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STUDIES ON METAL CHELATES
OF
SOME SCHIFF'S BASES

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IN
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BY

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UNDER THE GUIDANCE
OF

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The work included in the thesis is my own work under the supervision of ***Dr. P. K. Patel*** and leads to some contribution in chemistry subsidized by a number of references.

Dt. : -06-2007 ***(B. M. Bheshdadia)***
Place : Morbi

This is to certify that the present work submitted for the Ph.D. Degree of Saurashtra University by ***B. M. Bheshdadia*** is his own work and leads to advancement in the knowledge of chemistry. The thesis has been prepared under my supervision.

Date : -06-2007
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Mr. B. M. Bheshdadia

DEDICATED
TO MY
BELOVED FAMILY

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[A] Studies on Metal Chelates

Chapter-I

Introduction

A comprehensive summary of the work to be incorporated in the thesis entitled **“STUDIES ON METAL CHELATES OF SOME SCHIFF’S BASES”** included investigation pertaining to Schiff bases, metal chelates and corrosion inhibitory action of 1,2,4-triazole which have been described as under.

[A] STUDIES ON METAL CHELATES

[B] STUDIES ON CORROSION INHIBITION ACTIVITY OF SCHIFF BASES

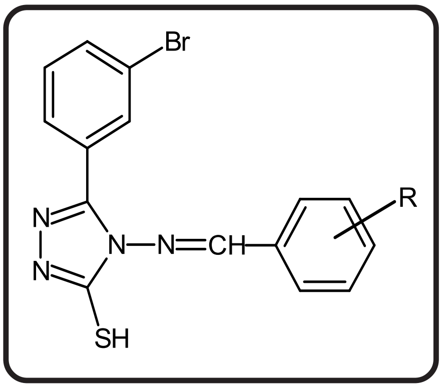
[A] STUDIES ON METAL CHELATES

Among the large number of synthetic and naturally occurring nitrogen donor molecules, schiff bases are of the greatest interest. Schiff bases play the role of an important class of ligands in the formation of metal coordination compounds. Owing to certain reasons like, manifestation of novel structural features, thermal stabilities, abnormal magnetic properties and relevant biological properties, the Schiff bases have been extensively studied.

Part-I : STUDIES ON SCHIFF BASES

The schiff’s bases synthesized by condensation of primary amine with compound containing carbonyl group. Compounds containing azomethine group are basic in nature, as N atom of this group has a lone pair electrons and the double bond has electron donating character. To attempt to develop a potentially active agents synthesis of some new schiff bases have been undertaken, which have been described as under.

Section-1: 5-(3-Bromophenyl)-4-{[(1*E*)-(4-arylphenyl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols

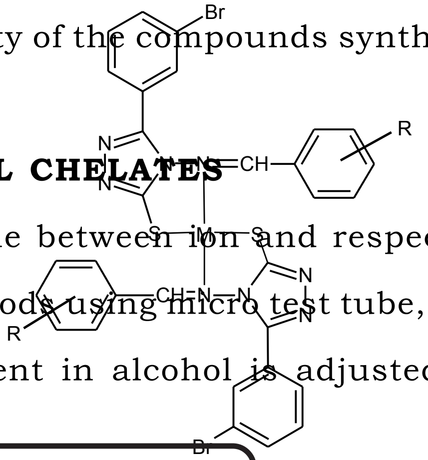


The synthesis of Schiff's bases have been undertaken by the condensation of 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol with different aromatic aldehydes in the presence of sulphuric acid.

All the Schiff bases were characterized by the elemental and spectroscopic analysis. The purity of the compounds synthesized was checked by TLC.

Part-II : STUDIES ON METAL CHELATES

A qualitative study is made between ion and respective schiff base adopting conventional methods using micro test tube, spot plate, etc. pH of the solution of reagent in alcohol is adjusted by using buffer solution.



Aqueous ethanolic solution of metal Cu (II), Ni (II), Fe(III), Mn(II) and Zn (II) were added to hot ethanolic solutions of the ligands in 1:2 molar ration which resulted in the formation of the metal derivatives in all the cases.

Part-III : STUDIES ON PHYSICOCHEMICAL PRINCIPLES AND METODS OF STUDY.

Schiff bases have been used as complexing ligands towards large number of transition and non-transitions metals. Use of organic compounds as analytical reagents are gaining importance because of their high analytical value in inorganic microanalysis, complexometry, spectrophotometry, masking agents, spot tests etc. Looking through the analytical application of schiff bases it was worthwhile to study the spectrophotometric determination of Cu (II), Ni (II), Fe(III), Mn(II) and Zn (II) with schiff bases derived from aromatic aldehydes and 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol.

The optimum condition of the present study have been investigated by examining parameters viz, effect of the pH, buffer solution, reagent concentration and divers-ions has also been studied.

[B] STUDIES ON CORROSION INHIBITION ACTIVITY OF SCHIFF BASES

The corrosion can be defined as the destructive results of chemical reaction between a metal of metal alloy and its environment. It is probably the commonest electrochemical phenomenon experienced in day to day life corrosion causes, huge losses to buildings, automobiles, industries etc. and it possibly the greatest consumer of metal today.

In the present study an attempt has made to study the influence of varying concentration of schiff' bases 5-(3-bromophenyl)-4-{[(1*E*)-(4-arylphenyl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols on mild steel in different concentration of HCl and H_2SO_4 employing mass loss technique.

All the compounds have been evaluated for their antibacterial activity towards Gram +*Ve* and Gram –*Ve* bacterial strains and antifungal activity towards ***Aspergillus niger*** at concentration 40 μg/mL. The biological activities of the synthesized compounds have been compared with standard drugs.

INTRODUCTION

Schiff bases have recently assumed greater importance in view of the fact that several of them have been found to be biologically active and have found uses in biology, medicine as well as in industry. They have been widely used in pigments and dyes[1], photographic emulsions[2], heart resistant polymers[3], high temperature stabilizers[4], lubricating oils[5], anticorrosive agents[6], antiknocking agents[7] and liquid crystal display composition[8,9]. They also have been used as antibacterials[10], antivirals[11], antifungals[12,13], antitumors[14-15], insecticides[16], antihelmintics[17] and antiemetcs[18]. Several schiff bases which are reported to be therapeutically active possess cytotoxic[19], antiinflammatory[20], antipyretic[21], analgesics[22], diuretic[23], and antispasmodic[24,25] activity.

The corrosion inhibition activity of Schiff bases have extensively been studied and reported[26-34].

The metal complexes of schiff bases have been used as active drugs against tumor[35] and tuberculosis[36] and also as insect repellents[37] and fungicides[38].

Schiff bases derived from sulpha drugs and salicylaldehyde have been found to be good chelating agents[39-40]. Therefore Iron (III), Cobalt (II), Nickel (II), complexes of schiff bases derived from sulphadiazine with 5-nitro-salicylaldehyde have been reported[41].

An organic compound may be regarded as any substance which used for the detection or evaluation of another. Organic reagent that have been utilized in analytical work for following purposes.

(1) They may be utilized as entrants of extraction purposes

(2) End point detectors.

(3) In qualitative (gravimetric) analysis.

(4) Many metals form complexes with organic reagents. These complexes are useful for colourometric and spectrophotometric determination of metals.

(5) Chelating agents which form stable water soluble metal complexes, are very useful as titrants for metals.

(6) Organic reagent have been widely been used as masking reagents, which increase the selectivity of reagents.

The formation of co-ordination compounds of metal ions with organic reagent has been extensively used in analytical methods. Large number of organic compounds have been used for the analytical determination of various metal ions. Most of the applications are based on complex formation reaction. The introduction of modern instruments and advanced techniques such as spectrophotometry, polarographic determinations and atomic absorption have changed the face of rapidly expanding field of analytical chemistry. More and more researches have been done to look for more sensitive reagents which would be extremely selective and sensitive for metal ions.

The survey of the literature shows that an organic reagent, which forms a chelate with a metal ions is better suited than any other reagents for the quantitative determination of metal ions. The chelates are the complexes containing one or more rings in which one of the member is metal ion. The ligands which form chelate are generally multidentate. The chelates are characterized by their low solubility in water and many of them are highly coloured. They have high molecular weight. Ethylene diamine tetra acetate (EDTA) which has changed a face of titrimetric methods is also a multidenate ligand and it is so strong ligand that it can form the complexes not only with transition elements but many of the pre and post transition elements. If an organic molecule is to form a chelate it should contain one or more acidic group such as –COOH, -SO_3H, -OH, -SH, =N-OH, -NO, =NH etc. From these more or less weakly ionized acids, hydrogen can be replaced by metal. The chelate formation also depends on the relative positions of the groups present in an organic compound. The group must be so located with respect to one another that the ring formed will contain four to eight atoms and the ring has less strain. Several workers[42-47] have studied a variety of chelates of metal ions with organic reagents having two coordination sites. They have two coordination sites. They have reported that when a group like –COOH, -SO_3H or –OH is suitably placed with a =S, -NH_2, =NH, -OH, of =N-OH, the later groups are found to be coordinating with a metal ion which is linked through a primary valence to the former. Many of such coordination systems are described in the various literature.

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Chapter-II

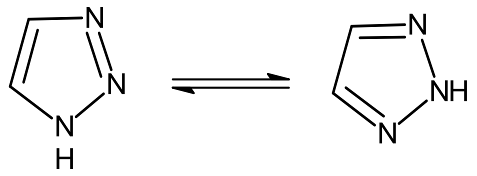
Studies on 1,2,4-triazoles

Studies on 1,2,4-triazoles

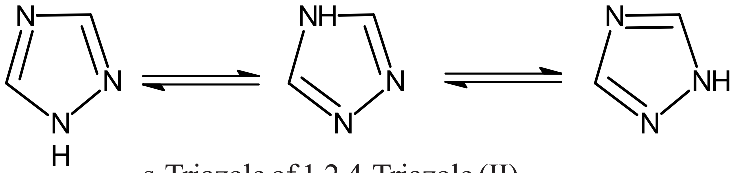
Triazoles are well known five membered heterocyclic compounds and several procedures for their synthesis have been extensively studied. Such studies have been stimulated by various promising applications, especially in the case of nitrogen containing heterocyclic entities. In fact, certain nitrogen containing heterocycles are used as pharmaceutical e.g. Analgesic, anti-inflammatory, antipyretic, agrochemicals where as some other is being studied for their medicinal interest.

The knowledge of such applications has point out that nitrogen containing heterocycles are important target to be prepared to our research on medicinally interesting chemical entities.

Triazoles have occupied an important place in the drug industry. Triazoles are of two types 1,2,3-triazole (I) and 1,2,4-triazole (II).



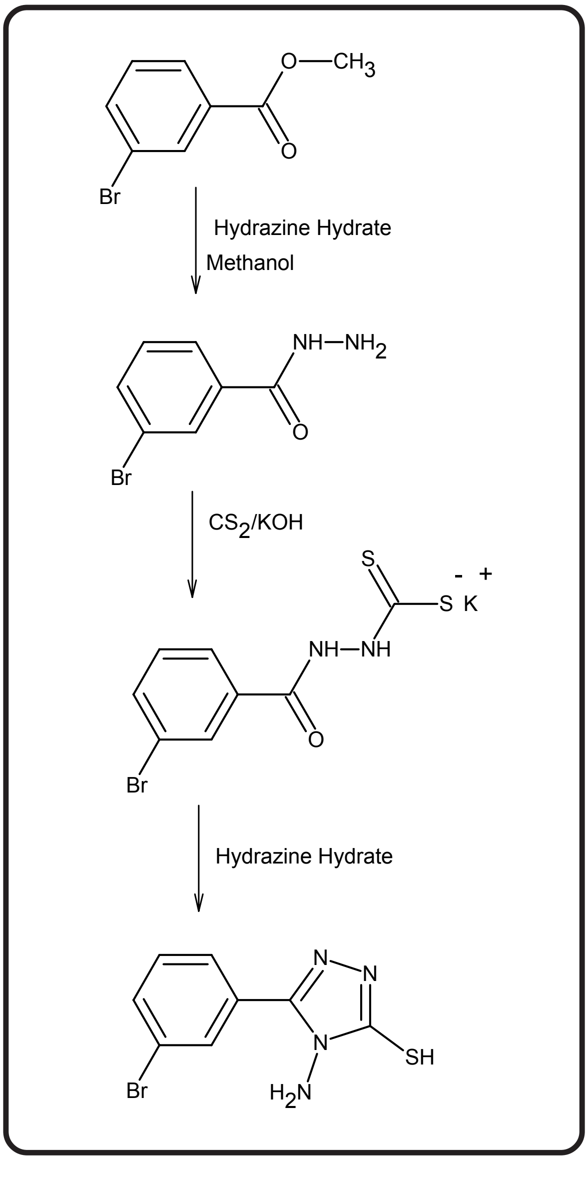
s-Triazole of 1,2,3-Triazole (I)



s-Triazole of 1,2,4-Triazole (II)

Hoggarth[1] and Meyer[2] have been studied briefly with the chemistry of 1,2,4-triazoels. Bladin[3-4] is a pioneer scientist in the field of triazole, who had synthesized the first derivative of 1,2,4-triazoel in 1885. 1,2,4-triazole derivatives not only known for their medicinal applications, but they are also used as analytical reagents[5], dyes and photographic chemicals[6], corrosion inhibitors[7,8] and in the preparation of polymers[9].

