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Kerbala University
College of Science

Preparation and Identification of Azo Reagent to Determine Ag(I) and Nickel(II) Ions as a Complex by using Spectrophotometric Method

A Thesis
Submitted to the College of Science
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By

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(2013 – 1434)

بسم الله الرحمن الرحيم

اللهُ نورُ السمواتِ والأرضِ مثلُ نُورِهِ
كمشكاةٍ فيها مصباح المصباحُ في
زجاجةٍ الزجاجةُ كأنها كوكبٌ دريٌّ
يوقدُ مِن شجرةٍ مباركةٍ زيتونةٍ لاشرقيةٍ
ولا غربيةٍ يكادُ زيتُها يضئ ولو لم
يمسَسهُ نارٌ نُورٌ على نورٍ يَهدي اللهُ
لنورهِ من يشاء

صدق الله العلي العظيم

سورة النور أية "35"

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

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Dedication

To the great man, my father

To the most kindhearted woman in my life who pushed me to go on … my mother

To the brave man, my dear husband

To my lovely kids….my sons

To the big heart… to the rare woman…to my only sister

To my brothers

Abstract

A new reagent, 2-[4-hydroxy phenyl)azo] 4,5-diphenyl imidazole,[HPAI] was prepared by mixing a diazonium salt solution of chloride with 4,5-diphenyl imidazole. The prepared reagent was used to prepare the two complexes, silver(I)(orange) and nickel(II)(red) complexes at λ_{max} =514 and λ_{max} =540, respectively. The characterization of prepared complexes was evaluated by using available techniques such as FT-IR, UV-Visible and C.H.N. analysis. In this study, the optimum conditions such as pH, reagent concentration, stability constant, linearity, limit of detection, molar absorptivity, sandel's sensitivity and thermodynamic functions were under taken for the two complexes. Firstly, the results show that the metal to reagent ratio for the two complexes was (1:2;M:L). Secondly, the reaction between Ag(I) and Ni(II) ions with the reagent was exothermic which lead to increase the production of complex. Finally, the value of pH, stability constant, linearity, detection limit, molar absorptivity, and sandel's sensitivity for Ag(I) and Ni(II) complexes was found to be (4, 1.520×10^{9}, $(0.372\times10^{-5}$- $4.09\times10^{-5})$M, 1.91×10^{-6} M, $(0.220\times10^{4}$ $L.mol^{-1}.cm^{-1}$ and $0.049 \mu g.cm^{-2})$ and (9, 4.150×10^{9}, $(0.681\times10^{-5}$-$8.177\times10^{-5})$M , $(3.14\times10^{-6}$ M), $(0.240\times10^{4}$ $L.mol^{-1}.cm^{-1})$ and $0.025 \mu g.cm^{-2})$, respectively. Furthermore, the effect of temperature, masking agents and sequence of addition was also studied. Moreover various conductivity, melting point and the stability in different solvent were determined for the prepared complexes. The precision level of an instruments was checked by using the relative standard deviation (%RSD). In general, good level of precision were obtained with perfect rang of %RSD (1.129-2.180)%, and (1.439-2.787)% for Ag(I) and Ni(II), respectively. The study was applied by determing the levels of silver in certified reference material, namely dental filling.

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Symbol	***Meaning***
HPAI	2-[4-Hydroxy phenyl)azo] 4,5-diphenyl imidazole
Ag	Silver
Ni	Nickel
Abs	Absorbance
B	Stability constant
RSD	Relative standard deviation
ΔG	Free energy
ΔH	Enthalpy
ΔS	Entropy
L	Ligand
M	Metal
FT-IR	Fourier transform infrared spectrometers
λ_{max}	Maximum wavelength
Nm	Nanometer
Re%	Recovery%
S.D	Standared deviation
E%	Relative error%

Symbol	***Meaning***
D.L	Detection limit
ICP-MS	Inductively coupled plasma – mass spectrometry
SPE	Solid-phase extraction
C–SPE	Colorimetric–solid-phase extraction
(CBT)	Synthesized triazene ligand, 1,3-bis(2-cyanobenzene)triazene
FAAS.	Flame atomic absorption spectrometry
APTES	3-Aminopropyltriethoxysilanes
APTES-PSE	3-Aminopropyltriethoxysilanes porous silicon electrode
FIA	Flow injection analysis
TLS	Thermal lens spectrometric
QADEAA	2-(2-Quinolylazo)-5-diethylaminoaniline
ETAAS.	Electrothermal atomic absorption spectrometry
PAA	Photon activation analysis
APDC	Ammonium pyrrolidine dithiocarbamate
UV–vis	Ultra violate-visible spectrometry
MPMP	2- [(2-Mercaptophenylimino)methyl]phenol

(1-1) Introduction

The electronic transition that takes place in the visible and ultraviolet regions of the spectrum is due to the absorption or radiation by specific types of groups, bonds, and functional groups within the molecule. The wavelength of absorption and the intensity are dependent on the type. The wavelength of absorption is a measure of the energy required for the transition. Its intensity is dependent on the probability of the transition occurring when the electronic system and the radiation interact and on the polarity of the excited state(1). All organic compounds are capable of absorbing electromagnetic radiation because all contain valence electrons that can be excited to higher energy levels. The excitation energies associated with electrons forming most single bonds are sufficiently high that absorption by them is restricted to the so called vacuum ultraviolet region (*A.* < 185 nm), where components of the atmosphere also absorb strongly. The experimental difficulties associated with the vacuum ultraviolet are formidable as a result, most spectrophotometric investigations of organic compounds have involved the wavelength region greater than 185 nm. Absorption of longer wavelength ultraviolet and visible radiation is restricted to a limited number of functional groups called (chromophores) that contain valence: electrons with relatively low excitation energies. The electronic spectra of organic molecules containing chromophores are usually complex, because the superposition of vibrational transitions the electronic transitions leads to an intricate combination of overlapping lines; the result is a broad band of continuous absorption. The complex nature of the spectra makes detailed theoretical analysis difficult or impossible. Nevertheless, qualitative or semiquantitative statements concerning the types of electronic transitions responsible for a given absorption spectrum can be deduced from molecular orbital considerations(2).

(1-2) Organic reagent

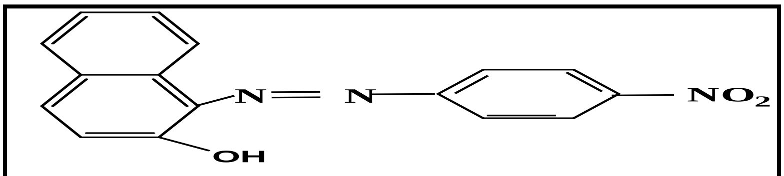
Organic reagents are chemical compounds used for quantitative and qualitative determination of elements to produce colored complex by joining the element with the function group of organic reagent by forming covalent , coordinative bond or both of them(3). The organic reagent has one or more function groups and this group contains atoms that have a pair of electron nonbonding that inter in the chemical structure of organic reagent like {C=S,N=N,C=N,C=O,N=O } and some of the organic reagents have a substitution called chromophore which will affect the color for this reagent such as{-OH,-NH_2,-Br,-SH,-CH_3}. Most of these groups donate the electrons so they increase the solubility of these organic reagents and their complexes. Then lead to increase the sensitivity of the organic reagent(4). The importance of these organic reagents comes from the ability of these group to determine the micrograms of metals and nonmetals compared with inorganic reagents. The main advantages of organic reagents are: high selectivity for some elements instead of another elements, high molecular weight and capability to dissolving in organic solvent(5,6). In addition, the organic reagents lead to produce colored solutions which can be used in various determinations such as spectrophotometric or colorimetric. Therefore, they are used to determine the micro amounts for many metals ions in different samples, for example, glass, bullions(7), samples of water(8), soil(9), and biological(10), as well as pharmaceutical chemistry(11).

(1-3) Azo compound

Azo compound constitutes the largest and most important groups of synthetic dyes. Azo compound contains one or more azo groups (N =N) which are linked to sp^2 hybridized carbon atoms, based on the number of such groups(12). The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups. Synthetic azo compound manufacturing started in 1856, when the English chemist W.H. Perkin, in an attempt to synthesize quinine, obtained instead a bluish substance with excellent dyeing properties that later became known as aniline purple, Tyrian purple or mauveine. Perkin, 18 years old, patented his invention and set up a production line. This concept of research and development was soon to be followed by others and new azo compounds began to appear on the market, a process that was strongly stimulated by Kekules discovery of the molecular structure of benzene in 1865(12). In the beginning of the 20thcentury, synthetic dyestuffs had almost completely supplanted natural azo compound(12) . Azobenzenes, the simply azo compound, (benzene rings connected by an N=N bond) like another azo compound have an extended conjugated system that causes them to absorb light from the visible region of the spectrum and have at least one chromophore (colour-bearing group). Some substituted azobenzenes are used commercially as dyes. Varying the extent of conjugation and the substituent attached to the conjugated system provides a large number of different colors(12). There are at least 3000 azo dyes in use. These dyes are used widely in textiles, leather, printing, paper making, drug and food industries there complexes have a general role in analytical, industrial, agriculture and pharmacological applications(13-15). The chemistry of azo compound complexes represents a wide field of the practical side. These types of compounds are very important in the biological field because they contain atoms such as oxygen, nitrogen and sulfur, which make them able to connect with different metal ions(15) .Thus little amounts of these elements may lead to decrease bioactivities(16,17). These reagents and their complexes are widely used as dyes for tissues, which increase their industrial importance(18). Azo compound known as monoazo have only one (N = N) group while diazo and triazo dyes contain two and three (N = N) groups, respectively. The azo compound classify according to the type of ring that linked to both of azo side to homocyclic azo compounds this compounds contain aromatic rings without presence hybrid atoms (O,S,N) within the ring but this compounds may be contain function group out of ring like ($-SH$,$-OH$,$-NH_2$,$-COOH$,$-SO_3H$) and heterocyclic azo compounds. These compounds contain heterocyclic aromatic ring on the azo group from one side or both(19). In addition they are very important reagents in analytical chemistry(20) which can be used as spectrophotometric reagents, indicators and solvent extraction reagents because they form color complexes that don't dissolve in aqueous solutions. Heterocyclic azo compounds contain more than one position to coordinate with the metal(21). Many of researchers succeeded to prepare some of organic azo reagents and study its characteristics and its biological activities(22). In addition, there are different ways to prepare these reagents. They differ according to the raw material, solvent, means, and the way followed for the dizaonium and coupling processes(23,24).

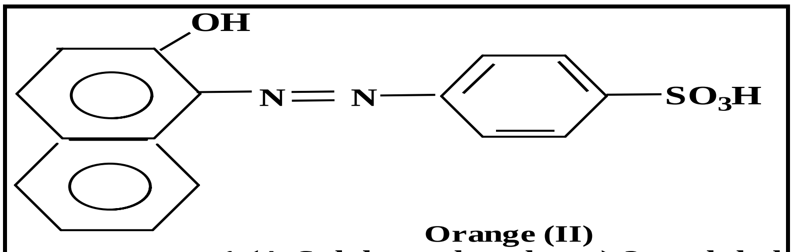
Three categories of azo compounds had been diagnosed(25) as shown below:-

1- compounds used as ingrain dyes that mean that have been used to dye fiber for example Para Red R dyes.
[1-(4-Nitrobenzen azo)-2-naphthol]



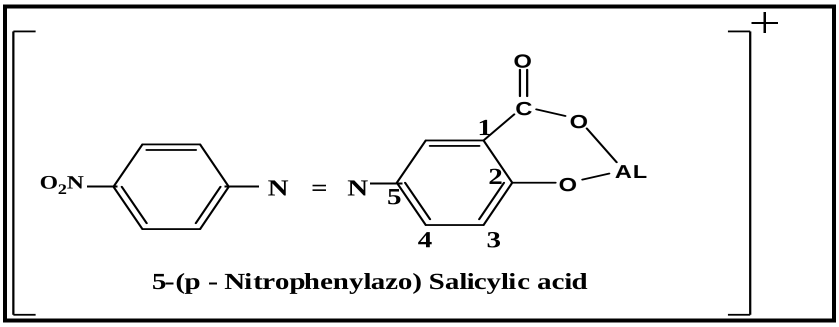
Para Red R
1-(4- Nitrobenzen azo)-2-naphthol

2- Azo compounds containing an amine or a sulphonic acid absorbed by the fiber in aqueous solutions such as:-
(5-Br- PADAB) [1,3-Diamino-4-(5-bromo-2-pyridyl azo)benzene and orange(II) [1-(4-Sulphonophenyl azo)-2-naphthol]



Orange (II)
1-(4- Sulphonophenyl azo)-2-naphthol

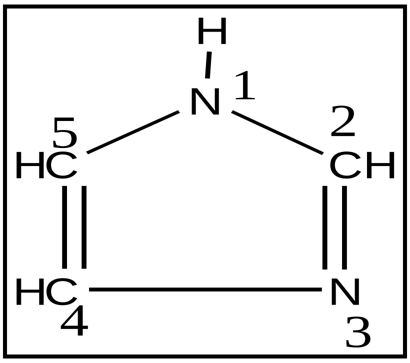
3-Azo compounds containing groups capable of configuring chelating compounds when they are coordinating with metallic ions, such as Alizarin yellow R[5-(p-Nitrophenylazo)Salicylic acid]$^{(26)}$



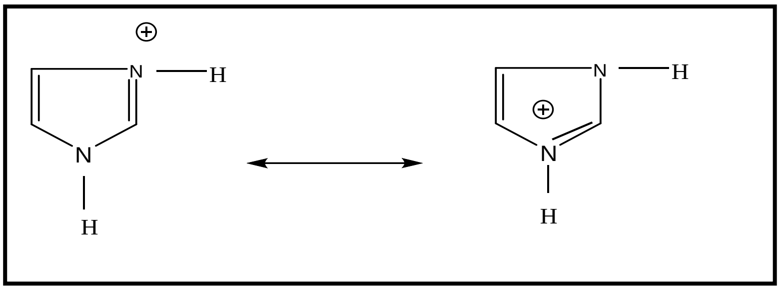
5-(p - Nitrophenylazo) Salicylic acid

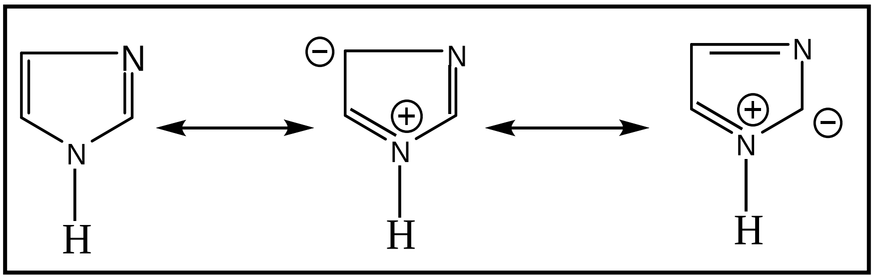
(1-4) Azo imidazole

Azo imidazole derivatives constitute a very important class of chemical compounds receiving the attention of scientific research$^{(27)}$. They are highly colored and have been used as dyes for a long time. They are important in drugs, cosmetics, biological activities including antibacterial, coordination capacity and participate in azo coupling reactions(28-30). It is five heterocyclic ring containing amino group and a nitrogen atom additional. The structure below shows the numbering imidazole ring:-

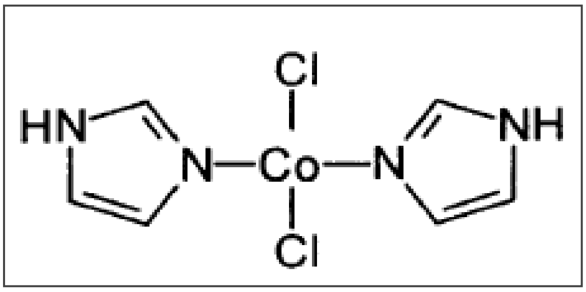


The coupling of diazonium salt occurs in position 2 or 4 of imidazole ring in alkaline medium to give shining azo imidazole dyes(31,32). Azo imidazole molecule being the azo imine group($-N{=}N-C{=}N-$), which is π-acidic and stabilized low valent metal redox state(33,34). Numbers of these azo dyes have been used as chelating ligands(27,29,35). In addition, they can be used as reagents in analytical chemistry(30,36,37). The resonance forms of imidazole are :-





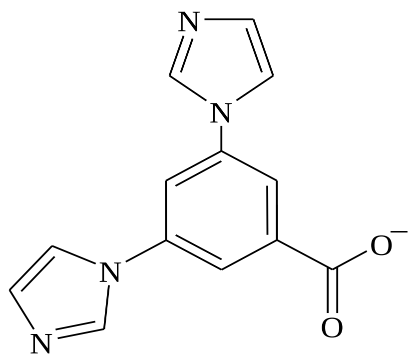
Imidazole is an organic compound with formula $(CH)_2N(NH)CH$. colourless crystals, m.p. 90C°, b.p. 25C°, is soluble in water. The values of melting and boiling points were found to be higher when compared to pyrrole, oxazole and thiazole. This is due to the imidazole molecule is a doner, an acceptor of hydrogen bonds, and only intermolecular hydrogen bridges can be formed. In the solid state, imidazoles forms chainlike associations with angled structures imparting a fibrous texture to the crystals. When dissolved in water, N– H---N bonds replaced by N–H---O and N---H–O bonds. In contrast, 1-methylimidazole is a liquid, mp-6°C, bp 180°C. It is only slightly soluble in water. Imidazole are extremely thermally stable and decomposes above 500°C. Haemoglobin is an iron(II) complex of haem with the imidazole ring of the amino acid histidine contained in the protein globin. The preparing of reagent from imidazole not only by coupling of diazonium salt with imidazole, but also by preparing a new organic reagent contained heterocyclic ring linked with the imidazole ring by azo group. Imidazole complexes with many metal ions in which the pyridine-like N-atom provide the donor, e.g., dichlorodiimidazole cobalt(II)(31)



The workers Martins et al.(38) synthesized two new reagent, namely [(2-hedroxybenzil) (2-(imidazole-2-il)amine](HLl) and [(2hedroxybenzil) (2-(piridil-2-il)amine], then have prepared their complexes with copper(II).

