Chapter (I)
Introduction

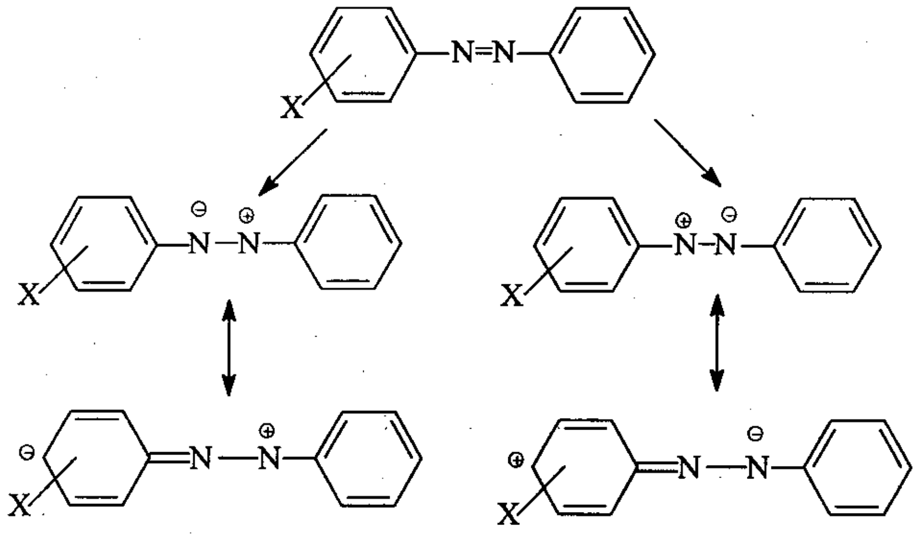
CHAPTER I

INTRODUCTION

1-1 Literature Survey on Absorption Spectra of Azo Compounds

It is well known that, the absorption spectrum of an organic molecule is essentially for the summation of the absorption bands of the different molecular fragments. So, the absorption spectra of the azo compounds should have bands due to electronic transitions within the aromatic moieties, as well as bands due to electronic transition within the N=N group. Moreover, one should consider the interaction between the different parts of the molecule leading to the phenomenal of intramolecular charge transfer which leads to either the appearance of new bands, or a shift in the position of the absorption bands due to transitions within the molecular parts influenced by charge migration.

In the spectrophotometric investigation of solvent and substitution effects on the electronic spectra of 4-hydroxyazobenzene, ***Issa et al.***(1) revealed that the absorption spectra involved bands in uv region due to electronic transition within the moieties attached to the azo group, and bands in the visible region corresponding to the electronic excitation of the π-and n-electrons on the N=N system. The strong π-π* transition of the N=N system was influenced by charge transfer interaction with the benzene rings and masked the n-π* band. At the same time, the π-π* transition was influenced by an interaction with π-electrons of the benzene ring i.e., involved a charge transfer character. The charge transfer took place from the azo group if the phenyl ring has an acceptor substituent, while the reverse direction occurred if the substituent is a donor one. The excitation of the azo group can be represented as follows:

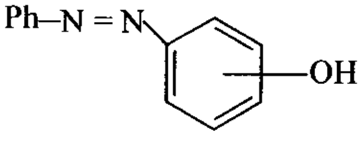


X = acceptor X = donor

Nagakura and Baba⁽²⁾, found that the absorption and dipole moment of p-aminoazobenzene and p-dimethylaminoazobenzene depends essentially on the refractive index of the solvent except for media leading to H-bond formation. The results were explained in terms of the electron migration effect. The energy of H-bond was determined from the extinction of the absorption spectra in mixed solvent e.g. ether and hexane.

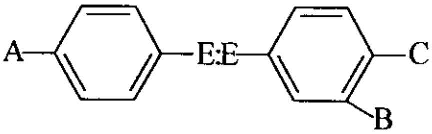
The uv-absorption spectra of azobenzene and several mono substituted derivatives and their conjugate acids and of benzaniline had been recorded by ***Jaffe et al.***(3). The spectra were analysed in terms of simplified (linear combination of atomic orbitals) molecular orbital theory. The strong 320 nm, which due to π-π*, band of azobenzene was shifted to 420 nm in acid medium. The weak n-π* transition of azobenzene near 440 nm (which may be doubled due to the separation of the n_a and n_b levels of the two N's) was blue shifted to 310 nm in acid solution and was also narrowed (because only n_a-π* remains possible). Weak Φ-Φ* transition (localized at position 2,2`, 3,3`) were observed at about 320 nm in all cases. Some weak bands, burried in the short wavelength shoulder of the π-π* bands were tentatively assigned as Φ-π*.

Mcdowell(4) found that alkali produced changes in the absorption spectra of azo dyes. The changes were completely reversed by acids. Dyes of the type:



Showed the displacement of the absorption bands by 50-60 nm wavelength with a widening of the bands. If the OH is in the o-position, the displacement is 30-40 nm and the weakening is more pronounced. If the dye molecule contains 2 azo bridges with OH groups ortho to both, the displacement was in the opposite direction by 10-20 nm.

Skulski and Urbansk(5) studied the absorption spectra of 4-hydroxy and 4-acetoxyazobenzene derivatives. The electron accepting substituents in ortho position to the phenolic group of 4-hydroxyazobenzene and its derivatives produced a hypsochromic shift of the primary band. Spectra of 4-acetoxyazobenzene derivatives contain a band near 260 nm (suggested term : K-band) which did not occur in 4-hydroxyazophenol. The electron acceptor substituents in the analogous derivatives of azobenzene obliterated completely the action of $OCOCH_3$ group on the chromophoric system in azobenzene. A means of marking the activity of groups, which were not included in the conjugate system, was suggested. The described effect may be found in compounds of the type:



Where E: E = N: N, CH:N, CH:CH

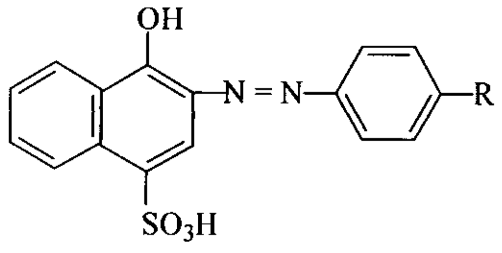
A = H, NO_2, CHO

B = OH, $CONH_2$, NH_2, $NHCOCH_3$

C = NO_2, CHO, $COCH_3$, COOH

Elenius(6) recorded the absorption spectra of some azo dyes in (heptane-ethanol) and (ethanol-H_2O) mixtures. 4-monomethylamino, 4-diethylamino and 4-diethylamino-4-hydroxyazobenzene showed an absorption band near 400 nm in heptane and a new band near 465 nm in ethanol and H_2O. This indicated the formation of new species in solution through intermolecular H-bonding. 4-dimethylamino-4-nitro azobenzene showed an absorption band at 445 nm which was progressively shifted to longer wavelength on increasing the concentration of the hydroxylic solvent. In 4-dimethylamino-2-carboxyazobenzene (o-methyl red) the intermolecular H-bond between the carboxyl group and the N-atom of the azo group was affected by hydroxylic solvents and a new species was formed with the free azo dye absorbing near 400 nm.

Khalifa et al. (7) studied the electronic absorption spectra of Neville Winther acid azo dye derivatives of the type:



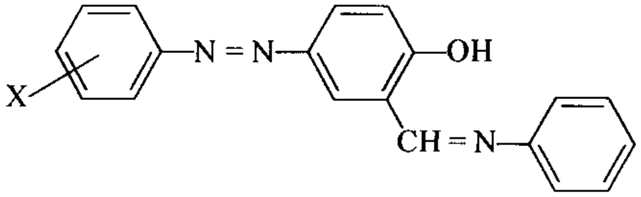
Where R=H, MeO, Cl, SO_3H or NO_2. The dissociation constants of the naphthalenic OH group were determined spectrophotometrically and the constant for the SO_3H group were determined potentiometrically.

Skulski(8) studied the uv-spectra of 2-acetamidobenzene, 1,2-benzamidoazobenzene and 2-hydroxy-5-methylazobenzene in a variety of polar and non polar solvents and compared them with the spectra of several related compounds not expected to exhibit intermolecular H-bonding. The effect of polar and non polar solvents on the band at 380 nm region indicates that the above mentioned azo dyes form each a fairly strong chelate ring due to intramolecular H-bonding.

Kamel et al.(9) studied the relation between the electronic absorption spectra and molecular structure of some mono azo dyes containing the benzothiophene, benzothiodiazole or benzotriazole nucleus. They concluded that the position of the absorption band corresponding to the N=N center is dependent on the type of moieties attached to the azo group. Band shifts were explained on the basis of the magnitude of the mesomeric shift and charge migration through the molecule.