Several methods have been reported in the literature for the synthesis of 1,2,4-triazoles. The starting material for the synthesis of triazoles is thiosemicarbazide or dithiocarbamate derivatives having nitrogen containing functions. The procedures for synthesizing 1,2,4-triazoles have been described as under.



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Chapter-III

Studies on
Schiff Bases

STUDIES ON SCHIFF BASES

Introduction:

Schiff bases are prepared by condensation of primary amine with a compound containing an active carbonyl group[1]. They are also known as ‘azomethines’, ‘anils’ or ‘imines’. When this compounds are prepared by ketones they are known as ‘kitimines’ and when prepared by aldehydes, they are known as the ‘aldimines’. Among the large number of synthetic and naturally occurring nitrogen donor molecules, schiff bases are of the greatest interest. In general, schiff bases are represented by the general formula RCH=NR’ where >C=N is the azomethine group. The colour of the schiff bases is due to the presence of this azomethine (>C=N) linkage and can vary by introducing other auxochromic groups. When functional groups, such as –OH, -SH, -COOH are present in these ligands in suitably tailored positions, they enable them to be powerful chelating, biological and analytical reagents.

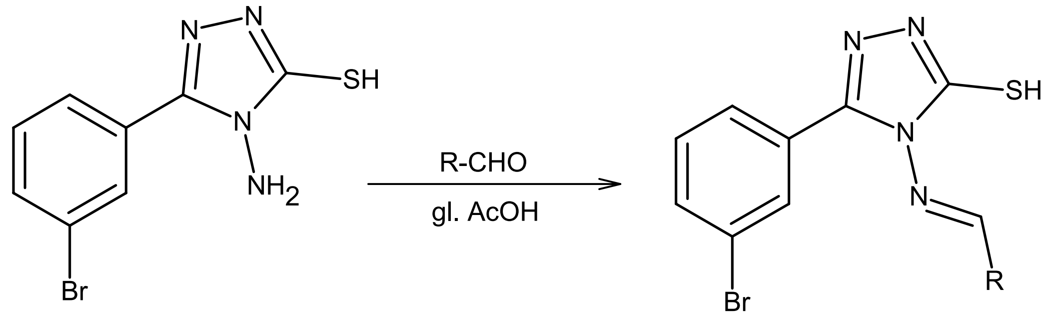
On this basis of such groups present, the schiff bases may be di, tri, tetra or polydentate in nature. Compounds containing azomethine group are basic in nature, as N atom of this group has a lone pare of electrons and the double bond has electron donating character.

In the field of coordination chemistry, schiff bases and their allied derivatives continue to provide the most interesting facts as evident by their long list of publications[2-7].

Schiff bases displayed the phenomenon of tautomeris[8], thermochromy and photochromy[9] and geometrical isomerism[10]. They possess both types of hydrogen bonding i.e. intramolecular as well as intermolecular[11].

SYNTHESIS AND BIOLOGICAL SCREENING OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-ARYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOLS.

Schiff's bases posses a wide range of therapeutic activities and intermediate for many heterocyclic compounds, hence it appeared on interest to synthesize some new Schiff bases of type (I) in association with 1,2,4-triozole nucleus. It has been prepared by the condensation of 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol with the different aromatic aldehydes in the presence of glacial acetic acid.



Type (II), R = Aryl

The constitution of newly synthesized compounds have been supported by using elemental analysis, IR, ^{1}H-NMR and EIMS . Purity of all compounds has been checked by thin layer chromatography.

All the compounds have been screened for their *in vitro* biological assay like antibacterial activity towards Gram positive and Gram negative bacterial strains and antifungal activity towards

Aspergillus niger at a concentration of 40 ì g/mL. The biological activities of the synthesized compounds have been compared with standard drugs. Some compounds have been found to have moderate activity as compared to known antibiotics recorded in Table No.1.

ANTIMICROBIAL ACTIVITY

Method : Cup-Plate[12]

Gram positive bacteria: Bacillus coccous
Bacillus substillis

Gram negative bacteria : Proteus Vulgaris
Escherichia Coli

Fungi : Aspergillus niger

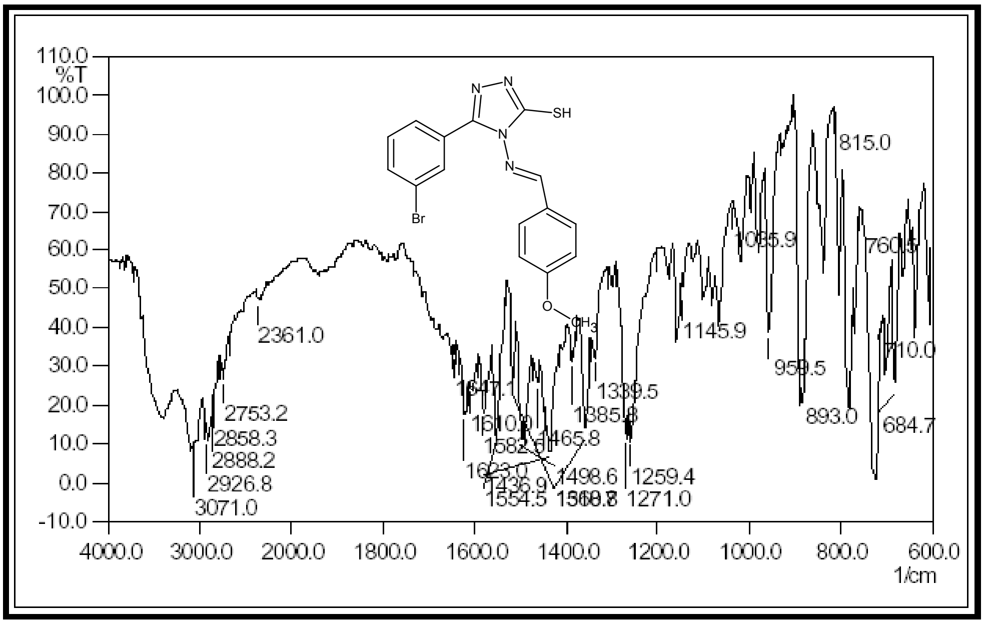
Concentration : 40μg/ml

Solvent : Dimethyl formamide

Standard drugs : Amoxicillin, Ampicillin, Benzyl penicillin,Norfloxacin, Greseofulvin

The antimicrobial activity was compared with standard drug viz Amoxicillin, Ampicillin, Benzyl penicillin, Norfloxacin and antifungal activity was compared with viz Greseofulvin. The inhibition zones measured in mm.

IR SPECTRAL STUDIES OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-METHOXYPHENYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOL

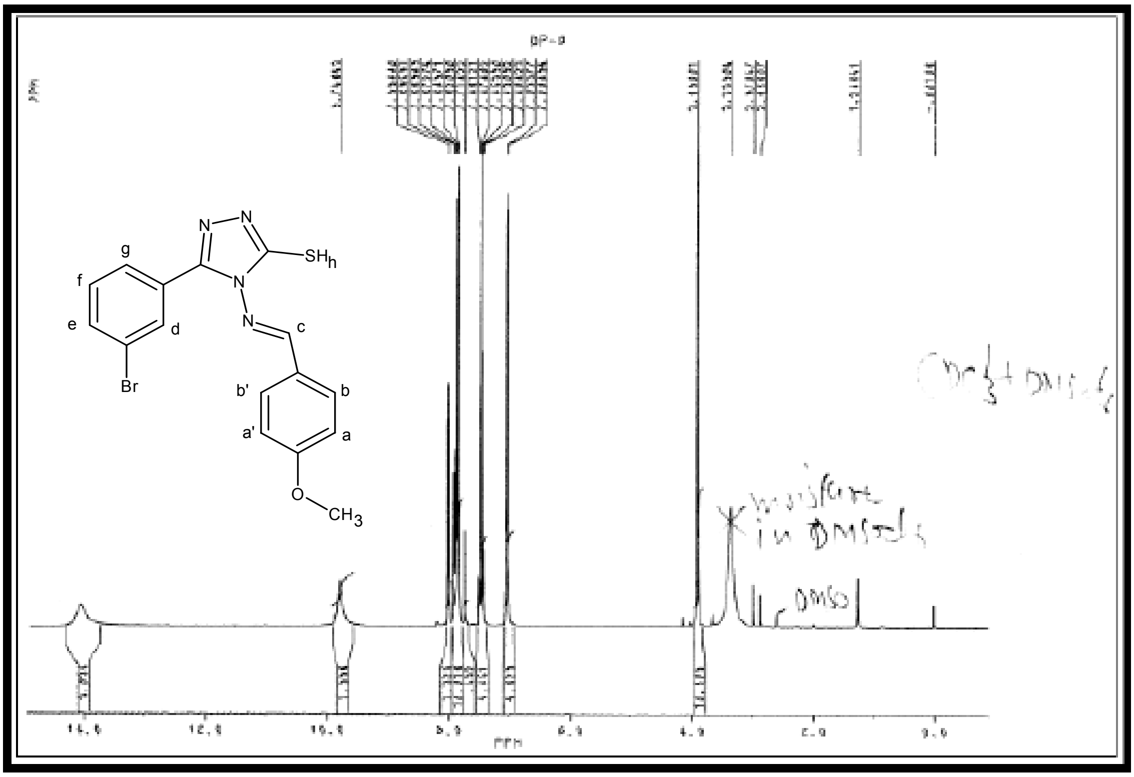


Instrument : SHIMADZU-FT-IR 8400-Spectrophotometer ;

Frequency range : 4000-400 cm-1 (KBr disc.)

Type	Vibration Mode	Frequency in cm-1		Ref.
		Observed	Reported	
Alkane	C-H str. (asym.)	2926	2975-2950	13
-CH_3	C-H str. (sym.)	2858	2880-2860	13
	C-H i.p.def. (asym.)	1465	1475-1435	13
	C-H o.o.p.def. (sym.)	1385	1390-1360	13
Aromatic	C-H str.	3071	3080-3030	14
	C=C str.	1560	1520-1480	14
	C-H i.p.def.	1145	1070-1000	14
	C-H o.o.p.def.	815	835-810	15
Triazole	C=N str.	1623	1640-1500	15
	C-N str.	1145	1220-1220	14
	N-N str.	1035	1050-1010	15
	C-S str	959	1050-950	14
	S-H	2753	2550-2440	15
Ether	C-O-C str. (asym.)	1271	1275-1200	15
(Ar-O-R)	C-O-C str. (sym.)	1035	1075-1020	14
Schiff's base	-C=N str.	1610	1660-1580	13
Halide	-C-Br	500	600-500	13

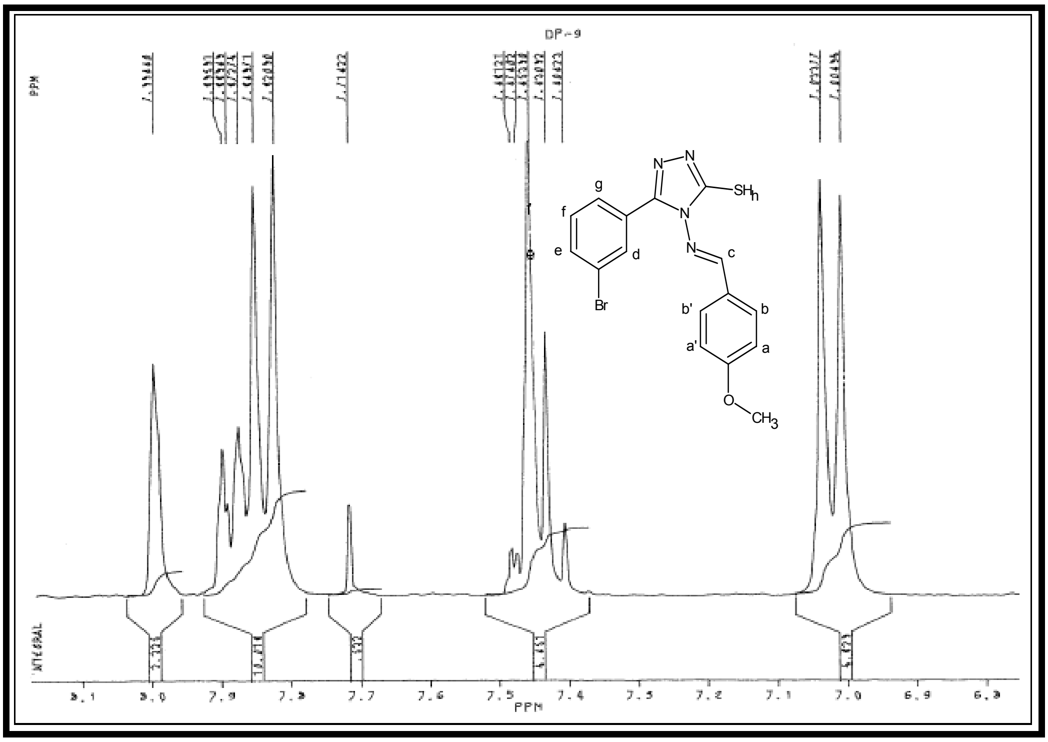
NMR SPECTRAL STUDIES OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-METHOXYPHENYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOL



