# CHAPTER I

# INTRODUCTION

## 1.1 Introduction

Spectrophotometry is an instrumental method of analysis widely adopted because of the high precision, sensitivity, and availability of the instruments used. Spectrophotometric methods enable nearly all the elements to be determined over a wide range of concenteration in most materials. They are of particular importance in trace analysis, testing of high purity materials, environmental studies and biochemistry. The basis of spectrophotometric methods is the simple relationship between the absorption of radiation by a solution and the concentration of the coloured species in that solution. This relationship is governed by ***Beer's*** law. In order to determine species spectrophotometrically it is usually converted into a coloured compounds. The colour of the substance itself is utilized much less than often.

However, spectrophotometry is one of the most useful tools for elucidating the complex ions in solution and for determining their formation constants. The power of technique lies in the fact that quantitative absorption measurements can be performed without fear of disturbing the equilibria under consideration. Although most spectrophotometric studies of complexes involve systems in which one of the reactants or the products absorbs, this condition is not necessary provided that one of the components can be caused to participate in a complete equilibrium that does produce an absorbing species.

There is a close relation between the absorption spectrum of a substance and its electronic structure. A molecule (or ions) exhibits absorption in the visible or ultraviolet range, when radiation (photons) causes an electronic transition, of some of the valancy electrons from ground state to an exited state. Irradiation causes variation in the electronic energy of molecules containing one or more chromophoric groups i.e; groups with unsaturated linkages. Some examples of common chromophoric groups are :C=O,-N=N-, C=N-NH-, C=N, C=N and C=S. Two or more chromophoric groups in the molecule often enhance one another's effect, to deepen the colour by displacing the absorption maximum ( $\lambda_{max}$ ) toward longer wavelength.

As the pH increased, spectrophotometric reagents ionize and their electronic structures change, leading mostly to a shift in the absorption maximum. Ionization also causes polarization of the chromophoric system.

The term ionization constants refers to those constants which are used to express the strength of acids and bases. In heterocyclic chemistry, the study of such constants has many useful applications, e.g; they can be used to investigate the point of equilibrium in tautomeric substances and to help in establishing the structure of newly isolated substances.

Various methods are known for determining the ionization constant of chemical compounds, the most important of which are the potentiometric, polarographic and spectrophotometric methods. Raman spectroscopy and nuclear magnetic resonance were also used for determining low pK values, vis, strong acids and weak bases. The determination of ionization constants by conductometry is also known to be an accurate method but not very versatile for measuring second or third ionization constant in polyionic substances.

Measuring the increase in solubility at various pH values may give approximate ionization constants in cases where potentiometry, polarography, spectrophotometry and conductometry can not be used, e.g; highly insoluble substances with no useful spectra.

Some organic compounds, especially those containing ionizable center directly attached to the π-system of the molecule undergo a remarkable colour changes through their ionization process. Mostly these compounds can be used as acid-base indicators. The importance of such compounds increases if they have chromophoric properties, thus, acting as metal indicators.

The chromophoric reagents are capable of forming complexes with a number of cations, the formation of these complexes is being accompanied by a change in colour at a certain pH value. Such chelates are characterized by their high stability. A large number of such organic reagents giving visible colour reaction with metal ions are known to analytical chemists. Their investigation was directed toward their application in colorimetric analysis specially for substances in small amount or traces, where application of other convential methods of analysis is impossible. The utility of such compounds is hence most frequently important from several points, namely, high selectivity of reaction, high solubility of the coloured complex, exact stoichiometric composition, sensitivity of colour reaction and stability of the coloured complex.

A good metal indicator must meet a number of requirements:

a ) The absorption maximum of its chelate must be sufficiently far from that of the free indicator at the same pH value.

b ) Both the indicator and its chelates must be sufficiently soluble in water or any other suitable solvent.

c ) The reaction with cations must be sensitive and practically instantaneous.

d )The stability of the metal indicator complexes must meet the requirements of the purpose of use.

From the structural point of view, chromophoric reagents must posses a grouping capable of chelate formation joined directly to the resonant system of a ligand. The free electron pairs of suitable disposed oxygen and nitrogen ligand atoms in hydroxy, -azo, azomethine, Schiff bases, for example will coordinate with the metal ion, forming stable five or six membered chelate rings.

The mode in which these electrons (originally participate in the electron system of the ligand, corresponding to the light absorption at a particular wavelength), is altered by the process of chelate formation and as a result the absorption maximum is displaced to a different wavelengths. Experiments show that the majority of the metal indicators also behave as acid-base indicators. This is due to the fact that changes in colour will also accompany by the dissociation of protons.