The electronic absorption spectra of some azo-azomethine dyes were investigated by ***Issa et al.***(10) in organic solvents of different polarities and in aqueous buffer solutions. The spectra displayed apparent shifts on changing the aromatic moiety attached to the azomethine center.

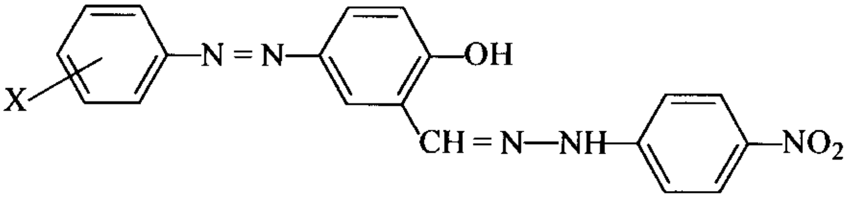
El-Kersh et al. (11) studied the spectral behaviour of some azo-azomethine dyes of the type:



X = p-Cl, p-Br, p-CH_3, p-COOH, and p-$COCH_3$.

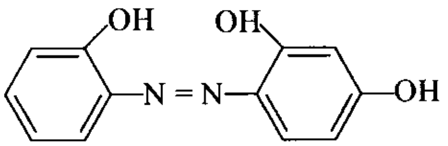
The study included the electronic absorption spectra in organic solvents of different polarities and also the ir and ^{1}H-nmr spectra. The uv-region displays two bands A and B in cyclohexane assigned to the moderate energy π-π* transition of the aromatic ring representing the ($^1L_a \leftarrow {}^1A$) state and the low energy π-π* transition corresponding to the ($^1L_b \leftarrow {}^1A$) state. These two bands strongly interacted in ethanol. A third band located at 350 nm was assigned to the intramolecular charge transfer involving the whole molecule. This band displays small solvent shifts except in DMF where two bands appeared at 330 and 470 nm. The authors reported that this splitting in the CT band is due to the weakly and strongly solvated molecules liable to exist in equilibrium.

The electronic absorption spectra of some azohydrazone dyes of the type:



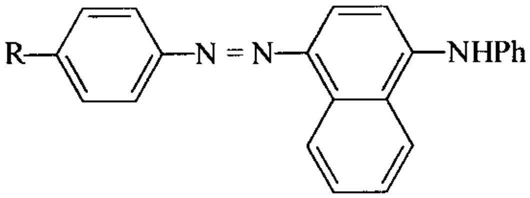
X = p-NO_2, p-Cl, p-Br, p-CH_3, p-OCH_3, p-COOH and p-$COCH_3$, have been studied by ***Issa et al.*** (12) in organic solvents of different polarities. The charge transfer band (CT) showed a wide variation in its position indicating some solvent dependence, but no regular variation in band position was observed. The study revealed that solute-solvent interaction leading to hydrogen bonding or solvation of both the ground and excited states are of higher contribution to the solvent effect.

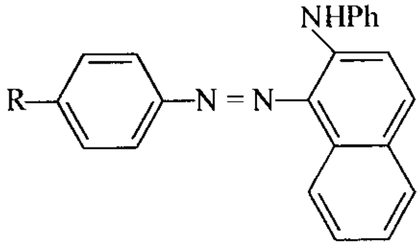
Issa and Harfoush(13) investigated the uv visible absorption spectra of 2-hydroxy-1-(2`,4`-dihydroxy) phenylazo containing more than one hydroxyl group in organic solvents.



The absorption bands were assigned to definite electronic transitions. The effect of solvent and molecular structure on band position was also discussed. The formation constant of the molecular complexes formed in ethanol was determined.

Kostyuchinko et al.(14) studied the visible spectra of mono azo dyes and their 2`-ph-NH-isomer

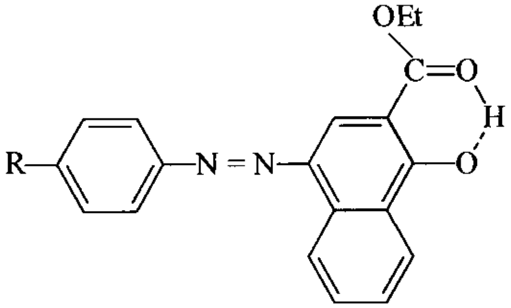


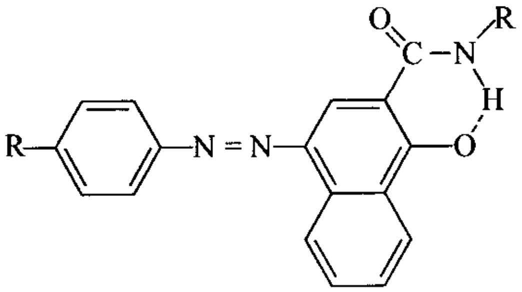


(R = H, OCH$_3$, Br, N(Et)$_2$ and NO$_2$)

They found that all compounds exist in azo form in neutral solvents such as dioxane and also in acetic acid, but exist in the quinone-hydrazone form in 30-90% aqueous acid mixture. The azo form of the o-substituted naphthyl moeity was stabilized by intramolecular H-bonding.

Traven et al.(15) studied the colour and azo-hydrazone tautomerism for 4-(arylazo)-1-naphthols.





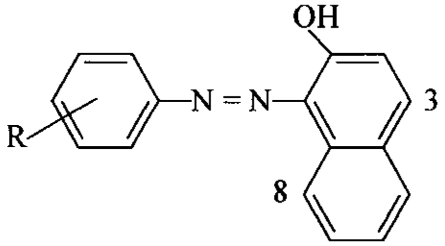
They found that ester group in position 2 stabilizes the azo tautomer by H-bonding where as a COOH or CONHR group stabilizes the quinone-hydrazone tautomer. A strong electron-donating substituents at R tends to stabilize the azo tautomer regardless of the functionality at position 2- of the naphthol ring.

Mahmoud et al.(16) investigated the low excitation energy band which appeared in the electronic spectra of some 4-hydroxyazobenzene derivatives and assigned the band as being due to electronic transition of the type n-π*. Hence 4-hydroxyazobenzene derivatives exist mainly in the true azo form, the visible spectra of 4-hydroxy-2-carboxyazobenzene was interpreted on the basis that this compound existed in a tautomeric equilibrium of the azo-hydrazone type.

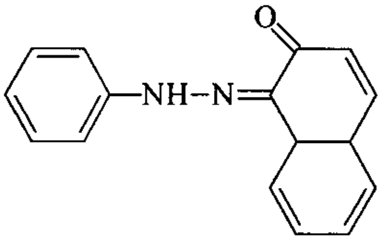
Solvent effect on the thermal cis-trans isomerization and position of the charge-transfer absorption of 4-(diethylamino)-4`-nitroazobenzene has been studied by ***Schanze et al.***(17). The isomerization rates, activation parameters and the absorption maxima were determined in a variety of protic and aprotic solvents. The data were analyzed and interpreted by using the Taft-Kamelt multiparameter linear free energy relationship (LFER). The correlation suggested that the isomerization was accelerated in H-bonding solvents relative to aprotic solvents of similar polarity due to a H-bonding interaction between the solvent and the NO_2 group of the dye.

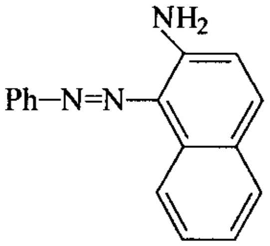
The uv and visible spectra of some hydroxy azo compound of increasing fused benzene rings were investigated by ***Hammam et al.***(18) in organic solvents of varying polarities in relation to molecular structure and polarity of the medium. The spectra were studied in aqueous buffer solutions and in buffer solutions containing 30% dioxane. The variation of absorbance with pH was utilised for the determination of pK values of the compounds. The effects of substituent on λ_{max} and pK were also studied.

Haessner et al.(19) studied the azo-hydrazone tautomerism in substituted 1-phenylazo-2-naphthols (R = 2-NO_2, 4-F, 3-OCH_3, 4-OH, 4-NH_2, etc).



