# Chapter (1)
# Introduction

# INTRODUCTION

## 1.1. Literature survey on azo dye and Schiff base compounds

### 1.1.1. Literature survey on azo dye compounds

Synthesis and characterization of [*o*-carboxyphenylazo] moiety of barbituric acid, thiobarbituric acid, thiouracil, citrazinic acid, and disodium chromotropate were studied[1]. The structure of the prepared azo compounds were confirmed by C, H, N analysis, IR, and $^1$H-NMR spectra. The dissociation constants of the free azo ligands were evaluated by spectrophotometric methods.

Synthesis of azo dye ligands and their optical and thermal properties were studied[2]. Several kinds of novel azo dyes based on benzoic acid, 6-methylbenzothiazole, benzothiazole-6-carboxylic acid, and benzimidazole have been synthesized. All structures of the azo dyes compounds were confirmed by $^1$H-NMR, C, H, N analysis and FT-IR analyses. The optical and thermal properties of azo dyes were characterized by UV-Vis and TGA analyses.

Gaber et al. [3] 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, the variation of absorbance with pH was utilized for the determination of $pK_a$. The IR spectra were recorded in the solid state as KBr pellets. The $^1$H-NMR spectra of some compounds in relation to their molecular structures were also discussed.

Goyal, et al [4] studied the electrochemical behavior of the bis azo dye. Direct Red-81, when the electroreduction of this dye occurs at two groups at the dropping mercury electrode and at the pyrolytic graphite

electrode. A comparison of the redox couple $III_a/III_c$ observed in cyclic voltammetry with p-phenylenediamine as a product of electroreduction. The analysis of products at various pH's and potentials indicated that the $4e^-$, $4H^+$ reduction of the first azo group occurs with cleavage of the α-naphtholazo derivative and is followed by the $4e^-$, $4H^+$ reduction of the second azo group in 4-amino-4-sulfoazobenzene.

### 1.1.2. Literature survey on Schiff base compounds

The synthesis and characterization of novel Schiff base liquid crystalline crown ethers prepared from the intermediates 4-(4`-alkoxylbiphenyl-4-carbonyl)benzaldehyde, *cis* and *trans*-4,4`-diamino-dibenzo-18-crown-6 were described[5]. The structure of these compounds has been well characterized by elemental analysis, IR, $^1H$ NMR and MS spectroscopy. The liquid-crystalline behavior of these compounds was also investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) with a heating stage and polarimetric analysis.

Synthesis of two potentially heptadentate ($N_4O_3$) Schiff base ligands derived from condensation of *tris* (3-aminopropyl) amine and salicyladehyde or 4-hydroxysalicyladehyde[6] which have been characterized by various spectroscopic methods (IR, MS, NMR). They are derived from the condensation reactions of *tris* (3-aminopropyl) amine (tpt) with 3 equivalents of either salicyladehyde or the ring-substituted salicylaldehyde, 4-hydroxy-salicylaldehyde. Complete condensation of all primary amino groups was confirmed by the lack of N-H stretching bands in the IR 3150-3450 $cm^{-1}$ region and the presence of strong C=N stretching bands. This conclusion was also supported by the $^1H$-NMR data.

Synthesis and characterization of a Schiff base of *p-tert*-butylalix[4]arene ($H_2L$) was described[7]. The synthesis of ($H_2L$) has been achieved by the condensation of salicylaldehyde with the amine group of upper rim monoamine-*p-tert*-butylicalix[4]arene in ethanol. This ligand has been characterized on the basis of elemental analysis and spectra data. Solvatochromisirty was observed for the ligand i.e. in different solvents depending on the solvent polarity, its $\lambda_{max}$ of absorption in electronic spectra appeared in different wavelength. Therefore these compounds can be good candidates for non linear optical active (NLO) applications.

Synthesis and characterization of some Schiff base compounds were described[8]. A Schiff bases containing an organometalic substituent. N, N`-[bis(ferrocenyl-1-oxo-3-methyl)propenyl]ethylene-diamine have been prepared and characterized by elemental analysis, IR, UV and $^1$H-NMR analyses. In the IR spectrum of this ligand, there were very strong characteristic absorptions at 1598, 1557 and 1520 $cm^{-1}$ due to the $\nu$ (C=O), $\nu$ (C=C) and $\delta$ (N-H) respectively.

## 1.2. Electroanalytical methods

### 1.2.1. Literature survey on conductimetric and potentiometric studies

Randhawa, et al. [9] investigated the conductimetric behavior of molecular complexes of charge transfer type formed between azo-aromatics and haloanils. The method depends on electrical conductivity technique which has been employed to investigate molecular interaction of azo-aromatics viz. pyridine, o-picoline with haloanils, namely chloranil, bromonil and fluoranil. The stoichiometry of the charge transfer (CT) complexes has been determined by molar conductivities of the complexes. A model has been proposed for determining the

equilibrium constant (K) for 1:1 molecular complexes of CT type. by conductimetric measurements. The observed and theoretical values of thermodynamic parameters for the azo-aromatic chloranil system revealed that the interaction of azo aromatic with haloanils is occurring through the lone pair of the nitrogen ring atom.

Mohamed, et al. [10] illustrated potentiometric and conductimetric studies on some diphenyl formazan and their metal chelates. The acid dissociation constant -$pK_a$ values of 1-aryl-5-(o-hydroxybenzoyl formazan) derivatives in ethanol water mixture has been determined using pH meter (25 ± 0.2 °C). Increase in the concentration of ethanol, caused the increase of $pK_a$ for all formazan derivatives. The formation constant $K_{ML}^{M}$ values of some lanthanide complexes were determined in 70% ethanol. The potentiometric and conductimetric studies revealed that 1:1 and 1:2 (metal: ligand) complexes were formed in solution.

The thermal dynamics of substituted pyrazolones; potentiometric and conductimetric studies of complexes of some transition metals with 4-(4-acetophenyl) hydrazono-3-methyl-2-pyrazolin-5-one was studied[11]. The proton-ligand dissociation constants of the above ligand (AHMP) and metal-ligand stability constants of its complexes with some transition metal ions were calculated potentiometrically in 0.1 M KCl and 50 % (v/v) ethanol-water mixture. The order of stability constants was found to be $Th^{4+} > UO_2^{2+} > Ce^{3+} > La^{3+} > Mn^{2+}$. The dissociation constants of AHMP and the stability constants, log k, of their complexes were determined at different temperatures (298, 308 and 318 K). The corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were determined and discussed. The dissociation process was nonspontaneous,

endothermic and entropically unfavourable. The formation of metal complexes was found to be spontaneous, exothermic and entropically favorable. The stoichiometry of these complexes was determined conductimetrically and indicated the formation of 1:1 and 1:2 (metal: ligand) complexes.