The function of a metal indicator follows from a just position of its properties as a chelating agent and as an acid-base indicator. The competition between protons and metal ions for the complex forming grouping of the indicator will lead within a certain pH limits, to an interference with the normal course of the acido-basic changes. The cation will, to an extent, depend on the factors normally affecting chelation, viz, ionic radius, number of charges, electron affinity ($E_A$) and the prevalent pH, induce in the ligand an electronic configuration capable of existence at this pH in absence of metal ions . This leads to a shift in the absorption maximum toward the position characteristic of that particular form of the unchelated ligand whose electronic structure resembles closely that of the chelate.

From the above consideration, it follows that the necessary attributes of a metal indicator is essentially dependent on a suitable balance of three structural features of the molecule. viz, the electronic system of the ligand, the acid-base properties and the complex forming grouping. The resonant system of the organic molecule is in fact the source of colour and as such it is present in practically every true organic ligand

The presence of acid-base properties in metal indicators is by no means fortuitous, but is indeed, on of the necessary attributes of such compounds. The only point of importance is its ability to undergo marked change in colour with progressive change in acidity. Thus, from a knowledge of the pH indicator properties of a given compound, it is possible to predict probable scope of its metallochromic or its chromophoric properties.

The chelate forming system of the known metal indicators as a rule involves two separate groups placed so as to allow the formation of a chelate ring, at least one of these groups being directly linked to the conjugated system of the molecule. In most of the indicators in current use, this is an (OH) group which is also responsible for the acid-base properties of such a ligand and hence it constitutes a common factor in both acid-base and chelate forming properties.

Vibrational spectroscopy is also a very helpful technique in the study of metal complexes. It has been concerned with the determination of molecular symmetry, but many applications of this method have as their objectives only the identification of molecule or a functional groups. In such fingerprinting applications, the frequency, shape and intensity of a band are all useful characteristics. Vibrational spectra of metal complexes can be classified into ligand vibrations which occur in the high frequency region (4000-600 $cm^{-1}$) and metal ligand vibrations which appear in the low frequency region(below 600 $cm^{1}$) The former provides information about the effect of coordination on the electronic structure of the ligand while the latter provides direct information about the structure of the coordination sphere and the nature of the metal-ligand bond. Since the main interest of coordination chemistry is focused on the coordination bond, the latter has attracted particular interest of inorganic chemists.

The ir, $^1H$-nmr and the uv-visible spectroscopy as well as the conductometric and potentiometric techniques, all were employed successfully in our studies in order to determine the nature of newly formed metal complexes, as explained in the next chapters.

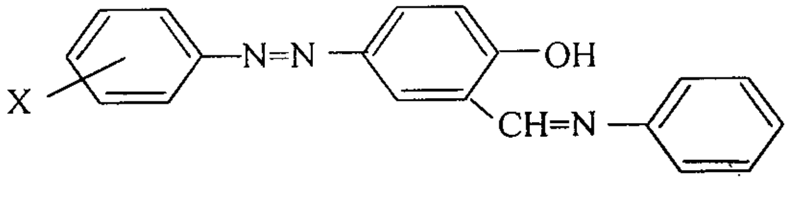
## 1.2. Literature survey on azo compounds and their metal chelates :

The visible, $^1H$-nmr and ir spectra of 1-phenylzo- 2-naphthol were studied in DMSO or in solid state(1). These compounds are known as mixture of azo and hydrazo tautomers in solution. When solutions of the compounds were diluted, both azo and hydrazo bands were shifted to shorter wavelength. The phenyl ring substituent effects on the absorption maximum were observed clearly and good LFER were observed between absorption maximum and $\sigma^0$ or $\alpha$ number. Substituent effects on molar extinction coefficients, were observed in the absorption bands for either the azo or hydrazo tautomers. The NH and OH proton peaks were not observed in the $^1H$-nmr spectra, only one peak was detected. The chemical shifts were correlated with $^aR$ or $^aR^+$. Broad absorption bands were observed in the range of 2500-500 cm$^{-1}$ instead of the characteristic absorption bands due to the azo ( OH and N:N ) and hydrazo (NH and C:O) forms in the ir spectra.

***Elsirafy*** et.al(2) studied the acid-base properties of the chloroazoxines dyes. The pK$_a$ of the sulfo-group in (I) [R=o-Cl, m-Cl, p-Cl and H] was determined, poteniometrically. The indicators were prepared and obtained in the acid form by perculation through a cation exchange resin, and titrated with NaOH. The $pK_a$ values were 3.69, 4.25, 3.65 and 3.71 respectively.

The electronic absorption spectra of some azo-azomethine dyes were investigated by ***Issa*** et. al(3) in organic solvents and aqueous solutions. The authors reported that the spectra display apparent shifts on changing the aromatic moiety attached to the azomethine centre.

***El-Kersh*** et. al(4) studied the electronic absorption spectra of some azo-azomethine dyes in different organic solvents of varying polarities. X=p-Cl (a), p-Br (b) ; p-$CH_3$ (c) p-COOH (d) and p-$COCH_3$ (e). the spectra of compounds (a)-(c) are studied in ethanol, ether, DMF and cyclohexane. The ir spectra of the different functional groups in these compounds are assigned, the plots of the wavenumber of the N=N and N=C bands as a function of $\sigma_x$ (Hammett constants) give more or less linear relationships. Also, the signals of the $^1$H-nmr spectra have been discussed in terms of substituent effect.