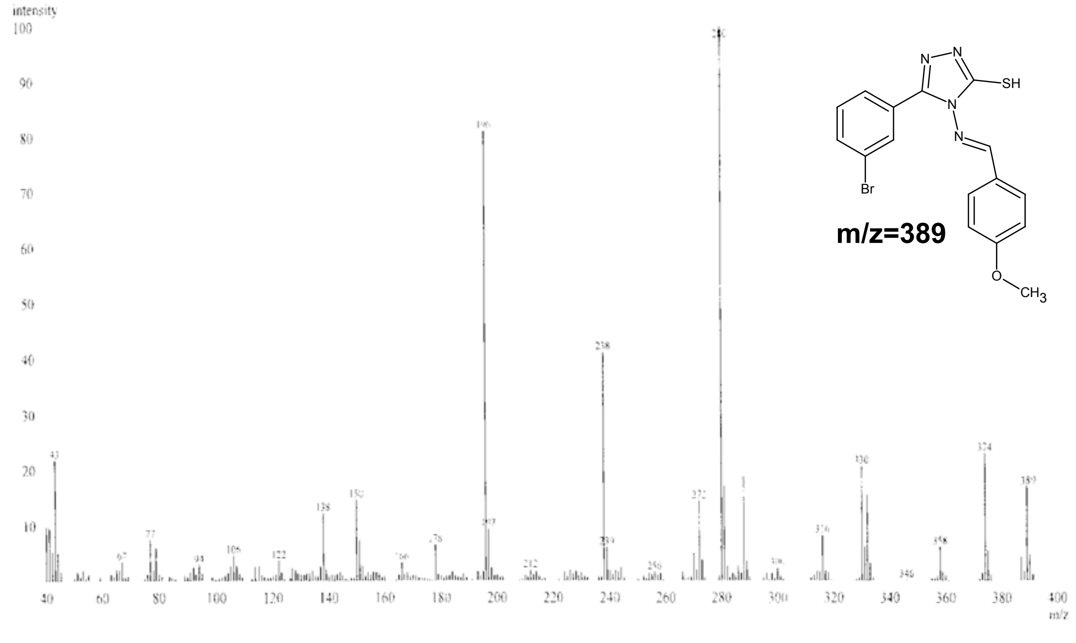
Instrumental Standard : TMS; Solvent: CDCl3 ; Instrument : BRUKER Spectrometer (300MHz)

Signal No.	Signal Position (δ ppm)	Relative No. of protons	Multiplicity	Inference	J Value In Hz
1	3.89	3H	singlet	Ar-OCH$_3$	-
2	7.01	2H	doublet	Ar-Haa'	Jab=8.7
3	7.45	2H	doublet	Ar-Hfg	Jfe=6.9
4	7.83	2H	doublet	Ar-Hbb'	Jba=8.7
5	7.88	1H	doublet	Ar-He	Jef=6.9
6	7.99	1H	singlet	Ar-Hd	-
7	9.76	1H	singlet	Ar-Hc	-
8	14.00	1H	broad	Ar-Hh	-

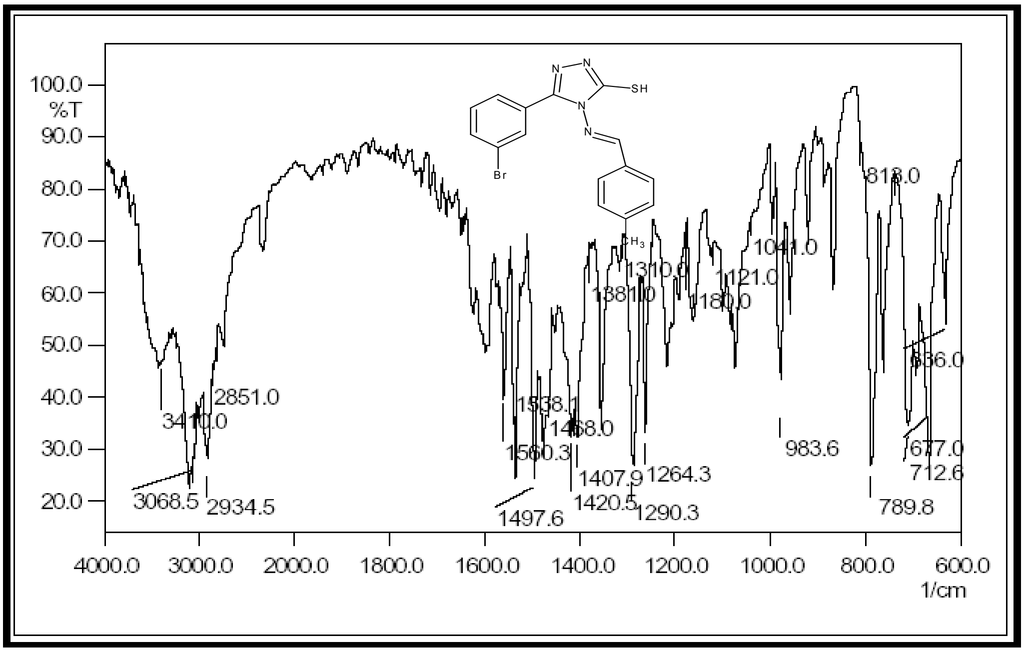
Expanded aromatic region of NMR spectra



MASS SPECTRAL STUDIES OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-METHOXYPHENYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOL



IR SPECTRAL STUDIES OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-METHYLPHENYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOL

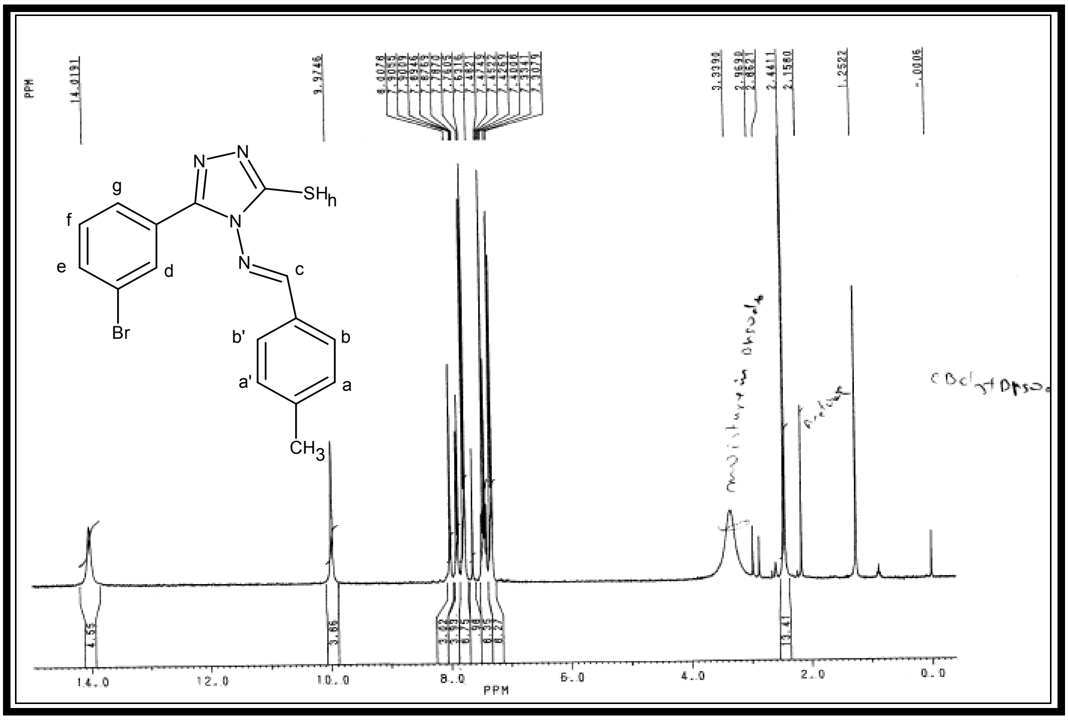


Instrument : SHIMADZU-FT-IR 8400-Spectrophotometer ;

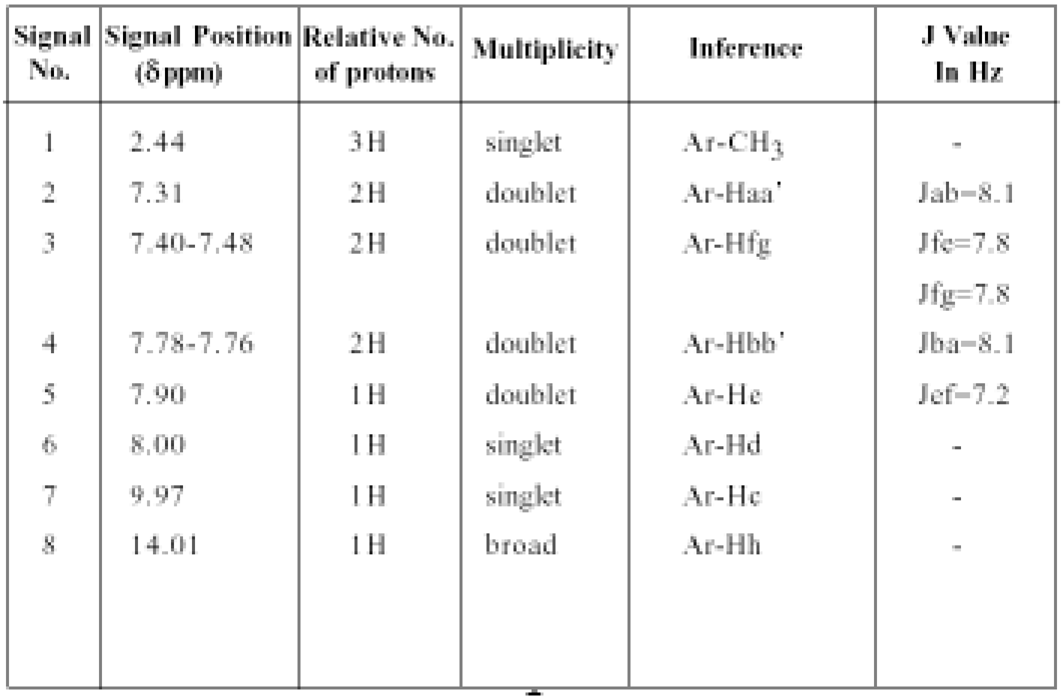
Frequency range : 4000-400 cm-1 (KBr disc.)