From the ^{1}H-nmr chemical shift of H(8) and H(3) using pyridylazonaphthols and the phenylazonaphthylamine as model compounds:

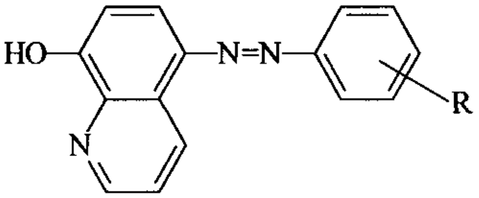




The equilibrium constant for tautomerization gave a linear free energy relationship with **Hammett** constant (σ). The studied reaction entropy for the conversion of the azo form into the hydrazone form was always negative and substituent independent. The quinonid hydrazone has a higher tendency to aggregate than does its tautomer.

Gaber et al.⁽²⁰⁾ studied the electronic absorption spectra of some phenylazohydrazone derivatives in ethanol and cyclohexane, as well as in some other organic solvents of different polarities and in buffer solutions of varying pH values. The variation of absorbance with pH was utilized for the determination of pK_a values. The ir spectra was recorded in the solid state as KBr pellet. The ^{1}H-nmr spectra of some compounds in relation to their molecular structure were also discussed.

The solvent and substituent effects on the absorption spectra of 5-arylazo-8-quinolinols [R = H, Cl, Br, OEt, $N(Me)_2$, $AsO(OH)_2$, SO_3H, OMe, Ac, Me, OH and NO_2].



were studied by ***El-Ansary et al.*** ⁽²¹⁾ in organic solvents of varying polarities. The four absorption bands observed in ethanol were assigned to the corresponding electronic transitions. The effect of solvent polarity on the band shift was interpreted in terms of the dielectric constant of the medium. Deviation in highly polar solvents was attributed to H-bond formation between the solute and solvent molecules. The ir-absorption bands were also identified for each dye.

The electronic absorption spectra of some chelating monoazo compounds have been studied in organic solvents of varying polarities by ***Dessouki et al.***(22). The uv-bands in ethanol and cyclohexane were assigned in the light of electronic transitions. The effect of microscopic and macroscopic solvent polarity parameters was also discussed. The ir spectra of the solid compounds as KBr discs as well as the ^{1}H-nmr have also been assigned and discussed in relation to molecular structure. The azo-hydrazone tautomerism in some of these compounds was assured. The study indicated that the colour of the materials depends on the polarity and the formation of intermolecular H-bond with the solvent molecules.

The electronic absorption spectra of some azo dyes with a condensed ring system had been investigated in organic solvents, and buffer solutions by ***Hammam et al.*** (23). The spectra in organic solvents were discussed in terms of molecular structure and medium effects.

The changed annulation in the condensed ring system was found to influence the position of the charge transfer band (CT) and the contribution of the o-hydroxyazo or the o-quinone-hydrazone forms to the tautomeric equilibrium. The spectra in buffer solutions were used for the determination of the pK_a values which were considered in relation to molecular structure. The main bands in the ir spectra were reported and discussed.

The state of symmetric carbocyanines and asymmetric styryls dyes has been studied by ***Kormosh et al.***(24). The specrophotometric characteristics, protonation and hydrolysis constant have been estimated. The charge distribution in the dyes has been evaluated by quantum-chemical calculations. Protonation mechanism is discussed based on the data UV-Vis and ^{1}H-NMR spectroscopy.

1-2 Literature Survey on The Applications of Azo Compounds in Spectrophotometric Determination of Metal Ions

Spectrophotometry is, now, one of the most important instrumental methods for analysis widely adopted with high precision, sensitivity and availability of the instrument used. Many reagents have been used for microdetermination of metal ions spectrophotometrically. Among them appear the azo compounds to be of the most interest. The chromogenic reagent reacts with the metal ions to give intense colourd products which can be colorimetrically or spectrophotometrically monitored. In the last few decades, many investigations had been carried out using different derivatives of azo compounds as new reagents for metal ions determination.

Fifteen azo dyes containing the m-dimethylaminophenol group were synthesized and their analytical potential for determination of some metal ions such as Cu^{2+}, Zn^{2+} and Ni^{2+} was studied spectrophotometrically by ***Shibata et al.***(25). It was found that, among these reagents, the heterocyclic azo derivatives were the most suitable as chromogenic reagents. The best reagents are the 2-pyridylazo compounds. These complexes with Cu^{2+}, Zn^{2+} and Ni^{2+} showed molar absorptivities of the order 10^5 1 mol^{-1} cm^{-1}. In these reagents, the para substituted dimethylamino group ortho to the azo group seems to play an important role in achieving high molar absorpitivity and stability of the metal complexes.

Kucher et al.(26) prepared 1-(7-oxo-5, 5-dimethyl-4,5,6,7-tetrahydrobenzothiazol-2-azo-2-hydroxy-naphthalene-6-sulfonic acid (LH_2) and investigated its acid-base properties spectrophotometrically. In slightly acidic medium, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Fe^{3+} formed a coloured chelates with (LH^-). The stability constant of Cu^{2+}-LH (1:1) complex was 1.28 x 10^{10} and hence, Cu^{2+} was determined spectrophotometrically by measuring the absorbance of this complex at 600 nm (molar absorptivity = 2.80 x 10^4 l $mole^{-1}$ cm^{-1}). Beer's law was obyed up to 7.8 μg/ml. LH_2 was used as metallochromic indicator in visual titration of Cu^{2+} with EDTA.

Domagalina et al.(27) examined the reactions of nine azo dye derivatives of thiadiazol with metal ions. The dyes formed a coloured complexes with Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+} and Fe^{2+} with ligand/metal ratios of 2:1 for Ni^{2+}, Co^{2+} and Fe^{3+}, and 1:1 for Cd^{2+} and Cu^{2+}. The dissociation constants for the complexes were determined. The results showed that the stability of the complexes decreased in the order Co > Ni > Fe > Cd > Cu.

Chauhan et al.(28) used 1-(5`-choloro-2`,3` dihydroxypyridyl-4`,azo) benzene-4-sulfonic acid as reagent for the spectrophotometric determination of Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} ions. They found that the ligand formes a dark coloured water-soluble complex with Fe^{2+} with a maximum absorbance at 580 nm in the pH range 5.2-7.5. The freshly prepared complex had 2:3 (metal:ligand), after

2-3 hour, Cu^{2+}, Ni^{2+} and Co^{2+} formed 1:3 (metal: ligand) red-violet complexes with a maximum absorbances at 650, 550 and 550 nm, respectively. The optimum pH range, Sandell sensitivity, molar absorpitivity, ranges in which Beer's law was obeyed and the optimum concentration ranges were determined.

Yusupov et al.(29) found that the introduction of a nitro group into the 5-position of the thiazol heterocyclic compounds improved the selectivity and sensitivity of the thiazolylazo reagents for the spectrophotometric determination of transition metal ions. The analytical properties of the reaction between the new reagents and Cu^{2+}, Ni^{2+}, Co^{2+} and Pd^{2+}, Such as optimum pH of the complexation. Spectral constant, metal/ligand ratio, molar absorpitivity (ε) of the complexes and selectivity were studied.

Purmal et al.(30) tested fourteen azo dyes with hydroxyaryl, 4-$Et_2NC_6H_4$, and substituted thiazolyl functional groups as potential analytical reagents for sensitive spectrophotometric determination of some metal ions viz Al^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, In^{3+}, V^{5+}, Sb^{2+} and Ge^{2+}. The molar absorpitivities of the complexes were $\leq 9.50 \times 10^4$ $l\,mol^{-1}\,cm^{-1}$.

Varma et al.(31) studied the reaction of Cu^{2+} with ammonium (2-amino-3-hydroxy-4-pyridylazo) benzene-4-arsonate spectrophotometrically in ascorbic acid medium at pH 5.6-7.0 where the red-violet 1:1 complex formed was used for determination of Cu^{2+}

ion by measuring the absorbance at 560 nm ($\varepsilon = 2.0 \times 10^4$ l mol^{-1} cm^{-1}). Beer's law was obeyed up to 2.4 µg/ml and Sandell sensitivity was 0.0032 µg/cm^2. The method was used to determine copper in alloys.

Varma et al.$^{(32)}$ evaluated the composition, molar absorpitivity and stability constant for Ni^{2+} ammonium complex with (2`-amino-3`-hydroxypyridyl-4`-azo) benzene-4-arsonate of stoichiometric ratio 1:2 (M:L). The optimum conditions for the spectrophotometric determination of Ni^{2+} with this reagent were obtained with samples containing 3.5-21.0µg/ml Ni^{2+} in the presence of excess reagent, with the absorbance measured at λ_{max} 540 nm.