Synthesis and structure studies of complexes of some metals with 1-(phenylacetyl and phenoxyacetyl)-4-phenyl-3-thiosemicarbazide were investigated[12]. The synthesis of the new complexes of 1-phenylacetyl-4-phenyl-3-thiosemicarbazide ($H_2$papts) and 1-phenoxyacetyl-4-phenyl-3-thiosemicarbazide ($H_2$pxapt); $[Ru(HL)_2(H_2O)_2]$, $[Rh(HL)_3]$, trans- $[UO_2.(HL)(bipy)(AcO)(H_2O)_2]$($H_2L$ = $H_2$papts), $[Ag(H_2\ Papts)\ (bipy)]^+$ and [Pd (Hpapts)(bipy)] was described. Characterization of these complexes by IR, electronic absorption spectra, conductimetric titration and thermal analysis was included. Complexes $[Ru(HL)_2(H_2O)_2]$ were found to be efficient catalysed for oxidation of primary alcohols to aldehydes and acids.

Potentiometric studies of copper(II) complexes of some substituted salicylideneanilines were illustrated[13]. The overall stability constants of copper(II) complexes with some substitued salicylideanilines have been determined in dioxane- water mixture. The trend in the values of the stability constants of Schiff base copper(II) complexes were explained in terms of the nature ligand and the mole fraction of dioxan in solvent mixtures. The relations between protonation constants of Schiff bases and the stability constants of copper(II) complexes have been discussed.

Deiv, et al [14] carried out potentiometric and $^1$H-NMR studies of binary and ternary complexes of thiamine hydrochloride with copper(II), zinc(II), nickel(II) or cobalt(II) with various secondary ligands. The

procedure was based on interaction of thiamine hydrochloride with Cu(II), Zn(II), Ni(II) and different secondary ligand like imidazole, tryptophan, 2,3-dicarboxylic acid, thiodiacetic acid; and thiodipropionic acid, which have been studied potentiometrically. The interaction of these ligands with thiamine and tryptophan or thiamine and imidazole has also been studied by $^1$H-NMR and the characters observed confirmed the inter-ligand interactions between thiamine and tryptophan and thiamine and imidazole. The electronic spectra also confirmed the inter-ligand interactions between thiamine and TRP or phenylalanine.

Potentiometric and spectroscopic studies of copper(II) binding to tobramycin was carried out[15]. The protonation and Cu(II) binding by tobramycin was studied by potentiometry, UV-Vis, and EPR spectroscopic methods. Mononuclear complexes of a general formula Cu $H_nL$ were found between 3 and 2.

Horria, et al. [16] illustrated potentiometric and spectroscopic studies on transition metal complexes with Glylys (Gly) and Asp-ε-lys. The method depended on formation of complexes between copper(II), nickel(II) and Zinc(II) with peptides glyly and Asp-ε-lys, containing the amide functions at the ε-amino groups of residues which were studied by potentiometric, UV-Vis and EPR spectroscopic methods. The stoichiometry of the major species formed in the copper-Glylys (Gly) system is $[CuH_{-1}L]$ and EPR spectroscopic data indicated the existance of two isomeric forms of the complex. The nickel(II) and zinc(II) Glylys (Gly) systems have been characterized by the formation of complexes containing bis ($NH_2CO$) coordination and macrochelating. Deprotonation and coordination of the amide groups were detected for copper(II) and

nickel(II) complexes. The stoichiometry of the dinuclear complexes can be given as $[M_2L_2]$, containing only amino acid binding sites.

Potentiometric and spectrofluorimetric ability for complexation of tenoxicam with some metal ions was investigated[17]. The interaction of tenoxicam with six metal ions, viz. Fe(III), Bi(III), Sb(III), Cr(III), Cd(II) and Al(III) was studied using potentiometric and fluorimetric methods. In the potentiometric method the ionization constants of the ligand and stability constants of the complexes formed have been tabulated at 25 ± 0.1 °C, ionic strength of $NaNO_3$ in 50 % (v/v) aqueous-acetonitrile solution that was 0.05 mol $L^{-1}$. Complexes of 1:1; 1:2 and 1:3 metal to ligand ratios were formed. The fluorescence of tenoxicam in the presence and absence of the metal ions was studied. The drug can be determined fluorimetrically in 0.5M $HNO_3$ at an emission wavelength of 450 nm (excitation at 350 nm). The linear range was 0.04-0.20 μg $mL^{-1}$ in the absence of Al(III) and in presence of 0.016-0.1 μg $mL^{-1}$ Al(III). Tenoxicam was determined by this method in tablets, suppository and injections where recovery percent ranged from 98.16 to 102.22 %.

### 1.2.2. Literature survey on voltammetric studies of azo dye compounds

Polarographic and voltammetric investigation of 3-allyl-4-hydroxyazobenzene was studied[18] at room temperature using various electrochemical techniques. In this study, the electrode reaction for the azo compound was investigated using SWV, DPP, DCP and CV. The reduction of the azo group to amino group in acidic media and hydrazo step in neutral and basic media was observed. From the observation an electrode reaction mechanism has been suggested for the compound.

Remazol brilliant orange 3R azo dye was determined by cathodic stripping voltammetry at a hanging mercury drop electrode[19]. The measurements were made in Britton-Robinson buffer at pH 4 and 10 at an accumulation potential of 0.0 V vs. Ag/AgCl reference electrode for 40 sec. The calibration graph was linear for 30-300 ng m $L^{-1}$ at pH 4 and 6.2-62 ng $mL^{-1}$ at pH 10.

The polarographic and voltammetric behavior and determination of two triazine dyes was examined [20]. The working electrode was dropping or hanging mercury drop electrode, with a vitreous carbon auxiliary electrode and Ag/AgCl reference electrode. Direct current and differential pulse polarography in acetate buffer of pH 4.5 gave a single wave or peak for the two dyes. Calibration graphs for the two dyes by differential pulse polarography, based on the first peak at -0.42 to -0.45 V, due to reduction of the azo group, were linear for 0.1-10 μM. the dyes were strongly adsorbed to a hanging mercury drop and could be determined by accumulation for 60 sec. at -0.1 V in a carbonate buffer.