Type	Vibration Mode	Frequency in cm-1		
		Observed	Reported	
Alkane	C-H str. (asym.)	2934	2975-2950	13
-CH_3	C-H str. (sym.)	2851	2880-2860	13
	C-H i.p.def. (asym.)	1468	1475-1435	13
	C-H o.o.p.def. (sym.)	1381	1390-1360	13
Aromatic	C-H str.	3068	3080-3030	14
	C=C str.	1497	1520-1480	14
	C-H i.p.def.	1121	1070-1000	14
	C-H o.o.p.def.	813	835-810	15
Triazole	C=N str.	1588	1640-1500	15
	C-N str.	1121	1220-1220	14
	N-N str.	1041	1050-1010	15
	C-S str	983	1050-950	14
	S-H	2851	2550-2440	15
Schiff’s base	-C=N str.	1618	1660-1580	13
Halide	C-Br str.	550	600-500	13

NMR SPECTRAL STUDIES OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-METHYLPHENYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOL

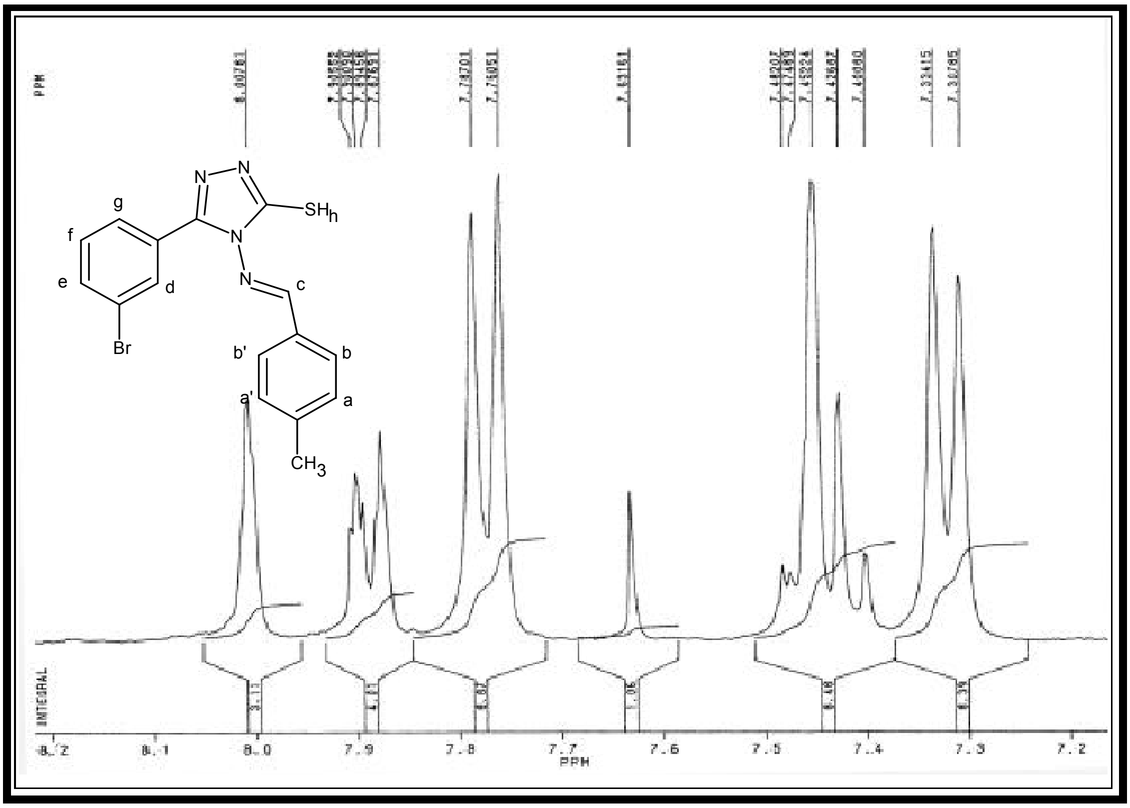


Instrumental Standard : TMS; Solvent: CDCl3 ; Instrument : BRUKER Spectrometer (300MHz)

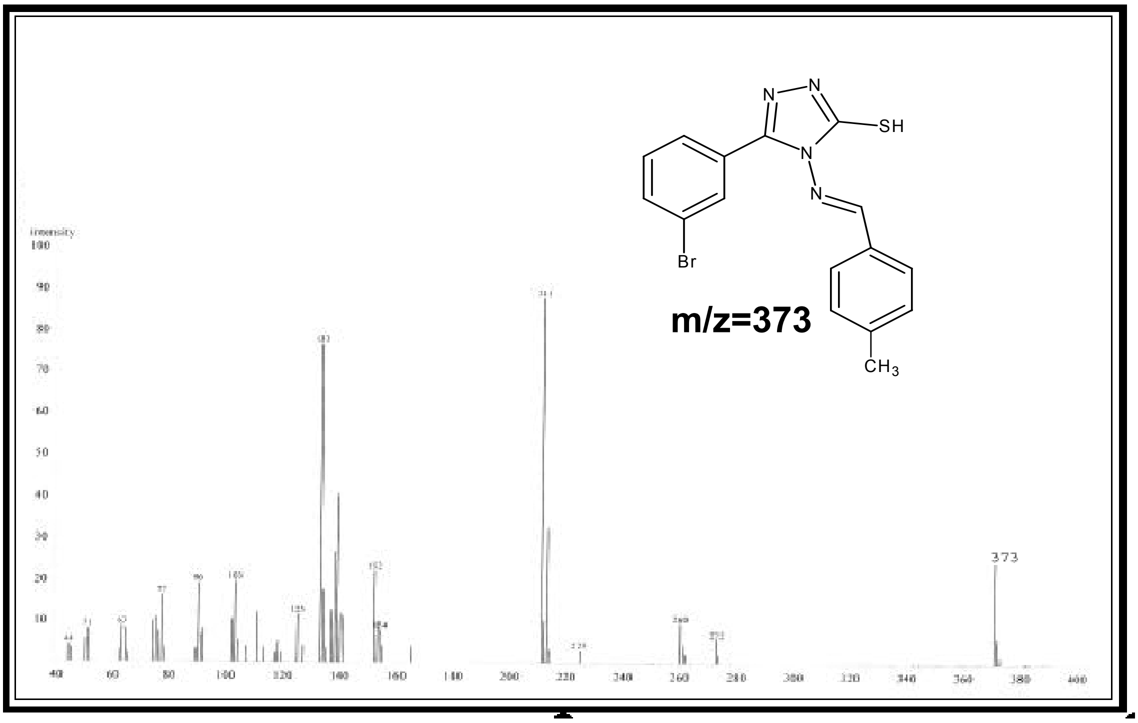


Signal No.	Signal Position (δ ppm)	Relative No. of protons	Multiplicity	Inference	J Value In Hz
1	2.44	3H	singlet	Ar-CH_3	-
2	7.31	2H	doublet	Ar-Haa'	Jab=8.1
3	7.40-7.48	2H	doublet	Ar-Hfg	Jfe=7.8 Jfg=7.8
4	7.78-7.76	2H	doublet	Ar-Hbb'	Jba=8.1
5	7.90	1H	doublet	Ar-He	Jef=7.2
6	8.00	1H	singlet	Ar-Hd	-
7	9.97	1H	singlet	Ar-Hc	-
8	14.01	1H	broad	Ar-Hh	-

Expanded aromatic region of NMR spectra



MASS SPECTRAL STUDIES OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-METHYLPHENYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOL



EXPERIMENTAL

SYNTHESIS AND BIOLOGICAL SCREENING OF 5-(3-BROMOPHENYL)-4-{[(1*E*)-(4-ARYL)METHYLENE]AMINO}-4*H*-1,2,4-TRIAZOLE-3-THIOLS.

[A] Preparation of potassium-3-bromobenzyl dithiocarbamate.

To a mixture of potassium hydroxide (8.40 gm, 0.15 mol) and 3-bromobenzohydrazide (0.1 mol) in methanol (25 mL), carbon disulphide (11.4 gm, 0.15 mol) was added. This mixture was stirred for 12-14 hours. It was then diluted with dry ether (200 mL) and thus the solid obtained was filtered and washed with ether and dried. There is no need to purify the salt for further reaction.

[B] Preparation of 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol.

A suspension of the potassium salt (32.5 gm, 0.1 mol), hydrazine hydrate (10 ml, 0.2 mol) and water (2 mL) was refluxed with stirring for 3 hours. The color of the reaction mixture changed to green, hydrogen sulfide was evolved (lead acetate paper and odour) and a homogenous solution resulted. Dilute the solution with cold water (100 mL) and neutralized with glacial acetic acid, precipitated a white solid. The product was filtered, washed with cold water and crystallized from dioxane yield 60%, m.p. 190°C.

[C] Preparation of 5-(3-bromophenyl)-4-{[(1*E*)-(4-methoxyphenyl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols.

To a solution of 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol (2.71 gm, 0.01 mol) in 10 mL DMF, 4-methoxybenzaldehyde (1.36 gm, 0.01 mol) was added with constant stirring. To this mixture

1.0 ml glacial acetic acid (1 mL) was added as a catalyst. The reaction mixture was refluxed for 8 hrs. The content was cooled and poured on to crushed ice and triturated with sodium bisulphate solution. The product was isolated and crystallized from methanol. Yield 70%, m.p. 213°C, Anal Calcd. For $C_{16}H_{13}BrN_4OS$: C, 49.37; H, 3.37; N, 14.39%; Found C, 49.32; H, 3.33; N, 14.31%.

Similarly 4-methyl bezaldehyde was condensed. The physical constants are recorded in Table No. I.

[D] Antimicrobial activity of 5-(3-bromophenyl)-4-{[(1*E*)-(4-aryl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols.

All the compounds have been evaluated for antimicrobial and antitubercular activity as described under.

(a) Antimicrobial activity

It was carried out by cop-plate diffusion method which has been described as under.

[I] Antibacterial activity

The purified products were screened for their antimicrobial activity. The nutrient agar bath prepared by the usual method, was inoculated aseptically with 0.5 ml of 24 hrs. old subcultures of B. coccous, B. substillis, E. Coli, P. vulgaris in separate conical flasks at 40-50°C and mixed well by gentle shaking. About 25ml content of the flask were poured and evenly spreaded in a petridish (13cm in diameter) and allowed to set for 2 hrs. The cups (10 mm in diameter) were formed by the help of borer in agar medium and filled with 0.04ml (40mg) solution of sample in DMF.

The plates were incubated at 37°C for 24 hrs. and the control was also maintained with 0.04 mole of DMF in a similar manner and the zones of inhibition of bacterial growth were measured in millimeter and are recorded in Table NO. 2.

[II] Antifungal activity

A. niger was employed for testing antifungal activity using cup-plate method. The culture was maintained on subouraud's agar slants. Sterilized sabouraud's agar medium was inoculated with 72 hrs. old 0.5 ml suspension of fungal spores in a separate flask.

About 25 ml of inoculated medium was evenly spreaded in a petridish and allowed to set for two hrs. The plates were incubated at 30°C for 48 hrs. After the completion of incubation period, the zone of inhibition of growth in the form of diameter in mm was measured. Along the test solution in each petridish one cup was filled with solvent which act as control. The zones of inhibition are recorded in Table No. II.

Table-I: Physical constant of 5-(3-bromophenyl)-4-{[(1*E*)-(4-aryl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols

Sr. No.	R	Molecular Formula	Molecular Weight	M.P. °C	Yield %	% of Nitrogen		Rf Value	Solvent System
						Calcd.	Found		
1	2	3	4	5	6	7	8	9	10
SB_I	$4-OCH_3-C_6H_4-$	$C_{16}H_{13}BrN_4OS$	389	213	60	14.39	14.31	0.42	S1
SB_{II}	$4-CH_3-C_6H_4-$	$C_{16}H_{13}BrN_4S$	373	182	58	17.32	17.21	0.47	S2

S1 Hexane:Ethyl acetate(5:5), S2 Hexane:Ethyl acetate(6:4)

Table-II: Antimicrobial activity results of 5-(3-bromophenyl)-4-{[(1*E*)-(4-aryl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols

	SB_I	SB_{II}	Amoxicillin	Ampicillin	Benzyl penicillin	Norfloxacin	Greseofulvin
B. coccous	14	13	20	18	28	21	0
B. substillis	20	17	24	17	18	24	0
P. Vulgaris	12	12	21	25	15	25	0
E. Coli	12	19	22	24	18	25	0
A. niger	14	09	00	00	00	00	24

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Chapter-IV

Studies on
Physico Chemical Principles and Methods of Study

The metal chelate is formed when a proper chelating agent is added to a solution of metal ion. The chelate formed may be water insoluble or water soluble. The water insoluble chelate when formed quantitatively, it may be filtered and the composition and structure of the chelate can be determined by various analytical physico-chemical methods. If, however, the chelate is soluble and if its isolation is difficult, special method has to be used to find out its composition and other characteristics.

when a chelate is formed, there is a change in the properties of the metal ion solution and many characteristics of the solution are altered. The few important properties which are changed on complexation are,

(i) Change in conductivity of the solution,
(ii) Change in colour of the solution,
(iii) Change in qualitative properties of the solutions.
(iv) Change in colligative properties of the solutions.

If such a change in property is followed by suitable phsico-chemical measurements, then it may be of large importance in elucidating the composition and structure of the complexes[1,2].

Different workers have used different methods for the study of complexes in solution as well as to study the properties of water insoluble complexes. Few of these methods used by different workers are listed below:

(i) Potentiometric measurements[3],
(ii) Ion-exhange method[4,5],
(iii) Polarographic method[6,7],
(iv) Solubility method[8-11],
(v) Reaction kinetics[12],
(vi) Electrical conductance
(vii) Magnetic susceptibility
(viii) Infrared spectra

(ix) Elemental analysis

(x) Absorptiometric methods

(xi) Thermogravimetric analysis[13].