Pesavento et al.$^{(33)}$ examined the complexation equilibrium between Ni^{2+} and some sulfonated azo dyes in 0.1 M $NaClO_4$ aqueous solution at 25°C. The investigated azo dyes were composed of three couples. The first had the thiazolyl heterocycle diazo moiety; 1-(2-thiazolylazo)-2-naphthol-3,6-disulfonic acid and 2-(2-thiazolylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid. The second couple had the tetrazolyl heterocycle namely; T-azo-R and 4,5- dihydroxy -3-(1H-tetrazolyl -5- azo) 2,7- naphthalenedisulfonic acid, whereas the last couple was Amaranth and 2-(4-nitro-phenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid having no hetero atom. The use of these dyes for the spectrophotometric determination of Ni^{2+} was studied.

Horiguchi et al.(34) synthesized some of water soluble derivatives of pyridylazo-aminophenol and pyridylazo-aminobenzoic acid, which were found to be highly sensitive chromogenic reagents for some metal ions viz Zn^{2+}, Co^{2+}, Ni^{2+} and UO_2^{2+}. Among this series; 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino) phenol was highly sensitive for Zn^{2+} ($\varepsilon = 1.33 \times 10^5$ $1 mol^{-1} cm^{-1}$ at 552 nm), UO_2^{2+} ($\varepsilon = 6.6 \times 10^4$ $1 mol^{-1} cm^{-1}$ at 578nm), while 2-(3,5-dibromo -2- pyridylazo) -5- (N-ethyl-N-sulfopropylamino) benezoic acid was highly sensitive to Co^{2+} ($\varepsilon = 1.52 \times 10^5$ $1 mol^{-1} cm^{-1}$ at 670nm) and Ni^{2+} ($\varepsilon = 1.37 \times 10^5$ $1 mol^{-1} cm^{-1}$ at 620 nm).

Abdel Ghani et al.(35) determined the successive stability constants of complexes of 5-(arylazo)-8-hydroxyquinolines with Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} metal ions potentiometrically following the Bjerrum pH titration technique as adopted by Irving and Rossotti. Log β values are given for the 1:1 and 1:2 complexes. In a few cases, 1:3 complexes are also formed.

The complexes formed between 1-(2-pyridylazo)-2-naphthol (PAN) and Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+} and Pb^{2+} were studied spectrophotometrically in solution by **Zaky et al.**(36). The different complexes were characterized and their stoichiometric ratios were thoroughly investigated. Methods for the spectrophotometric determination of these metals and spectrophotometric titrations using

EDTA were reported. The complexes have been isolated in solid state and characterized on the basis of mass spectra and ir data.

Oiha et al.(37) described a method for spectrophotometric determination of traces of cobalt with 5-methoxy-2-(3-methoxybenzoyl) 3-methyl-7-nitro-4H-1,4-benzothiazine. A stable complex formed from Co^{2+} with the reagent and was quantitatively adsorbed on microcrystalline naphthalene at pH = 8.0. The adsorbed crystals were separated, dried at ~ 50°C and dissolved in DMF. From the absorbance measured at 510 nm, the molar absorpitivity and the sensitivity were determined.

1-(2-imdazolylazo)-2-naphthol-4-sulfonic acid was used for the determination of Cu^{2+} in solution of pH 3.0 by ***Fuyou and Sumwei***(38). The apparent molar absorpitivity of the complex was 1.94×10^4 $l\ mol^{-1}\ cm^{-1}$ at 530 nm. The 1:1 complex has an apparent stability constant of 6.96×10^6. Beer's law was obeyed in the range of 0.0-0.8 µg/ml. the method was applied for the determination of traces of Cu in magnesium alloys and iron ores.

The conditions for the formation and properties of the system of cobalt-2-(2-benzothiazolylazo)-5-dimethylaminobenzoic acid (BTAMB)- sodium laurylsulfate (Na LS) have been studied by ***Xie and Dong***(39). In the pH range of 5.2-7.7, cobalt reacts with BTAMB to form a Co^{2+} complex in the presence of thiourea as reducing agent; and to form Co^{3+} complex in the presence of $(NH_4)_2S_2O_8$ as the oxidant. The Co^{2+} complex has spectral properties of λ_{max} = 640 nm, ε_{max} = 1.12×10^5 l mol^{-1} cm^{-1}; the Co^{3+} complex has λ_{max} = 690 nm, ε_{max} = 9.7×10^4 l mol^{-1} cm^{-1}. The molar ratio of Co : BTAMB in the Co^{2+} and Co^{3+} was estimated to be 1:2 Beer's law was obeyed for Co^{2+} and Co^{3+} in the range of 0.0-6.0 µg/10 ml. The simultaneous determination of cobalt and nickel by Kalman filtering method was described and the method had been applied to the analysis of synthetic samples with satisfactory results.

A simple, sensitive and selective method for the spectrophotometric determination of nickel has been developed by ***Han et al.***(40) Nickel (II) reacted with -2-(5-bromo-2-pyridylazo)-5-dimethylamino aniline in the presence of sodium lauryl sulfate to form a 1:2 complex at pH 5.2-6.5. The molar absorptivity of the complex was 1.24×10^5 $lmol^{-1}cm^{-1}$ at 570 nm. Beer's law was obeyed for 0.0.4-µg/ml. In the presence of thiourea, ammonium flouride, Cu^{2+}, Pd^{2+} and Fe^{3+} do not interfere. The method had been applied for the determination of Ni^{2+} in aluminum alloys with satisfactory results.

A spectrophotometric method for the determination of trace amounts of nickel was described by ***Zhao et al.***(41) At pH 6.0, Ni^{2+} reacted with p-acetylarsenazo to form a 1:2 coloured complex with an absorption maximum at 630 nm. The apparent molar absorpitivity is 6.5×10^4 l mol^{-1} cm^{-1}. Beer's law was obeyed over the concentration range of 0-0.8 μg/ml. The method was selective and can be applied for the determination of nickel in aluminum alloy.

A sensitive colour reaction of Ni^{2+} with a new reagent; 2-arsono-4-methylphenyldiazoaminoazobenzene had been studied by ***Bincai and Liu***(42). A stable red complex was formed in a medium of pH 10.8-11.5. The ratio of Ni^{2+} to the reagent in the complex was 1:2. The apparent molar absorpitivity was $1.92x10^5$ 1 mol^{-1} cm^{-1} at 538 nm. Beer's law was obeyed in the range of 0.-0.32 μg/ml. The method had been applied for the determination of nickel in aluminium alloys and ores with satisfactory results.

The reaction of copper with the new reagent 2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminoaniline (3,5-diCl-PADMA) was studied spectrophotometrically by ***Yang et al.*** (43). In the pH range of 3.5-4.5, copper forms a stable 1:1 complex with 3,5-di Cl-PADMA showing maximum absorption band at 580 nm with a molar absorpitvitiy of $4.54x10^4$ 1 mol^{-1} cm^{-1}. The stability constant of the complex is 1.78 x 10^6. Beer's law was obeyed at 0.-24 μg/25 ml of copper. This method was used for the determination of traces of copper in aluminum alloy with satisfactory results.

Extensive study of composition, stability constant and optimum conditions for formation of Fe^{3+}, Ni^{2+} and Cu^{2+} complexes with four azo compounds based on 4-aminoantipyrene were done by ***Moustafa et al.***(44). The coloured complexes formed, at the optimum conditions can be successfully used in the microdetermination of above mentioned metal ions in synthetic solutions as well as in Incoloy 800 alloy. The method described was rapid, sensitive, highly accurate and reproducible.

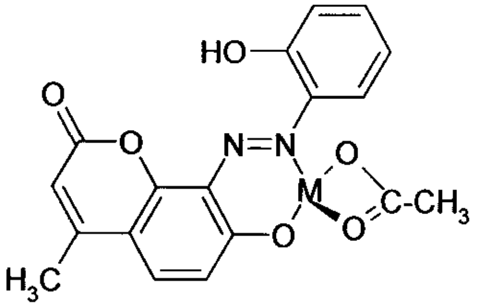
Abollino et al.(45) determine the stability constants for Cd^{2+}, Cu^{2+}, Ni^{2+} and Mn^{2+} complexes with three sulfonated azo-ligands, calamagite, alizarin violet N and Palatine chrome black. The ion-exchange flow method was performed by passing a 100 ml of buffered test solution containing 10 micro M-Ligand and 0.1 mg/L of metal ion through an AGMP-1 anion exchange column at 1.5 ml/min. the effluent was collected and analysed for the metal ion by ICPAES. The retained metal ions were eluted from the column with 10 ml of 2 M-HNO_3 and determined by ICPAES. The ion-exchange batch method used the same test solution and Anion-exchange resin (0.5 g) as described for the flow method. After shaking for 4-h, the solid and liquid phases were separated and the flow method was followed. The results agreed well with those obtained by a spectrophotometric method (details given) and also with literature data, the order of stability of the complexes with the same ligand is $Cu^{2+} > Ni^{2+} > Cd^{2+} > Mn^{2+}$.