The plarographic and voltammetric behaviors of 2-hydroxy-3-methoxy-5-(2-propenyl)azobenzene in Britton-Robinson buffer were studied[21] using differential pulse polarography, square-wave voltammetry, cyclic voltammetry and d.c. polarography. The working electrode was a dropping mercury electrode. The azo dye under investigation was determined using square-wave voltammetry in a pH 6-12 media with a detection limit of 0.1 micro M. From the polarographic and voltammetric behavior of the azo compound, the $pK_a$ value was determined to be 10.7 ± 0.02 and 11.08 ± 0.02, respectively.

The voltammetric behavior of Sunset Yellow FCF (food yellow 3) azo dye at platinum disc microelectrodes plated with mercury was studied[22] in phosphate and carbonate buffers and in KOH solution of pH 13. Calibration graphs of the diffusion limited currents vs. dye concentration are presented.

The polarographic and voltammetric behavior of five triazine-based azo dyes, which differed only in their potentially reactive group were studied[23] using differential pulse polarography at static mercury drop electrode. Differential pulse (DP) and adsorptive stripping voltammetry (ADSV) were also used to investigate the electrochemical behavior of the azo dyes at a hanging mercury drop electrode. The dyes under investigation were determined by each technique.

The surface reduction of nine monoazo dyes at a static mercury drop electrode has been studied by adsorptive square wave voltammetry[24]. Three types of surface reduction behaviors were seen among the nine azo dyes. Two of them are modeled as a two-step mechanism in which the first step is a quasi-reversible reduction followed by a totally irreversible reduction for those dyes having strong electron-donating groups such as amino or dimethylamino. The second reduction occurred at a potential almost the same as that of the first, and only one peak is observed. The second step gradually separated from the first step as the pH-value of the solution increases. For those azo dyes having methoxy or hydroxyl substituents, two peaks were observed, one quasi-reversible, the other is totally irreversible. The second irreversible step gradually overlaps the first step as the pH value of the solution decreases. The third type displays a single irreversible peak that was modeled as a four-electron one-step irreversible reduction.

### 1.2.3. Literature survey on voltammetric studies of Schiff base compounds and its complexes

Juan, et al. [25] studied the structure and cyclic voltammetry of three copper(II) complexes derived from bulky *ortho*-hydroxy Schiff bases, where these three complexes were synthesized and characterized by chemical analysis, UV-Vis, IR, $\mu_{eff}$ and mass spectrometry. The solid state structures of complexes were determined. The solid state X-ray diffraction studies of these compounds showed that the geometry is intermediate between square planar and tetrahedral. Moreover, cyclic voltammetry studies performed for these complexes, indicated a dependence of the cathodic potential upon conformational and electronic effects.

Electrochemical studies of copper(II) complexes with Schiff base ligand were studied [26]. The electrochemical reduction of copper(II) complexes with salen Schiff-base ligands derived from ethylenediamine or (R,R) or (S,S)-1,2-diphenyl-ethylenediamine and 5-methoxy.5-bromo and 5-nitrosalicyaldehyde have been studied by cyclic voltammetry in the potential range +1.0 to -2.3 V in dimethylsulfoxide (DMSO) as a solvent. The resulting voltammograms consisted of a single quasi-reversible one-electron transfer attributable to the couple [Cu(II)L]/[Cu(I)L]$^{-}$. Trends in cathodic peak potential ($E_{PC}$) values were observed which can be correlated with the electronic effects of 5-substituents of the Schiff base ligands. Changes in the basicity of the ligand groups were determinant for such electrochemical trends.

Losada, et al. [27] studied the electrochemical and spectroelectro-chemical properties of copper(II) Schiff base complexes. The electrochemical behavior of several copper(II) complexes with Schiff base ligands containing pyrrole groups has been investigated in aprotic

solvents by cyclic voltammetry and spectroelectrochemistry. Electrochemical oxidation of copper(II) complexes in acetonitrile produces conducting polymeric films at the electrode surface. The modified electrodes were electrochemically and spectrochemically characterized and their electrocatalytical properties have been examined.

Adsorptive stripping voltammetric behavior of $UO_2^{2+}$ complexed with the Schiff base N, N`-ethylene bis (salicylidemine) in aqueous 4-(2-hydroxyethyl)-1-piperazine ethanosulfonic acid medium, was examined[28]. The adsorptive stripping voltammetric behavior of uranyl ions complexed with the Schiff base SALEN in buffered aqueous solution of HEPES at the hanging mercury drop electrode (HMDE) versus Ag/AgCl (saturated KCl) was studied. The adsorptive stripping behavior was evaluated with respect to Schiff base's concentration, supporting electrolyte and pH, potential and pre-concentration time, scan rate dependence and analytical application. It was found that, in the pH range from 6.3 to 8.0 $UO_2^{2+}$-SALEN complex exhibited one large cathodic adsorptive reduction peak whose position depended on pH. Cyclic voltammetry showed that the reduction mechanism seemed to be quasi-reversible in the range of the scan potential rate employed. Due to the sensitivity of differential pulse adsorptive stripping current per unit of concentration even with low accumulation time, a new method for the uranium determination in the presence of SALEN was studied. The response of the system was found to be linear in the range of uranyl concentration from 5.0 to 25.0 $\mu g\ L^{-1}$. This method was applied to uranium determination in a glass SRM-610 certified sample.

Spectroscopy and electrochemistry of cobalt(III) Schiff base complexes were studied[29]. The structural, spectroscopic and electrochemical properties of cobalt(III) derivatives of bis(acetylacetone)

ethlenediimine and related ligands have been investigated. Electronic structure calculations indicated that the absorption between 340 and 378 nm in $Co^{3+}$ complex was attributable to the lowest $\pi$-$\pi^*$ intraligand charge-transfer transition. Equatorial ligand substitutions affected reduction potentials less than axial ligand changes. Consistent with an electronic structure model in which $d_{Z^2}$ is populated in forming the cobalt(II) complex. Also cyclic voltammogram of a Co(III) complex in the potential range from 0.7 to -2.1 V vs. Ag/AgCl in acetonitrile solution was done, which showed to types of processes. A first irreversible reduction wave at -0.8 V which was due to the process $[Co^{III} L(X_2)^+ + e^- \rightarrow [CO^{II}L] + 2x$. A second well-defined reversible process at -1.6 V was corresponding to the simple one-electron process $[Co^{II}L] + e^- \rightarrow [Co^{I}L]$.