HL1 HL2

A previous study(39) has synthesized the compound of 3,5-di(1H-imidazole -1-yl)-benzoate.



3,5-di(1H-imidazole-1-yl)-benzoate

Yabas et al.(40) reported a study of preparing some imidazole compounds such as 4[(4,5-Diphenyl-1H-imidazole)-2-yl-thio]phthalonitrile. In 2013, Türker Akçaya et al.(41) synthesized and characterized of novel organosoluble peripherally tetra imidazole substituted metal-free (4), zinc(II) (5), nickel(II) (6), cobalt(II) (7), lead(II) (8) and oxo-titanium(IV) (9) phthalocyanines. In addition, Sahraei et al.(42) have reported a study of preparing 3H-imidazo[4,5-a]acridine-11-carbonitriles.

(1-5) Silver

Silver is a chemical element with the chemical symbol Ag and atomic number 47. transition metal. The melting point of silver is 961.78°C, boiling point is 2,212°C. Pure silver has a brilliant white metallic luster. Silver is slightly harder than gold. It is a very ductile and malleable, exceeded in these properties by gold and palladium. It has the highest electrical and thermal conductivity and the lowest contact resistance when compared to all metals(43). Naturally, occurring silver is composed of two stable isotopes, ^{107}Ag and ^{109}Ag(44). Silver is stable in pure air and water. The most common oxidation state of silver is +1 (for example, silver nitrate, $AgNO_3$); the less common +2 compounds (for example, silver(II) fluoride, AgF_2); and the even less common +3(for example, potassium tetrafluoroargentate(III), $KAgF_4$) and even +4 compounds (for example, potassium hexafluoroargentate(IV), K_2AgF_6)(45) are also known. Silver metal dissolves readily in nitric acid (HNO_3) to produce silver nitrate ($AgNO_3$), the most important salt of silver(44).

(1-5-1) Physical Properties

White metal with brilliant metallic luster, face–centered cubic crystals, density 10.43 g/cm^3 at 20°C, and 9.18 g/cm^3 at 1,100°C vaporizes at 2,162°C vapor pressure 5 torr at 1,500°C. Electrical resistivity of pure metal at 25C° is 1.617×10^{-6} ohm-cm Poisson’s ratio 0.39 (hard drawn), 0.37 (annealed); viscosity of liquid silver 3.97. Inert to most acids; attacked by dilute HNO_3 and concentrated H_2SO_4. Soluble in fused caustic soda or caustic potash in the presence of air(44).

(1-5-2) Occurrence and Applications

Silver exists in native form, as an alloy with gold and in ores containing sulfur, arsenic, antimony or chlorine. Ores include argentite (Ag_2S), chlorargyrite,($AgCl$) which includes horn silver and pyrargyrite(Ag_3SbS_3) The principal sources of silver are the ores of copper(46). The alloys of silver have many commercial uses. Silver is used in photography, dental compounds, solder, electrical contacts, electronic industries, batteries, mirrors, jewelry, printed circuit(43,47) and used in numerous commercial products, including textiles, to prevent bacterial growth(48).

(1-5-3) Toxicity

Soluble silver salts, specially $AgNO_3$, are lethal in concentrations of up to 2g . Silver compounds can be slowly absorbed by body tissues, with the consequent bluish or blackish skin pigmentation , if liquid comes in contact with the eyes, may cause severe cornea injury. Repeated and prolonged contact with skin may cause allergic dermatitis. Exposure to high concentrations of vapors may cause dizziness, breathing difficulty, headaches or respiratory irritation. chronic overexposure to a component or components in this material has been found to cause the following effects in laboratory animals, kidney damage, eye damage, lung damage, liver damage, anemia and brain damage(43).

(1-6) Some different methods to determine silver

(1-6-1) Atomic absorption technique :-

The worker Zhang et al. (49) have determined a silver ion by using flame atomic absorption with good detection limit 1.1×10^{-6}M and perfect precision R.S.D 1.2%. Previous study(50) has determined the silver ion in environmental samples by electro thermal AAS. The detection limit was 5.0×10^{-9}M and the relative standard deviation was 8.2%. In addition Manzoori and Nezhad(51) have determined the levels of silver in samples of water by using flame atomic absorption spectrometry after extracting it by dithizone as a complexing agent, the detection limit was 0.56×10^{-6}M. Resano et al(52) used the solid sampling-graphite furnace atomic absorption spectrometry for direct determination of silver ion. Ingrid et al.(53) determined silver ion in geological samples by using high-resolution continuum source electrothermal atomic absorption spectrometry and direct solid sampling. The detection limit was 2×10^{-6}M. In another study(54) have separated of trace amounts of silver ions in water samples by using liquid–liquid microextraction and determined it by flame atomic absorption spectrometry. The detection limit was 1.2×10^{-3}M. Yuan et al.(55) determined the trace silver in environmental samples by room temperature ionic liquid (RTIL). The detection limit and the relative standard deviation were 0.28×10^{-6}M and 4.1% respectively. In another study Dasbasia et al.(56)have reported a method for separation /preconcentration procedure to determination of trace levels of Ag(I) by flame atomic absorption spectrometry. The calibration curve obtained was linear over the concentration range of $(0.2\times10^{-5} – 2\times10^{-5})$M. The detection limit of the method was 0.3×10^{-6}M while precision was 1.5% at the level of 1×10^{-5}M.

(1-6-2) Colorimetric–solid-phase extraction method :-

The workers Arena et al.(57) have determined silver (I), using the solid-phase extraction (SPE). In this method, the silver(I) was extracted by diffuse reflectance spectroscopy (DRS). This method, called colorimetric–solid-phase extraction (C–SPE), the detection limit was 4×10^{-6}M. A previous study (58) has determined the level of colloidal and dissolved silver in water samples using colorimetric solid-phase extraction, the detection limit was 0.1×10^{-3}M . A simple, reliable and rapid method for preconcentration and determination of the ultra trace amount of silver by Rofoueia et al.(59),the detection limit was 6.0×10^{-6}M.

(1-6-3) Electric method

Rohani and Taher(60) have prepared a carbon ceramic electrode modified by 4-(2-pyridylazo)-resorcinol in order to measure the level of silver The detection limit of silver(I) was 0.123×10^{-6}M and the calibration curve was linear for $(0.5\times10^{-6}$-$3\times10^{-4})$M. Another study reported by Ibrahim(61) has made carbon paste electrode for determined the potentiometric flow injection analysis of silver(I). The detection limit was 2.5×10^{-7}M. Firooz et al.(62) were reported the study of prepared sensitive and selective optical sensor for determination of ultra-trace amount of silver ions in range (2.27×10^{-11} to 1.13×10^{-3} M) with a low detection limit of 9.5×10^{-12}M. Haghnazari et al.(63) determined the level of silver ion in aqueous solutions using benzo crown-ether modified gold nanoparticles in simple optical determination. On the other hand, Jahandari et al.(64) have reported a silver(I) selective carbon paste electrode modified with multi-walled carbon nanotubes for determine Ag(I). The calibration curve was linear for range(0.5×10^{-6}M to 235 $\times10^{-6}$M) and with a detection limit 0.08 $\times10^{-6}$M. Li et al.(65) were prepared voltammetric sensor modified porous silicon electrode was elaborated and used for determine Ag(I) in aqueous solution. The calibration curve was linear for range (1×10^{-3}M to 1×10^{-7}M), with a detection limit of 3×10^{-8} M.

(1-6-4) The other methods

Katarina et al.(66) have developed novel chelating resins for silver ion using chitosan as a base material and to determine ultra trace amounts of silver by(inductively coupled plasma mass spectrometry) ICP-MS. Naik et al.(67) have reported a kinetic determination of silver at trace level based on its catalytic effect on a ligand substitution reaction. In another study Korte(68) et al. collinear dual beam thermal lens spectrometric (TLS) detection, combined with flow injection analysis (FIA), was developed and applied to determine simultaneously concentrations of ionic and colloidal silver in the Russian drinking water supplies of the International Space Station (ISS), the detection was 1.5×10^{-6}M. The workers(69) have developed rapid determination of silver ion with functional cadmium sulphide (CdS) nanoparticles as a fluorescence probe. On the other hand Zheng et al.(70) were reported the study of fluorescence of such nanorods NRs is quenched by silver ions, and this is accompanied by a gradual red shift of the peak from 585 nm to 605 nm. Bruzzonitia et al (71) were developed a flow injection method for determined silver. This method is based on a reduction reaction with sodium borohydride which leads to the formation of a colloidal species which is monitored at a wavelength of 390 nm.

(1-6-5) The spectrophotometric method

The scientists Hu et al.(72) synthesized a new chromogenic reagent, 2-(2-quinolylazo)-5-diethylaminoaniline (QADEAA) for the determination of silver(I). Beer's law is obeyed in the range of (0.01×10^{-3} -0.6×10^{-3})M The molar absorptivity of the complex is 1.39×10^{5}L mol^{-1} cm^{-1} at 580nm. Yang at el.(73) synthesized a new chromogenic reagent, 2-(2-quinolylazo)-5-diethylaminophenol (QADEAP) for determination of silver. Beer's law is obeyed in the range of (0.01×10^{-3} - 0.6×10^{-3})M. The molar absorptivity of the complex was 1.33×10^{5}L mol^{-1}.cm^{-1} at 590 nm. In another study Mohsen(74) was determined Pd(II) and Ag(I) by using the organic reagent 2- [(2- carboxy -4- iodophenyl) azo] -4,5- diphenyl imidazole. The detection limite 0.7×10^{-5}M and molar absorptivity of 3.243×10^{4}L.mol^{-1}.cm^{-1}.

(1-7) Nickel

Nickel is a chemical element (Ni) and atomic number 28. Nickel belongs to the transition metals in the first triad of group VIII(Group 10) after iron and cobalt, electron configuration [Ar]3d84s^{2} atomic radius 1.24Å, ionic radius(75). Naturally occurring nickel is composed of 5 stable isotopes,^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni and ^{64}Ni(45).It is high electrical and thermal conductivities, is quite resistant to corrosion. The most common oxidation state of nickel is +2, but compounds of Ni^{0}, Ni^{+}, and Ni^{3+} are well known, and Ni^{4+} has been demonstrated (46). Because of nickel's slow rate of oxidation at room temperature, it is considered corrosion-resistant(75).

(1-7-1) Physical Properties

The main properties of Ni are: silvery-white lustrous metal; face-centered cubic crystal structure, ductile, ferromagnetic, melts at 1,455°C, vaporizes at 2,730°C, electrical resistivity 6.97 microhm-cm at 20C° total emissivity 0.045, 0.060 and 0.190 erg/s.cm^{2} at 25, 100 and 1,000C°. Insoluble in water, dissolves in dilute nitric acid, slightly soluble in dilute hydrochloric acid and sulfuric acid and insoluble in ammonia solution(46).

(1-7-2) Occurrence and application

In nature, the nickel can be found in combination with different substance, namely sulfur and iron ,sulfur, arsenic and arsenic and sulfur to produce various materials such as pentlandite; millerite, mieral nickeline and nickel galena. Nickel is commonly found in iron meteorites as the alloys kamacite and taenite. The most important applications of nickel metal involve its use in numerous alloys. Nickel is used in many specific and recognizable industrial. It is also used for plating and as a green tint in glass. Nickel is preeminently an alloy metal, and its chief use as the nickel steels and nickel cast irons, of which there are many varieties. It is also widely used in many other alloys, such as nickel brasses and bronzes, and alloys with copper, chromium, aluminum, lead, cobalt, silver, and gold(76). Nickel anodes are used for nickel plating of many base metals to enhance their resistance to corrosion. Nickel-plated metals are used in various equipment, machine parts, printing plates, and many house hold items such as scissors, keys, clips, pins, and decorative pieces. Nickel powder is used as porous electrodes in storage batteries and fuel cells. Another major industrial use of nickel is in catalysis. Nickel and raney nickel are used in catalytic hydrogenation or dehydrogenation of organic compounds including olefins, fats, and oils(44).

(1-7-3) Toxicity

Skin contact with nickel-contaminated soil or water can cause dermatitis and a type of chronic eczema, known as “nickel itch” caused by hypersensitivity reactions of nickel on the skin. Although oral toxicity of the metal is very low, ingestion may cause hyperglycemia and depression of the central nervous system. Chronic inhalation of nickel dust can cause lung and sinus cancers in humans(77).

(1-8) Some of different method to determination of nickel.

(1-8-1) Atomic absorption technique

Baysal and Akman (78) determined copper and nickel in scalp hair by solid sampling electrothermal atomic absorption spectrometric. The limit of detection was 35×10^{-6}M. In another study Dobrowolski and Otto(79) determined nickel and cobalt in reference plant materials by graphite furnace atomic absorption spectrometry GFAAS technique. The limit of detection was 0.02×10^{-6}M. The workers Alizadeh et al.(80) reported selective dispersive liquid–liquid microextraction and preconcentration of Ni(II) into a micro droplet followed by ETAAS electrothermal atomic absorption spectrometry determination using a yellow Schiff's base bisazanyl derivative The calibration curve was linear over a nickel concentration range of $(1\times10^{-6}–5\times10^{-6})$M. The detection limit and relative standard deviation were 0.04×10^{-6}M and 2.1%, respectively. Amirkavei et al.(81) determined nickel, cobalt and copper with electrothermal atomic absorption spectrometry after liquid–liquid microextraction the detection limits of 1.2×10^{-9}M. In another study, Kowalewska(82) determine Ni(II) in xylene solutions of raw material for catalytic cracking with application of graphite furnace atomic absorption spectrometry with a detection limit of 1.2×10^{-9}M.