Pilipenko et al(46) studied the complex formation of copper with 4-methyl-2-(2-hydroxynaphthyl-1-azo). Thiazole [1-(4-methyl-2-thiazolylazo)-2-naphthol] and 4-admantal-2-(2-hydroxy-naphthyl-1-azo). Thiazole [1-(4-adamantyl-2-Thiazolylazo)-2-naphthol].The cited azo-dyes (I and II) form Cu-I (or II) (1:2) complexes insoluble in H_2O, but extractable into $CHCl_3$ at pH 3 to 14 (> = 4 fold molar excess of I or II relative to Cu is needed. The extracted complexes exhibit max. absorption at 600 nm (Є = 7.8 x10^4 l mol^{-1} cm^{-1}) for I or 565 nm (Є = 4.5x 10^4 l mol^{-1} cm^{-1}) for II. I has been used for determining ≥ 4 ng ml^{-1} of Cu in distilled water at pH 10 to 12; Fe, Co, Ni, Zn, Cd and Hg interfere. II is the more selective reagent; it has been used for determining ~ 60 to 300 ng ml^{-1} of Cu in industrial waste water at pH 3 to 4 in the presence of F-as masking reagent (Al, Fe(III), Zn and Pb do not interfere).

Extractive-spectrophotometric determination of traces of copper (II) with 2-amino-4-(4-nitrophenylazo) pyridin-3-ol as determined by ***Salillas, et al*** (47). The determination involved the extraction of Cu (II) from aqueous solution at pH 6 by shaking with a 10 mM solution of the cited azo dye (1) (preparation described) in isobutylmethyl ketone. After separation of the organic layer, the absorbance of the highly coloured, stable Cu (II) (2:1) complex formed was measured at 560 nm. Beer's law was obeyed from 0.1 to 2.2 μg ml^{-1}; Є was 51.900 and the sandell sensitivity was 1.2 ng cm^{-2}. The optimum concentration range was 0.2 to 1.2 μg ml^{-1}, and the relative error was 0.44%. Many foreign species were tolerated, but Sn (II) and Hg (II) interfered seriously; the interference from 10-fold amounts (relative to Cu) of Hg (II) could be eliminated. This method has been applied to the determination of Cu in whisky, fish liver and sea-water.

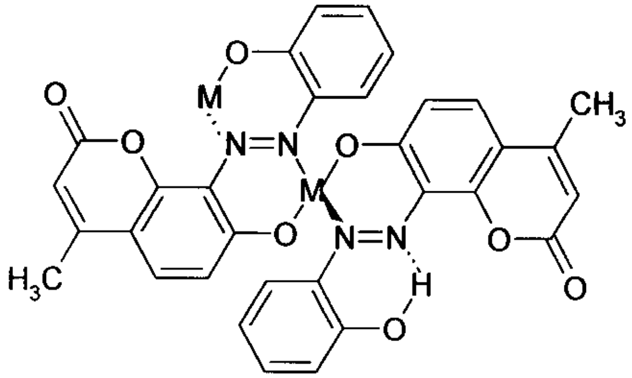
The spectrophotometric study and analytical applications of the complexes of copper (II) and zinc (II) with some sulphonated azo-dyes were studied by ***Pesavento and Fulle-Solid.***(48). A study has been made of the reacitons of Zn (II) and Cu (II) with five azo-derivatives of 3-hydroxy-or 4,5-dihydroxy-naphthaline-2,7-disulphonic acid in 0.1 M-$NaClO_4$ or–Hcloy medium. Both metals yield stable complexes with 3-hydroxy-4-(2-thiazolylazo) naphthalene-2,7-disulponic acid and with 3-(5-tetrazolylazo) chromotropic acid. Stability constants are reported, and are compared with earlier data for the complexes of Ni(II) with the same reagents and of all three metals with 3-hydroxy-4-(5-tetrazolylazo) naphthalene-2,7-disulphonic acid. Analytical applications of the reagents are discussed, and methods are given for the determination of Ni, Cu interferes and a correction must be applied. Results on four steels containing 0.14 to 0.18% of Cu and 0.07 to 0.14% of Ni agreed well with those found by independent methods.

Proton-ligand ionization and metal ligand stability constants of 8-(arylazo)-7- hydroxyl-4-methylcoumarin complexes with V(IV), Co(II), Ni(II), Cu(II) and Zn(II) ions have been determined.(49) pH-metrically in 70% (v/v) ethanol-water mixture at 25 °C and $\mu = 0.1$. The order of stability constants ($\log \beta_1$), $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ is inconformity with Irving-Williams series. The correlations between the properties of the ligand and stability of its complexes were studied. The structure of the solid complexes has been assigned on the basis of elemental analysis and IR spectroscopy. In the light of these findings, structures (A) and (B) may be assigned to the 1:1 and 1:2 complexes, respectively, of Co(II), Ni(II) and Cu(II) while structure (C) may be assigned to the 1:1 complex of Zn (II) as shown in shape the following sheet.



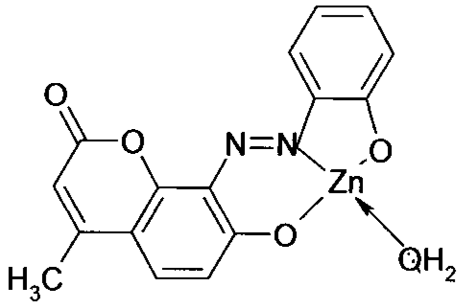
M = Co, Ni and Cu

(A)



M = Co, Ni and Cu

(B)



(C)

Awad and Ibrahim.(50) studied the synthesis of some new azosulphonamides based on salicylic acid and thiosallicylic acid, and having antibacterial and antifungal activity. The new azo-dyes have been prepared by diazotization of 4-aminobenzene 4-prime-(substituted heterocyclo) sulphonamide derivatives and coupling with salicylic or thiosalicylic acid in acid medium, to afford the corresponding substituted 4-azo-(4-Prime-substituted benzene sulphonamido)-salicylic and thiosalicylic acids as ligands. Interaction of these ligands with metal salts (Fe^{2+}, Cu^{2+} and Hg^{2+}) in solution afforded the corresponding metal chelates. The compounds were screened in vitro for antibacterial and antifungal activity.

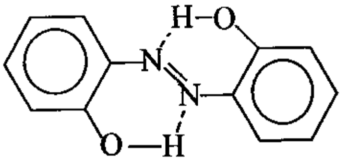
1-3 Literature survey on the Metal Chelates of azo compouds

Maurica et al.(51) studied the absorption spectra of Cu^{2+}, Ni^{2+} and Co^{2+} chelates of some simple o-hydroxy and o-amino azodyes. The absorption spectra of these compounds were recorded in the uv region, the spectra of the metal complexes did not differ appreciably from the spectra of the corresponding dyes, but in the visible region a new weak band due to the metal ion was found. This new band lies at ~ 590 and ~ 490 nm for Ni^{2+} and Cu^{2+}, respectively regardless of the dye with which the metal is combined, it is not due to vibration of the entire molecule but to transitions of one or more electrons in the bonds between the dye and the metals. It is likely that the electron (or electrons) which undergoes transition is one of those in the covalent or coordinate covalent bonds between the dyes and the metal since these are the electrons directly influenced by both dye and metal ion.

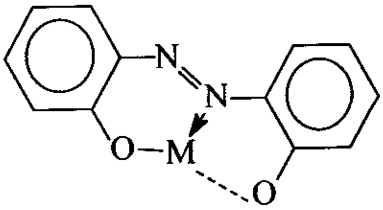
Karitsyna et al.(52) studied the complexes of azo compounds with metal halides. The uv spectra were reported for the following complexes: 2-$(CH_3)_2N$-C_6H_4N:N-Ph. 3 $SbCl_3$, 2-p-$(CH_3)_2NC_6H_4$ N:N-Ph_3 $BiCl_3$, p-O_2N-C_6H_4N:N-Ph. $BiCl_3$. $2H_2O$, Ph-N:N-Ph. $SbCl_5$. $2H_2O$ and Ph-N: N-Ph. $SbCl_5$. The spectra indicated that the metal complexes were formed through coordination with the azo group. In ethanol, the complexes were partially dissociated. Possible coordination at the aminonitrogen atom was suggested in addition to definite bond formation at the azo group.