Potentiometric and electrochemical behavior of some Zn(II). Schiff base complexes was studied [30]. Reactions of Schiff bases viz. salicylidene-2-hydroxy-aniline (SHA), acetophenone-2-hydroxyaniline (AHA), 4-hydroxyacetophenone-2-hydroxy aniline (HAHA) and 4-hydroxyacetophenone-2-hydroxy-5-chloroaniline (HAHCA) with same metal ions were investigated by potentiometric and voltammetric techniques. Formation constants of the complex type ML and $ML_2$ (where L-Schiff base as monodentate ligand at pH < 6) were calculated using potentiometric technique. Overall formation constants of the complexes of the type $ML_2$ (L is being a tridentate ligand at neutral pH) were determined by voltammetric technique. Thermodynamic parameters of Zn(II), chelates and their standard rate constants ($K_s$) were also calculated.

## 1.3. Literature survey on spectrophotometric determination of the metal ions under consideration

Simultaneous derivative spectrophotometric determination of zinc and cadmium with 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol in the presence of cetylpyridinum chloride was investigated[31]. A selective and sensitive derivative photometric method has been developed for the determination of trace amounts of $Zn^{2+}$ with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of cetylpyridinium chloride, as cationic surfactant. The molar absorption coefficient and analytical sensitivity of the 1:2 complex at 554 nm were $1.19 \times 10^5$ L $mol^{-1}$ $cm^{-1}$ and 0.56 ng $mL^{-1}$ respectively. The detection limit was $1.96 \times 10^{-2}$ ng $mL^{-1}$ and Beer's law was valid in the 0.02 – 0.66 μg $mL^{-1}$ range of $Zn^{2+}$. Complex matrices, including reference materials, environmental and biological samples or synthetic mixtures, have been successfully analyzed for trace amounts of the two metal ions.

Ahmed, et al [32] studied a simple spectrophotometric method for the determination of cadmium in industrial, environmental, biological and soil samples using 5, 7-dibromo-8-hydroxyquinoline. A very simple, ultra-sensitive and highly selective non-extractive spectrophotometric method for the determination of trace amounts of cadmium using 5,7-dibromo-8-hydroxyquinoline (DBHQ) has been developed. DBHQ reacted in a slightly acidic solution with cadmium to give a deep greenish-yellow chelate, which has an absorption maximum at 396 nm. The average molar absorption coefficient and Sandell's sensitivity were found to be $5.3 \times 10^3$ L $mol^{-1}$ $cm^{-1}$ and 20.0 ng $mL^{-1}$ of Cd, respectively. Linear calibration graphs were obtained for 0.1-30 μg $mL^{-1}$ of Cd. A large excess of over 50 cations, anions and some common complexing agents did not interfere with the determination. This method was successfully

used in the determination of cadmium in several standard reference materials as well as in some environmental, water, biological and soil samples.

Jiang, et al. [33] developed a spectrofluorometric method for determination of trace amounts of cadmium with 4-chlorosalicylic acid, EDTA, and cetyltrimethylammonium bromide. The complex formed by cadmium with 4-chlorosalicylic acid (CSA), EDTA and cetyltrimethyl-ammonium bromide (CTAB) has been used for the sensitive spectrofluorometric determination of cadmium in mixed rare earths. The effect of the experimental conditions on the fluorescence intensity was defined. Under the optimum conditions selected, the fluorescence intensity was linear with the cadmium concentration in the range of $3.0 \times 10^{-3} - 1.0 \times 10^{-5}$ mol $L^{-1}$.

A second and First-derivative spectrophotometric method for efficient simultaneous and individual determination of palladium and cobalt using 1-(2-pyridylazo)-2-naphthol in sodium dodecylsulfate micellar media, was studied [34]. PAN complexes of palladium and cobalt at neutral pH form green colored neutral complexes, which were soluble in aqueous SDS micellar media. Under optimum conditions, calibration graphs for individual determinations by zero and first-derivative spectrophotometry, and also for simultaneous determinations by second-derivative spectrophotometry were obtained. The method was suitable to determine the cobalt-to-palladium ratio 5:1 to 1:10 (wt/wt), accurately. The accuracy and reproducibility of the determination method for various known amounts of cobalt and palladium in their binary mixtures were tested. The effect of diverse ions on the determination of cobalt and palladium to investigate the selectivity of the method was also studied.

The recommended procedures were applied to a synthetic binary alloy, cobalt in vitamin $B_{12}$ and some synthetic palladium alloys.

A facile spectrophotometric method for cobalt determination using α-benzilmonoxime in sodium dodecylsulfate micellar solutions was studied[35] at pH 9.0. The linear range of calibration was 0.05-1.5 μg $mL^{-1}$ of cobalt at 380 nm with molar absorptivity of 3.72 x $10^4$ L $mol^{-1}$ $cm^{-1}$, which is about 1.5 times greater than that of the α-benzilmonoxime extraction based method. The relative standard deviations recoveries, detection limits and effects of diverse ions on the determination of cobalt were studied. These analytical results were satisfactory. This method was successfully applied to the determination of cobalt in the various samples.

Saran, et al. [36] developed a spectrophotometric method for the determination of trace silver with sodium 2-(8-hydroxyquinolin-5-ylazo) benzoate. The method depended on the reaction between silver and sodium 2-(8-hydroxyquinolin-5-ylazo)benzoate in aqueous media in presence of Na-K tartrate at pH 5.2-6.1 which resulted in an intense purple color, which was stable for at least 24h. The molar absorptivity and Sandell's sensitivity at 525 nm are 3.65 x $10^4$ L $mol^{-1}cm^{-1}$ and 0.0029 μg $cm^{-2}$, respectively. The method was applied to the determination of silver in geological samples.