(1-8-2) The other methods

Beiraghi et al.(83) were reported the study of simultaneous preconcentration of cadmium, cobalt and nickel in water samples by cationic micellar precipitation and their determination by ICP-OES., the detection limit was 0.004×10^{-6}M. Hashemi(84) determined nickel using dimethylglyoxime by flotation-spectrophotometric method. In another study, Zeng et al. (85) determined cobalt and nickel by atomic fluorescence spectrometry using APDC (ammonium pyrrolidine dithiocarbamate) enhanced chemical vapor generation. The limits of detection was 1×10^{-6}M. The calibration curves were linear in the range of (1×10^{-5}to30×10^{-5})M. Sekimoto et al.(86) determined nickel ion in cosmic spherules by photon activation analysis(PAA). The workers Volpe et al. (87) reported the quantification of cadmium, cobalt, chromium, and nickel by inductively coupled plasma-mass spectrometry (ICP-MS) in samples of eye shadows.

(1-8-3) The spectrophotometric method

A previous study(88) has determined the level of nickel in environmental samples by developing a new method which is RTILs. for cloud point extraction combined with UV–vis spectrophotometer the detection limit for Ni was (0.5×10^{-6}M). Relative standard deviations was 3.9%. Memon et al.(89) developed a single channel flow injection spectrophotometric for determination of nickel using furildioxime as complexing agent in micellar solution absorbance is linear from(0.2×10^{-4} to 0.1×10^{-2})M. Haji et al.(90) have produced an extraction spectrophotometric method for determination of nickel in water and wastewater using 2-[(2mercaptophenylimino)methyl] phenol (MPMP). The reagent reacts with nickel(II) at pH > 10 to produce brown complex. Beer’s law is obeyed over the range of (0.011×10^{-3} -0.30×10^{-3})M. The relative standard deviation at 0.018×10^{-3}M is 1.1 %. In another study Niazi and Yazdanipour(91) reported spectrophotometric determination of cobalt, copper and nickel using 1-(2-thiazolylazo)-2-naphthol. Beer’s law is obeyed over the range of(0.05×10^{-3}–0.80×10^{-3}) M. The workers Deng et al.(92) reported novel coupling of surfactant assisted emulsification dispersive liquid–liquid microextraction with spectrophotometric determination for nickel. The relative standard deviation at 0.25M was 3%.

(1-9) Stability of complex in solution

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Many complexes are relatively unreactive species remaining unchanged throughout a sequence of chemical or physical operations and can often be isolated as stable solids or liquid compounds. Other complexes have a much more transient existence and may exist only in solution or be highly reactive and easily converted to other species. All metals form complexes, although the extent of formation and nature of these depend very largely on the electronic structure of the metal. Stability of a complex in solution" refers to the degree of association between the two species involved in the state of equilibrium. Qualitatively, the greater the association, the greater the stability of the compound. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability(93).

Thus, if we have a reaction of the type:-

$M + 4L \rightarrow ML_4$

then the larger the stability constant, the higher the proportion of ML_4 that exists in the solution. Free metal ions rarely exist in solution so that M, will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

1. $M + L \rightarrow ML$ $K_1 = [ML] / [M] [L]$
2. $ML + L \rightarrow ML_2$ $K_2 = [ML_2] / [ML] [L]$
3. $ML_2 + L \rightarrow ML_3$ $K_3 = [ML_3] / [ML_2] [L]$
4. $ML_3 + L \rightarrow ML_4$ $K_4 = [ML_4] / [ML_3] [L]$

where K_1, K_2 etc. are referred to as "stepwise stability constants". Alternatively, we can write the "Overall Stability Constant" thus:

$$. \frac{[ML2]}{[ML][L]} . \frac{[ML3]}{[ML2][L]} . \frac{[ML4]}{[ML3][L]} = \frac{[ML4]}{[M][L]4} \frac{[ML]}{[M][L]}$$

$M + 4L \rightarrow ML_4$ $\beta_4 = [ML_4]/ [M] [L]^4$

The stepwise and overall stability constants are therefore related as follows:

$\beta_4 = K_1.K_2.K_3.K_4$ or more generally,

$\beta_n = K_1.K_2.K_3.K_4$--------------$K_n$

(1-10) Thermodynamics and equilibrium chemistry

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, and chemistry. Of the various branches of thermodynamics, the most important to chemistry is the study of the changes in energy occurring during a chemical reaction. Chemical systems spontaneously react in a fashion that lowers their overall free energy(94). At a constant temperature and pressure, typical of many benchtop chemical reactions, the free energy of a chemical reaction is given by the **Gibb's free energy** function(95)

$\Delta G = \Delta H - T\,\Delta S$ ---------------(1-10)

where T is the temperature in kelvins, and ΔG, ΔH, and ΔS are the differences in the Gibb's free energy, the enthalpy, and the entropy between the products and reactants. **Enthalpy** is a measure of the net flow of energy, as heat, during a chemical reaction. Reactions in which heat is produced have a negative ΔH and are called exothermic. Endothermic reactions absorb heat from their surroundings and have a positive ΔH. **Entropy** is a measure of randomness, or disorder. The entropy of an individual species is always positive and tends to be larger for gases than for solids and for more complex rather than simpler molecules. Reactions that result in a large number of simple, gaseous products usually have a positive ΔS. The sign of ΔG can be used to predict the direction in which a reaction moves to reach its equilibrium position. A reaction is always thermodynamically favored when enthalpy decreases and entropy increases. Substituting the inequalities $\Delta H < 0$ and $\Delta S > 0$ into equation (1-10) shows that ΔG is negative when a reaction is thermodynamically favored. When ΔG is positive, the reaction is unfavorable as written (although the reverse reaction is favorable). Systems at equilibrium have a ΔG of zero. At equilibrium the Gibb's free energy is zero, and equation below

$\Delta G^\circ = -RT \ln K$

where K is an **equilibrium constant** that defines the reaction's equilibrium position(94).

(1-11) Statistical treatment

The requirements of the analysis determine the best method. In choosing a method, consideration is given to some or all the following design criteria: accuracy precision, sensitivity, selectivity, robustness, ruggedness, scale of operation, analysis time, availability of equipment, and cost . The relative standard deviation(RSD) is widely used in analytical chemistry to express the precision and repeatability of an assay.

$$\mathrm{RSD} = \frac{\mathrm{S}}{\bar{\mathrm{X}}} \times 100$$

$$\mathrm{S} = \sqrt{\frac{\Sigma(\,\mathrm{Xi} - \bar{\mathrm{X}})^2}{\mathrm{N} - 1}}$$

Accuracy is a measure of how closely the result of an experiment agrees with the expected result. The difference between the obtained result and the expected result is usually divided by the expected result and reported as a percent relative error.

$$\%\ \mathrm{Error} = \frac{\text{measured result} - \text{expected result}}{\text{expected result}} \times 100$$

Analytical methods may be divided into three groups based on the magnitude of their relative errors. When an experimental result is within 1% of the correct result, the analytical method is highly accurate. Methods resulting in relative errors between 1% and 5% are moderately accurate, but methods of low accuracy produce relative errors greater than 5%(94).

Precision when a sample is analyzed several times, the individual results are rarely the same. Instead, the results are randomly scattered. **Precision**

is a measure of this variability. The closer the agreement between individual analyses, the more precise the results(94).

Sensitivity the ability to demonstrate that two samples have different amounts of analyte is an essential part of many analyses. A method's sensitivity is a measure of its ability to establish that such differences are significant. Sensitivity is often confused with a method's detection limit. The **detection limit** is the smallest amount or concentration of analyte that can be detected with statistical confidence(94).

(1-12) The Aim of Work

The main aim of this study was to develop and validate the preparation method for azo reagent 2-[4-hydroxy phenyl)azo] 4,5-diphenyl imidazole and used it to determine the level of Ag^+ and Ni^{++} using to optimum conditions. The study was applied by determing the level of Ag^+ in dental filling.

(2-1) Instrumentation

1- Single beam UV-visible spectrophotometer Sp-300, (Japan).

2- Double beam UV-visible spectrophotometer -1800, Shamadzu, (Japan).Equipped with quartz cells (1cm).

3- pH-meter-WTW-720-ionlab, (Germany).

4- Electrical shaker ,Scientific technical supplies, Maxi-MixIII, Type 65800,(Germany).

5- Melting point apparatus, MFB-600.010F, (England).

6- Digital conductivity meter-WT-270-ioolab, (Germany).

7- Temperature control circulator laboratory Supply Company BS-11,(Korea).

8- FT-IR 8400 spectrophotometer, Shamadzu , (Japan).

9- Digital balance, BL 210S, (Germany)

10- Flameless atomic absorption spectrophotometer-670 Shimadzu Japan).

11- Elemental analysis(C.H.N). Type GGG.WWW.(49),(Itali)

(2-2) Chemicals

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

Table (2-1) The chemical materials used in this study

Name	***Chemical structure***	***Purity***	***Manufactured by companies***
Ethanol	C_2H_5OH	96.0%	(B.D.H)
Nickel nitrate	$Ni(NO_3)_2.6H_2O$	99%	(B.D.H)
Silver nitrate	$AgNO_3$	99%	(B.D.H)
Nitric acid	HNO_3 (Laboratory)	65% v/v	(B.D.H)
Carbon tetrachloride	CCl_4	99.8%	(B.D.H)
Potassium bromide	KBr	99.0%	(B.D.H)
Potassium thiocyannate	KSCN	99.8%	(B.D.H)
Iron(III) nitrate	$Fe(NO_3)_3.9H_2O$	99%	(B.D.H)
Mercuric(II) nitrate	$HgNO_3$	99%	(B.D.H)
Ascorbic acid	$C_6H_8O_6$	99.5%	(B.D.H)

Name	***Chemical structure***	***Purity***	***Manufactured by companies***
Cuppric nitrate	$Cu(NO_3)_2.3H_2O$	99%	(B.D.H)
Cobalt nitrate	$Co(NO_3)_2.6H_2O$	99%	(B.D.H)
Leade(II)nitrate.	$Pd(NO_3)_2$	99%	(B.D.H)
Benzil	$C_{14}H_{10}O_2$	99%	(B.D.H)
Ammonium hydroxide	NH_4OH	97%	(B.D.H)
Cadumium nitrate	$Cd(NO_2)_2.4H_2O$	99%	(Merck)
Potassium carbonate	K_2CO_3	98.0%	(Merck)
Potassium nitrate	KNO_3	98.0%	(Merck)
Potassium Oxalate	$K_2C_2O_4$	99%	(Merck)
Sodium hydroxide	$NaOH$	98.0%	(Merck)
Sodium Potassiumtartarte	$KNaC_4H_4O_6.4HO$	99%	Fluka
Chrom(III)nitrate	$Cr (NO_3)_3. 9H_2O$	99%	Fluka
Potassium Sulfate	K_2SO_4	99%	Fluka

Name	***Chemical structure***	***Purity***	***Manufactured by companies***
Sodium nitrite	$NaNO_2$	98%	Fluka
Chloroform	$CHCl_3$	99.5%	(GCC)
Glacial acetic acid	CH_3COOH	99.6%	(GCC)
Hydrochloric acid	HCl	36% v/v	(PODH)
Ammonium acetate	NH_4CH_3COO	99.8%	GRIFFIM
Thiourea	CH_4N_2S	99%	Riedel-DeHaen AG
Potassium acetate	KCH_3COO	99%	(GCC)
Sulfuric acid	H_2SO_4	99%	(GCC)

(2-3) Preparation of standard solutions.

(2-3-1) Preparation of standard solution of silver (I)ion(1M).

The solution was prepared by dissolving (0.158gm) of $AgNO_3$ in double distilled water and the volume was completed to 100 mL with DDW. in a volumetric flask. Dilute Ag (I) solutions were prepared by diluting this standard solution with necessary volume of water.

(2-3-2) Preparation of standard solution of nickel (II)ion(1M).

The solution was prepared by dissolving (0.490gm) of $Ni(NO_3)_2.6H_2O$ in DDW. and the volume was completed to 100 mL with DDW. in a volumetric flask. Dilute Ni (II) solutions were prepared by diluting this standard solution with necessary volume of water.

(2-3-3) Preparation of reagent(1M).

The reagent was prepared by dissolving (0.100gm) of reagent [HPAI] in absolute ethanol and the volume was completed to 100 mL with ethanol in a volumetric flask.

(2-3-4) Preparation of nitric acid solution(0.1M).

The solution was prepared by transferring (6.920 mL) from concentrated nitric acid (65v/v%) the volume was completed to 100 mL with DDW. in a volumetric flask.

(2-3-5) Preparation of sodium hydroxide solution(0.1M)

The solution was prepared by dissolving (0.4gm) of NaOH solution in DDW. and the volume was completed to 100 mL with DDW. in a volumetric flask.

(2-3-6) Preparation of masking agents

The agents (0.1M) were prepared by dissolving the salts of [Potassium Thiocynaite, Ascorbic acid, Potassium sodium tartrate, Thiourea], in a (25 mL) of DDW.

(2-4) Preparation of reagent[HPAI].

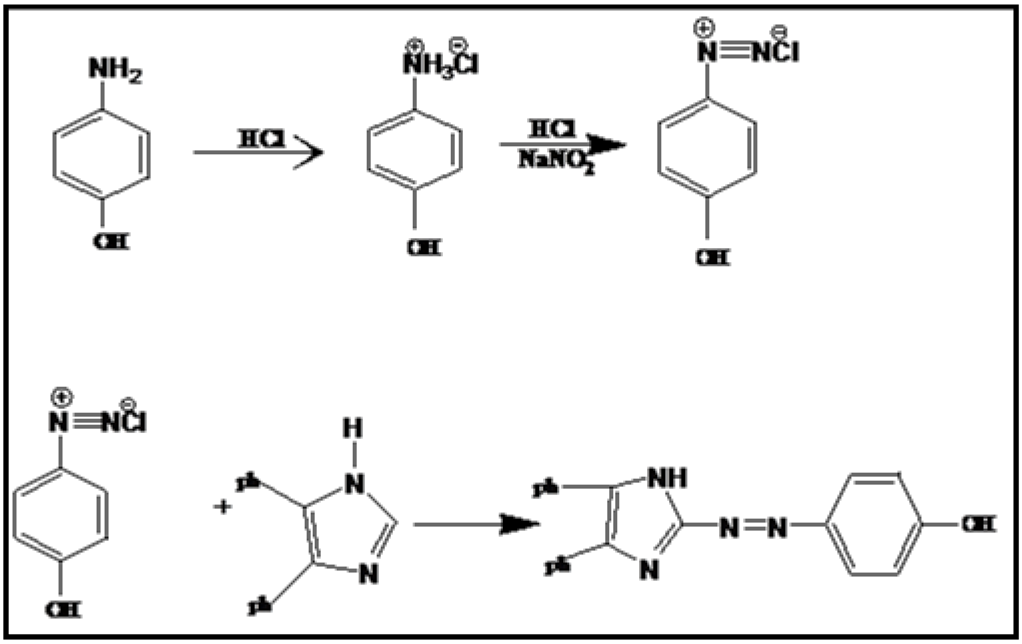
Preparation of starting materials (4,5-diphenyl imidazole)

A mixture of benzyl 2.1gm (0.01mol) ammonium acetate 6gm (0.8 mol) and hexamine 0.26 gm (0.02 mmol) in glacial acetic acid (50 mL) was heated under reflux for 2h. After refluxing, the reaction mixture was allowed to reach room temperature. The solid that appeared after the addition of DDW (400 mL) was filtered through filter paper. The filtrate solution was neutralized with ammonium hydroxide to give solid and was filtered. The solid mass obtained was dried in vacuum and recrystallized from absolute ethanol. Yield 77-86% .

(2-4-2) Preparation of 2-[4-hydroxy phenyl)azo] 4,5-diphenyl imidazole.