The composition and protonation constans of 2N-salicylidene-5- phenyl –1,3,4- thiadiazole (SPT) and 2N-3,5- dichlorosalicylidene-5- phenyl-1,3,4 thiadiazol (DCSPT) and formation constants of their metal-chelates with $Cu^{2+}$ and $Ni^{2+}$ in 50% ethanol-water system had been determined by ***Irving –Rossotti*** method at various ionic strength at 25±1 °C(5). The observed order of stability of the metal chelates was found to be $Cu^{2+} > Ni^{2+}$. The order of the ligand on the basis of relative strength was SPT>DCSPT. Solid complexes were also separated. Chemical analysis suggested a 1:2 stoichiometry of metal : ligand.

The ir-spectra of isomeric chloro-bromo and iodobenzene – (1-azo-1) –2-naphthols and their $Cu^{2+}$ complexes were studied(6). The assignments of the bands in the ir-spectra are the stretching vibration of N=N at 1463 – 1453 $cm^{-1}$ which during complexation shifted to 1375 – 1352 $cm^{-1}$. The stretching vibration of C=O is a weak band at 1570 – 1564 $cm^{-1}$ (only in the spectra of primary naphthols ); The stretching vibration of C-N in complexes is at 1473 – 1463 $cm^{-1}$ deformation vibration of OH of naphthols is at 1219 – 1210 $cm^{-1}$ (disappear during complexation), the stretching vibration of Cu-O in complexes are 2 bands 838 – 818 and 563 – 556 $cm^{-1}$, while the stretching vibration of Cu-N is at 453-448 $cm^{-1}$.

The vibration absorption spectra at 700-1620 $cm^{-1}$ and uv absorption spectra at 200 – 700 nm of uranyl and copper complexes of phenylazo and naphthylazo dyes 1:2 chelates were studied(7). The ir and uv spectra of the compounds were qualitatively evaluated and their structure were considered.

The stability constants of 2-(4-benzimidazolylazo) – R acid (I) and 5-(4-benzimidazolylazo) - 8 - hydroxy quinoline ( II ), and the optimum formation conditions of the $Co^{2+}$, $Ni^{2+}$ complexes with them were studied spectophotometrically(8). The metals form (1:1) and (1:2) (M:L) complexes with

I and II, except for Cu with I, where only the 1:2 complex is formed.. A rapid method for the spectrophotometric determination of the metals with I and II was developed. Both reagents can be used as indicators in the chelatometric titration of the metals with EDTA with spectrophotometric end point. On the other hand the formation constants of the complexes were determined.

The synthesis and characterisation of a series of Fe (II) , Co(II), Ni(II) and Cu(II) complexes with N-substituted hydrazones of 2,6-diacetylpyridine were carried out( 9 ) . The analytical data included elemental analysis, infrared spectra, electronic spectra, conductivity and magnetic measurements.

***El-Dissoukey*** et. al( 10 ) reported the complexes of phenyl-2- picolyl ketone hydrazone (ppkphy) and phenyl-2-picolyl ketone phenyl hydrazone (ppkphy), with hydrated copper (II) acetate or hydrated copper(II) nitrate in mole ratio 1:1 or 1:2 (metal : ligand). Various physical techniques indicating molar conductivity, spectral (ir, electronic, esr and $^1$H-nmr ) and magnetic measurements were used to study the nature and structure of the prepared complexes .

***Symal***( 11 ) synthesized new $Cu^{2+}$ complexes of Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 4-methoxy salicylaldehyde, 5-methoxysalicylaldehyde and 3-amino-thiophenol. The Schiff bases coordinated through O, N and S as tridentate dibasic ligands. The complexes, which were characterized by elemental analysis, ir, electronic spectra and magnetic susceptibility measurements were insoluble in common solvents and decompose above 250 °C without melting. The complexes possed subnormal magnetic moments ($\mu_{eff}$=1.31-1.54 B.M. at room temperature) and were involved in antiferromagnetic exchange with an S=O ground state. The electronic absorption spectra of the complexes exhibit one ligand field band at 15000 $cm^{-1}$.

Potentiometric and conductometric titrations were performed( 12 ) in order to study the reaction between $Ag^+$ and highly neutralized EDTA (95-99%) in the form of $Y^-$ anion. In the titration of $AgNO_3$ with $Y^-$, the product $Ag_4Y$ was precipitated but this re-dissolved in the presence of an excess of $Y^{-4}$ to form an $[AgY]^{-3}$ complex. Equilibrium constants and solubility products are reported and the thermal stability of $Ag_4Y$ was studied by DTA. Thermal decomposition begins at 135-157 °C and on heating to 600 °C a residue of pure Ag is formed.