Mikheeva et al. (53) examined the complexes of some azo compounds and their ir-spectra. The assignment of the bands in the spectra were restricted to some bands, namely the stretching vibration of N:N at 1463-1453 cm^{-1}, which during complexation shifted to 1375-1352 cm^{-1} the stretching vibration of the C=O was a weak band at 1570-1564 cm^{-1}. The stretching vibration of C-N in the complexes was found at 1473-1463 cm^{-1}, deformation vibration of OH naphthol was at 1219-1210 cm^{-1} and disappeared during complexation. The Cu-O in the complexes gave two bands at 838-818 and 563-556 cm^{-1}, whereas the stretching virbation of Cu-N was found at 453-448 cm^{-1}.

The structure and bonding of bivalent metal chelates of o, o`-dihydroxyazobenzene (DHAB) have been studied by ***Knoeck***(54) using PMR and absorption spectrocopic methods. This study indicated that fluorescence, which is observed only for the Mg DHAB chelate, many arise from a greater degree of ionic character in the metal-oxygen bonds of this compounds than in the other metal (II) chelates examined. NMR studies of DHAB and similar compounds showed that the phenol hydrogen atom, which gave peaks appearing far downfield, must be strongly hydrogen bonded, so the most probable structure of free ligand is the symmetric trans structure.

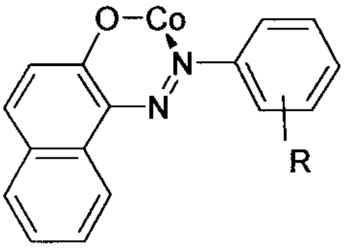


The infrared spectra also substantiated this structure. The following structure of the metal chelate was suggested:

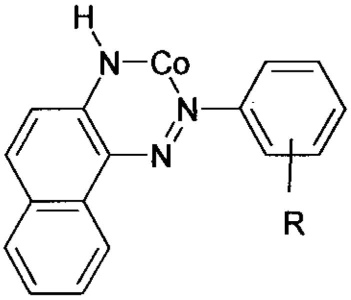


Konovalov et al.(55) studied the ir-spectra of the metallic complexes of p-aminoazobenzene. The spectra of the complexes of Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} and their λ_{max} were tabulated. The spectral shift revealed that the ligand was coordinated via the NH_2 group.

Alekseenko et al.(56) studied the metal chelates of cobalt (II) with o-hydroxy and o-aminonaphthalazobenzene (A and B) with R=H, p-OCH_3, o-CH_3 and 2,4-$(CH_3)_2$. The magnetic susceptibilities and magnetic moments of the complexes were determined.



(A)



(B)

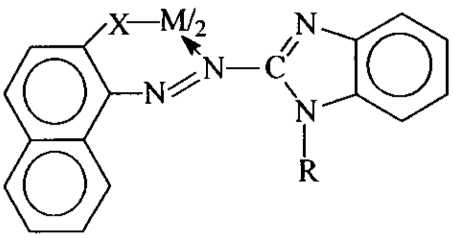
In (A), the magnetic moment varied with the nature of R, but with R=H, p-CH_3 or p-OCH_3, it was within the limits of spin-unpaird tetrahedral complexes of Co(II) with three unpaired electrons. In (B), the magnetic moment was that expected of one unpaired electron, and it was independent of the nature of R.

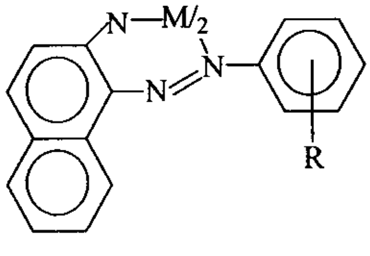
Fitzner(57) observed that unsymmetrical o,o`-dihydroxyazo compounds form 1:1 isomeric complexes with Cu^{2+} and Ni^{2+}. The isomers differed according to which of the azo N-atom is coordinated to the metal. The isomers are formed in almost equal unit and were separated by chromatography except in the case of complexes having a nitro group containing ligand. Cr^{3+} and Co^{2+} complexes with metal/Ligand ratio of 1:2 exist in three isomeric forms.

Masoud et al.(58) reported the acid dissociation constants of some 2-hydroxy-5-methyl-4-substituted azobenzenes and the formation constants of their chelates with Fe(III), Co(II), Ni(II) and Cu(II). The substituent and the solvent, beside the pH value, affect the tautomeric phenomena in the ligands. The ligands formed 1:1 and 1:2 complexes in solutions. The pK values of the complexes were evaluated spectrophotometrically, the solid complexes were found to have octahedral spatial configuration.

Dessouki et al.(59) studied the complex formation of Co(II), Ni(II) and Cu(II) with o-carboxyphenylazo salicylaldehyde by potentiometric and conductometric titrations. The stoichiometry of the complexes was also studied spectrophotometrically, the proton-reagent stability constant and conditional formation constants were determined. DTA and ir-spectra for the binuclear complexes were reported. This study showed that the ligand in the case of binuclear metal chelates functions as a dibasic tetradentate group.

Alekseenko et al.(60) studied the complexes of Cu^{2+} and Ni^{2+} with heterocyclic azo-ligands (type XVIII) and compared them with analogous complexes which did not contain a benzimidazole ring (type XIX).





(XVIII)

$X = N_2$-Ph, OH
$R = CH_3, C_8H_{17}$
$M = Ni^{2+}, Cu^{2+}$

(XIX)

R = H, p-CH_3, p-OCH_3
$M = Ni^{2+}, Cu^{2+}$

Magnetochemical, infrared and spectroscopic methods revealed that a tetrahedral coordination geometry took place for the metal cations in complexes when a heterocyclic ligand replaces any aryl ring.

Gromov et al.(61) studied the coordination compounds of Cu^{2+} and Ni^{2+} with 1-(4-methoxyphenylazo)-2-naphthol (L), 1-(4-methoxyphenylazo)-3-carboxy-2-naphthol ($\bar{L}$) and 1-(4-methoxyphenyl azo)-3-ethoxycarbonyl-2-naphthol ($\bar{\bar{L}}$). The chelates were found to be CuL_2, $Cu\bar{L}$, Cu_2L_3, $Ni\bar{\bar{L}}_2$, $Ni\bar{L}$, $Ni\bar{\bar{L}}$ and $Ni\bar{\bar{L}}_2$. ir and electronic spectroscopy in solution and in the solid state were used to prove that the complexes contain five and six-membered metal-chelate rings.

Dessouki et al.(62) investigated the complexes of some phenyl azosalicylaldehyde derivatives with Co(II), Ni(II) and Cu(II) using spectrophotometric and potentiometric methods in buffer solutions. The study revealed the formation of 1:1 and 1:2 (metal:ligand) complexes. The conditional stability constants K_f and ΔG° values were determined. The structure of the ligands in the solid chelates

A spectrophotometric study on o-hydroxyphenylazo acetylacetone (o-HPAA) and its Co^{2+} complexes was carried out by ***El-Atrash et al.***(64). The pK values were determined by spectrophotometric and potentiometric methods. The values of pK_1 and pK_2 were found to be 10.6 and 11.82, respectively. The reaction with Co^{2+} was studied spectrophotometrically in the visible region. Optimum conditions for complexation revealed that the formation of a 1:1 complex with log K = 4.37±0.03 at pH 9.6 and ionic strength 0.05 M . The stability constant was found to decrease with increase of the dielectric constant of the medium.

Gaber et al.(65) studied the chelates of Co(II), Ni(II) and Cu(II) with some 3-arylazo-1,2,4-triazol dyes by conductometric titration, ir and ESR spectra. The formation of 1:1 and 1:2 (metal: ligand) complexes was established by elemental analysis and conductometric titration.

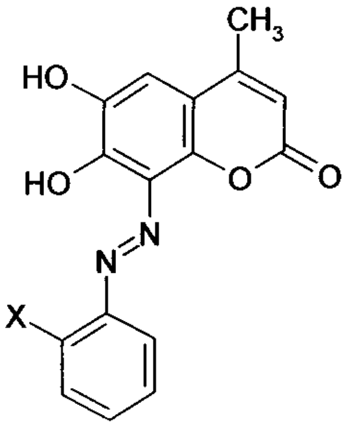
Khandar et al.(66) studied the syntheses and characterization of Bis[5(4-Alkoxyphenylazo)-N-nAlkyl-sallcylaldiminato]nickel(II) complex and the crystal structure of Bis[5-(4-propyloxyphenylazo)-N-pentyl salicylaldiminatol]Ni(II) by single crystal X-ray diffraction. Thermal properties of these compounds have been studied by polarizing microscopy.