The reagent was prepared according to the following general procedure(96).In this method, 4-hydroxy aniline (1.09 gm, 10 mmol) was dissolved in 30 mL of water and 3.0 mL of concentrated hydrochloric acid. This solution was diazotized below 5°C with 13 mL of aqueous sodium nitrite (1.0 mol L^{-1}). A drop of the reaction mixture is tested from time to time with starch-iodide paper until nitrous acid persists in the solution during a 10 min interval. The resulting diazonium chloride solution was mixed with 4,5-dipheny imidazole. (2.2 gm, 10 mmol) dissolved in 150 mL alkaline ethanol cooled below 5°C after leaving in the refrigerator for 24 hour, the mixture was acidified with (0.1 mol L^{-1})

hydrochloric acid until (pH= 6). The precipitate was filtered off, and twice recrystallized from hot absolute ethanol, and dried over anhydrous $CaCl_2$. The equation of reaction below:-



(2-5) Preliminary investigation

(2-5-1) General procedure:

Prepared complexes of silver(I) and nickel(II):-

a- Complex of silver(I):-

Complex of silver(I) was prepared by mixing (5ml) of silver solution in concentration (1.860×10^{-4}M), with 2ml of reagent (2.941×10^{-3}M) then the solution adjusted to (pH =4) using different amounts of nitric acid solution (0.1M) and/ or sodium hydroxide solution (0.1M). The blank solution prepared by mixing (5 mL) of DDW. with 2mL of reagent (2.941×10^{-3}M) then the solution adjusted to (pH=4) using different amounts of nitric acid solution (0.1M) and/ or sodium hydroxide solution (0.1M). The complex and the blank solutions were transferred into volumetric flasks of (10)mL and made up to the mark with DDW.

b- Complex of nickel(II):-

Complex of silver(I) was prepared by mixing (5ml) of nickel solution in concentration (3.407×10^{-4}M), with 2ml of reagent (2.941×10^{-3}M) then the solution adjusted to (pH =9) using different amounts of nitric acid solution (0.1M) and/ or sodium hydroxide solution (0.1M). The blank solution prepared by mixing (5 mL) of DDW. with 2mL of reagent (2.941×10^{-3}M) then the solution adjusted to (pH=9) using different amounts of nitric acid solution (0.1M) and/ or sodium hydroxide solution (0.1M). The complex and the blank solutions were transferred into volumetric flasks of (10)mL and made up to the mark with DDW.

(2-5-2) Study of UV – visible spectra:-

Absorption of UV-visible spectra for solutions were plotted for each solution to determine the λ_{max} for each complex :-

1. Absorption spectrum of reagent solution dissolved in ethanol was determined and ethanol used as a blank.
2. Absorption spectrum of complex Ag(I) with reagent [HPAI] was determined.
3. Absorption spectrum of complex Ni (II) with reagent [HPAI] was determined.

(2-6) Study the best conditions to form the complexes:-

In order to reach the best conditions that can be used to determine the levels of silver(I) and nickel(II) ions, the effects of the following factors was studied, as shown below: -

(2-6-1) The Effect of (pH)

The pH function ranged from (1 to 10) was organized by installing the concentration of Ag (I) and Ni(II) ions , separately, by using different amounts of nitric acid solution (0.1M) and/ or sodium hydroxide solution (0.1M) using the pH-meter. The absorbance of the complex was measured at (λ_{max}= 514 nm) and (λ_{max}= 540 nm) for silver(I) and nickel(II) respectively.

(2-6-2) The effect of reagent concentration

The influence of reagent concentration was carried out by using various concentration of reagent ranged from (0.360×10^{-3} to 2.941×10^{-3})M. 5mL of each solution was mixed with 2mL of reagent at pH=(4,9) and the value of absorbance at λ_{max}=(514,540)nm for silver and nickel respectively. Each mixture were determined against the blank of reagent solution.

(2-6-3) The effect of sequence of addition

Three different methods were used to prepare silver and nickel complexes by the sequence of adding the metal ion and the reagent processes as follows:

a- Complex of silver(I):-

1- A solution (5mL) of silver (1.86×10^{-4}M) transferred to a beaker. Two (mL) of reagent (2.941×10^{-3} M) was added. The value of pH was fixed to be 4 by using nitric acid or/and sodium hydroxide. The solution was transferee into a volumetric flask (10 mL) and the volume made up to the mark with DDW. The absorbance of sample measured at (λ_{max}= 514nm) against the absorbance of blank solution that prepared in the same sequence of addition except exchange the silver ion with DDW.

2- A solution (5mL) of silver ion (1.86×10^{-4}M) transferred to a beaker. The value of pH was fixed to be 4 by using nitric acid or/and sodium hydroxide. Then (2 mL) of reagent (2.941×10^{-3}M) were added, and the solution was transferee into a volumetric flask (10 mL) and the volume made up to the mark with DDW. The absorbance of sample measured at (λ_{max}= 514nm) against the absorbance measured by the blank solution that prepared in the same sequence of addition except exchange the silver ion with DDW.

3- A solution 2ml of reagent (2.941×10^{-3} M) was transferred to a beaker. The value of pH was fixed to be 4 by using nitric acid or/and sodium hydroxide. Five (mL) of silver ion (1.86×10^{-4} M) were added and the solution was transferred into a volumetric flask (10 mL) and the volume was made up to the mark with DDW. The absorbance measured at (λ_{max}=514nm) against the absorbance measured by the blank solution that prepared in the same sequence of addition except exchange the silver ion with DDW.

b- Complex of nickel(II):-

1- A solution (5mL) of nickel(3.400×10^{-4}M) transferred to a beaker. Two (mL) of reagent (2.941×10^{-3} M) was added. The value of pH was fixed to be 9 by using nitric acid or/and sodium hydroxide. The solution was transferee into a volumetric flask (10 mL) and the volume made up to the mark with DDW. The absorbance of sample measured at (λ_{max}= 540nm) against the absorbance of blank solution that prepared in the same sequence of addition except exchange the nickel ion with DDW.

2- A solution (5mL) of nickel ion (3.400×10^{-4}M) transferred to a beaker. The value of pH was fixed to be 9 by using nitric acid or/and sodium hydroxide. Then (2 mL) of reagent (2.941×10^{-3}M) were added, and the solution was transferee into a volumetric flask (10 mL) and the volume made up to the mark with DDW. The absorbance of sample measured at (λ_{max}= 540nm) against the absorbance measured by the blank solution that prepared in the same sequence of addition except exchange the nickel ion with DDW.

3- A solution 2ml of reagent (2.941×10^{-3} M) was transferred to a beaker. The value of pH was fixed to be 9 by using nitric acid or/and sodium hydroxide. Five (mL) of nickel ion (3.400×10^{-4} M) were added and the solution was transferred into a volumetric flask (10 mL) and the volume was made up to the mark with DDW. The absorbance measured at (λ_{max}=540nm) against the absorbance measured by the blank solution that prepared in the same sequence of addition except exchange the nickel ion with DDW.

(2-6-4) Effect of time on the stability of complex:-

The effect of this factor was studied under optimal experimental conditions for silver and nickel complexes. The stability of complex checked by measuring the absorbance of the solution at different time of intervals from (5-60) min.

(2-6-5) The effect of temperature

In order to assess the effect of temperature on the forming of silver and nickel complexes, this factor was studied under optimal experimental conditions using different temperatures ranged from(5-45)°C by thermostatic circulator.

(2-7) Building of calibration curves

To measure the absorption of standard solutions of Ag (I) and Ni(II), separately, The processes as follows: -

(2-7-1) Calibration curves of silver

Various concentrations of silver ion, ranged from(0.372×10^{-5} to 4.09×10^{-5})M where prepared from stock solution of silver (1M). Five (mL) of each solution was mixed with 2mL of reagent [HPAI] at 4 pH.

(2-7-2) Calibration curves of nickel

Various concentrations of nickel ion, ranged from(3.4×10^{-5}M) to (8.17×10^{-5}M) where prepared from stock solution of nickel (1M). Five (mL) of each solution was mixed with 2mL of reagent [HPAI] at 9 pH.

(2-8) The stoichiometry of the complexes

The metal to ligand ratio is studied under optimal conditions by both mole ratio method and Job’s method (continuous variations).

(2-8-1) Job's Method

This method was carried out by mixing different volumes of solutions that have equal concentrations (4×10^{-4} M) of Ag(I) ion and Ni(II) with reagent (HPAI).

(2-8-2) Mole Ratio Method

This method was carried out by mixing known constant concentration of Ag(I) and Ni(II) ions equivalent to (1×10^{-4} M) ,with increasing concentrations and proportionate of ligand (HPAI) , ranged from (0.5×10^{-4}- 4.5×10^{-4})M.

(2-9) The effect of temperature on the complexes of Ag^+ and Ni^{++}

A- In order to study the effect of temperature, 5mL (1.000×10^{-4} M), of silver(I) and nickel(II) ions were taken. Then 2mL (2.000×10^{-4} M) of reagent(HPAI) were added by using the optimum pH. The solution was transferred into a volumetric flask (10mL) and made up to the mark with DDW. The volumetric flask placed in water bath at different temperatures ranged from (5-13) °C. The absorbance measured refer to absorption at the stoichiometry (A_s).

B- Five (mL) (1.000×10^{-4} M) of silver(I) and nickel(II) ions were taken. Then 2mL (4.000×10^{-4} M), of reagent(HPAI) were added by using the optimum pH. The solution was transferred into a volumetric flask (10mL) and made up to the mark with DDW. The volumetric flask placed in water bath at different temperatures ranged from (5-13)°C. The absorbance measured refer to the greatest absorption (A_m).

(2-10) The effect of masking agents

The effect of masking agents were studied under optimal conditions for silver and nickel ion along with reagent (HPAI) by adding in (0.1M) of masking agents, namely potassium, thiocynaite, ascorbic acid, thiourea and potassium sodium tartrate.

(2-11) Preparing the complexes of silver(I) and nickel(II) with the reagent as a solid substance.

In order to prepare of silver and nickel complexes the reagent(HPAI) was added to the solution of silver(I) and nickel(II) in ratio (2:1), respectively. That mean (2.000mmol,0.680gm) of ligand with (1.000mmol, 0.1698gm) and (1.000mmol 0.290 gm) of silver and nickel, respectively. The mixture was stirred and refluxed for (2hour). The recrystallized was carried out by ethanol and the solution was left for 96 hours. The product has been precipitated as red powder.

(2-12) Determination of some physical properties for the complexes.

(2-12-1) The effect of solubility

The solubility for nickel and silver complexes were studied using various solvents such as chloroform, water, carbon tetrachloride, ethanol, n-hexane, ethyl acetate, dimethylether.

(2-12-2) Melting point

In general, the complexes and reagent were dried at room temperature, then the melting point was determined for each one by using melting point instrument.

(2-12-3) Electrical conductivity

The values of electrical conductivity for silver and nickel solutions complexes were studied by preparing solutions (1×10^{-3} M) of silver and nickel complexes.

(2-13) Study of FT-IR spectra:-

FT- IR spectra were recorded for the compounds:-

1- Infrared spectrum of 4,5-diphenyl imidazole.

2- Infrared spectrum of ligand (HPAI).

3- Infrared spectrum of complex for Ag (I).

4- Infrared spectrum of complex for Ni(II).

(2-14) The (C.H.N.) analysis for reagent

Elemental analysis is a process where a sample of some material is analyzed for its elemental. The most common form of elemental analysis, CHN analysis. In this technique, a sample is burned in an excess of oxygen, and various traps collect the combustion products—carbon dioxide, water, and nitric oxide. The masses of these combustion products can be used to calculate the composition of the unknown sample. The reagent was performed on a (C.H.N.) analyzer by (C.H.N) type GGG.WWW.(49),(Itali).

(2-15) AAS analysis for filling dental

The filling dental was performed on a (AAS) analyzer using flameless atomic absorption spectrophotometer-670 Shimadzu Japan. The atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state.

(2-16) Applications

Determination of silver(I) ion:-

The study method was checked by determing the level of silver in dental filling sample as a certified reference material(CRM). This (CRM) made in Australia by SDI limited. The procedure have been done according to the reference(97). In this case, 0.1g of sample the filler dissolved in 10ml of HNO_3. The solution was filtrated then the sulfuric acid (0.3M) was added to solution to remove the interference of copper. The solution was filtrated to remove the precipitate that contains copper. Two milliliters of reagent[HPAI] were added to 5mL of result solution at pH=4. The solution transferred to a volumetric flask (10mL) and the volume was made up to the mark with DDW. The absorbance for the sample and blank was determined at (λ_{max}=514nm). This can be used to evaluate the accuracy for analysis.

* In this study, the accuracy for nickel(II) was not determined as the certified because of the reference material for Ni(II) was not available at the time of measurement.

(2-17) The precision

Relative standard deviation was determined as a function of the precision of data in all experiments. For this purpose 5ml for silver (I) in concentrations(0.93×10^{-4},1.39×10^{-4},2.79×10^{-4}), and nickel (II) in concentration (1.7×10^{-4}, 2.55×10^{-4}, 5.11×10^{-4}), were taken. Tow mL of reagent [HPAI] added at the optimum pH. The solution transferred to volumetric flask (10mL) and the volume was made up to the mark with DDW. The absorbance for the sample and blank was determined at λ_{max}. The results obtained in tables (2-2).

(2-18) Limit of detection

The detection limit (LOD) was determined as a function of sensitivity(94).

$$LOD = \frac{S}{m}$$

S= Standard deviation , m= Slope of the calibration curve

The limit of detection was determined for silver (I) in concentrations (0.93×10^{-4}, 1.39×10^{-4}, 2.79×10^{-4}), and for nickel (II) in concentration (1.7×10^{-4}, 2.55×10^{-4}, 5.11×10^{-4}).

The results of (2-16) and (2-17) was obtained in Tables (2-2), (2-3).

Tables (2-2) the precision and detection limit of silver(I)

Calculation of RSD and D.L at (2.79×10^{-4}M) of Ag(I)

No. Read	**Abs.(Xi)**	**Mean ($\bar{X}$)**	**($Xi-\bar{X}$)**	**$\Sigma(Xi-\bar{X})^2$**	$S = \sqrt{\frac{\Sigma(Xi - \bar{X})^2}{N-1}}$	$RSD = \frac{S}{\bar{X}}\times100$	**D.L (M)**
1	0.370	0.371	-1.25×10^{-3}	5.275×10^{-5}	4.193×10^{-3}	1.129%	1.91×10^{-6}
2	0.367		-4.25×10^{-3}				
3	0.377		5.75×10^{-3}				
4	0.371		-2.5×10^{-4}				

Calculation of RSD and D.L at (1.39×10^{-4}M) of Ag(I)

No. Read	**Abs.(Xi)**	**Mean ($\bar{X}$)**	**($Xi-\bar{X}$)**	**$\Sigma(Xi-\bar{X})^2$**	$S = \sqrt{\frac{\Sigma(Xi - \bar{X})^2}{N-1}}$	$RSD = \frac{S}{\bar{X}}\times100$	**D.L (M)**
1	0.299	0.297	1.75×10^{-3}	7.675×10^{-5}	5.058×10^{-3}	1.70%	2.30×10^{-6}
2	0.291		-6.25×10^{-3}				
3	0.303		5.75×10^{-3}				
4	0.296		-1.25×10^{-3}				

Calculation of RSD and D.L at (0.93×10^{-4}M) of Ag(I)

No. read	**Abs.(Xi)**	**Mean ($\bar{X}$)**	**($Xi-\bar{X}$)**	**$\Sigma(Xi-\bar{X})^2$**	$S = \sqrt{\frac{\Sigma(Xi - \bar{X})^2}{N-1}}$	$RSD = \frac{S}{\bar{X}}\times100$	**D.L (M)**
1	0.270	0.268	1.75×10^{-3}	1.027×10^{-4}	5.852×10^{-3}	2.18%	2.67×10^{-6}
2	0.267		-1.25×10^{-3}				
3	0.275		6.75×10^{-3}				
4	0.261		-7.25×10^{-3}				

Tables (2-3) the precision and detection limit of nickel (II)

Calculation of RSD and D.L at (1.7×10^{-4}M) of Ni(II)

No. read	**Abs.(Xi)**	**Mean ($\bar{X}$)**	**(Xi-$\bar{X}$)**	**Σ(Xi-$\bar{X}$)^2**	$S = \sqrt{\frac{\Sigma(Xi - \bar{X})^2}{N-1}}$	$RSD = \frac{S}{\bar{X}}\times100$	**D.L (M)**
1	0.317	0.308	9.25×10^{-3}	1.747×10^{-4}	7.632×10^{-3}	2.479	3.14×10^{-6}
2	0.310		2.25×10^{-3}				
3	0.299		-8.75×10^{-3}				
4	0.305		-2.75×10^{-3}				

Calculation of RSD and D.L at (2.55×10^{-4}M) of Ni(II)

No. read	**Abs.(Xi)**	**Mean ($\bar{X}$)**	**(Xi-$\bar{X}$)**	**Σ(Xi-$\bar{X}$)^2**	$S = \sqrt{\frac{\Sigma(Xi - \bar{X})^2}{N-1}}$	$RSD = \frac{S}{\bar{X}}\times100$	**D.L (M)**
1	0.342	0.336	6.25×10^{-3}	2.627×10^{-4}	9.358×10^{-3}	2.787	3.85×10^{-6}
2	0.331		-4.75×10^{-3}				
3	0.345		9.25×10^{-3}				
4	0.325		-0.01075				

Calculation of RSD and D.L at (5.11×10^{-4}M) of Ni(II)

No. read	**Abs.(Xi)**	**Mean ($\bar{X}$)**	**(Xi-$\bar{X}$)**	**Σ(Xi-$\bar{X}$)^2**	$S = \sqrt{\frac{\Sigma(Xi - \bar{X})^2}{N-1}}$	$RSD = \frac{S}{\bar{X}}\times100$	**D.L (M)**
1	0.734	0.728	6.5×10^{-3}	3.290×10^{-4}	0.010	1.439	4.11×10^{-6}
2	0.715		-0.0125				
3	0.723		-4.5×10^{-3}				
4	0.738		0.0105				

(3-1) Study of UV –visible Spectrum

The aim of this analysis is either to verify the purity of reagent or the interaction and formation of complexes.