ABSORPTIOMETRIC METHOD :

H. Ley[14] recognised that the development of a characteristic colour is one of the most important and distinguished feature of a chelate compound. He made use of absorption spectra to distinguish between free metal ions and their chelates. Besides, to indicate the chelate formation, spectrophotometry can also be used to study the composition of chelates or complexes in solution. As the quantity of the coloured chelate formed is directly proportional to the concentration of metal ion, spectrophotometry can also be used to find out the concentration of metal ion if the standard data are available. The advances made in the design of sophisticated spectrophotometers have helped to exploit this technique to the maximum possible extent.

Two basic laws of spectrophotomety are of much importance. The first known as Lambert's law and the second Beer-Lambert law. According to the Lambert's law, when a monochromatic light is passed through a transparent medium, the intensity of the transmitted light decreases exponentially as the thickness of the absorbing medium incereases. Mathematically, this can be written as,

$$- \frac{dI}{dt} = KI \qquad \text{........ (1)}$$

Where 'I' is the intensity of the incident light, dI is the small decrease in intensity on passing through the small thickness dt and K is a constant. Integration of above equation (1) gives,

$$\text{In} \frac{I_o}{I_t} = Kt \quad \text{or} \quad I_t = I_o e^{-kt} \qquad \text{........ (2)}$$

Where, I_o and I_t are the intensities of incident radiation and that of transmitted radiation respectively.

Beer studied the effect of concentration of the coloured constituent in solution on the absorption of radiation. He found that "the intensity of a beam of monochromatic radiation decreases exponentially as the concentration of the absorbing substance incereases".

Combining Lambert's law and Beer's law, we have the law known as Lambert-Beer law or simply known as Beer's law. It is stated mathematically as follows:

$$I_t = I_o e^{-kct} \qquad \text{........ (3)}$$

Where 'c' is the concentration of the solution and 't' is the thickness. Converting equation (3) to natural logarithm, we can write down:

$$\log \frac{I_o}{I_t} = \varepsilon ct$$

Where, I_o and I_t have usual meanings, ε is a constant which is a characteristic of absorbing species, it is termed as molar absorptivity. The term log I_o/I_t is known as absorbance denoted by A. Thus,

$$A = \varepsilon ct \quad \text{or} \quad \varepsilon = A/ct$$

Concentration 'c' is expressed in mole/lit and thickness 't' in cm and so molar absorptivity will have the unit lit mol^{-1} cm^{-1} .

Beer law is obeyed well in dilute solution. In concentrated solution, the index of refraction for the absorbed radiation is changed and hence the system shows deviation from Beer's law. In the present study, the maximum concentration limit up to which the Beer's law is obeyed, is studied.

ABSORPTION SPECTRA OF METAL COMPLEXES :

For a metal chelate, two types of light absorption occur, in the visible and ultraviolet region.

(i) the absorption due to an electronic transition in a conjugated system in which a metal may or may not have taken part, and

(ii) the absorption resulting from electronic transition in the metal ion itself.

The former, which is due to the ligand, is very strong and is known as 'K' type absorption. It has been investigated in several cases [15-17].

The absorption bands characteristics of a metal ion alone are relatively weak and they result from the so-called forbidden transitions in the electron shells of the metal itself. This transition which corresponds to an electron shift in the unfilled 'd' orbitals of the transition metals and which are frequently intensified due to coordination may be observed in a free metal ion as well as metal chelate. M. Calvin and coworkers[15-17] observed absorption in the visible region due to the forbidden transition and also 'K' type absorption bands characteristics of the ligands in the UV region in case of Cu(II)- ethylacetoacetate and other substituted β-diketo chelates. They concluded from the experimental data that the influence of a metal ion on the characteristic absorption is much weaker than the ligand, which has a large conjugated system.

The transition metal cations have characteristic absorption bands in the visible and near UV region. These are considerably changed according to stereochemical forms and the ligand strength with the same solvent. In case of a non-polar solvent being used the absorption bands may be due to electron transition from 'd' orbital of lower energy to 'd' orbital of higher energy due to charge transfer. According to Franck-Condon principle, during electronic transition the atom in a molecule does not change the relative position. In charge transfer process,the absorption of light occurs when an electron is transferred from an orbital lying principally on the metal to that of ligand or viceversa. The absorption bands due to charge transfer are intense. Generally, such bands are at higher frequencies compared to d-d transition bands. Polar solvents shift the charge transfer bands to lower wavelength[18]. In case of d-d transition, the selection rule may be obeyed.

(i) Transitions in which the number of unpaired electrons change in going from the ground state to the excited state are referred to as "spin or multiplicity forbidden."

(ii) Transitions within a given set of p or d sub-shell are "Laporte forbidden," if the molecule has a centre of symmetry.

In transition metal complexes, there is always a centre of symmetry, which does not change during transition, and hence d-d transitions are forbidden. However, the distortion in the orbital symmetry due to ligand field or solvent effect causes the transition and as a result absorption is observed in many cases.

ML_6 complex of Ni(II) exhibits a simple spctrum involving 3 spin allowed transitions in the range of 7000-13000 cm^{-1}, 11000-20000 cm^{-1} and 19000-27000 cm^{-1}. In addition, two spin forbidden bands are also observed. ML_4 square-planar complexes of Ni(II) gives strong absorption bands between 15000-25000 cm^{-1}, and 23000-30000 cm^{-1}. On the other hand, ML_4 tetrahedral complex of Ni(II) gives one less intense band nearly at 16000 cm^{-1} [19-23]. In the visible region, spectra of Cu(II) complex formed with 2-hydroxy-4-ethoxyacetopnenone oxime, two bands have been observed. One weak band at 650 nm could be assigned to the transition $^1A_{1g} \leftarrow {}^2B_{1g}$[24]. A strong band that observed at 365 nm could be assigned to charge transfer. In case of Ni(II) complex with the same oxime, two bands have been observed. One weak band at 620 nm could be assignd to $^1B_{1g} \leftarrow {}^1A_{1g}$ transition and the strong band at 380 nm could be assigned to charge transfer.

METHOD FOR THE DETERMINATION OF THE COMPOSITION OF THE METAL CHELATE:

Reaction between metal ion and ligand can be written in general form as follows:

$$M + nL \rightleftharpoons ML_n$$

The number or ligand molecules 'n' required for each mole of metal ion i.e. metal : ligand ratio can be determined from absorption measurements. Several methods have been used since long for this purpose:

(i) The method of continuous variation[25],
(ii) The mole ratio method[26],
(iii) The slope ratio method[27],
(iv) The logarithmic method[28],
(v) The method of isobestic point and straight-line method.

In the present work, the first two methods are employed for determining the composition of the chelates and hence a brief resume of these two methods is given here.

METHOD OF CONTINUOUS VARIATON:

I. Ostromisslensky[29] in 1910 and R.B. Denison[30] in 1912 first worked out the basis of the method of continuous variation. P. Job[25] published the details of this method along with the discussion.

In a reaction of the type,

$$M + nL \rightleftharpoons ML_n$$

in which the complex MLn is formed from the metal M and ligand L. Solutions of metal ions and ligands of the same concentration are mixed in varying proportion.

$$M + nL \rightleftharpoons ML_n \qquad \text{........ (1)}$$

$$K = \frac{[ML_n]}{[M]\,[L]^n} \qquad \text{........ (2)}$$

Where,[ ] represents activities = molar concentrations. If we impose the restriction,

$$M_t + L_t = \text{constant}$$

Where, 'M_t' and 'L_t' are the total molarities of M and L respectively, which can be shown when concentration $[ML_n]$ is maximum.

$$\frac{d\,[\,ML_n\,]}{dM_t} = 0 \qquad \text{........ (3)}$$

$$L\,/\,M = n \qquad \text{........ (4)}$$

In other words, for a constant, total concentration of the metal and the chelating agent, the concentration of the chelate is the greatest when the metal and the chelating agent are brought together in the same ratio in which they exist in the chelate. This can be evaluated in terms of the absorbance. If a solution of a ligand 'L' is mixed with a solution of a metal ion 'M', so that the total molar concentration of the ligand and metal ion is maintained constant then,

$$M = M_t - [ML_n] \qquad \text{........ (5)}$$

$$L = L_t - n\,[ML_n] \qquad \text{........ (6)}$$

$$M_t + L_t = \text{constant} \qquad \text{........ (7)}$$

The absorbance 'A' of the solution at a given wavelenght represents the total absorption by all the species in the solution, and that is expressed by

$$D = t\,[\,E_1\,(M) + E_2\,(L) + E_3\,(ML_n)\,] \text{........ (8)}$$

Where, t = length of the light path through the solution and E_1, E_2 and E_3 are the respective molar absorptivities of 'M', 'L' and 'ML_n' respectively.

Function 'Y' which represents the difference in the absorbance of equation (8) and the corrsponding absorbance in absence of the reaction between the solutions of 'M' and 'L' can be given by,

$$Y = t\,[\,E_1\,(M) + E_2\,(L) + E_3\,(ML_n)\,] - I\,[E_1M_t + E_2L_t\,] \quad \text{........ (9)}$$

where the chelating agent is optically transparent and cell path is 1.0 cm. Equation (9) may be rewritten by putting $E_2 = 0$ and $t = 1.0$ as follows:

$$Y = [\,E_1\,(M) + E_3\,(ML_n)\,] - [E_1M_t] \qquad \text{........ (10)}$$

Differentiation of the equation (10) with respect to 'L_t' and combination with the differentiated form of equation (9) gives,

$$\frac{dY}{dL_t} = (E_3 - E_1)\,\frac{d\,[\,ML_n\,]}{dM_t} \qquad \text{........ (11)}$$

Equation (11) represents the basis for the Job's method of continuous variation

If the chelate is the only coloured substance present, the absorbance of the solution is proportional to the concentration of the chelate and hence, the graph of the absorbance against the ratio of metal ion concentration to total concentration of metal and ligand would give a curve showing maximum at the ratio corrsponding to the composition of the chelate.

This method had been used to determine the composition of Cu(II), Fe(II), Fe(III) and UO_2(II) chelate with several salicylic acid derivatives. Foley and Anderson[31], Turner and Anderson[32] Yoe and Harvey[33], Moss and Mellon[34] employed this method for various complexes. K. Hussain Reddy and D. Venkata Reddy[35], K. Hussain Reddy, K. Giridhara Reddy, K. M. M. S. Prakash and D. Venkata Reddy[36] used this method to determine the compositon of Ni(II), Fe(III) and Cu(II) chelates with 2,4 dihydroxyacetophenone thiosemicarbazone and 2,4-dihydroxyacetophenone semicarbazone. Y. G. Patel[37] and G. H. Bhatt[38] have employed this method for the determination of the composition of metal complexes.

MOLE RATIO METHOD :

The stoichiometric ratio between metal ions and these above was also studied by the mole ratio method.

J.H. Yoe and A. L. Jones[39] described the mole ratio method in which a series of solutions are prepared containing a constant amount of the metal ion but with incerasing ratio of the metal to the reagent or vice versa. The absorbances of the solutions are measured and plotted against the concentration ratios. For a stable complex, the curve rises from the origin as a straight line and breaks sharply at a constant absorbance at the molar ratio of the components in the complex, if both the interactants are colourless. However, a complex that undergoes appreciable dissociation in solution, gives a continuous rising curve which becomes approximately parallel to the molar ratio axis only when an excess of the variable components is added.

In many cases, the results obtained by extrapolation of this curve are uncertain. It is often seen that such curve may be made to break sharply at the correct molar ratio, if the ionic strength of the solution is adjusted to a suitable value by the addition of an indifferent electrolyte. In such cases, it is possible to get information about the composition of the complex by this method. Also the mathematical treatment of the mole ratio method for deducing the stoichiometry of complexes in solution for situations in which several complexes exist under a given set of conditions has been fully worked out by Mayer and Ayres[40].