Spectrophotometric and simultaneous derivative spectrophotometric determination of gold(III) and silver(I) with Rhodanine derivative in miceller medium was illustrated[37]. The determination methods of the gold(III) and silver(I) with 5-(4-hydroxy-3-methoxybenzylidene) rhodanine (3,4-MHBR) using benzyldimethyltetradicylammonium chloride (zephiramine), and 5-(3,4-dihydroxybenzylidene) rhodanine (3,4-DHBR) in the presence of cetyltrimethylammonium bromide

(CTAB) have been described. The application of first and second derivative spectrophotometry to simultaneous determination of gold(III) and silver(I) in their mixtures have been assayed using "zero-crossing" technique of measurement. In the pH ranges 8.8-9.8 and 9.0-10.2 the ternary 1:3:3 and 1:2:2 complexes gold(III) -3,4-MHBR-zephiramine and silver(I) -3,4-MHBR-zephiramine have been formed with molar absorptivities of $4.98 \times 10^4$ and $4.64 \times 10^4$ L $mol^{-1}cm^{-1}$ at 529 and 522 nm, respectively. The ternary 1:3:4 and 1:2:3 complexes for gold(III) -3,4-DHBR-CTAB and silver(I) -3,4-DHBR-CTAB have been formed in the pH ranges 9.4-10.2 and 9.0-10.5 with molar absorptivities of $8.63 \times 10^4$ and $7.76 \times 10^4$ L $mol^{-1}$ $cm^{-1}$ at 560 and 555 nm, respectively. The first and second derivative spectra of these complexes allowed the determination of one metal in the presence of an excess of the other. Gold(III) (0.21-3.6 μg $mL^{-1}$) and silver(I) (0.12-2.63 μg $mL^{-1}$) in different ratios have been determined simultaneously with good precision and accuracy using the proposed methods. The statistical analysis of the experimental results were presented. The methods have been applied to simultaneous determination of gold and silver in silicate rocks.

2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline was used as an analytical reagent for the spectrophotometric determine-ation of micro amounts of gold(III) and silver(I) by Amin, et al [38]. The synthesis, spectral characteristics, and analytical application of 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline(DCHNAQ) were described. A simple, rapid, and sensitive spectrophotometric method for the determination of microgram amounts of gold alone, or in the presence of associated metals, was developed, based on the color reaction between the metal ion and the reagent. The yellowish brown complex ($\lambda$ = 575 nm) has stoichiometric ratio (1:1) (metal : ligand) over the pH

Spectrophotometric determination of copper(II), silver(I), and palladium(II) with 4-(2,6-diamino-4-pyrimidylazo) phenol was studied[41]. 4-(2,6-Diamino-4-pyrimidylazo)phenol (DAPP) interacted with copper(II), silver(I) and palladium(II) to give 1:2 violet, 1:1 violet and 1:1 green complexes, respectively. The Sandell's sensitivity of the color reaction was 1.1 x $10^{-3}$ μg $mL^{-1}$ at 535 nm for copper(II), 3.1 ng $mL^{-1}$ at 550 nm for silver(I) and 5.8 ng $mL^{-1}$ at 625 nm for palladium(II). Other optical constants have been evaluated. Effect of foreign ions in the determination of the three metal ions has also been studied.

Reddy, et al.[42] investigated the spectrophotometric determination of cobalt(II) and gold(III) in the presence of potassium persulphate using resacetophenone oxime. The procedure based on reaction of cobalt(II) and gold(III) with 2,4-dihydroxy acetophenone oxime (RPO) leading to form yellowish brown and greyish green colored soluble complexes, respectively. The reactions were very slow but became fast in the presence of $K_2S_2O_8$. This was ascribed to the enhancement of oxidation of metal complexes with RPO in their lower oxidation states [Co(II), Au(III)] to colored complexes with higher oxidation state [Co(III), Au(V)]. The Co(III)-RPO complexes showed $\lambda_{max}$ at 390 nm and at pH 9.5 obeying Beer's law in the range 0.12-1.80 μg $mL^{-1}$. Determination of Au(III) was carried out at 630 nm and pH 3.5 where Beer's law was obeyed in the range 0.39-5.12 μg $mL^{-1}$ of Au(III). The effect of foreign ions on the method was studied. The method was applied for the analysis of Co(II) in vitamin $B_{12}$ and Au(III) in Rheumartho pharmaceutical sample.

Extractive spectrophotometric determination of cadmium was studied[43]. The binary complex formed between $Cd^{2+}$ and N-phenylcinnamohydroxamic acid (PCHA) was extracted with chloroform

at pH 9.5, and showed maximum absorbance at 380 nm with optimum range for estimation 1.41-11.25 μg $mL^{-1}$. The sensitivity of the method was increased by the addition of 4-(2-pyridylazo)resorcinol (PAR) after extracting $Cd^{2+}$ with PCHA at pH 9.5. The Cd-PCHA-PAR complex was reddish orange with maximum absorbance at 510 nm and obeyed Beer's law over the range 0.23-2.25 μg $mL^{-1}$. The method was applied to blood, urine and other samples.

The complexing ability of standard humic acid with cadmium ions was determined by Pommery, et al. [44], where complex formation of cadmium with Fluka humic acids was studied by UV-Visible spectrophotometry, differential pulse anodic stripping voltammetry and ion selective electrodes. The first method failed to characterize the interaction sites, but the 113Cd NMR demonstrated that two kinds of complexes existed. This was confirmed by applying Scatchard's graphical method. The two sites had 1 and 10 Cd ions per humic acid molecule.

Extraction, separation and spectrophotometric determination of cadmium and mercury using triphenylphosphine oxide and its application to environmental sample was investigated[45]. A method was proposed for the solvent extraction of cadmium and mercury from salicylate media using triphenylphosphine oxide as extractant. The optimum extraction conditions were evaluated from a critical study of the effect of pH, sodium salicylate concentration and the concentration of triphenyl-phosphine oxide. The probable composition of the species has been deduced from log-log data and an extraction mechanism was suggested. The method has been used to separate zinc, cadmium and mercury from binary and ternary mixtures and for the spectrophotometric determination of mercury or cadmium in environmental samples.

Jankiewicz, et al. [46] investigated a spectrophotometric determination of cadmium(II) in soil of allotment gardens in Lodz. The formed cadmium(II) dithizonate was determined by the extraction-spectrophotometric method. In all cases, soil pollution with cadmium increased with the proximity of busy roads. The molar absorptivity and Sandell's sensitivity of the method were determined. Also, the relative standard deviation from six replicable determinations were calculated. The interference of various ions has been studied and conditions were developed for the determination of cadmium in soil.