Neutral copper (II) complexes of Schiff bases derived from substituted salicylaldehyde and 2-aminopyridene methyl derivatives had been synthesized by an electrochemical procedure( 13 ). The crystal and molecular structure of bis {N-(2-[3-methyl pyridyl]}-5 methoxy salicylideneiminato} copper (II) and bis{N-[6-methylpyidyl]}-salicylideneiminato} copper (II) had been determined by X-ray diffiraction. In both structures, the metals adopt square-planer coordination geometries and the pyridyl nitrogen atoms are not coordinated. The electronic and ir spectra of complexes were discussed and related to the structure.

Potentiometric studies has been carried out on metal complexes of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$ with N- (2hydroxy -1-naphthalidene ) – 4 - carbomethoxy aniline (14). The formation constant (logK) of the reagent and the stability constants of its metal complexes had been determined by ***Bjerrum's*** method at 30± 0.1 °C and at ionic strength 0.1M. The order of stability constants of chelates was found to be $Cu^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$

The proton- ligand dissociation and metal- ligand stability constants of malonic acid hydrazone derivatives with some transition metal ions were investigated potentiometrically(15). The order of stability constants was found to be $Cr^{3+} > Fe^{3+} > Co^{2+} > Ni^{2+} > Cu^{2+} > Cd^{2+}$. The effect of temperature on the stability of the complexes formed was studied and the corresponding thermodynamic functions were derived and discussed. The results were reported for the formation of the complexes under investigation with three substituents of malonic acid hydrazones by pH-metric method of ***Irving*** and ***Rosstti*** in 40% (v/v) ethanol-water medium at $\mu$=0.1 M (KC1). The ratio of the metal: Ligand was determined conductometrically. The structure of the investigated ligands has been elucidated by ir and $^1$H-nmr spectrocopy.

### 1.3. Literature survey on the determination of the studied metal ions :

The spectrophotometric micro determination of copper (II), silver (I) and gold (III) was studied(16) using azastyrene Schiff bases as reagents. The optimum pH, sequence of reagent addition, wavelength maxima and other data were determined and listed for determination of $Cu^{2+}$, $Ag^{+}$ and $Au^{3+}$ with $\alpha$[5 bromo-2 hydroxy and $\alpha$[2- (hydroxy-3methoxy benzylidene) amino] o.cresol. ***Beer's*** law was obeyed up to 5.00, 8.64 and 11.82 $\mu g\ ml^{-1}$ for Cu, Ag and Au, respectively acid] as indicator was reported(19). A sample solution of $CuSO_4$ is adjusted to an optimum pH of 6.0 to 6.5 with acetic acid and titrated with EDTA in the presence of 2 or 3 drops of the cited indicator. The end point was marked with a sharp colour change from yellow to green. Results were in good agreement with these obtained with fast sulphon black F as indicator. The titration was carried out at 25 °C to 40 °C.

***Wang*** et.al(20) studied the reaction of 5-(4chloro-2-carboxyl phenyl azo) rhodamine with silver. Synthesis of the cited reagent was reported. A 0.5 ml portion of 0.1 mg $ml^{-1}$ of Ag solution was mixed with 10 ml of citirate buffer of pH 5, 2 ml of 1 mM of reagent and 2 ml of 1% Triton X-100 and then diluted with $H_2O$ to 50 ml. After 20 min, the absorbance was measured at 475 nm ($\varepsilon = 1.1x10^5$)vs. a reagent blank. The solution was stable for up to 100 min. ***Beer's*** law was obeyed for $\leq 2$ µg $ml^{-1}$ of $Ag^+$. Most foreign species including $Au^{3+}$ and $Cu^{2+}$ were permitted.

Silver has been determined spectrophotometrically by ***Zhu*** et.al(21). In the presence of Triton X-100- sodium dodocyl sulphate, Ag forms a complex with cadion 2B that has an absorption maximum at 560 nm ($\varepsilon$=1.23x$10^5$) at pH 9.2. Beer's law was obeyed for up to 0.64 µg $ml^{-1}$ of Ag and the colour was stable for 24 h. The method was applied in the analysis of water and waste water.

Copper (II), iorn (III) and nickl (II) were determined using some 4-amino - antipyrine azo- derivatives(22). Sample solution was mixed with 2 ml of 10 mM ethanolic solution of 4 aminoantipyrine derivative. The mixture was diluted to 25 ml with universal buffer and absolute ethanol so as to obtain a 30% solution. Optimum pH values and $\lambda_{max}$ used for each derivative were tabulated. ***Beer's*** law was obeyed for up to 12.5, 5.02 and 5.21 $\mu g\ ml^{-1}$ of $Fe^{3+}$, $Ni^{2+}$ and $Cu^{2+}$, respectively. The method was also used to determine these metals in different alloy samples.