The complexes formed between 4-(o-hydroxy or carboxy phenylazo)-1,3-diphenyl-2-pyrazoline-5-one and Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions have been studied in solution using conductometric, potentiometric and spectrophotometric methods(67). Interference from several metal ions was found. The stoichiometry and stability constants of the chelats were determined. The complexes formed were characterized by molar conductance, elemental, thermo-gravimetric analysis, ir , ^1H NMR , ESR and electronic absorption spectra. The bonding of the metal ions to the ligand took place through coordination of N in the N=N and O in the C=O groups and covalent bonding with the O of the hydroxy or carboxylic groups through proton displacement.

The nature of the complexes produced from the reaction of Zn^{2+} or Cd^{2+} with (2-pyridylazo)-resorcinol (PAR), sorbed on a sephadex QAE anion exchanger were studied(68). The visible and ir absorption spectra of the species fixed on the exchanger were established, the stoichiometry of the complexes was found to be 1:2 (Metal: ligand).

The structure of the dianionic form of PAR (L_2^{2-}) and for its complex ZnL_2^{2-} and CdL_2^{2-} was established by the SPARTAN program. The role of molecular orbitals of the ligand in possible coordination to metal ions was discussed and a distorted octahedral structure was proposed for both complexes. For comparison, $[Zn(HL)_2,H_2O]$ and $[Cd(HL)_2.H_2O]$ were synthesized and characterized by the normal instrumental techniques.

The solid complexes of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} with 8-arylazo-6,7-dihydroxy-4-methylcoumarin have been synthesized and charactrized by elemental and thermal analysis, magnetic susceptibility, molar conductance as well as ir spectroscopy(69). These azo compounds as new chromophoric reagents for the spectrophotometric determination of the metal ions were studied by extensive investigation of the optimum conditions favouring the formation of coloured complexes in solution.



X = H(1), OH(2), COOH(3), NO_2(4), OCH_3(5) and $AsO(OH)_2$(6)

Saha et al.(70) studied the complexes of Mn(II) and Co(II) with new tridentate ligands of N-aryl-2-pyridylazo phenylamines [NH_4C_5N:$NC_6H_4N(H)C_6H_4(R)$; where R = H or CH_3]. These complexes have low spin electronic configuration. While the manganese complexes are paramgnetic with one unpaired electron (1.65-1.70 μB), the cobalt complexes are diamagnetic. The characterization of the ligand and complexes was made by elemental analysis, magnetic susceptibility; ir , electronic absorption spectra as well as from esr-spectral data.

Optimum conditions for Er(III) complexation by 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [5-Br-PAAP] in the presence of surfactants are described (71). The calculated molar absorptivity (1.02 x 10^5) shows high sensitivity of the complexing agent towards Er(III) in the presence of surfactants. The effects of ionic strength and organic solvent on the Er-5-Br-PAAP-surfactant system are studied.

El-Saied et al.(72) studied the Fe(III), Co(II), Ni(II) and Cu(II) complexes of 4-azomalanonitrile antipyrine. The characterization of the complexes was made by elemental analysis, ir , electronic absorption spectra and ESR spectra as well as magnetic susceptibilities and molar conductivities.

Oxidative coupling of 2-aminopyrimidine with LiOCl produces 5-chloro-2,2`-azobis(pyrimidine) and 2,2`-azobis (5-chloropyrimidine) (abcp) both of which were structurally characterized(75). The symmetrical abcp was used as strongly π-accepting mono- and bis-chelate ligand in complexes with $[(bpy)_2Ru]^{2+}$, $[(H_6C_6)ClRu]^+$, $[(Ph_3P)_2Cu]^+$ and $(OC)_3$ ClRe. The π-acceptor capability of abcp results in low-energy MLCT transitions and facile reduction to isolable radial complexes of which the DFT calculated and structurally characterized dicopper (I) species {(μ-abcp)$[Cu(pph_3)_2]_2$} (PF_6) was studied by X- and W- band EPR and the complex $\{(\mu\text{-abcp})\ [Ru(bpy)_2]_2\}(PF_6)_3$ at 906, 230 and 285 GHZEPR frequency. The results indicate considerable metal:ligand orbital mixing in the singly occupied molecular orbitals.

A ^{13}C NMR and UV-Visible study of the tautomeric behaviour of azo functinalized PAMAM (polyamidoamine) dendrimers and the corresponding model compounds in a variety of solvents is reported(74). The results of these studies indicate that the azo functionlized PAMAM dendrimers exist as an equilibrium mixture of azo and hydrozone tautomers. A comparison of the behaviour of the dendmers with model compounds suggests that the dendrimer periphery affects the tautomeric equilibrium between the azo and the hydrazone forms. The results further show that the proportion of the azo tautomer increases with dendrimer generation as well as in the presence of hydrogen-bond donor solvents such as acetic acid and 2,2,2-trifluoroethanol. Results of MO calculations suggest that the more planar azo tautomer would be favored because it stacks better on the dendrimer surface, which is consistent with experimental results.

The colour reaction of Cu^{2+} with a new thiazolylazo reagent of 2-[2-(6-methylbenzothiazolyl)azo]-5-diethylaminobenzoic acid was presented(75). A stable blue complex with the ratio of 1:1 was formed in pH 2.5-6.3, AcOH-AcONZ buffer solution in the presence of ethanol. The maximum absorption of the complex was at 655 nm, the apparent molar absorptivity 7.94×10^4, and Beer's law was obeyed at 0.24 μg/25 ml. NaF, diacetyldioxime and thiourea were used as mesking agents. The method was used for the determination of Cu in Al alloy samples with the RSD 0.67-1.86%.

Spectrophotometric determination of Pd(II) and tartaric acid was studied by using the colour reactions between 2 (5-nitro-2-pyridylazo)-5-(N-propyl-N-3-sulfopropylamino)phenyl, (5-NO_2-PA PS), and Pd(II) in strong acidic media, and between 5-NO_2-PAPS, Nb(V), and tartaric acid in weak acidic media(76). The calibration graphs were linear at 0-25 μg/10ml Pd(II), with an apparent molar absorption coefficient (ε) of 6.2×10^4 1 mol^{-1}. cm^{-1} at 612 nm, 0-23 μg/10 ml tartaric acid with $\varepsilon = 1.08 \times 10^6$ L mol^{-1}. cm^{-1} at 612 nm, respectively. The proposed methods were selective and sensitive in comparison with other chelating pyridylazo dyes Pd(II) or metavanadic acid-tartaric acid method, and the effect of foreign ions such as Cu(II) was negligible for the assay of Pd(II) with 5-NO_2, PAPS.

A method for the photometric determination of Fe(III) was developed based on the colour reaction of Fe(III) with a new chromogenic reagent α-quinolylazoquercetin(77). A yellow complex was formed in pH 5.6 KH_2PO_4-NaOH buffer solution. The absorption maximum of the complex was at 430 nm, the apparent molar absorptivity 1.15×10^5, and Beer's law was obeyed at 0.6-1.2 μg/10ml. The method was used for the determination of Fe in tea samples with the recovery 94.6-104.3% and the RSD 0.5-2.1%.

The synthesis, characteristics and analysis reactions of a new reagent, namely 5-(6-methoxy-2-benzothiazoleazo,8-aminoquinoline (MBTAQ) with Co^{2+} and Ni^{2+} were described(78). Sensitive spectrophotometric methods for the determination of Co and Ni by using this reagent were developed. In the presence of the ionic surfactants cetyltrimethylaminonium bromide (CTAB) and borax buffer solution, Co^{2+} and Ni^{2+} form blue coloured, 1:2 and 1:3 (metal: ligand) complexes with MBTAQ, respectively. The apparent molar absorptivities were 1.15×10^5 (Co) and 1.28×10^5 (Ni) 1 mol^{-1}, cm^{-1} at 655 and 623 nm. The methods obeyed Beer's law for 0-0.40 μg ml^{-1} of Co and 0-0.32 μg ml^{-1} of Ni and the detection limits were 0.00050 and 0.00045 μg ml^{-1}. The relative standard deviations (RSD) for measurement of 0.24 μg ml^{-1} Co^{2+} and of 0.20 μg ml^{-1} of Ni^{2+} were 0.7% and 1.1%, respectively. The methods were successfully used to determine trace amounts of Co in draingage sediment and trace amounts of Ni in Al alloy.