1- The (UV –vis.) spectrum for the reagent [HPAI] dissolve in ethanol in Figure (3-1).

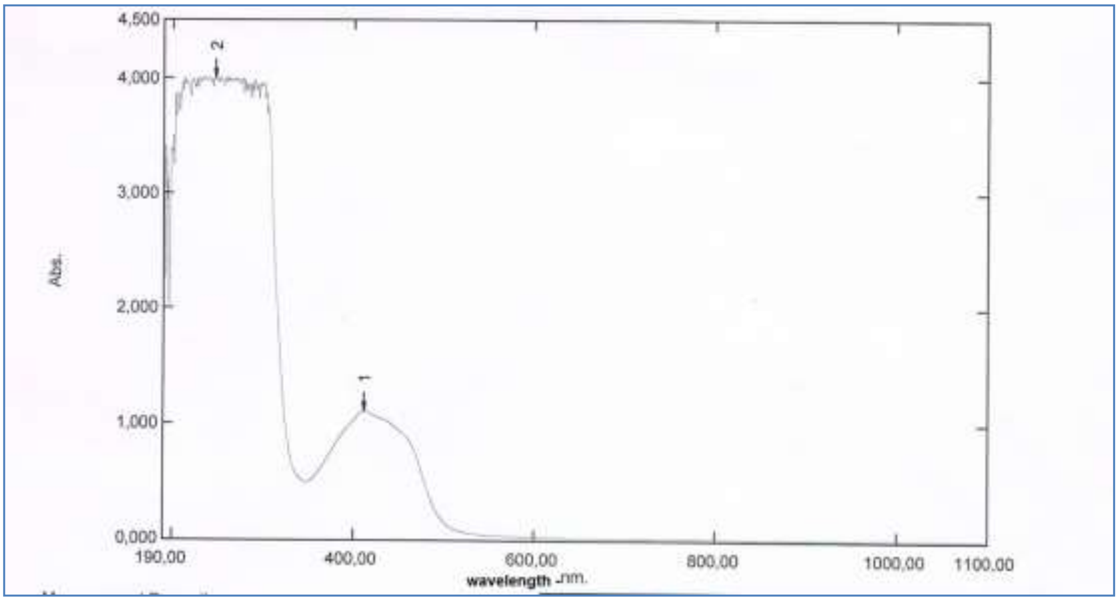


Figure (3-1) UV – visible spectrum for the reagent

2- The (UV –vis.) spectrum for the complex Ag(I) with the reagent [HPAI] in Figure (3-2).

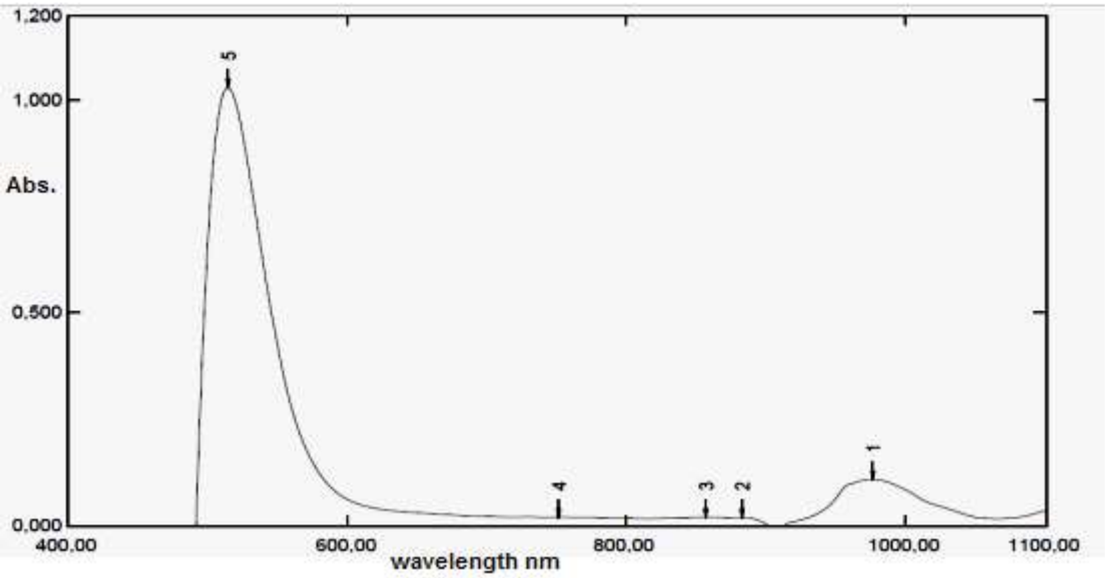


Figure (3-2) UV – visible spectrum for the Ag (I) complex

3- The (UV –vis.) spectrum for the complex Ni(II) with the reagent [HPAI] in Figure (3-3).

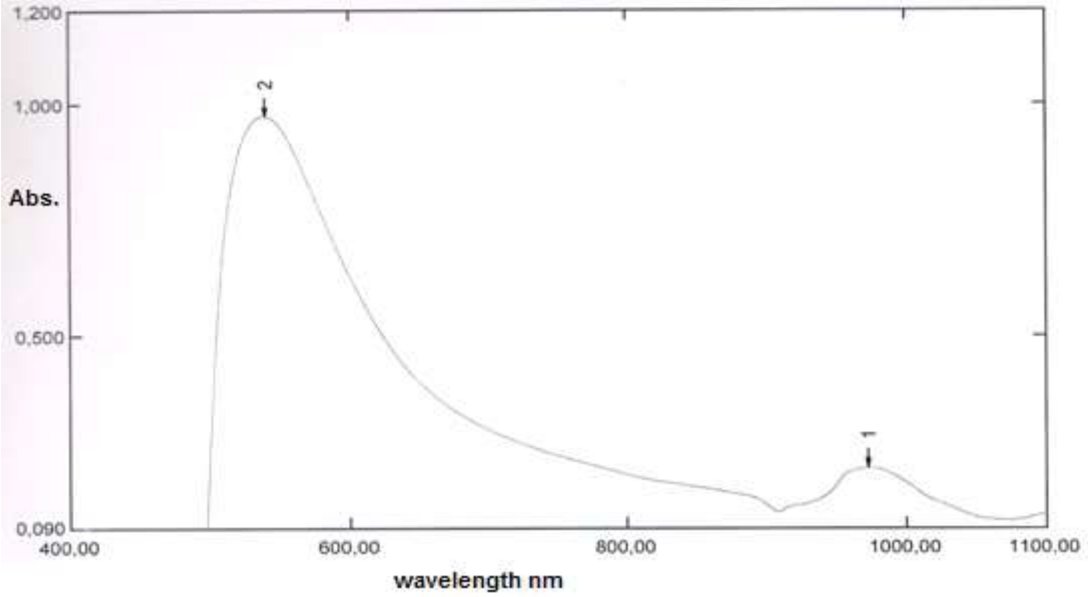


Figure (3-3) UV –visible spectrum for the Ni (II) complex

Figures(3-1), (3-2) and (3-3), show the UV – visible spectrums for reagent, complex of silver(I) and complex of nickel(II) respectively. It was found that high absorbance of reagent, complex of silver(I) and complex of nickel (II) was λ_{max} =412, λ_{max} =514, λ_{max} =540 respectively. The deference in λ_{max} refer to red shift found in the two complexes when compared with reagent.

(3-2) Study the best conditions to forming the complexes

(3-2-1) The Effect of (pH)

The effect of pH was studied. The results are illustrated in Figures (3-4) and (3-5).

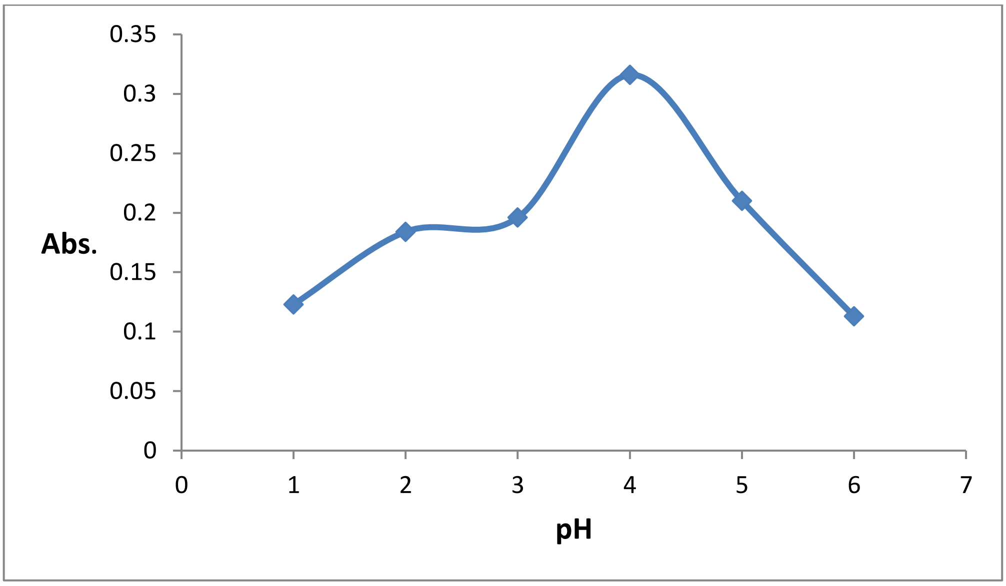


Figure (3-4) Effect of pH on the absorbance of the complex of Ag^+

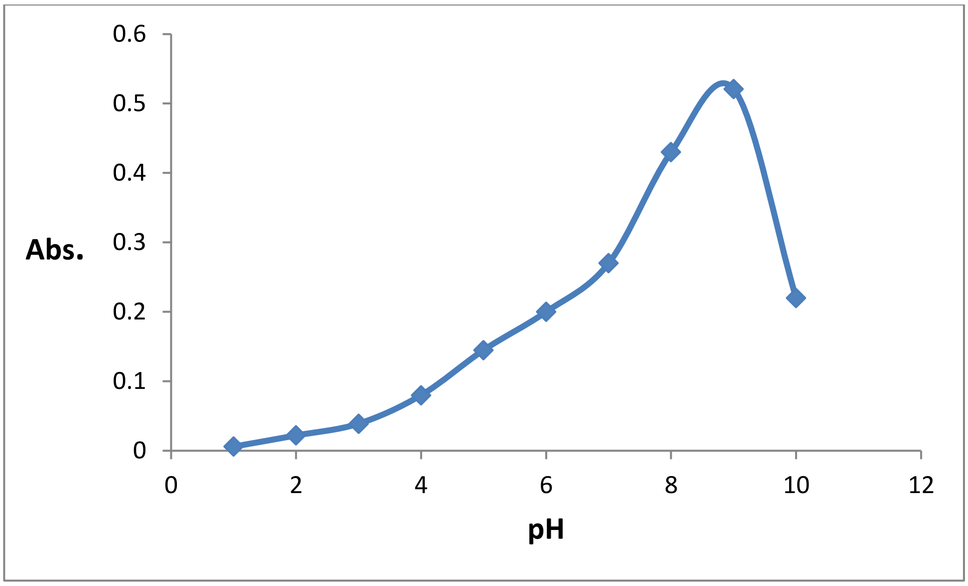


Figure (3-5) Effect of pH on the absorbance of the complex of Ni^{+2}

From the results in the Figure (3-4) the absorbance of silver increases with increasing pH up to 4 then decrease until pH =7 precipitate appears . The decreasing of the absorbance could be due to the precipitation of the ion or forming unstable complex (98,99). From the results in the Figure (3-5) the absorbance of nickel complex increases with increasing of pH. The absorbance was maximum at pH 9.0 when pH=10 the absorbance decrease. These results are in agreement with studies(84,89).

(3-2-2) Effect of reagent concentration

The effect of the organic reagent concentration upon absorbance was studied. The results are illustrated in Tables (3-1).

Table (3-1) Effect of reagent concentration on the absorbance of ions.

Conc. of reagent 10^{-4}	**Abs. of Ag^+**	**Abs. of Ni^{+2}**
3.60	0.017	0.091
7.30	0.056	0.166
11.02	0.109	0.234
14.70	0.145	0.289
18.38	0.175	0.367
22.05	0.23	0.433
25.73	0.28	0.458
29.41	0.307	0.521

The results show that the absorbance for both complexes increases with increasing the concentration of reagent [HPAI]. This result may be due to push the interaction to form of complex and give the best color intensity(100).

(3-2-3) Effect of sequence of addition

In order to illustrate the effect of sequence addition on the absorbance of the two complexes there were three sequence method of addition are described in Table (3-2).

Table (3-2) Effect of sequence of addition

sequence of addition number	sequence of addition	Abs. of Ag complex	Abs. of Ni complex
I	M+L+pH	0.316	0.521
II	M+ pH + L	0.355	0.480
III	L + pH + M	0.341	0.504

The three sequence of addition effected on the absorbance of the two complexes. The sequence of addition (II) and (III) show higher absorbance than the sequence of addition (I) for the Ag, complex but the sequence of addition (I)had been selected in this work because the other data not stable and the absorbance had been recorded after 20 minute. The sequence of addition (I) had been depended in case of Ni complex because it was recorded the higher absorbance than the sequence of addition (II) and (III). These results are in agreement with previous studies(101).

(3-2-4) Effect of time on the stability of complexes:-

Results of this study are described in table (3-3).

Table (3-3) Effect of time on the absorbance

Time\min	Abs. of Ag complex	Abs. of Ni complex
5	0.316	0.510
10	0.316	0.517
15	0.316	0.518
20	0.316	0.521
25	0.315	0.519
30	0.315	0.519
35	0.315	0.517
40	0.311	0.517
45	0.310	0.515
50	0.306	0.513
55	0.306	0.509
60	0.306	0.508
24h	0.306	0.508

Table (3-3) shows that the absorbance values of the silver complex, reaches its maximum after mixing the components and remains stable for at least 24 hour. These results are in agreement with previous studies(102). While the absorbance values of the nickel complex reaches to maximum value after (20) minutes and remains stable for at least 24 hours. These results are in agreement with previous studies (103).