The organic ligand [5-(4 sodium sulphonate-phenylazo )-8 aminoquinoline was applied for determination of gold( 23 ). The cited reagent was synthesized from diazotized sulfanilinic acid and 8 amino quinoline, the product was dissolved in $H_2O$ to give a 0.2 mM concentration. To a solution containing< 50μg of $Au^{3+}$ were added 3.0 ml of 0.2% hexamethyltrimethyl ammonium bromide solution. 4.0 ml of reageant solution and 2.5 ml of 0.5 M NaOH and the mixture was diluted to 25 ml with $H_2O$. After 15 min the absorbance of the blue green complex formed was measured at 605 nm vs. a reagent blank ($\varepsilon = 1.46 x 10^6$ ). ***Beer's*** law was obeyed up to 2 $\mu g\ ml^{-1}$ of $Au^{3+}$. Interference from $Fe^{3+}$ was masked with NaF and from $Cu^{2+}$ and $Hg^{2+}$ with EDTA. The method was applied to the determination of gold in ores .

The synthesis of the new long-chain saturated fatty hydrocarbon substituting group compound, N-undecy -N- (sodium p-aminobenzensulfonate)-thiourea (UPT) was described( 24 ). According to the studies on its analytical performance, it was found that this reagent can be used to identify $Cu^{2+}$ (PD 6.3) and determine microamounts of copper ( $\varepsilon_{300.4} = 2.39 x 10^5\ l\ mol^{-1}\ cm^{-1}$) in aqueouus solution. Both of their sensitivities and selectivity's are better than other common methods(25-27). These new methods are simple and convenient and can provide satisfactory results on samples.

The reaction between $Cu^{2+}$ and 5-(4- bromo-2- carboxyphenylazo) rhodamine (I) was studied by ***Wang*** et.al(28). This reaction was applied for determination of $Cu^{2+}$ in aluminium alloy using sodium acetate/ acetic acid buffer as best media. In presence of Triton X-100 the absorbance of $Cu^{2+}$- I (1: 2) complex was measured at 504 nm ($\varepsilon$=8.9x$10^4$) after 20 min. ***Beer's*** law was obeyed for up to 2.7 μg $ml^{-1}$ $Cu^{2+}$. Recoveries were found to be 98-99 %.

Copper was determined by new sensititive spectrophotometric method(29). The method depends on the determination of $Cu^{2+}$ as a complex with N- (2,5 dimethylphenyl)-p- toluimdoylphenylhydrazine (I) using borate buffer (pH=8) and cetyltrimethyl ammonium bromide. The method applied for determination of $Cu^{2+}$ in water where the formed complex was extracted with pentanol for 1min. The solution was dried with 2 gm $Na_2SO_4$ and the absorbance was measured at 410 nm. ***Beer's*** law was obeyed from 0.01-0.135 μg $ml^{-1}$of $Cu^{2+}$. Various metal and other ions at concentrations of 10-100 mg $l^{-1}$ caused an error of ≤ 2% at 70 μg $l^{-1}$ of $Cu^{2+}$ ions.

The reaction of N-octyl-N-(sodium p- aminobenzenesulfonate) thiourea with copper (II) was described(30). A standared solution of $Cu^{2+}$ was mixed with acetic acid/ sodium acetate buffer (pH=4.2), NaF (if required) and the listed reagent. The solution was heated at 100 °C for 2min, cooled to room temperature. The absorbance was measured at 301.4 nm ($\varepsilon$=1.82x10$^5$) vs. a reagent blank. ***Beer's*** law was obeyed up to 10 µg of Cu/25 ml. Interference from $Al^{3+}$ was masked with NaF. The method was applied to the analysis of alloy steels and milk powder, with recoveries of 97.1-97.8% and relative standared deviation (RSD) of 1.48-2.8%.

A resin containing imidazolylazo functional group has been used for the separation and preconcentration of palladium (II) and silver (I) from other metal ions in synthetic mixture, ores, alloys and medicinal samples(31). No interference could be observed from alkali and alkaline earth metal. Palladium (II) was quantitatively separated from ores and platinum wire without interference's.

Determination of gold using 3,3,5,5-tetramethylbenzidine was reported by ***Gu*** et.al(32). Standered $Au^{3+}$ solution (10 µg ml$^{-1}$) was treated with 1 ml of the cited reagent in ethanol and mixed with an amount of 0.1 M HCl. The absorbance was measured at 450 nm ($\varepsilon$=1.03x10$^4$) vs. a reagent blank. ***Beer's*** law was obeyed for$\leq$ 40 µg Au in 25 ml of the solution. Interference's from $Ag^+$, $Pt^{4+}$, $Fe^{3+}$ and $Ce^{4+}$ could be overcome by addition of NaF, potassium citerate and EDTA. The method was used in the analysis of coarse copper, with recovery of 96-105%.

Determination of gold was also available(33) by its reaction with molybdate and nile blue in the presence of polyvinyl alchohol (PVA). In this method 3 ml of 0.2% ammonium molybdate solution was added to 8 µg of $Au^{3+}$.