DETERMINATION OF STABILITY CONSTANT :

One of the most important factors relating to the coordination compound is their stability constants or formation constants. A reaction between a metal ion and a ligand may be represented as,..... (1)

$$mM + nL \rightleftharpoons M_m L_n$$

and the stability (or formation) constant K_s is given by .... (2)

$$K_s = \frac{[M_mL_n]}{[M]^m [L]^n}$$

and dissociation (or instability) constant, K_i of the chelate is given by

$$K_i = \frac{[M]^m [L]^n}{[M_mL_n]}$$

if 'a' represents the initial concentration of the metal, 'b' that of the ligand and 'X' the concentration of the chelate formed at equilibrium, then the stability constant K_s is given by,

$$K_s = \frac{X}{(a - mX]^m [b - nX]^n} \quad .... (3)$$

Hence, the determination of 'X' permits a calculation of the value of K_S, a and 'b' being known. The stability constant is a measure of the stability of the complex in solution with reference to the dissociation into metal ions and free ligands. From a precise knowledge of the stability constant, thermodynamic constants may be evaluated. However, the method involves many difficulties and it is doubtful whether true thermodynamic quantities of chelation can be determined except in very simple cases. The stability constants of chelates are studied mainly by two principle proceducers. G. N. Lewis and M Randall[41] first intoduced the concept of ionic strength which later received theoretical justification from the Debye-Huckel theory. The classical approach for the evaluation of thermodynamic equilibrium constants involves the determination of equilibrium constant in media of low ionic srength followed by an extrapolation to zero ionic strength (infinite dilution). Some workers have used the value of a single determination and attempted to correct this value to a thermodynamic equilibrium constant by the application of Debye-Huckel theory. The second method was intorduced by the G. Biederman and L. G. Sillen[42] and the fundamental idea of their method is to control the activity coefficient by keeping the ionic strength constant, because in dilute solution the activity coefficient of a given strong electrolyte is the same in all solutions of identical ionic strength.

F. C. Rossotti and H. R. Rassotti[43] have modified the methods for determining stability constant. The values of the stoichiometric constants are reliable under a given set of experimental conditions and are useful for practical purposes. In the present study, the constants determined are those obtained at room temperature and pH as mentioned. At the particular pH, the effect of hydolysis of the metal salt has not been taken into account. This constant has been termed as stability constant in the present work. Attempts to maintain the ionic strength with indifferent electrolyte could not succeed in the present study as the metal chelates either precipitated by the addition of an electrolyte or there was a gradual fading of colour.

There are various methods for detemining the stability constant. The mole ratio method, which has been used here, is dscribd below in brief.

DETERMINATION OF STABILITY CONSTANT BY MOLE RATIO METHOD:

The stability constants may be calculated from the mole ratio method. A series of solutions is prepared which contain equal formal concentrations of the metal ion but different formal concentrations of ligand. The ratio of these concentrations should usually vary from about o.1 to 10.0 or 20.0. The absorbance of each solution is measured at a wavelength where the complex ion absorbs but the aquometal ion does not. These absorbances are proportional to the equilibrium concentration of the complex ion in the solution, and a plot of the absorbance against the ratio of the number of moles of ligand to the number of moles of metal ion will resemble inverted obtuse angle.

The extent of the curvature in the vicinity of the end point depends, of course, on the degree of dissociation of the complex. However, the stoichiometric formula of the complex can be found by extrapolating the straight line portions of the graph, which is to say that the point at which these lines intersect corresponds directly to the ratio of the ligand to metal ion in the coplex. This procedure works very well for weakly dissociated complex, but, if the dissociation constant of the complex is too large, the molar ratio plot will become a smooth continuous curve and it will be impossible to locate the stoichiometric point. In such cases, better results can often be secured by the slope ratio or continuous variation method.

Within a certain rather restricted range, however, the curvature around the “end point” of a molar ratio plot can be turned to good advantage and used for the calculation of the stability constant of the complex. Let the dissociation of the complex can be represented as,

$$\begin{array}{llcll} ML_n & M & + & nL & \\ C & 0 & & 0 & \text{. . . Initial concentration} \\ C\,(1 - \alpha) & C & & n\,(\alpha C) & \text{. . . Equilibrium concs.} \end{array}$$

Where, C is the total concentration of the complex in the moles per litre assuming no dissociation and is the degree of dissociation, the stability constant (reciprocal of dissociation constant) may be written as,

$$K_s = \frac{C\,(1 - \alpha)}{C\,(n\,\alpha^2\,C)^n}$$

The value of n for the complex having been established, the value of a may be obtained from the mole ratio curve by the following relationship:

$$\alpha = \frac{E_m - E_s}{E_m}$$

Where, E_m is the maximum absorbance obtained from the horizontal portion of the curve, indicating that all the metal is present in the form of the complex, E_s is the absorbance at stoichiometric molar ratio of the metal to reagent in the complex. Actually, however, the formation of the complex is not quite complete at the stoichiometry point due to backward dissociation reaction and so the value E_s at this point is smaller than E_m.

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Chapter-V

Studies on Experimental Parameters, Preparation of Solution and Reagents

EXPERIMENTAL PARAMETERS :

Temperature :

All the experiments, including the preparation of the solutions, extraction of the complex, recording the observation etc. were done at room temperature.

Instruments :

(i) Spectrophotometer :

The absorbance measurements were done on a "Shimadzu-UV-160-A spectrophotometer".

(ii) pH meter :

The pH of the solutions were measured on EQUIP TRONICS 614 pH meter and solutions of required pH were obtained using sodium-acetate-acetic acid, sodium acetate-HCl, NH_3-NH_4Cl or Borax-HCl buffer of suitable concentration.

(iii) IR spectrophotometer :

All IR spectra were recorded on SHIMADZU-FOURIER TRANSFER (FTIR)-8400 Spectrophotometer using KBr pellet.

(iv) Thermogravimetric Analysis :

Thermogravimetric Analysis of the chelates were done on "Mettler TOLEDO STAR Systems".

Materials :

All chemicals used throughout this work were of analytical grade.

Effect of time on the absorbance of chelate :

The colour development due to the formation of the metal chelates was found attain constancy in absorbance values, within five to ten minutes and were found to be constant. Details for each chelate are given with the study of respective chelate.

Effect of order of addition of the reagents :

The effect of the order of the addition of the reagent was observed in all experiments. It is found that the order of addition of the reagent has no effect.

Number of complex species formed :

In order to ascertain the number of complexes formed in each case under the experimental conditions, the method of Vosburgh and Copper[84] was applied. Several mixtures containing metal ion and ligand in the ratio 0:1, 1:0, 1:1, 1:2, 1:3 and 1:4 were prepared at selected pH. The absorbance of the solutions were measured between a selected range of wavelengths. In second experiment, several mixtures containing stoichiometry amount of metal ion and ligand were prepared at different pH values and the absorbance of the complex were measured by the number of shifts in the region of maximum absorbance of the mixtures. From the λmax of the reagent itself, the number of complexes formed was ascertained during the studies, it was found that only one complex was formed in all cases under experimental conditions.

Determination of the composition of chelates :

The stoichiometric ratio of metal to reagent in the complexes were determined by -

(i) Job's Method of continuous variation,

(ii) Yoe and Jones Mole ratio method,

(iii) Gravimetric Method.

Determination of conditional stability constant :

The conditional stability constants of the complexes were determined from Yoe and Jones mole ratio method and Job's method. The Gibbs free energy changes ΔG^{o} corresponding to the complex formation reactions were also calculated.

Analytical Application of the Metal Chelates :

Beer's Law :

The obeyance of the Beer law was studied for metal chelates under investigation by varying metal ion concentration and adding the excess reagent in constant amount and measuring the absorbance of at wavelength of maximum absorbance and at pH of maximum absorption. The range of concentration for obeyance to the Beer's law expressed in ppm for each system has been determined from the graphs.

Molar Absorptivity :

The values of molar absorptivity was calculated for all complexes. That was expressed in litre $mol^{-1}cm^{-1}$.

Preparation of metal ion solution :

	Metal salts	Mole wt.
1.	$CuSO_4 . 5H_2O$	249.68
2.	$NiSO_4 . 6H_2O$	256.71
3.	$MnSO_4 . H_2O$	169.00
4.	$FeCl_3$ (Anhy.)	162.22
5.	$ZnSO_4 . 7H_2O$	287.54

were used to get the solutions of corresponding metal ions.

Standard solutions of the salts (i) to (v) were prepared by dissolving the requisite quantity of sample in doubly distilled water. Little acids were added to prevent hydrolysis of metal salts. Solutions of desired concentrations were obtained by suitable dilution of the stock solutions.

Chapter-VI

Spectrophotometric Determination of Cu(II), Ni(II), Mn(II) and Fe(III) with 5-(3-bromophenyl)-4-{[(1E)-(4-methoxyphenyl)methylene]amino}-4H-1,2,4-triazole-3-thiol (SB_I)

6.1 STUDY OF Cu(II) COMPLEX :

Preparation of standard solution of Copper(II) :

Stock solution of Cu(II) (0.05 M) was prepared by dissolving 3.121 g of $CuSO_4.5H_20$ in distilled water and little acid and diluting it to 250 ml. This solution was standardised volumetrically using EDTA[1-A]. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

*** Reaction of SB_I with Cu(II) :**

1.0 % solution of the schiff base in dioxane was used in all detection and gravimetric determination.

*** Reaction with Cu(II) at different pH values :**

5 ml schiff base (SB_I) solution was added to 2 ml of standard 0.05 M Cu(II) solution at different pH. The results are Tabulated in Table-I.

*** Stability of chelate :**

The buff colour Cu(II) chelate is insoluble in water and ethanol, while it is soluble in chloroform, dioxan, DMF, ethyl acetate. The solution of the chelate was stable and could be kept for long time without any decomposition.

*** Limit of identification and dilution limit :**

The limit of identification (X) is the quantity of material in microgram (γ) per ml of the sample solution which is detectable by the particular technique and expressed in gram (γ/ml) (1γ : 1 microgram = 0.001 mg). The following simple relation exists between the dilution limit, the volume of the test solution and identification limit.

$$\text{Dilution Limit} = \frac{\text{1: Volume of the test solution in ml}}{\text{Limit of identification in } \gamma/\text{ml}} \times 10^6$$

The limit of identification (X) was determined with the standard copper sulphate solution employing spot plate technique, 1.0 ml of the metal ion solution of different concentration at pH 5.0 was treated with 5 ml of 0.05 M solution of the reagent. The limit of identification was found to be 6.876 γ/ml and corresponding dilution limit is 1:1, 45, 458.

TABLE - I

pH	Buffer	Observation
2.0	HCl + CH_3COOH	Colouration
2.5	HCl + CH_3COONa	Buff precipitate
3.0	HCl + CH_3COONa	Buff precipitate
4.0	CH_3COOH + CH_3COONa	Buff precipitate
5.0	CH_3COOH + CH_3COONa	Buff precipitate
6.0	CH_3COOH + CH_3COONa	Buff precipitate
7.0	NaOH + KH_2PO_4	Buff precipitate
8.0	NH_3 + NH_4Cl	Buff precipitate
9.0	NH_3 + NH_4Cl	Buff precipitate
10.0	NH_3 + NH_4Cl	Buff precipitate

* Gravimetric determination of Cu(II) with SB_I :

A 1.0 % solution of the schiff base in dioxane was used.

Copper sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 3.0 to 4.0 using sodium acetate - hydrochloric acid buffer. The solution was warmed at 60°C and small excess of schiff base-SB_I was added (1%, 30 ml). A buff precipitate obtained were digested on water bath for 60 minutes at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by 50% dioxane-ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

* Calculations :

10 ml solution gave 0.4221 g of Cu(II) SB_I

Found Copper = 0.03195 g

10 ml Copper sulphate contains = 0.03180 g of Cu(II)

Error = 0.00015 g

= 0.47 %

TABLE - II

Estimation of Cu(II) using SB_I Ligand :

Cu(II) taken = 0.03180 g.

Drying temperature = 115 - 120^{O}C

pH	Cu(II) complex in (g)	Cu(II) found in (g)	Error in (g)	Error %
2.5	0.4077	0.03086	-0.00094	-2.9
2.5	0.4087	0.03094	-0.00086	-2.7
3.0	0.4094	0.03099	-0.00081	-2.5
3.0	0.4116	0.03116	-0.00064	-2.0
3.5	0.4140	0.03134	-0.00046	-1.44
3.5	0.4149	0.03141	-0.00039	-1.22
4.0	0.4157	0.03147	-0.00033	-1.03
4.0	0.4168	0.03155	-0.00025	-0.78
4.5	0.4176	0.03161	-0.00019	-0.59
4.5	0.4186	0.03169	-0.00011	-0.34
5.0	0.4198	0.03178	-0.00002	-0.062
5.0	0.4206	0.03184	+0.00004	+0.027
5.5	0.4221	0.03195	+0.00015	+0.47
5.5	0.4227	0.03200	+0.00020	+0.62
6.0	0.4239	0.03209	+0.00029	+0.91
6.0	0.4250	0.03217	+0.00037	+1.16

*** Spectrophotometric study of Cu(II) complex :**

The Cu(II) - SB_I chelate has been found to be soluble in chloroform, benzene, carbon tetrachloride, DMF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

*** Absorption Spectra :**

To record the absorption spectra, 5 mg of chelate was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the range of 350-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 410 nm and hence all the measurements were carried out at 410 nm. Absorption spectra is given on page No. 53.