Simultaneous determination of Cd(II), Cu(II) and Pb(II) in surface waters by solid phase extraction and flow injection analysis (FIA) with spectrophotometric method was studied[47]. A method for heavy metal moitoring using spectrophotometric detection was presented. Traces of Cu(II), Pb(II) and Cd(II) at the low μg level can be determined simultaneously after both selective removal of metal interferences and preconcentration using "extraction chromatograhic resins". Lewatit TP 807'84, which contains di-(2,4,4-trimethylpenthyl)phosphinic acid as active component, was used as solid adsorbent. Two minicolumns containing this resin were used: one at pH 3.2 for the removal of interferences, such as Zn(II) and Fe(II), and the other at pH 5.5 for the selective preconcentration of the target analytes. Spectrophotometric determination was performed using FIA methodology with sulfarsazene as chromogenic reagent and partial least-squares multivariate calibration. The method was successfully applied to the analysis of surface waters from the Llobregat river, Barcelona, Spain, and ground water samples from wells in the Guadiamar basin, Sevilla, Spain. Accuracy, expressed in terms of recoveries, was in the range 80-120% and relative standard deviations were below 10%.

citrate, nitroso-R salt and Chugaev's reagent were added as masking agents. Soils from several sources have been analysed by this method, and the results obtained were satisfactory.

Application of macrocyclic Schiff bases for selective extraction and spectrophotometric determination of copper was investigated[51]. A method was described for selective extraction of copper using macrocyclic Schiff base compounds against a background of many other metals, followed by spectrophotometric analysis. The distribution constants for the reagents in the chloroform-water system, the composition of the copper(II) complexes extracted, and the extraction constants were determined. Copper extraction depended on the length of the hydrocarbon chain, the changing size of the cavity and the conformation of the macrocycle.

Spectrophotometric determination of copper in vinegar with glyoxal bis(4-phenyl-3-thiosemicarbazone) was studied [52]. Both glyoxal bis(4-phenyl-3-thiosemicarbazone) and bathocuproine disulphonate methods were used to estimate copper content of vinegars produced in different plants from Andalusia, Spain. For routine estimation, the first procedure was fast and sufficiently precise and was suitable for a programme where large numbers of analyses were made. Cu content of five samples analysed ranged from 0.50 to 15.73 $\mu g\ mL^{-1}$.

Wada, et al. [53] investigated a direct determination of copper in serum by flow-injection analysis. A flow-injection system was used to estimate copper in serum based on spectrophotometry using 2-(2-thiazolylazo)-4-methyl-5-(sulphomethylamino)benzoic acid (TAMSMB) as chromogenic reagent. A serum sample (30 μL) was directly injected into the carrier containing 0.5 M acetic acid-sodium acetate buffer of pH 4.2, 1.0 % Triton X-100 and 3.0 % ethanol. The carrier merged into the

stream of 2.5 M guanidine hydrochloride containing 4.5 x $10^{-3}$ M $KIO_3$ and 4.0 x $10^{-4}$ M KI, and then Cu(II) reacted with TAMSMB in the flow system. The absorbances were monitored at 600 nm and the sampling frequency was 60 $h^{-1}$.

Spectrophotometric determination of trace copper with a Cu-diethyldithiocarbamate-β-cyclodextrin colour system was illustrated[54]. A simple, selective and accurate spectrophotometric method for the determination of trace Cu(II) with diethyldithiocarbamate (DETC) in the presence of β-cyclodextrin (β-CD) in ammonia media was described. The method can be directly conducted in aqueous solution without any need for separation. The color development was almost instantaneous and the stability of the inclusion complex was very high. Beer's law was obeyed for Cu(II) in the range 0.150-2.500 μg/25mL. This method was applicable to a variety of Cu(II) containing samples e.g. soils, wheat flour, Al alloys, vegetables, herbs and some traditional Chinese medicinal plants.

Derivative spectrophotometric determination of copper(II) in nonionic micellar medium was studied[55]. The complexation reaction between 1-(2-pyridylazo)-2-naphthol(PAN) and Cu(II) ions in the presence of a neutral surfactant, Triton X-100, was examined in normal and derivative photometric modes, to develop a rapid, reproducible, sensitive and selective spectrophotometric method for the determination of Cu(II) in standard reference materials, alcoholic beverages (Whisky, rum, gin and brandy) and biological samples (goat liver and human hair). The molar absorption coefficient (ε) and Sandell's sensitivity (S) of PAN-Cu(II) complex at 555 nm and pH 6.5, were 5.21 x $10^4$ L $mol^{-1}$ $cm^{-1}$ and 1.22 ng $cm^{-2}$, respectively. The detection limit of Cu(II) was 4.0 ng $mL^{-1}$ and Beer's law was obeyed in the range 0.08 - 4.00 μg $mL^{-1}$ of the

analyte. The results obtained agreed with those obtained using atomic absorption spectroscopy.

The use of 1-[pyridyl-(2)-azo]-naphthol-(2) in the presence of Triton X-100 and N,N`-diphenylbenzamidine for the spectrophotometric determination of copper in real samples was investigated[56]. A simple and sensitive field detection and spectrophotometric method for determination of copper was described based on the formation of a red colored species of copper(II) with 1-[pyridyl-(2)-azo]-naphthol (PAN), Triton X-100 and N,N`-diphenylbenzamidine (DPBA) in the pH range 7.8-9.4. The red colored Cu(II)-PAN-(TX-100)-DPBA complex in chloroform showed maximum absorbance at 520 nm with molar absorptivity value $1.14 \times 10^5$ L $mol^{-1}$ $cm^{-1}$. The detection limit of the method was 2.0 ng $mL^{-1}$ in organic phase. The system obeys Beer's law up to 0.6 μg Cu(II) $mL^{-1}$ in organic solution. Most of the common metal ions generally found associated with copper, do not interfere. The repeatability of the method was checked by finding the relative standard deviation (RSD) (n =10) value for solutions each containing 0.2 μg of Cu(II) $mL^{-1}$ and the RSD value of the method was 1.5 %. The validity of the method has been satisfactorily examined for the determination of copper in soil and airborne dust particulate samples.

Extraction and spectrophotometric determination of copper(II) with S,S`,-bis(2-aminophenyl)oxalate was illustrated[57]. A new selective reagent, S,S`-bis(2-aminophenyl)oxalate ($H_2L$), for the extractive spectrophotometric determination of copper has been prepared. The ligand, $H_2L$, forms a 1:1 complex with copper(II) in methanol. The molar absorptivity of Cu(II)-S,S`-bis(2-aminophenyl) oxalate complex in methanol was 5365 L $mol^{-1}$ $cm^{-1}$ at 504 nm. The method has been applied for the determination of copper in pharmaceutical formulations, environmental and foodstuff samples.

benzene-4-sulphonic acid and the corresponding 5`-chloro-substituted acid were proposed as sensitive reagents for Zn. Cyanide masking and selective demasking of Zn could be used to deal with the interference of many metal ions, Cd could be masked with thiosemicarbazide, and thiosulphate could be used for masking Hg(II), Pd(II) and Os(VIII). The molar absorptivity was about $1.3x10^5$ L $mol^{-1}$ $cm^{-1}$. The method has been used for determining Zn in milk, with recoveries from spiked samples of cows', buffaloes', goats', camels', and human milks ranging from 91 to 104%, for additions of 1.6 and 3.25 μg/10 mL.