The mixture was diluted and left to stand for 10 min. After adding 5 ml $HClO_4$, the mixture was diluted with $H_2O$ and 1 ml 2% PVA followed by 2 ml 0.05% nile blue. The absorbance was measured at 595 nm after 15 min. ***Beer's*** law was obeyed up to 16 µg of Au. The molar ratio of the $Au^{3+}$-nile blue ion association complex formed was 1:2. The method was applied to the determination of trace amount of $Au^{3+}$ in powdered carbon and ores.

***El-Zawawy*** et.al(34) used 5-(2,4-dihydroxybenzylidene) rhodanine and cationic surfactants for the determination of both $Ag^+$ and $Au^{3+}$ where sample solution containing ≤ 45µg $Ag^+$ or < 56 µg $Au^{3+}$, was mixed with 0.5ml ethanolic reagent solution. The solution was mixed with 0.01 M cetyltrimethyl ammonium bromide (for Ag determination) or cetylpyridinum bromide (for Au determination) At pH=10 using borax buffer the absorbance was measured at 547 nm ($\varepsilon=7.11x10^4$) or 558 nm ($\varepsilon=8.45x10^4$) for Ag and Au respectively. The Ag-complex was stable for at least 3 days; whereas Au-complex was stable for 2 h. The calibration graphs were linear for 0.13-1.83 and for 0.16-2.24 µg $ml^{-1}$ of Ag and Au, respectively. Interference was investigated showing a high tolerance limits for other metal ions. The methods were applied to the determination of Au in silicate rocks and Ag and Au sulfide ore.

The reaction of 4- ( 2,3- dihydro-1,4 - phthalazinedione-5-triazeno ) azobenzene as a new reagent for spectrophotometric determination of $Cu^{2+}$ ions was described(35). A standard solution containing 5 µg Cu was mixed with 3 ml $Na_2B_4O_7$ / NaOH buffer of pH 11.5, 1 ml aqueous 2% tween 80 and 1.5 ml ethanolic solution of the cited reagent. The mixture was then diluted by $H_2O$ to 10 ml. The absorbance was measured at 520 nm ($\varepsilon$=6x$10^4$ ). ***Beer's*** law was obeyed up to .6 μg $ml^{-1}$of $Cu^{2+}$. The method was applied to Al-alloys, with a recovery of 98.2% and a relative standard deviation of 2.4%.

***Shen*** et.al ( 36 ) studied the reaction of $Au^{3+}$ and p-bromophenylazo-rhodamine. In this method a portion of standard $Au^{3+}$ ions solution, containing 20 μg of gold, was treated with 5 ml HCl (1:1), 2 ml aqueous o.2% sodium dodocylbenzenesulfonate and 3 ml of ethanolic solution of the reagent described. The mixture was diluted by $H_2O$ to 25 ml and stored at room temperature for 5 min. The absorbance was measured at 545 nm ($\varepsilon$=7.7x$10^4$ ) vs. a reagent blank. ***Beer's*** law was obeyed up to 1.6 μg $ml^{-1}$ $Au^{3+}$. Only Pd and Ag interfered seriously. The method was applied to waste water, with recoveries of 98.5-103% and RSD of o.47-1.08%.

Copper interference on the spectrophotometric determination of iron was studied by ***Baraj*** et. al( 37 ) using bathophenanthrolinedisulfonic disodium salt. In this method factorial design was used to optimize the conditions for the similtaneous determination of Cu and Fe by two wavelength measurements. Samples were mixed with 0.5 ml of 10% ascrobic acid solution, 5 ml acetate buffer (pH=5.6) and 1.0 ml aqueous reagent. The mixture was diluted with water to 10 ml. After 15 min, absorbance was measured at 425 nm for the Cu-reagent complex and at 535 nm for the $Fe^{2+}$complex. Çalibration graphs for Cu were linear up to 8 μg $ml^{-1}$, with a detection limit of 0.1 μg $ml^{-1}$. The method was applied to the analysis of two samples from a water treatment plant, befor and after treatment.

The catalytic Spectrophotometric determination of trace amounts of silver was reported ( 38 ). The determination was based on oxidation of o-hydroxybenzenediazo-aminoazobenzene with solubilization of nonionic surfactant. Portions of standard Ag solution were treated with 2 ml acetic acid / sodium acetate buffer (pH=5.3), 1.5 ml 0.3% of 2,2-bipyridyl, 1ml 5% Triton X-100 and 2 ml ethanolic 0.02% o-hydroxybenzenediazoaminoazobenzene. The mixture was diluted to 25 ml with $H_2O$, heated at 80 °C for 10 min and cooled with water. The absorbance was measured at 435 nm vs. a $H_2O$ blank. An uncatalytic run was also performed to evaluate the absorbance difference for calculation of amount of Ag. The calibration graph was linear from 0.001-0.02 mg $l^{-1}$ Ag with a detection limit of 50 ng $l^{-1}$. There was no interference and the method was used in the analysis of synthetic samples and gold ores.