(3-2-5) The effect of temperature

This study was performed at temperature between (5-50)C° at room temperature(14C°).the results of this study are described in Table (3-4).

Table (3-4) Effect of temperature on the absorbance of ions

Temperature/C°	Abs. of Ag complex	Abs. of Ni complex
5	0.330	0.540
10	0.320	0.530
15	0.310	0.520
20	0.300	0.510
25	0.290	0.500
30	0.280	0.490
35	0.270	0.480
40	0.260	0.470
45	0.250	0.460
50	0.240	0.450

The absorbance is gradually decreased when the temperatures increase that may be due to dissociation of the complexes(104,105).

(3-3) Calibration curves of complexes

The calibration curves were constructed according to the general procedure under the optimum condition. The results are shown in Figures (3-6) and (3-7).

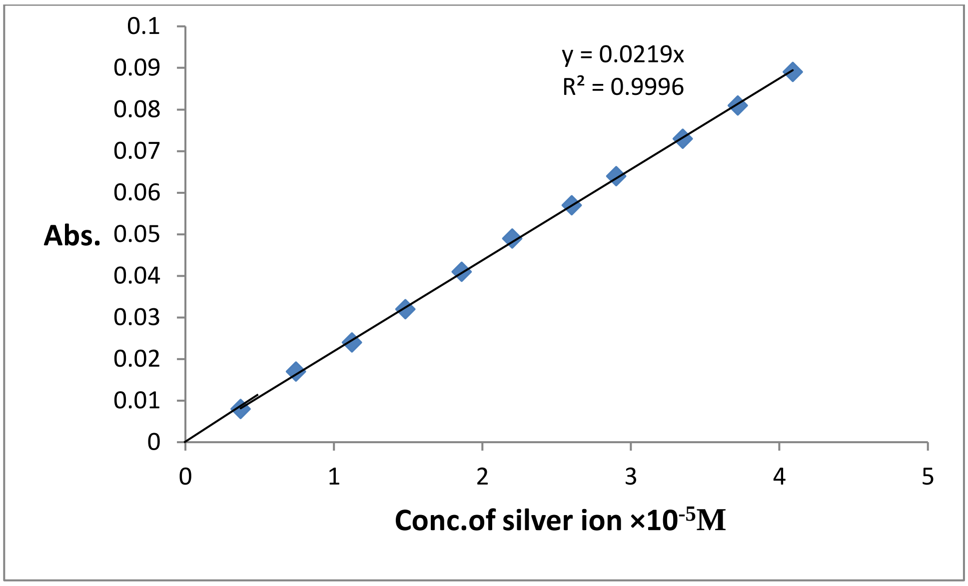


Figure (3-6) Calibration curve of Ag^+ complexes

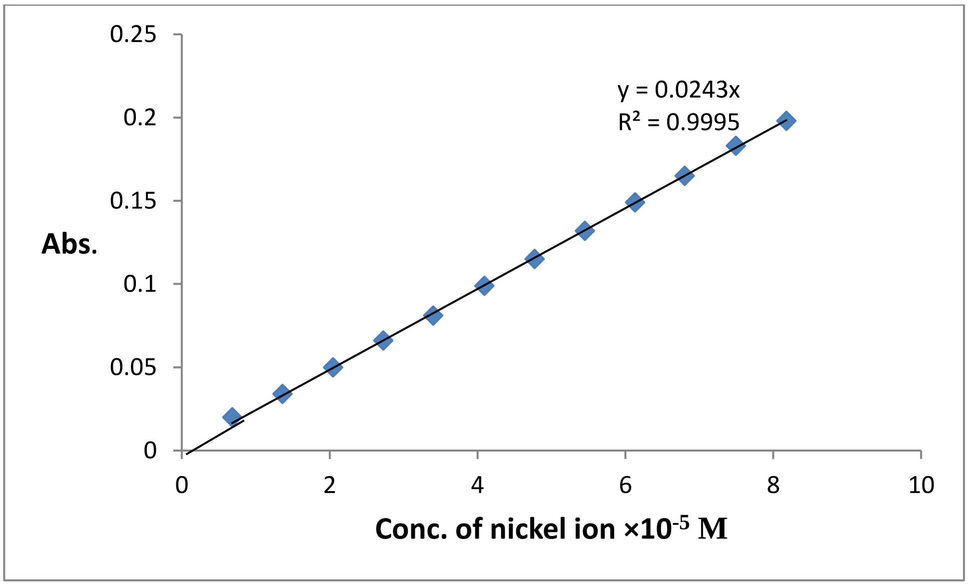


Figure (3-7) Calibration curve of the Ni^{2+}complex

A linear relationship between absorption and concentration had been obtained by plotting the relationship between the absorbance and concentration. The figure (3-6) shows that the silver ion is obeyed Beer's low in the concentrations range (0.372×10^{-5}- 4.09×10^{-5})M, the molar absorptivity (0.22×10^{4} L.mol^{-1}.cm^{-1}) and the sandel's sensitivity (0.049 µg.cm^{-2}), The result in figure (3-7) shows that the nickel ion is obeyed Beer's low in the concentrations range(0.681×10^{-5}- 8.177×10^{-5})M with molar absorptivity of (0.24×10^{4}L.mol^{-1}.cm^{-1}) and sandel's sensitivity (0.025µg.cm^{-2}). The results show that the nickel and the silver ions with ligand [HPAI] in the complexes absorb in intensity in the visible region and that mean it will be able to determine the low concentration of the nickel and the silver ions in this method.

(3-4) The stoichiometry of the complex

The stoichiometry (M : L) was determined by different methods to produce the best structure of complexes. In this study, there are two methods have been used as shown below.

(3-4-1) Job's Method

The Job's method was carried out by mixing different volumes of solutions with [HPAI] so that the final volume is equal to (10mL), Table (3-5) shows the results of this method(95).

Table (3-5): The results of Job's method (continuous variation) for the Ag (I) ion by using (HPAI) dissolved in ethanol.

(Vm/Vm+Vl)	Abs of Ag$^+$ complex	Abs. of Ni^{+2}complex
0.1	0.167	0.067
0.2	0.301	0.149
0.3	0.359	0.191
0.4	0.288	0.162
0.5	0.190	0.127
0.6	0.163	0.099
0.7	0.114	0.078
0.8	0.029	0.046

The Figures (3-8) and (3-9) show the relationships between the values of absorbance and volume ratio.

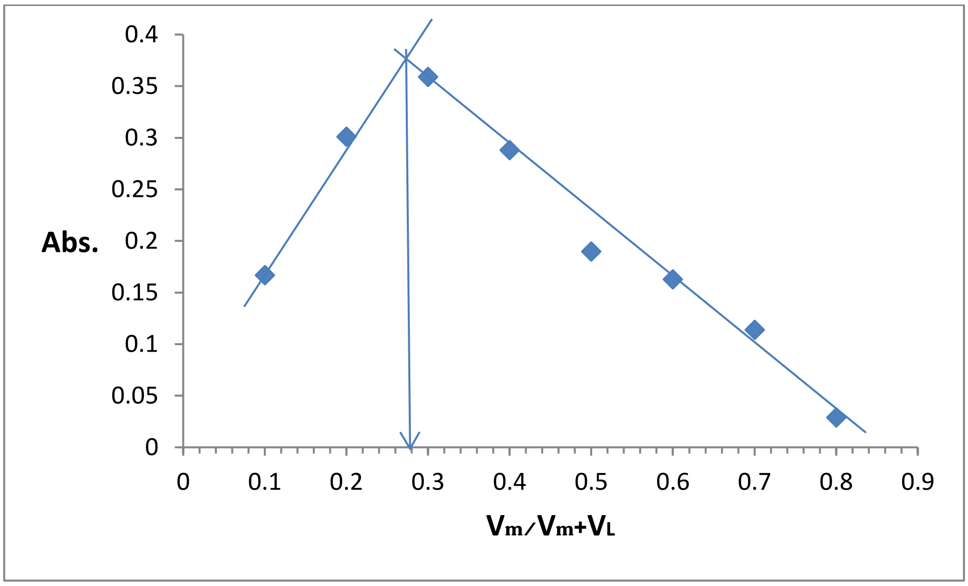


Figure (3-8) Job's method (continuous variation) for the Ag (I) ion with (HPAI).

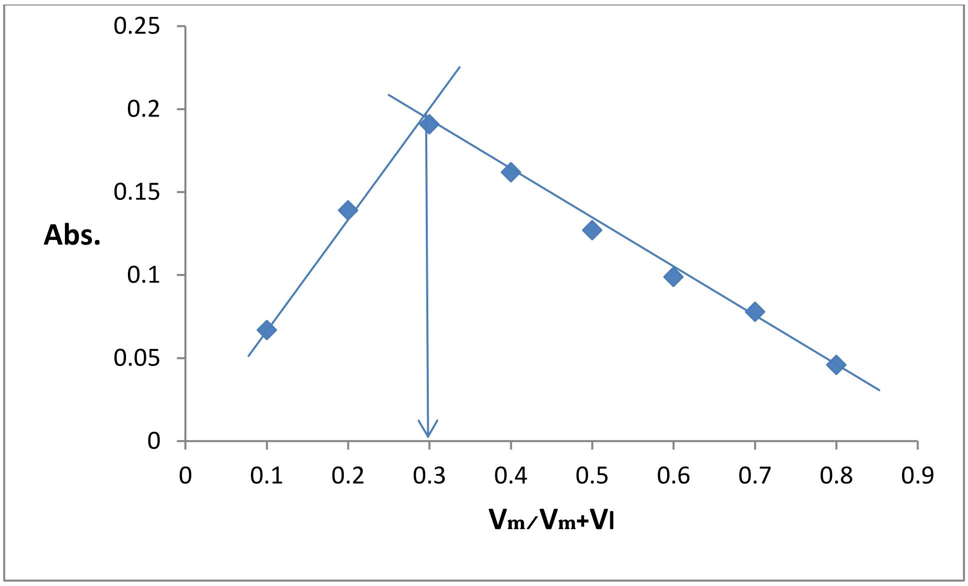


Figure (3-9) Job's method (continuous variation) for the Ni(II) ion with (HPAI).

From the results in the table (3-5) and figures (3-8), (3-9) show that the committed in complexes are (1:2) (M: L), which means one mole of metal with two mole of reagent (ML_2).

(3-4-2) Mole Ratio Method

The composition of the complex was studied by another method which is the mole ratio method. The fixed concentration of Ag(I) and Ni(II) ions, with proportionate and increasing volumes from (HPAI) ranged from (0.5–4.5) mL under optimum condition. Tables (3-6)and Figures (3-10), (3-11) show the results of this method(106).

Table(3-6) Mole ratio to Ag (I) ion andNi (II) ion by using the reagent(HPAI).

Cl/Cm	Abs. of Ag$^+$ complex	Abs. of Ni^{+2}complex
0.5	0.042	0.085
1	0.081	0.167
1.5	0.157	0.223
2	0.250	0.305
2.5	0.258	0.357
3	0.276	0.371
3.5	0.285	0.377
4	0.321	0.411
4.5	0.326	0.422

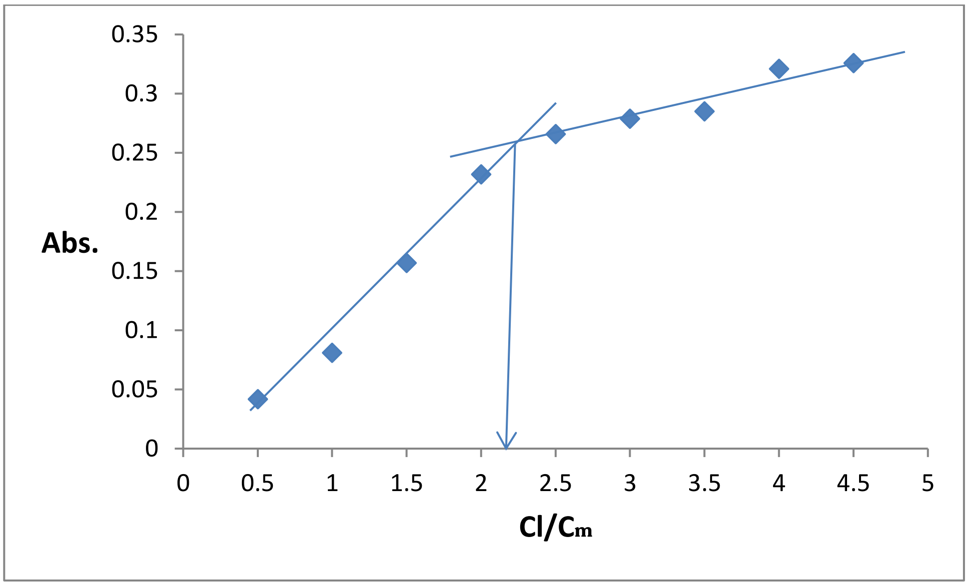


Figure (3-10) The mole ratio method to Ag(I) ion by using (HPAI).

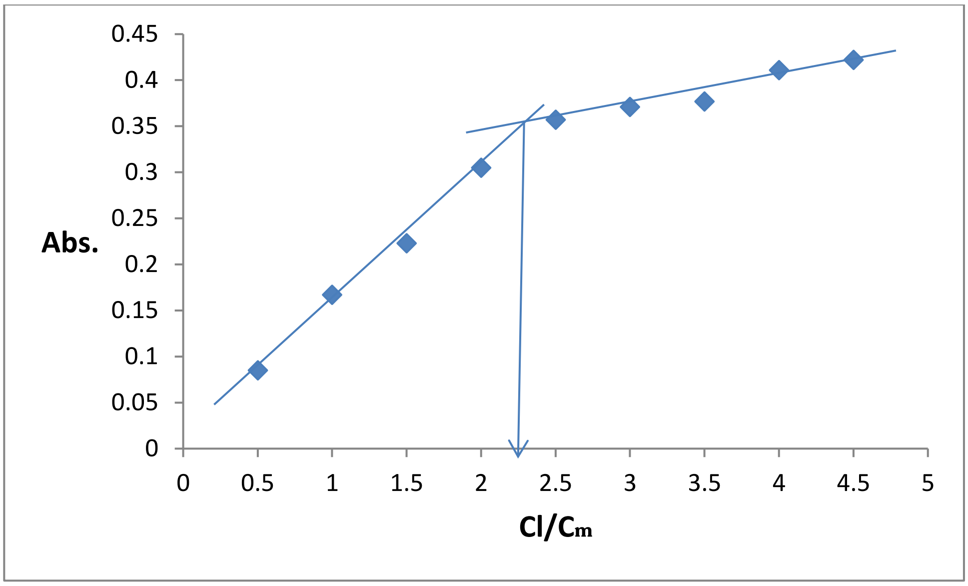


Figure (3-11) The mole ratio method to Ni(II) ion by using (HPAI).

In comparison with Job's method, similar ratio (1:2) (M: L) was found in silver and nickel complexes shown in Table (3-6) and Figures (3-10) and (3-11).

(3-5) Study the stability for the complexes.

Stability constants of the two complexes were calculated from the results of mole ratio method specially if the complexes are colored(107). This was carried out by drawing the equilibrium reaction for the complexes as shown below(108).

$$M^{+n} + nL^{-} \rightarrow MLn$$

$$\alpha c \qquad 2\alpha c \qquad (1-\alpha)c$$

$$K = \frac{[ML^{+n}]}{[M^{+n}][L^{-}]^{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3-1)$$

$$K = \frac{(1-\alpha)c}{\alpha c(n\alpha c)^n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3-2)$$

$$\alpha = \frac{Am-As}{Am} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3-3)$$

Where α : the degree of dissociation.