Determination of zinc in honey by spectrophotometry with 5,10, 15,20-tetrakis(4-trimethylammoniumphenyl)prophine was illustrated[65]. Honey samples were dissolved in water, treated with HCl, diluted with water, and filtered. The filtrates were treated with buffer solution of pH 4.5 and 5,10,15,20-tetrakis(4-trimethylammonium-phenyl) prophine, heated in boiling water for 10 min, cooled, treated with buffer solution at pH 2.3, and zinc was measured at 420 nm. The recovery was 100-108%. Plots of absorbance vs. zinc concentration were linear for 0.0-2.0 μg. No interference by other metal ions was detected. Results were comparable to those obtained by atomic absorption spectrometry.

Application of a new specrophotometric method for zinc determination in beverages and condiments was investigated[66]. A new spectrophotometric method, based on the interaction of zinc with 1-[di-(2-pyridyl)-methylidene]-5-(salicylidene)-thiocarbohydrazone forming a single, DMF/water-soluble, yellow complex, was used to estimate zinc concentrations in bottled mineral water (carbonated and uncarbonated), soft drinks, vinegar and table salt. There were few interferences which were eliminated by simple masking.

Determination of zinc in plants by flow injection spectrophotometry with ion-exchange separation was investigated[67]. A flow injection system was proposed for the spectrophotometric estimation of zinc in plants. Ashed samples dissolved in 2.0 M hydrochloric acid were injected into a slightly acidic sodium chloride carrier steam flowing through an anion-exchange resin (Dowex 1XB, 100 to 200 mesh) where zinc chloro complexes were retained. Elution was accomplished with dilute sodium hydroxide solution and on-line estimation was made after addition of zinc ion. Schlieren noise was overcome by using dual-wavelength spectrophotometry. Reagent constitution, chloro-complexation conditions, resin operation, system dimensions, interferences and comultating times were investigated. The proposed system handled 45 samples per h with Zn contents in the range 0.00 to 2.00 μg $mL^{-1}$. The results are precise (relative standard deviation usually < 0.02) and in agreement with data obtained by atomic absorption spectrometry.

Cherian, et al. [68] studied a spectrophotometric determination of zinc using 4-carboxyphenyldiazoaminoazobenzene and its application in complex materials. The method was based on the reaction of zinc with the reagent in alkaline medium where the reagent was in the acid form. The complex exhibited an absorption maximum at 530 nm and Beer's law was valid over the concentration range 2.5-20 μg zinc per 25 mL solution. Various analytical parameters for color development have been studied. The method has been successfully applied for the determination of zinc in milk and standard zinc samples.

Simultaneous determination of zinc(II), manganese(II) and iron(II) in pharmaceutical preparations was illustrated [69]. Beer's law was obeyed in the range 0.025-13 μg $mL^{-1}$ for zinc 1-20, for manganese and 0.025-0.2

for iron ion. The elaborated method was applied successfully for determination of the mentioned ions in pharmaceutical preparations without previous separation. The error of the determination did not exceed ±3.0 %.

## 1.4. Literature survey on solid chelates

A mixed metal carboxylate, cadmium(II) bis(oxalate) cobaltate(II) pentahydrate, has been synthesized[70] and characterized by elemental analysis, IR spectral, reflectance and X-ray powder diffraction studies. Thermal decomposition studies (TG, DTG and DTA) in air showed that the compound decomposed to $CdCoO_3$ at 370 °C through the formation of an anhydrous compound at ~ 194 °C. Finally, $CdCoO_2$ is generated at 1000 °C. DSC study in nitrogen up to 550 °C showed the formation of a mixture of CdO and $Co_3O_4$ as end products. The kinetic parameters have been evaluated for the dehydration and decomposition steps using four non-mechanistic equations, i.e., **Freeman** and **Carroll**, **Coats** and **Redfern**, **Flynn** and **Wall**, **MacCallum** and **Tanner** equations. Using seven mechanistic equations, the rate controlling processes of the dehydration and decomposition mechanism are also inferred. The kinetic parameters, ΔH and ΔS obtained from DSC are discussed. IR and X-ray powder diffraction studies identified some of the decomposition products.

A thermal study of zinc(II) salicylate complex compounds with bioactive ligands was investigated [71]. Five new complex compounds of general formula $Zn(Hsal)_2.L_2.nH_2O$ (where Hsal = $OHC_6H_4COO^-$, L = thiourea (tu), nicotinamide (nam), caffeine (caf), theobromine (tor), n = 2-4), were prepared and characterized by chemical analysis, IR spectroscopy and some methods of thermal analysis (TG/DTG, DTA). It was found that the thermal decomposition of the hydrated compounds

starts with the release of water molecules during the thermal decomposition of hydrated compounds. The decomposition of the anhydrous starts with the release of organic ligands followed by the decomposition of salicylate anion. Zinc oxide was found as the final product of the thermal decomposition heated up to 800 °C. IR spectra and chemical analysis were used for the determination of products of the thermal decomposition.

Aly et al. [72] studied the thermal and photochemical behavior of Zn(II) complexes of some cephalosporins, where Zn(II) complexes of some cephalosporin antibiotics namely cephalexin, cephapirin, cefamandole, cefuroxime, cefotaxime and ceftazidime were synthesized and characterized. The stoichiometrics and the mode of bonding of the complexes were deduced from their elemental analysis, IR and electronic spectroscopies. Thermal stabilities and the photochemical behavior of the complexes were studied. The Zn(II) complex of cephalexin exhibited a high light sensitivity. The remaining Zn(II) complexes behaved similarly to their free antibiotics, upon irradiation.