The spectrophotometric determination of $Cu^{2+}$ using 2-hydroxy 3carboxy-5-sulfobenzenediazoaminobenzene was reported( 39 ). Portions of standard $Cu^{2+}$ were mixed with 2 ml $Na_2B_4O_7$ / NaOH buffer (pH =10.6), 1.2 ml Triton-N101 and 2 ml ethanolic 0.03% of the cited reagent. The mixture was diluted to 10 ml with $H_2O$. After 10 min, the absorbance was measured at 530 nm ($\varepsilon=1.3\times10^5$ ) vs. a reagent blank . ***Beer's*** law was obeyed up to 0.24 µg $ml^{-1}$of $Cu^{2+}$ion. The solution was stable for 1.5 h and the method was applied to Pb-Zn ores and peanuts, with RSD of 0.6-1.6%

***Mori*** et.al( 40 ) described a new and sensitive spectrophotometric method for the determination of gold (III) using NN-dimethyl-p-phenylenediamine and potassium persulphate. In this method a 2.5 ml portion of 0.2 M potassium persulphate was mixed with 1ml 10 mM-NN- dimethyl-p- phenylenediamine and 3 ml buffer solution of pH 4 comprising 0.1 M citrate buffer and 2 mM- EDTA before addition to $Au^{3+}$ solution. The resulting solution was diluted with $H_2O$ and laft to stand for 25 min before measuring the absorbance at 552 nm. The calibration graph was linear up to 30 $ng\ ml^{-1}$ with an RSD of 4.5% (n=5) and $\varepsilon = 1.9 \times 10^6\ l.mol^{-1}.cm^{-1}$.

The reaction of antipyridyldiazoamino-2.4-dinitrobenzene with silver and its application was studied( 41 ). An appropriate amount of Ag was treated with 5 ml ***Britton-Robinson*** buffer solution of pH 7-9 followed by 2 ml aqueous 1% Tween-80 solution and 3 ml ethanolic 0.025% 1-antipyridyldiazoamino-2,4-dinitrobenzene. After dilution with $H_2O$ to 25 ml and storing for 15 min, absorbance was measured at 485 nm ($\varepsilon = 7.2 \times 10^4$) vs. a reagent blank. ***Beer's*** law was obeyed for $\leq 0.6\ \mu g\ ml^{-1}\ Ag^+$. The method was applied to the analysis of synthetic samples and photographic development solutions.

Salicylaldehydehydrazone was used for spectrophotometric determination of copper (II)( 42 ). The absorbance of the $Cu^{2+}$ N,N- oxalybis (salicylaldehyde hydrazone) complex in aqueous 60% DMF (pH =2 )is measured at 422 nm. ***Beer's*** law was obyed for 0.4 to 1.8 $\mu g\ ml^{-1}$ of $Cu^{2+}$

In the presence of sodium dodecyl sulphate at pH 2.5 to 4.5 $Au^{3+}$ ion reacted with thiomichler ketone( 43 ) to form a stable 1:4 complex with $\varepsilon = 1.6\times10^5$ at 545 nm. ***Beer's*** law was obyed to 3 μg $ml^{-1}$ of Au. The recovery was 99 to 101% and the method was applied to the determination of gold in minerals with satisfactory results.

Copper (II) and iorn (II) were determined spectrophotometrically by ***Bansal*** et.al( 44 ) using pyridin -2,6- diol. In this method portion of solution containing 1 to 84 μg of $Fe^{2+}$ or 1.2 to 116 μg of $Cu^{2+}$ were mixed with 1 :15 separately, with pyridine-2,6-diol solution . The $Cu^{2+}$ solution was adjusted to pH 7.5 to 10.8. after dilution to 20 ml with water, the absorbance was measured at 535 nm vs. a reagent blank. ***Beer's*** law was obeyed up to 0.6 to 5.8 μg $ml^{-1}$ $Cu^{2+}$. The method was applied for the determination of $Fe^{2+}$ and $Cu^{2+}$ in their alloys.

The complexation reaction of $Cu^{2+}$ with N-(4-hydroxy-3methoxy benzylidene)-hydrazene carbothiamide was reported( 45 ). Aliquots of solution containing 5 to 77.5 μg $Cu^{2+}$ were mixed with $KH_2PO_4$-NaOH buffer solution of pH 11.98 (5 ml), ethanol (6 ml) and 4 ml of 0.3% of the cited reagent .The solution was diluted with $H_2O$ to 25 ml and the absorbance was measured at 410 vs. a reagent blank. ***Beer's*** law was obeyed from 0.1 to 3.2 μg of $Cu^{2+}$ ($\varepsilon = 1.2\times10^4$, ***Sandell*** sensitivity 5.15 ng.$cm^{-2}$). the method was applied for the determination of $Cu^{2+}$ in simulated copper alloys.