C : Concentration of metal.

K : Stability constant.

Am : The greatest absorption.

As : Absorption at the stoichiometry.

Table (3-7) The value of stability constant for silver(I)and nickel(II) complexes.

Complex	**Am**	**As**	**α**	**Ksta.**
$Ag[(HPAI)_2]^+$	0.326	0.250	0.233	1.520×10^9
$Ni[(HPAI)_2]^{+2}$	0.422	0.350	0.171	4.150×10^9

(3-6) The effect of temperature and the thermodynamic functions for the two complexes.

(3-6-1) The effect of temperature on the stability constant.

The values of stability constant of Ag (I) and Ni(II) ions, with (HPAI) were determined at different temperatures ranged from (5-13) °C. Tables (3-8)and (3-9) show the results of this study.

Table (3-8) The effect of temperature on the stability constant for the complex of silver(I).

t(C º)	**T/K**	**Am**	**As**	**α**	**K×10^9**
5	278	0.137	0.102	0.255	11.23
7	280	0.133	0.097	0.271	9.20
9	282	0.129	0.093	0.279	8.30
11	284	0.125	0.089	0.288	7.46
13	286	0.121	0.085	0.297	6.71

Table (3-9) The effect of temperature on the stability constant for the complex of nickel(II).

t(C º)	T/K	**Am**	**As**	α	K×10^9
5	278	0.224	0.186	0.170	4.22
10	280	0.220	0.182	0.173	3.99
15	282	0.216	0.178	0.176	3.78
20	284	0.212	0.174	0.179	3.58
25	286	0.208	0.170	0.182	3.40

(3-6-2)Determination of thermodynamic functions for the two complexes :-

The effect of the temperature on thermodynamic functions for the silver and nickel complexes was determined from the results in the previous section(3-6-1)and the equations from the introduction, so the results of determined the thermodynamic functions(ΔH, ΔG, ΔS) are illustrated in tables (3-10),(3-11).

Table (3-10) The effect of temperature on thermodynamic functions for the silver complex

T(K)	$1/T10^{-3}.K^{-1}$	Log K	ΔH	ΔG(K.J/mol)	ΔS(K.J/mol.K)
278	3.61	9.050	-36.780	-48.070	0.041
280	3.57	8.964		-48.056	0.040
282	3.55	8.920		-48.019	0.039
284	3.52	8.873		-48.147	0.040
286	3.49	8.826		-48.229	0.040

Table (3-11) The effect of temperature on thermodynamic functions for the nickel complex

T(K)	$1/T10^{-3}.K^{-1}$	Log K	ΔH (K.J/mol)	ΔG(K.J/mol)	ΔS (K.J/mol.K)
278	3.59	9.625	-17.960	-51.124	0.119
280	3.57	9.601		-51.358	0.119
282	3.55	9.577		-51.563	0.119
284	3.52	9.554		-51.820	0.119
286	3.49	9.531		-52.082	0.119

From the Tables (3-10) ,(3-11) that the negative sign of the values of enthalpy shows that the reaction between Ag(I) and Ni(II)ions, with [HPAI] were exothermic and these means increase in the possibility of formation complexes with decreasing temperature in general for this type of reaction ligand (109).The negative sign of the free energy of Ag(I) and Ni(II) ions, with ligand (HPAI) explain that reactions are spontaneously. The values of entropy approach to zero and each other demonstrated to the spontaneous. Reaction (less random) and stability of complex, these study are in agreement with a previously studies(110,111).

(3-7) The effect of masking agent

To test the effect of masking agent on the selectivity on determination of silver(I) ion and Ni(II) ion. The result show in the figure (3-12).

Table(3-12): The effect of some masking agent on the absorbance of Ni(II) ion and Ag(I) ion

Masking agent	Abs. of Ag^{+} complex	Abs. of Ni^{+2} complex
Without masking agent	0.316	0.521
Thiourea	0.144	0.811
Potassium Thiocynaite	0.125	0.901
Ascorbic acid	0.891	0.040
Potassium sodium tartrate	0.020	0.692

The result in table (3-12) shows that the value of the absorbance for all the masking agent in the table except ascorbic acid decrease the absorbance of the silver complex and the value of the absorbance of potassium sodium tartrate refer to that it masking the silver ion from the solution. In the other hand the value of the absorbance of the nickel complex increase with all the masking agent in the table except ascorbic acid decrease the absorbance of nickel complex. That mean the ascorbic acid masking the nickel from the solution.

(3-8) Determination of some physical properties for the complexes

(3-8-1) Melting point

Melting point of two complexes and ligand (HPAI) were measured. Table (3-13) shows the results.

Table (3-13) Melting points for the silver, nickel complexes and [HPAI] reagent.

Material	**Melting point °C**
HPAI	**210-213**
$Ag[HPAI]^+$	**215-217**
$Ni[HPA]^{++}$	**198-203**

(3-8-2) The effect of solubility

The solubility of two complexes had been tested with some of polar and nonpolar solvent. Results of this study described in tables (3-14)

Table (3-14) The solubility of complexes

Solvent	**Complex of Ag^+**	**Complex of Ni^{+2}**
Chloroform	+	+
Water	+	+
Carbon tetrachloride	÷	÷
Ethanol	+	+
N-hexane	÷	÷
Ethel acetate	**-**	**-**
Dimethylether	+	+

÷ :soluble - :insoluble + :slightly soluble

Table(3-14) show that the two solid complexes soluble in chloroform, water, ethanol and dimethylether. In the other hand insoluble in ethel acetate and slightly soluble in n-hexane and carbon tetrachloride.

(3-8-3) Electrical conductivity

The electrical conductivity measured is very important to know the structures of the compounds in it's solutions(108). The electrical conductivity helps to reaching forms the stereochemistry of complexes. As the complexes charged is directly proportional to the degree of the electrical conductivity(112). Preferred to use polar solvents such as ethanol, methanol, Nitromethan, etc. because they have high insulation electrical constant and low viscosity(113) .The table (3-15) show the electrical conductivity for electrolytes in different solvent.

Table (3-15) electrical conductivity for different electrolyte at concentration (1×10^{-3})M(114)

Solvent	**Non-Electrolyte**	**Electrolyte type**			
		1:1	**1:2**	**1:3**	**1:4**
Water	**0.0**	**120**	**240**	**360**	**480**
Ethanol	**0-20**	**35-45**	**70-90**	**120**	**160**
Nitromethan	**0-20**	**75-95**	**150-180**	**220-260**	**290-330**
Methyl	**0-30**	**120-160**	**220-300**	**340-420**	**500**
DMF	**0-30**	**65-90**	**130-170**	**200-240**	**300**
DMSO	**0-20**	**30-40**	**70-80**	**-----**	**-----**

Table (3-16) electrical conductivity for Ag^+ and Ni^{+2}

No	**Complex**	**Electrical conductivity μS.cm-1**
		In ethanol
1	$[Ag(HPAI)]^+$	45
2	$[Ni(HPAI)]^{++}$	72

By compared the results in Table (3-15) with the table (3-14) that shows the two complexes have charged and the ratio of the charge for silver was(1:1) and for nickel (1:2).

(3-9) Study of FT-IR spectra(115-116)

The result of FT-IR analysis are shown in figures (3-12), (3-13), (3-14) and (3-15).

(3-9-1) FT-IR of reagent[HPAI]

FT-IR spectrum of reagent was determined, in comparison with that for (4,5-Diphenylimidazole) as shown in Figure (3-12)and (3-13). A new reagent bands at ν(1373cm^{-1}), ν(1026cm^{-1}), ν(3061cm^{-1}) were found in spectrum due to ν(N=N) for azo group , ν(C-O) and ν(O-H) for phenol respectively. In addition other new bands were also found as well as the presence of joint bands of reagent with spectrum of 4,5-diphenylimidazole. This results can be explained that the reagent [HPAI] was produced. The comparison results between the bands of the reagent and 4,5diphenylimidazole show in Table(3-17).

Table (3-17) Typical FT-IR absorption frequencies for reagent and 4,5-diphenyl imidazole

Compound	ν (N-H)	ν(O-H)	ν(C=N)	ν(N=N)	ν(C-N)	ν(C-O)	δ (O-H)
4,5-Diphenyl imidazole)	3400$_{(m)}$	/	1600$_{(s)}$	/	1050$_{(m)}$	/	/
[HPAI]	3392$_{(w)}$	3061$_{(w)}$	1597$_{(s)}$	1373$_{(m)}$	1072$_{(m)}$	1026$_{(w)}$	696 ,650$_{(s)}$

(3-9-2) FT-IR for complex[Ag(HPAI)]$^{+}$

The FT-IR spectra were determined for complex of silver as shown in Figure (3-14):-

1-The stretching frequencies of the (N-H) group have shifted from (3392cm^{-1}) in the ligand to (3421cm^{-1}) in the complex which suggests that the electron pairs on N group is involved in bonding.

2-Apeak in (1600cm^{-1}) due to ν(C=N).

3-The peak in (1026cm^{-1}) due to ν(C-O).

4-The peak at (1072 cm^{-1}) due to ν(C-N).

5-Two strong peak at (761 cm^{-1}),(700 cm^{-1}) which is assigned to the δ (O-H) out of plan.

6-The weak peak at (1384cm^{-1}) was assigned to the ν(N=N).

7-The peak at (497cm^{-1}) due to ν(Ag-N).

(3-9-3) FT-IR for complex[Ni(HPAI)]$^{++}$

The FT-IR spectra were determined for complex of nickel as shown in Figure (3-15):-

The stretching frequencies of the (N-H) group have shifted from (3392cm^{-1}) in the ligand to (3448cm^{-1}) in the complex ,which suggests that the electron pairs on N group is involved in bonding .

2-strong peak in (1602cm^{-1}) due to ν(C=N).

3-The peak in (1026cm^{-1}) due to ν(C-O).

4-The to peak at 1602cm^{-1}) was assigned to the ν(C=N).

5-The peak at (1072 cm^{-1}) due to ν(C-N).

6-Two strong peak at (763 cm^{-1}),(700 cm^{-1}) which is assigned to the δ (O-H) out of plan for phenyl.

7-The strong peak at (1384cm^{-1}) was assigned to the ν(N=N)

8-The peak at (450cm^{-1}) due to ν(Ni-N).

Table (3-18) Typical FT-IR absorption frequencies for reagent and complexes

Compound	**Stretching vibration ν N-H**	νC=N.	νO-H	**δO-H** out of plan	**νC-O**	**νN=N**	**νC-N**	**νM-N**
[HPAI]	3392$_{(w)}$	1597$_{(s)}$	3061$_{(w)}$	696-650$_{(s)}$	1026$_{(w)}$	1373$_{(m)}$	1072$_{(m)}$	——
[Ag(HPAI)]$^{+}$	3421$_{(w)}$	1600$_{(w)}$	3506$_{(w)}$	761-700$_{(s)}$	1026$_{(w)}$	1384$_{(m)}$	1072$_{(m)}$	497$_{(w)}$
[Ni(HPAI)]$^{++}$	3448$_{(w)}$	1602$_{(w)}$	3647$_{(w)}$	763-700$_{(s)}$	1026$_{(w)}$	1384$_{(s)}$	1072$_{(m)}$	450$_{(w)}$