New metal complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with salicylidene-2-aminobenzimidazole (SABI) are synthesized[73] and their physicochemical properties were investigated using elemental and thermal analysis, IR, conductometric, solid reflectance and magnetic susceptibility measurements. The base reacted with these metal ions to give 1:1 (Metal: SABI) complexes; in case of Fe(III), Co(II), Cu(II), Zn(II) and Cd(II) ions; and 1:2 (Metal:SABI) complexes, in case of Fe(III), Co(II), Cu(II), Zn(II) and Cd(II) ions, and 1:2 (Metal: SABI) complexes, in case of Ni(II) ion. The conductance data reveal that Fe(III) complex is 2:1 electrolyte, Co(II) is 1:2 electrolyte, Cu(II), Zn(II) and Cd(II) complexes were 1:1 electrolytes while Ni(II)

was non-electrolyte. IR spectra showed that the ligand was coordinated to the metal ions in a terdentate manner with O, N, N donor sites of the phenolic-OH, azomethine-N and benzimidazole-$N_3$. Magnetic and solid reflectance spectra were used to infer the coordinating capacity of the ligand and the geometrical structure of these complexes. The thermal decomposition of the complexes was studied and indicated that not only the coordinated and/or crystallization water was lost but also that the decomposition of the ligand from the complexes was necessary to interpret the successive mass loss. Different thermodynamic activation parameters were also reported, using Coats-Redfern method.

Badaa, et al. [74] studied the thermal stability of some azo-derivatives and their complexes. The thermal stability of two 1-(2-benzothiazolyl)-3-methyl-4-azo-pyrazil-5-one derivatives and their Cu(II) coordination compounds of type $\{(C_4H_9)_4N_2[Cu(L)_2]\}$ was investigated. The main decomposition steps of these two azo-derivatives and their complexes have been evidenced. In order to confirm the nature of some of the intermediates, the IR spectra and chemical analyses were used.

The complex formation of cobalt(II), nickel(II) and copper(II) sulphate hydrates with 3,5-dimethyl-1-thiocarboxamidepyrazole (HL) was studied[75]. The influence of the anions on the course of the reaction was also examined, using nickel(II) salts with various anions. Beside the $NiSO_4.7H_2O$ the reaction has been carried out with $Ni(OAc)_2$, $Ni(CF_3COO)_2$ and $Ni(SCN)_2$. Compounds with the following composition were obtained: $Co(L)_3$, $Ni(L)_2$ and $[Cu(SCN)L]_2$. The structure of the ligand and the $Co(L)_3$ complex was determined by single crystal X-ray analysis, while that of the $Ni(L)_2$ was solved by analysis of powder diffraction X-ray data. The most probable structure of the copper(II) complex was proposed on the basis of the elemental analyses

data. FT-IR spectrometry and magnetic measurement. The thermal decomposition of the complexes was investigated by thermogravimetry, DSC and coupled TG-MS measurements. In the case of the nickel(II) complex, a relatively stable intermediate was detected in the 550-650 K temperature range. The composition of the intermediate, Ni(SCN) (NCS), was determined by FT-IR spectrometry.

Thermal and spectral properties of halogenosalielato-Cu(II) complexes were illustrated[76]. This method was dependent on an investigation of thermal and spectral properties of the complexes $Cu_2$(3,5-$Cl_2$sal)$_4$.$H_2O$ (I), Cu(3,5-$Br_2$sal).$2H_2O$ (II), Cu(3,5,$I_2$sal)$_2$.$2H_2O$ (III) and Cu(5-Isal)$_2$.$2H_2O$ (IV). (where sal = salicylate). TG, DTG, DTA, IR, EPR and electronic spectra have been applied to investigate thermal and spectral properties of these complexes. The chemical composition of the complexes has been identified by means of elemental analysis and complexometric titration. Schemes of destruction of these complexes were suggested. Heating of these compounds first resulted in a release of water molecules. The thermal stability of these complexes can be ordered in the sequence, IV = I < II < III. The final product of the thermal decomposition was CuO in all cases IR data suggested unidentate coordination of carboxylates to Cu(II) in complexes I-IV.

Mixed complexes of the type, Zn(Hsal)$_2$(Him)$_2$, Zn(Hsal)$_2$(Him)$_5$, Zn(Hsal)$_2$(4-MeHim)$_2$ and Zn(Hsal)$_2$(1,2-diMeim)$_2$ (where Hsal = $OHC_6H_4COO^-$, Him = imidazole, 4-MeHim = 4-methylimidazole, 1,2-diMeim = 1,2-dimethylimidazole) have been synthesized[77]. The application of chemical, thermal and X-ray methods enabled to analyze the complexes and their sinters. The gaseous products of pyrolysis of Zn(Hsal)$_2$(Him)$_2$ and Zn(Hsal)$_2$(4-MeHim)$_2$ have been investigated.

Thermal decomposition pathways have been postulated for the synthesized complexes. The molecular structures of the $Zn(Hsal)_2(Him)_2$ and $Zn(Hsal)_2(1,2\text{-diMeim})_2$ have been solved.

The Schiff base 2,5-dihydroxyacetophenone isonicotinoyl hydrazone ($H_2I$) has been synthesized[78] by condensation of 2,5-dihydroxyacetophenone with isonicotinoyl hydrazide in ethanol. Metal complexes of the Schiff base were prepared from salts of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and $UO_2$(VI). Characterization of the ligand and its metal complexes were carried out by elemental analysis, molar conductivity, magnetic susceptibility measurements, IR, $^1$H-NMR, electronic and thermogravimetric analysis in air. The Schiff base behaved as flexidentate ligand and commonly coordinated through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. The thermal data have been analyzed for the kinetic parameters by Broido and Horowitz-Metzger methods. All the compounds were also screened for their antimicrobial activity by agar cup-plate method against organisms and the results have been compared.

1,2-Benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4 azaheptane was synthesized[79] by the reaction of 1,2-benzylidenedioxy-3-chloropropane with 1,3-diaminopropane and subsequent condensation of 1,2-benzylidenedioxy-7-amino-4-azaheptane with salicyladehyde. Complexes of 1,2-benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4-azaheptane with cobalt(II), nickel(II), and copper(II) salts were obtained. The structure of the ligand and its complexes was established on the basis of their elemental compositions, IR, UV, and $^1$H NMR spectra, magnetic susceptibilities, and thermogravimetric data.

Kocaokutgen et al. [80] studied the thermal behavior of some azo dyes containing sterically hindered and water-soluble group. The thermal behavior of six azo dyes containing steric hindered groups such as tert-butyl, sec-butyl and isopropyl, were investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG). The thermal decomposition points and amount of volatile pyrolysis products, were determined in nitrogen atmosphere using TG, DTA and DTG curves.