*** Verification of Beer's Law :**

To 5 ml of solution (0.01 M) of the schiff base-SB_I, varying amounts of the metal ion solution (0.005 M) were added and the pH was adjusted to 5.0 using CH_3COONa + CH_3COOH buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and final volume of the chloroform extract was adjusted to 25 ml. The absorbance of these solutions were measured at 410 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 30.48 ppm of Cu(II). The standard graph thus obtained may be used for the determination of copper in a unknown solution using schiff base-SB_I. The results are tabulated in Table-III. The graph is shown on page 47.

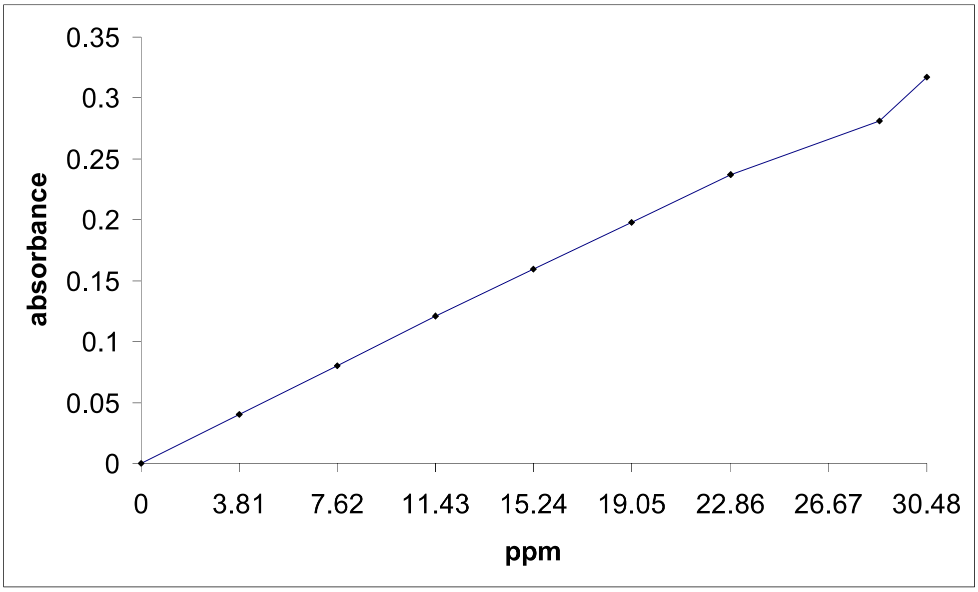
Molar absorptivity calculated from Beer's law plot was found to be $10x10^2$ lit.mol^{-1} cm^{-1} for Cu(II)-SB_I reagent at 410 nm.

Verification of Beer's Law

Cu(II) SB_I

Varying amount of metal solution	: 0.005M
Ligand solutin	: 5.0 ml (0.01M)
Final volume of chloroform extract	: 25 ml
Wavelength	: 410 nm.
pH	: 5.0

Cu(II) Solution taken in ml	Cu (II) Taken in ppm	Absorbance
0.3	3.81	0.0401
0.6	7.62	0.0802
0.9	11.43	0.121
1.2	15.24	0.159
1.5	19.05	0.198
1.8	22.86	0.237
2.1	26.67	0.281
2.4	30.48	0.317



Verificaiton of Beer's Law: Cu(II) SB_I Complex

Composition of Chelate :

The composition of Cu(II) chelate with the reagent SB_I has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

(i) Composition of Cu(II)-SB_I complex by Job's method of continuous variation :

A 0.005 M solution of Cu(II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.005 M) was prepared in dioxane. The solution of metal salt and the reagent were mixed in varying proportions as under :

Metal ion solution : 0, 1, 2, 3, - - - - 11, 12 ml
Reagent solution : 12, 11, 10, 9, - - - - 1, 0 ml

pH of the solution was adjusted to 5.0. The precipitated complex was extracted with three 5 ml portions of chloroform and final volume of chloroform extract was adjusted to 25 ml. The absorbance of chloroform extracts were measured at 410 nm. The results are tabulated in Table-IV.

From the graph (page No. 50), it has been found that maximum occurs at 0.33 ratio of metal ion concentration to the total metal and ligand concentration indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In this method, equimolar solutions of the copper (II) and the reagent (0.005 M) were used. A series of solutions were prepared, keeping the reagent solution (6.0 ml) constant while varying the amount (from 1 to 8.0 ml) of 0.005 M metal solution.

pH of the solutions were adjusted to 5.0. The resulting precipitate were extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 410 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V. Graph on page No. 51.

It is evident from the graph that absorbance gradually increases upto molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

- Evaluation of stability constant :

$$MLn = M + nL$$

$$C(1-\alpha) \qquad C[n.c\alpha]^n$$

$$K_s = \frac{C(1-\alpha)}{C[n.c\alpha]^n}$$

taking n = 2 in this case the equation reduce to,

$$K_s = \frac{1-\alpha}{4c^2\alpha^2}$$

where $$\alpha = \frac{E_m-E_s}{E_m}$$

E_m : Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines ;

E_s : absorbance at the stoichiometric molar ratio of the metal to reagent in complex

*** Calculation of stability constant :**

The stability constant is calculated from the above relation :

From mean K_s value, the standard free energy change ΔG^o for the formation reaction of complex has been calculated at 25°C using the formula $\Delta G^o = - RTlnk$

Method	**E_M**	**E_s**	**α**	**K_s**
Job	0.288	0.278	0.0347	8.0×10^6
Mole ratio	0.205	0.192	0.0634	2.3×10^6

Means K_s = 5.15×10^6

ΔG^o = -9.151 k.cal/mole

Cu(II) SB_I

Metal solution : 0.005M

Ligand solutin : 0.005M

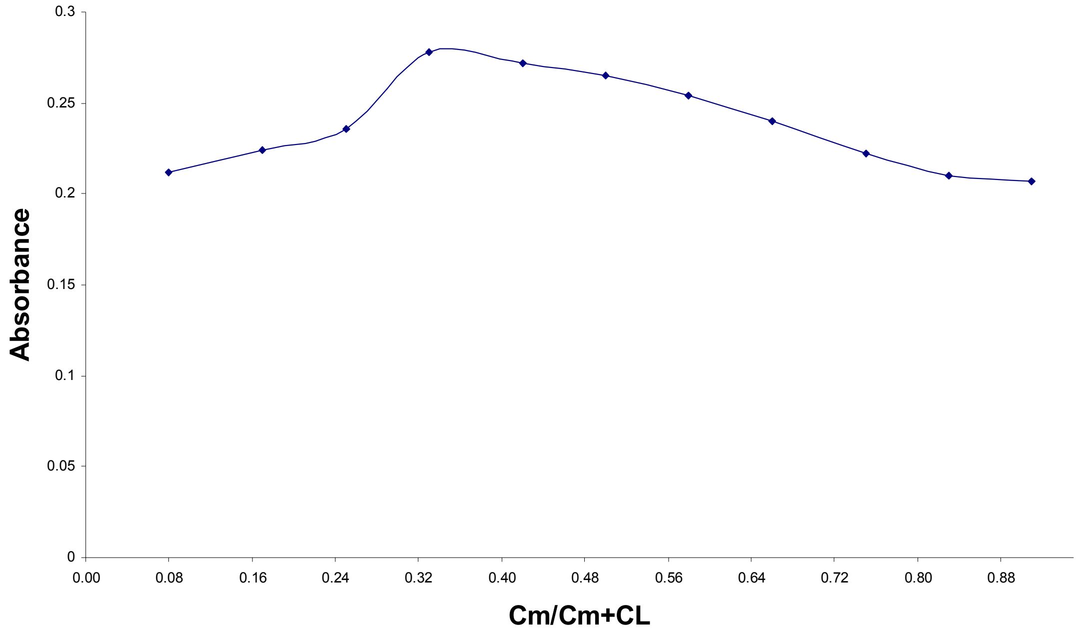
Final volume of chloroform extract : 25 ml

Wavelength : 410 nm.

pH : 5.0

TABLE-IV

Metalion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.212
2	10	0.17	0.224
3	9	0.25	0.236
4	8	0.33	0.278
5	7	0.42	0.272
6	6	0.50	0.265
7	5	0.58	0.254
8	4	0.66	0.240
9	3	0.75	0.222
10	2	0.83	0.210
11	1	0.91	0.207



Composition of Cu(II) SB_I Complex of Job's method

Cu(II) SB_I

Metal solution : 0.005M

Ligand solutin : 0.005M (6.0 ml.)

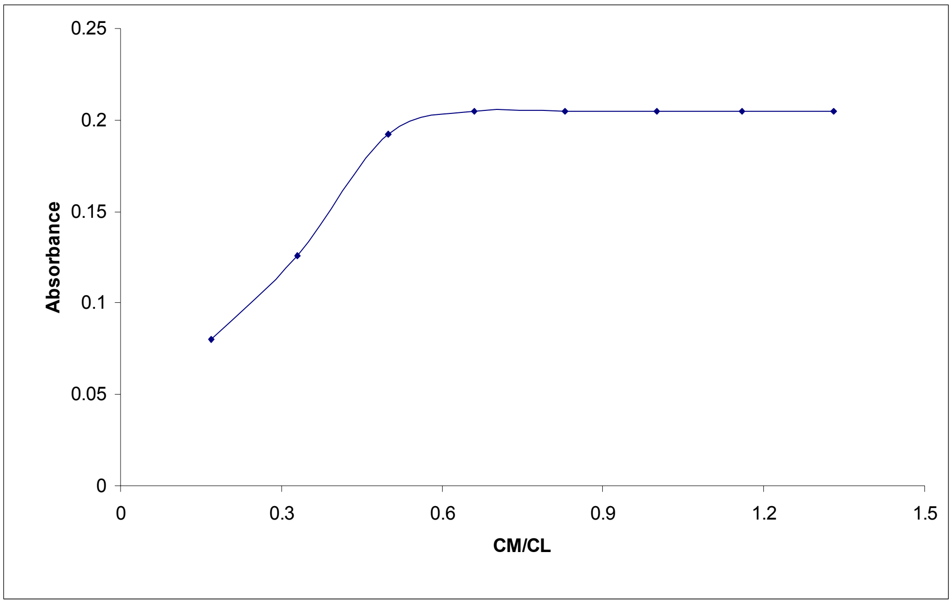
Final volume of chloroform extract : 25 ml

Wavelength : 410 nm.

pH : 5.0

TABLE-V

Metal ion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.08
2	6	0.33	0.126
3	6	0.50	0.192
4	6	0.66	0.205
5	6	0.83	0.205
6	6	1.00	0.205
7	6	1.16	0.205
8	6	1.33	0.205



Composition of Cu(II) SB_I Complex of mole-ratio method

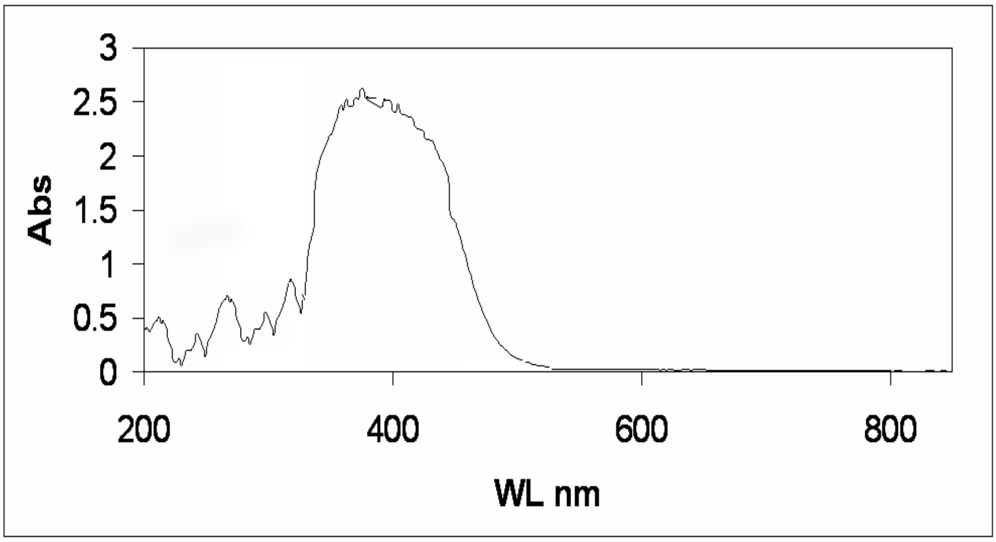
* Effect of diverse ions :

To study the effect of foreign ions on gravimetric determinations of Cu(II), 8-10 mg of various cations were added to a known amount of Cu(II) solution at pH 5.0 and gravimetric estimations were done. It was observed that Ba(II), Sr(II), Mg(II), Mn(II), do not interfere at this pH, but Fe(III), Co(II), Pd(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

* Estimation of copper and copper oxide from its chelate :