Amine et al.(79) reported the reaction of mercury with 4-(2-benzothiazolylazo)-2, 2-biphenol, 5-(2-benzo-thiazolylazo) -8-hydroxyquinoline; 1-(2-benzo-thiazolylazo)-2, 3-naphthalenediol and 8-(2-benzothiazolylazo)-1,4-naphthalendiol. The potentiality of the prepared compounds as new chromogenic reagents for the spectrophotometric determination of Hg^{2+} ions were assessed by extensive studies of the optimum conditions favoring the formation of the coloured complexes. The method allows the determination of Hg^{2+} ions at 0.1-6.5: 0.1-7.2, 0.1-4.8 and 0.1-6.5 μg ml^{-1} at wavelengths 590; 629, 606 and 591 nm on using reagents. The molar absorptivity and Sandell sensitivity are also calculated. The effect of various interfering ions and their tolerance limits were studied. The conditions developed were used successfully for the determination of Hg^{2+} ions in environmental and human (urine and blood) samples.

The colour reaction of Ag^+ ions with 5-(2-hydroxy-4-sulfo-5-chlorophenol-1-azo)thiorhodanine (HSCT) was studied and a method for spectrophotometric determination of Ag^+ ions in waste water was presented(80). In a buffer solution of pH = 2.8 in the presence of Triton X-100, HSCT reacted with Ag^+ ions to form 1:1 stable red complex with the molar absorptivity 6.33 x 10^4 L mol^{-1} cm^{-1} at 540 nm. Beer's law is obeyed in the range of 0.0-20.0 μg Ag^+ per 25 ml solution. The method was used to the determination of Ag^+ ions in waste water with satisfactory result.

The method is established for the determination of Fe(III) by spectrophotometry using the reagent of 4-(2-pyridylazo)pyrocatechol and sodium dodecylsulfonate as surfactant(81). The method is used for analysis of Al alloy with a relative standard deviation of 1.0-1.2% and a recovery of 99.9-100.2%. A complex was formed by Fe(III) and the reagent having a composition ratio of 1:3 and an apparent stability constant of 9.33 x 10^{14}.

V- Synthetic zeolite, e.g. the permutites which are used in water softening.

These materials can behave as selective sorbents and ion exchangers and it must be conditioned before use in an effort to overcome their limited resistance to acids and alkalis and limited mechanical stability.

1-4-2 Distribution coefficient (K_d)

The k_d values were calculated using the simplest proposed formula:

$$K_d = \frac{I-F}{F} X \frac{V}{m} \qquad \text{ml/g} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where

I is the initial activity of the cation.

F is the final activity of the cation after equilibrium.

m is the weight of the exchanger in grams.

V is the volume of the cation solution (ml).

When the ion exchange proceeds by the reaction

$$\overline{nH^+} + M^{n+} \rightleftharpoons \overline{M^{n+}} + nH^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

In sufficiently diluted solution, where activity coefficient may be neglected, the selectivity coefficient can be defined by the following equation(84).

$$K_H^M = \frac{\overline{[M^{n+}]}\,[\mathrm{H}^+]^n}{[M^{n+}]\,\overline{[H^+]^n}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

vigorous agitation to disperse the precipitate in the effluent and to aid the entrainment of the activity.

1-4-6 Advantages of chemical treatment:

Chemical treatment has many advantages and can be listed in the following points:

i- At least in batch processes it is relatively easy to change the chemical precipitates in order to accommodate changes in the composition of the liquid feed.

ii- It's relatively low cost.

iii-Big liquid flows can be handled economically.

iv-The process allows the separation of activity from inactive solutes which may have a large bulk.

1-4-7 Disadvantages of chemical treatment:

Treatment of liquid radioactive waste by chemical treatment show some disadvantages such as:

i- Difficulties with continuous automatic operation.

ii- The relatively large volume of radioactive sludge's which has to further treated, conditioned and disposed off.

iii-The relatively low decontamination factors being achieved as compared to other method.

iv- High inactive salt content of the treated water, which is also undesirable from the environmental protection point of view.

1-4-8 Evaporation:

Evaporation is probably the best technique for wastes having relatively high salt content for nitric acid containing effluents, i.e. having a high electrical conductivity, a relatively low volume and needing high decontamination factor. Because of its relatively high operating costs and high decontamination efficiency, evaporation is preferably confined to the treatment of intermediate-and high-level radioactive liquid wastes. Although it can be considered a fairly simple operation which has been successfully applied in the conventional chemical industry for many years its application in the treatment of radioactive waste can give rise to many problems such as corrosion, scaling, or foaming. All of these problems should be considered as potential limitations of the evaporation process.

1-4-9 Decontamination and volume reduction factor:

The main advantage of an evaporation process is its ability to reduce the volume of a radioactive liquid that must be disposed off. At the same time as the solvent is removed most of the radioactive or other dissolved material in the original solution remains in the reduced volume. The presence of volatile nuclides such as tritium and some forms of iodine and ruthenium will reduce the decontamination factor. By adding alkalinity of the feed solution the volatility of iodine and ruthenium may be reduced; tritium separation cannot be effected in evaporation.

1-4-10 Antimonates as inorganic ion exchangers

A wide range of compounds of this type have shown a great promise in preparation reproducibility, ion-exchange behavior and both chemical and thermal stabilities. Many elements have been used for preparing materials such as zirconium (IV), cerium (IV), tin (IV), aluminum (III), uranium (IV)…..etc.

These double salts acting mostly as cation-exchangers, due to presence of readily exchangeable hydrogen ions. These are gel-like or micro-crystalline materials with the composition and properties depending upon the method of preparation(87,88). These exchangers can be applied in chemical processing of radioactive materials, treatment of contamination moderator, cooling water in nuclear reactor which working at high temperatures and pressures, in water desalination processes and in fuel-cell employing ion-exchanging membranes for transport of hydrogen ions(89).

El-Naggar et al.(90) studied the various antimonate compounds which are well known as important inorganic ion exchangers, since they have radiation and chemical stabilities and also high selectivities towards some elements. Ceric, silicon, titanium and ferric antimonates were prepared as inorganic ion exchangers. Characterization of these materials has been described using different techniques, including thermal analysis, surface area measurements, X-ray diffraction and ir -spectroscopy. In batch distribution experiments the influence of HNO_3 molarities and Mo concentration for Mo sorption on different matrices is described in terms of their retention capacities and distribution coefficients. The selectivities of these prepared exchangers towards molybdenum are in the order; CeSb> SiSb> FeSb> TiSb.

Mathew and Tendon(91) have reported that zirconium antimonate was prepared under varying conditions of precipitation. Its properties, composition and ion exchange behavior are reported. The log K_d are given for Rb, Cs, Zn and Ti ions. The K_d values of 26 metal ions were measured at pH 2-3, and several separation of analytical and radiochemical importances were achieved.

Antimony silicate (KSiSb and SiSb) are acidic ion exchangers in character and have significantly higher affinity for ^{85}Sr in acidic conditions than several commercially avaliable ion exchangers. The ^{85}Sr K_d values have two or three orders of magnitude higher for the amorphous KSiSb and pyrochlore SiSb at pH $\approx$ 2.5 than for sodium titanosilicate (TSil) and the natural zeolite clinoptilolite(92).

1-4-11 In-situ precipitation of some radioactive wastes in inorganic ion exchange materials:

The nuclear industry produces large volumes of radioactive solution waste, which requires treatment prior disposal or storage. A highly efficient treatment concept is the removal of harmful radionuclide from the bulk waste solution. Application of such a technique will result in considerable reductions in the volumes of waste that require solidification prior to final disposal, as well as in radioactive discharges from storage containers into the environment. The method for efficient removal of trace radio nuclides from effluents, which contain large amounts of inactive metal ions (Cs^+, Co^{2+}....etc.), must be selective for the radioactive component. This requirement can be met with the use of inorganic ion exchangers. Ion exchange as a separation process is relatively facile and energy-efficient compared to other common solution phase separation procedures used in industry (e.g. solvent extraction and precipitation). The challenge in nuclear waste treatment is the efficient separation of the radio nuclides present in trace amounts from complex solutions, which contain high concentrations of interfering inactive components, or extreme acidity or alkalinity. Therefore, the method for effective separation in such conditions must be selective only for the trace ions in question. The major attraction in the use of inorganic ion exchangers in such applications is their good chemical and thermal stability, and the possibility for obtaining very high selectivities and thus, good separation efficiencies.(92)

Acid salts of metal oxides, such as phosphates, molybdates and antimonates proved to be superior to many organic resins in this respect. These materials also had other importance and advantageous properties needed in efficient separation of ions, such as high selectivity and capacity. However, these sorbents were mostly amorphous in nature and elucidation of the ion exchange mechanism, and their physical and chemical properties, was very difficult and limited. The discovery of a crystalline phase of zirconium phosphate in 1964 made it possible to explain its observed ion exchange behavior in structural terms(93,94).