w: weak, s:strong, m:medium

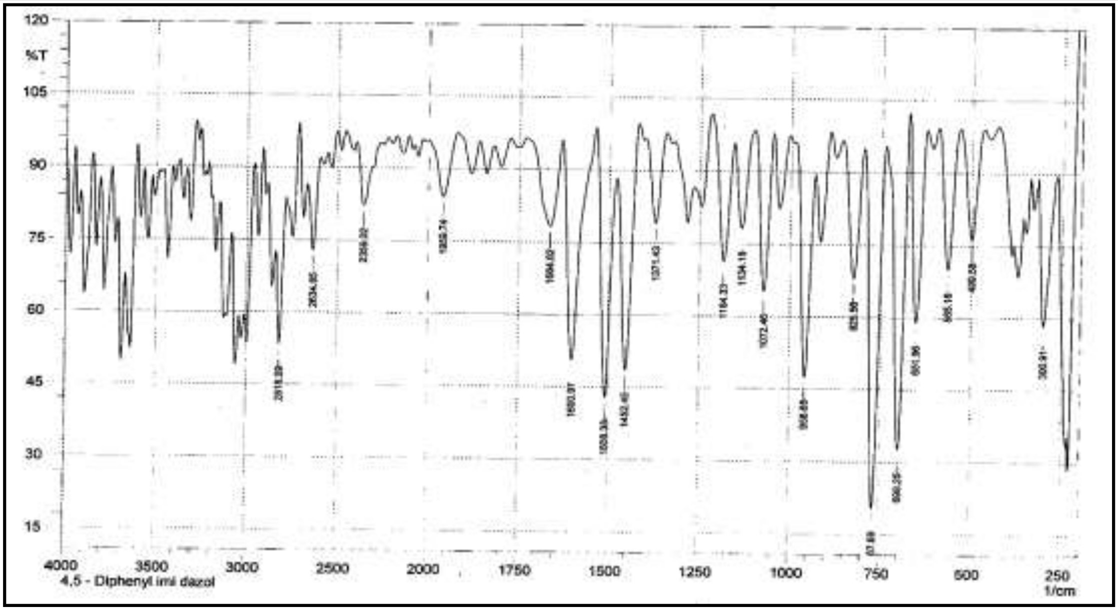


Figure (3-12) FT-IR spectrum of the starting material 4,5- diphenyl imidazole

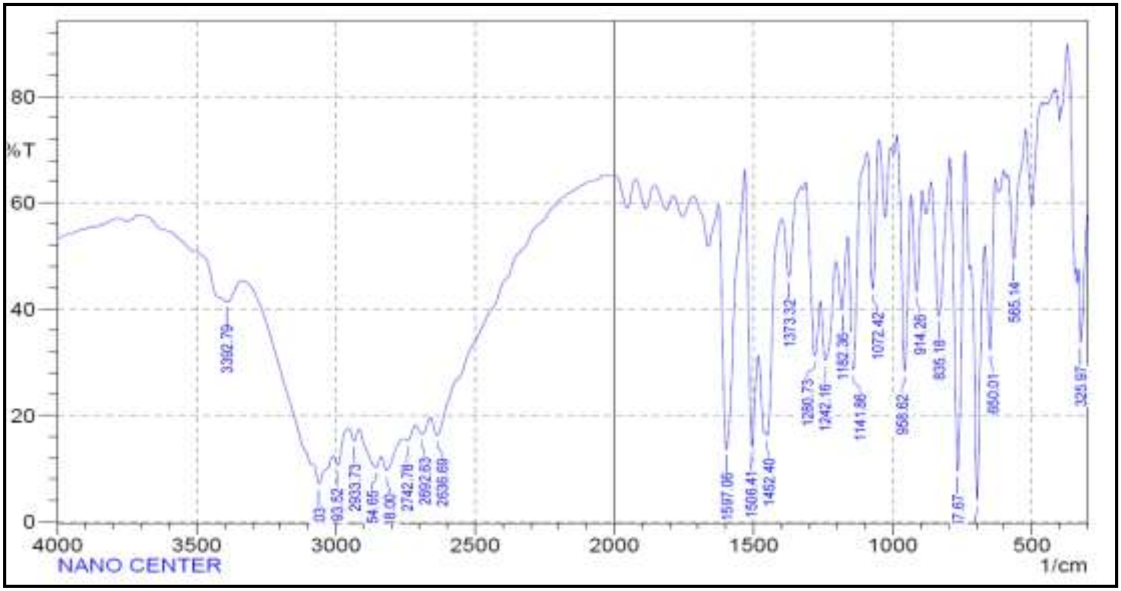


Figure (3-13) FT-IR spectrum of reagent

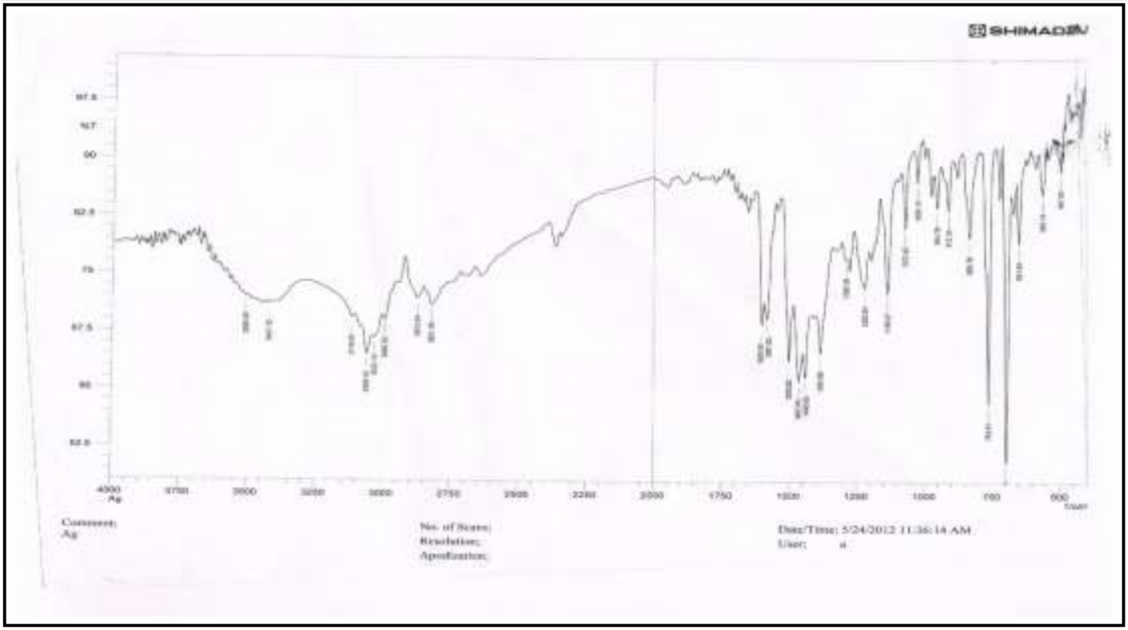


Figure (3-14) FT-IR spectrum of silver(I) complex

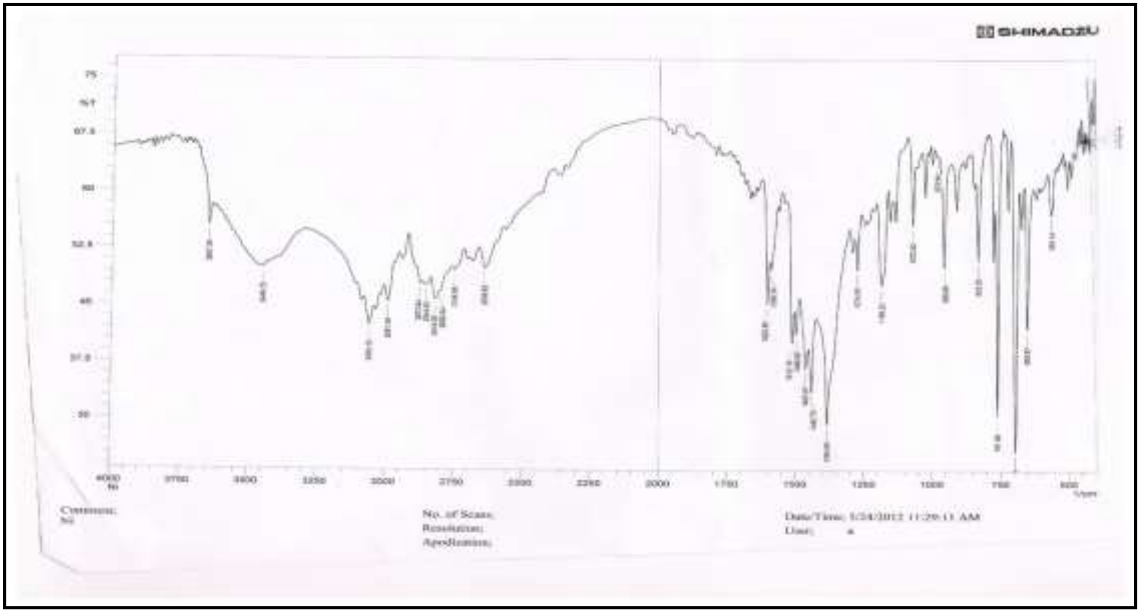


Figure (3-15) FT-IR spectrum of nickel(II) complex

(3-10) Elemental analysis (C.H.N)

The reagent investigated by technology quantitative analysis of elements. The results have been shown in Table(3-19), when comparison the values obtained in practice with the theoretically calculated values observed a rapprochement between them, which confirms the true formulas proposed reagent.

(3-19) Some of physical properties and C.H.N analysis for reagent [HPAI]

Compound	**M.wt**	**colour**	**M.P. C^0**	**Yield%**	**C%**	**H%**	**N%**
4,5-Diphenyl imidazol	220	White	229-230	75%	/	/	/
[HPAI]	340	Yellow	210-213	80%	74.10 73.83	4.74 4.55	16.46 16.21

(3-11) Application

The Silver(I) ion

The concentration of the silver was determined in a sample of filler and it was (41.3%) for four value at the trust level 95%. The components ratios were on the cover of the filler and the concentration of Ag was (40%), Sn(30.3%), Cu(28.7%). The two analytical results had been compared and Table (3-20)shows the results.

Table (3-20) The results of the application for silver(I) in sample of filler

Contain	Spectrophotometric method	Er%	Re%
40%	41.300%	-1.300	101.300

The results in Table (3-20) emphasized the success of a new spectrophotometric method way to determine the silver(I) ion, Where the results from the new analytical spectrophotometric method is close to results which showed on the cover of the filler. This result indicate that we can use this method with the different samples.

(3-12) The suggested figure for complexes

From FT-IR spectra of complexes, the suggested structures of complexes for silver(I) complex was linear and hybridization sp$^{(117)}$ Figure(3-16), for nickel(II) complex was tetrahedral $^{(118)}$ Figure(3-17).

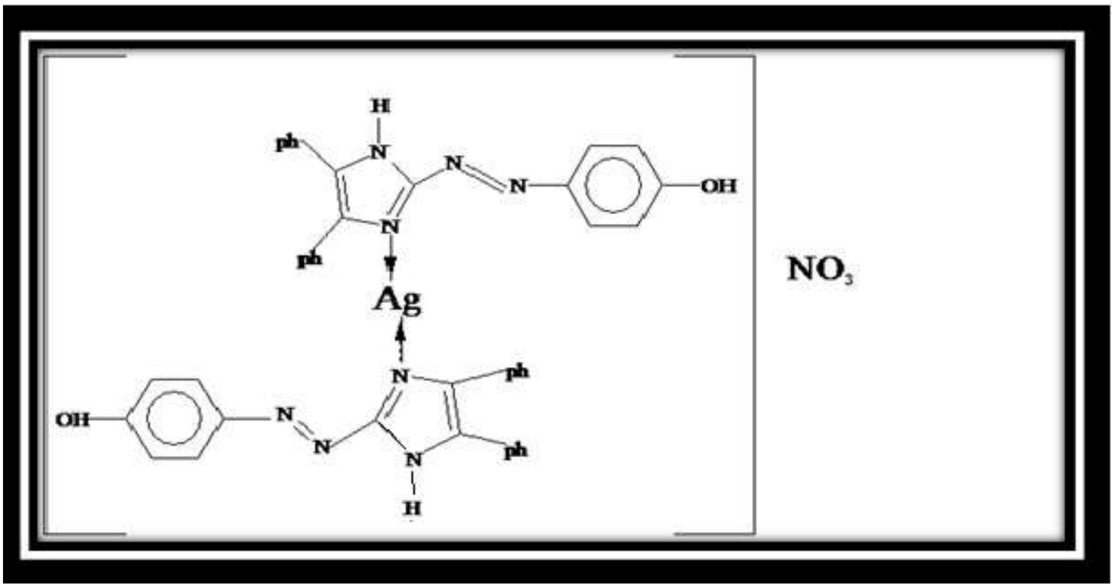


Figure (3-16) The suggested figure for the silver complex

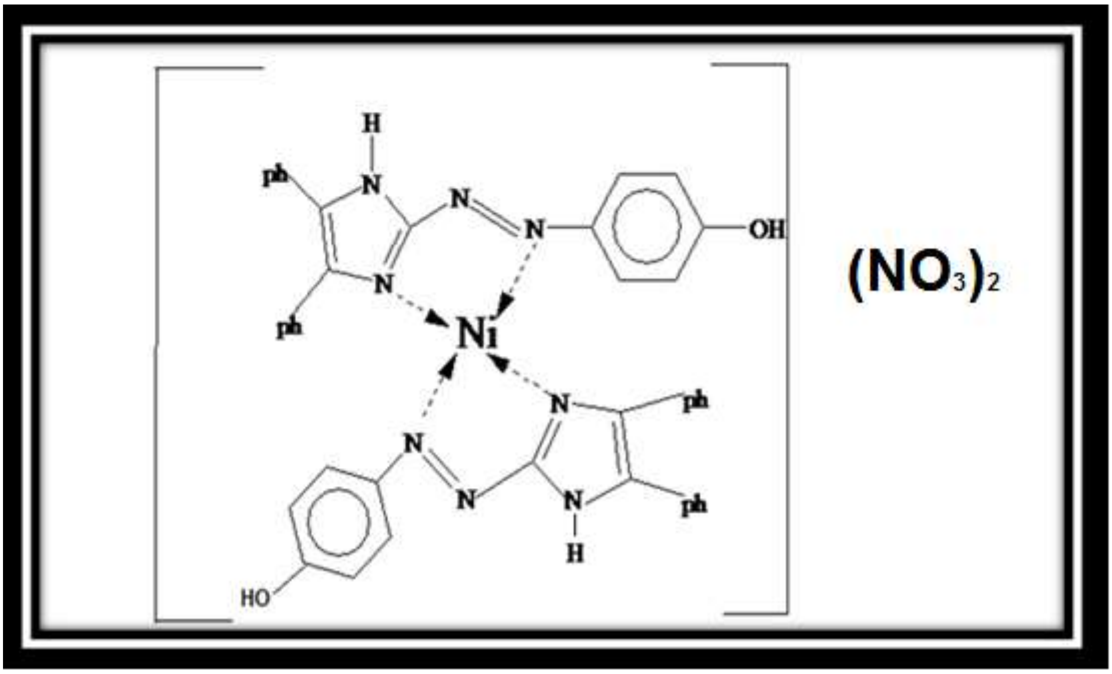


Figure (3-17) The suggested figure for the nickel complex

(3-13) The sensitivity of the spectrophotometric method.

The term (detection limit) used to show the sensitivity of the spectrophotometric method. The detection limit of the silver(I) ion was (1.9×10^{-6}M), while the detection limit of the nickel(II) ion was (3.14×10^{-6}M), These values that show the spectrophotomtric method used to determinate of the silver and the nickel is sensitive

(3-14) Conclusions

1- The simplify of preparation the reagent [HPAI] by mixing derivatives of imidazole with diazonium chloride solution.

2- The λ_{max} for the two complexes were higher than reagent that show the ability of using the reagent to determinate the silver(I) and the nickel(II) ion.

3- The determination of Ag^+ and Ni^{+2} should be done under the optimum conditions that reached to them in this study.

4- The stoichiometry of reagent to metal were 2:1.

5-The values of stability constant show that the complexes in high stable and the nickel(II) complex more stable than the silver(I) complex.

6-The values of ΔH show that the forming of the silver and the nickel complexes exothermic.

7- The negative charge of ΔG show that the reaction of forming of the two complexes was spontaneously.

8- The study of conductivity show that the two complexes were charged.

9- The values of relative standard deviation show that the analytical method is a highly precision and rapid method for the determination of the silver(I) and the nickel(II) ions.

(3-15) Recommendations

1- Possibility of determination some another ions with the reagent [HPAI].

2-Study the possibility of use the reagent [HPAI] and its complexes in industrial.

3-Using the reagent [HPAI] as an intermediate in organic chemistry to prepare the derivatives reagent.

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الخلاصة

حضرالليكند الجديد 2-[4-hydroxy phenyl)azo] 4,5-diphenyl imidazole بواسطة مزج محلول كلوريد الديازونيوم مع ال 4,5-diphenyl imidazole. الليكند المحضر شخص بواسطة طيف الاشعة تحت الحمراء وطيف الاشعة المرئية – فوق البنفسجية وبتحليل العناصر C.H.N. الفضة الاحادي يكون معقد ذو لون برتقالي عند الطول الموجي الاعظم λ_{max} =514 وبينما يعطي النيكل معقد ذو لون احمر عند الطول الموجي الاعظم λ_{max} =540 . تمت دراسة الظروف المثلى لتكوين المعقدين فوجد ان افضل دالة حامضية لمعقدي الفضة وللنيكل هي 4و9 على التوالي مع بقاء المعقدين ثابتين لاكثر من 24 ساعة عند تلك الدالة الحامضية. كما ودرست نسبة الكاشف الى الفلز بواسطة طريقتي جوب والنسب المولية وكانت نسبة الليكند الى الفلز1:2. حسبت الدوال الثرموديناميكية ΔH و$\Delta S, \Delta G$ و بينت النتائج ان التفاعل بين الليكند وكل من ايوني الفضة والنيكل هي تفاعلات باعثة للحرارة وهذا يدل على زيادة في تكوين المعقد مع الانخفاض في درجات الحرارة. وان قيمة ثابت الاستقرارية هي 1.520×10^{9} و 4.150×10^{9} للفضة والنيكل على التوالي, وهذا يدل على الاستقرارية العالية للمعقدين. ايون الفضة يخضع لقانون لامبرت - بير في مدى من التراكيز $(0.372\times10^{-5}-4.09\times10^{-5})$M وكان حد الكشف $(1.91\times10^{-6}$ M) مع امتصاصية مولارية مقدارها $(0.22\times10^{4}$ L.mol^{-1}.cm^{-1}) وحساسية ساندل $(0.049\mu g.cm^{-2})$. ايون النيكل يخضع لقانون لامبرت –بير ضمن مدى من التراكيز$(0.681\times10^{-5}-8.177\times10^{-5})$M وكان حد الكشف $(3.14\times10^{-6}$M), مع امتصاصية مولارية $(0.24\times10^{4}$ L.mol^{-1}.cm^{-1}) وكانت حساسية ساندل $(0.025\mu g.cm^{-2}\mu g.cm^{-2})$. درست تاثيرات مختلفة على تكون المعقدات منها تأثير اضافة الايونات الموجبة والسالبة وعوامل الحجب وتغير تركيز الليكند وتعاقب الاضافة وتاثير درجة الحرارة. كما ودرست بعض الخواص الفيزياوية للمعقدين مثل التوصيلية, درجة الانصهار وقابلية ذوبانية المعقدين في مذيبات مختلفة . شخصت المعقدات المحضرة بواسطة طيف الاشعة تحت الحمراء وطيف الاشعة المرئية – فوق البنفسجية .كان الانحراف القياسي النسبي %(1.129-2.18) و %(1.439-2.787) لكل من الفضة والنيكل على التوالي. اختبرت هذه الطريقة التحليلية بواسطة تقدير الفضة في حشوة الاسنان وتقدير النيكل في عينة من ماء جدول الحسينية والنتائج المستحصلة تبين ان هذه الطريقة حساسة وسريعة وغير مكلفة في تقدير كل من الفضة والنيكل.

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة كربلاء

كلية العلوم

تحضير وتشخيص كاشف أزو

لأستخدامه في تقدير أيوني الفضة الأحادي والنيكل الثنائي كمعقدات بأستخدام الطريقة الطيفية

رساله مقدمة
الى جامعة كربلاء - كلية العلوم
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من قبل

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بأشراف

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