The reduction of gold (III) with cobalt (II) was studied potentiometrically (46). In this method sample solution was mixed with suitable volume of 1,10-phenanthrolene or 2,2-bipyridyl having a molar concentration at least ten times that of the Au(III) present and the mixture was adjusted to pH 4 - 5 with acetate buffer solution. The mixture was heated to 50 °C and titrated with 10-25 mM $CoCl_2$ to a potentiometric end point. Only $Hg^{2+}$, $Pt^{4+}$ and $Fe^{3+}$ interfered and the method was used to determine $Au^{3+}$ in alloys.

The catalytic-kinetic spectrophotometric determination of silver (I) was described (47). Portions of standard $Ag^+$ solution were treated with 4 ml $Na_2HPO_4/NaOH$ buffer of pH 11, 0.6 ml $H_2O_2$ and the solution was diluted to 25 ml with water. The solution was heated at 50 °C for 4 min, 2 ml of 0.32 mM rhodamine B was added and the solution was heated for a further 15min . After cooling with running water to room temperature , the absorbance was measured at 556 nm ($\varepsilon=2.41x10^5$)vs. water as blank. At the same time, a blank run was conducted so that the absorbance difference could be evaluated for the calculation of the amount of Ag. The calibration graph was linear up to 0.116 $\mu g\ ml^{-1}$ of $Ag^+$.

Copper in $CuSO_4.5H_2O$, $CuCl_2.2H_2O$, $Cu(NO_3)_2$ and CuO (powder) was determined spectrophotometrically (48) at 630 nm after complexation with salicylaldhyde thiosemicarbazone in HCl-sod.acetate buffer solution of pH 2.5 containing ascorbic acid as a masking agent. The calibration graph was still linear up to 160 $\mu g\ ml^{-1}$ of $Cu^{2+}$ with recovery of 98.5 to 99% .

***Saran*** et.al( 49 ) reported the spectrophotometric determination of silver using sodium 2-(8-hydroxyquinolin-ylazo)benzoate. Sample solution adjusted to pH 5.2 to 6.1 with dilute $NH_3$ and $HNO_3$ was treated with 1% sodium potassium tartarate solution and 1mM sodium 2-(8-hydroxyquinolin-5ylazo ) benzoate. After 30 min, the absorbance of the intense purple complex formed was measured at 525 nm ($\varepsilon=3.6\times10^4$). ***Sandell's*** sensitivity was 0.0029 $\mu g\ cm^{-2}$ whereas ***Beer's*** law was obeyed for 0.05 to 0.65 $\mu g\ ml^{-1}$ of $Ag^+$ ions .The method was applied to the determination of $Ag^+$ in geological samples .

Copper (II) formed 1:1 complex with 1-(2-imidazolyazo)-2-naphthol-4-sulphonic acid in acetate buffer of pH =3 and in the presence of 2 ml 10% citric acid( 50 ). The absorbance was measured at 530 nm vs. a reagent blank. ***Beer's*** law was obeyed up to 0.8 $\mu g\ ml^{-1}$ $Cu^{2+}$ and the method was used to determine $Cu^{2+}$ in magnesium and iron ores .

In borate buffer solution , in the presence of Triton X-100 silver reacted with 2,4-dibromo-6-carboxybenzenediazoaminoazobezene( 51 ). For determination of $Ag^+$, test solution containing $\leq$ 10 $\mu g$ of $Ag^+$ was mixed with borate buffer (5 ml), 3 ml Triton X-100 solution and 3 ml ethanolic solution of the cited reagent. The mixture was diluted to 25 ml with water and absorbance of the resulting solution was measured at 552 nm vs. a reagent blank. ***Beer's*** law was obeyed up to 0.4 $\mu g\ ml^{-1}$ of $Ag^+$. The method was applied to the determination of trace $Ag^+$ in waste water and geological samples.

# Aim of the work

Though many studies were carried out on the spectrophotometric behaviour of azo compounds yet the work carried out on the azo dyes derived from phenylazo malonic acid with aniline derivatives as chelating agent is not satisfactory. The aim of the present investigation is to carry out studies on the possibility of using such compounds as analytical reagents for the spectrophotometric determination of some transition metal ions ( $Cu^{2+}$, $Ag^{+}$ and $Au^{3+}$). The investigation used different methods for characterizing the structural formula and geometries of the metal chelates formed such as spectrophotometry, conductometry, potentiometry, in addition to the elemental analysis, DTA – TGA, ir and magnetic susceptibility measurements. Also the stepwise formation constants of the chelates are determined potentiometrically, and spectrophotometrically.

The present work aims also to investigate the optimum conditions for determining the selected ions and the optimum spectral methods for determining the stability constants of the complexes formed. The spectrophotometric methods are aimed to be used as a trace analysis for these ions and azo compounds under study as a chromophoric reagents.