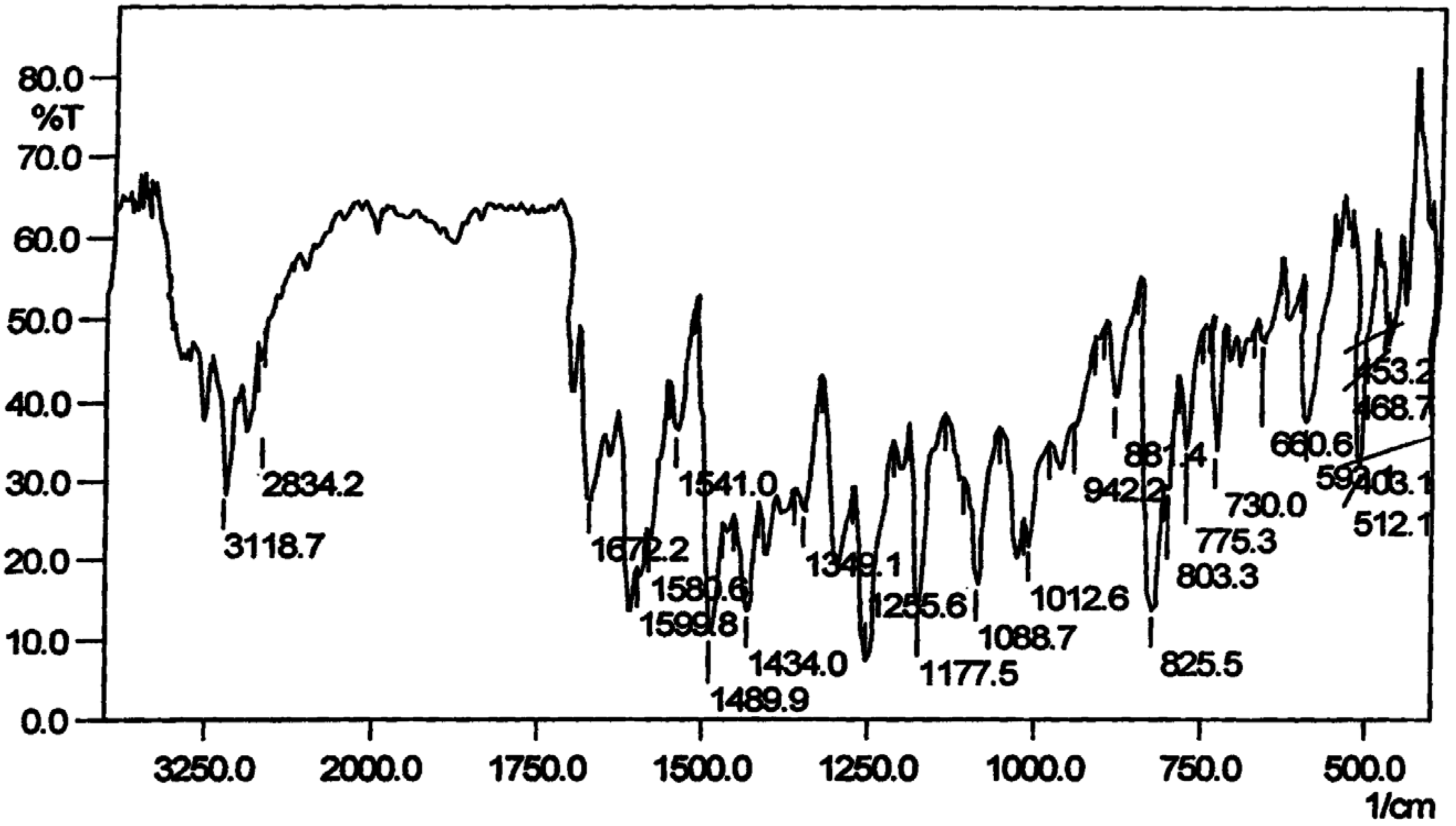
Copper (II) - SB_I (0.250 g) was ignited in a covered crucible. The ignited mass was then treated with a drop of concentrated nitric acid and then excess of acid was evaporated off by heating the crucible over low flame. The temperature was gradually raised to a dull red heat to ensure complete conversion to copper oxide. It was cooled and weighed as copper oxide. The results are tabulated below.

Chelate	Weight of chelate ignited in mg.	Weight of CuO obtained in mg.	Percentage of metal	
			Calc.	Found
Cu II - SB_I	250	25.59	8.32	7.93



Absorption Spectra of Cu(II)-SB_I Complex

IR SPECTRA OF Cu(II)-SB$_I$ COPMLEX



6.2 STUDY OF Ni(II) COMPLEX :

Preparation of standard solution of Nickel (II) :

Stock solution of Ni(II) (0.05 M) was prepared by dissolving 3.208 g of $NiSO_4.6H_20$ in distilled water with little acid and diluting to 250 ml. This solution was standardised volumetrically using EDTA[1-B]. Experimental solutions of required concentration were prepared by suitable dilution of the above stock solution.

*** Reaction of SB_I reagent with Ni(II) :**

1.0 % solution of the reagent in 50% dioxane was used in all detection and gravimetric determination.

*** Reaction with Ni(II) at different pH values :**

5 ml reagent (SB_I) was added to 2 ml of standard 0.05 M Ni(II) solution at different pH. The results are Tabulated in Table-I.

*** Stability of chelate :**

The light green Ni(II) chelate is insoluble in water and ethanol, while it is soluble in chloroform, dioxan, DMF, THF, ethylacetate. The solution of the chelate was stable and could be kept for long time without any decomposition.

*** Limit of identification of dilution limit :**

The limit of identification (X) was determined in a similar way as done for Cu(II)-SB_I using the standard nickel sulphate solution at pH 8.5. The limit of identification was found to be 7.4063 γ/ml and corresponding dilution limits is 1:1, 3.5, 0.20

TABLE - I

pH	Buffer	Observation
7.5	NaOH + KH_2PO_4	Small amount of light green precipitate
7.5	NH_3 + NH_4Cl	Light green precipitate
8.0	NH_3 + NH_4Cl	Light green precipitate
8.5	NH_3 + NH_4Cl	Light green precipitate
9.0	NH_3 + NH_4Cl	Light green precipitate
9.5	NH_3 + NH_4Cl	Light green precipitate
10.0	NH_3 + NH_4Cl	Light green precipitate

* Gravimetric determination of Ni(II) with SB_I reagent :

A 1.0 % solution of the reagent in 50% dioxane was used.

Nickel sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 7.5 to 8.0 by using NH_3-NH_4Cl buffer. The solution was warmed at 60^{O}C and small excess of reagent SB_I was added (1%, 25 ml). A light green precipitate obtained were digested on water bath for 60 minutes at 60-70^{O}C. The precipitate were filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by 50% dioxane-ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115^{O}C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

*** Calculations :**

10 ml solution gave 0.4208 g of Ni(II)-SB_I reagent complex

Found nickel = 0.02956 g

10 ml nickel sulphate contains = 0.02950 g of Ni(II)

Error = 0.00006 g

= + 0.20 %

TABLE - II

Estimation of Ni(II) using SB_I Legand :

Ni(II) taken = 0.02950 g.

$NiSO_4.6H_2O$ Drying temperature = 110 - 115°C

pH	Ni(II) complex in (g)	Ni(II) found in (g)	Error in (g)	Error %
7.5	0.4146	0.02913	-0.00037	-1.25
7.5	0.4157	0.02921	-0.00029	-0.98
8.0	0.4169	0.02929	-0.00021	-0.71
8.0	0.4182	0.02938	-0.00012	-0.40
8.5	0.4196	0.02948	-0.00002	-0.067
8.5	0.4203	0.02953	+0.00003	+0.10
9.0	0.4214	0.02961	+0.00011	+0.37
9.0	0.4226	0.02969	+0.00019	+0.64
9.5	0.4230	0.02972	+0.00022	+0.74
9.5	0.4243	0.02981	+0.00031	+1.05
10.0	0.4259	0.02992	+0.00042	+1.42
10.0	0.4270	0.03000	+0.00050	+1.69

* Spectrophotometric study of Ni(II) complex :

The Ni(II) - SB_I chelate has been found to be soluble in chloroform, dioxane, DMF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

* Absorption Spectra :

To take the absorption spectra, 5 mg of chelate was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the region 350-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 450 nm and hence all the measurements were carried out at 450 nm. Absorption spectra is given on page No. 65.

* Verification of Beer's Law :

To 6 ml of solution (0.01 M) of the reagent SB_I, varying amount of Ni(II) solution (0.005 M) were added. The pH was adjusted to 8.5 using NH_3-NH_4Cl buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and the final volume of chloroform extract was diluted to 25 ml in volumetric flask. The absorption of these solutions were measured at 450 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 30.48 ppm of Ni(II). The standard graph thus prepared may be used for the determination of nickel in unknown solution using SB_I reagent. The results are tabulated in Table-III. The graph is shown on page 59.

Molar absorptivity calculated from Beer's law plot was found to be 16×10^2 lit.mol^{-1} cm^{-1} for Ni(II)-SB_I complex as 450 nm.

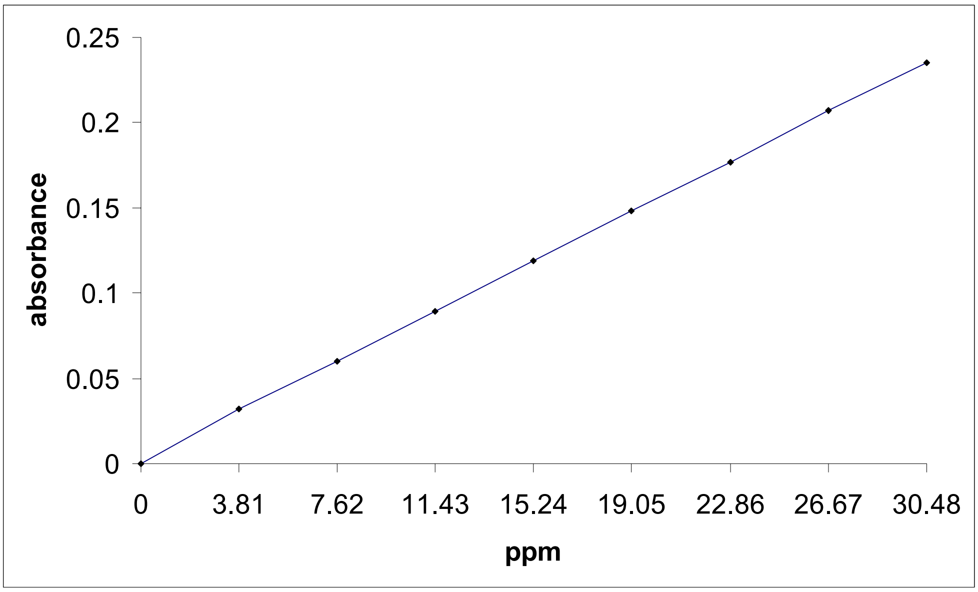
Verification of Beer's Law

Ni(II) SB_I

Varying amount of metal solution	: 0.005M
Ligand solutin	: 6.0 ml (0.01M)
Final volume of chloroform extract	: 25 ml
Wavelength	: 450 nm.
pH	: 8.5

TABLE-III

Ni(II) Solution taken in ml	Ni(II) Taken in ppm	Absorbance
0.3	3.81	0.032
0.6	7.62	0.06
0.9	11.43	0.089
1.2	15.24	0.119
1.5	19.05	0.148
1.8	22.86	0.177
2.1	26.67	0.207
2.4	30.48	0.235



Verificaiton of Beer's Law: Ni(II) SB_I Complex

* Composition of Chelate :

The composition of Ni(II) chelate with the reagent SB_I has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

(i) Composition of Ni(II)-SB_I complex by Job's method of continuous variation :

A 0.005 M solution of Ni(II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.005 M) was prepared in dioxane. The solution of metal salt and the reagent were mixed in varying proportions as under :

Metal ion solution : 1, 2, 3, - - - - 9, 10, 11 ml

Reagent solution : 11, 10, 9, - - - - 3, 2, 1 ml

pH of the solution was adjusted to 8.5. The precipitated complex was extracted with three 5 ml portions of chloroform. The volume of chloroform extract was adjusted to 25 ml in volumetric flask. The absorbance of chloroform extracts were tabulated in Table-IV.

From the graph (page No. 61), it has been found that maximum occurs at 0.33 ratio of metal ion concentration to the total concentration of metal and ligand indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In this method, equimolar solutions of the nickel (II) as well as the reagent (0.005 M) were used. A series of solutions were prepared by keeping the reagent solution (6 ml) constant while varying the amount (from 1 to 8.0 ml) of 0.005 M metal solution.

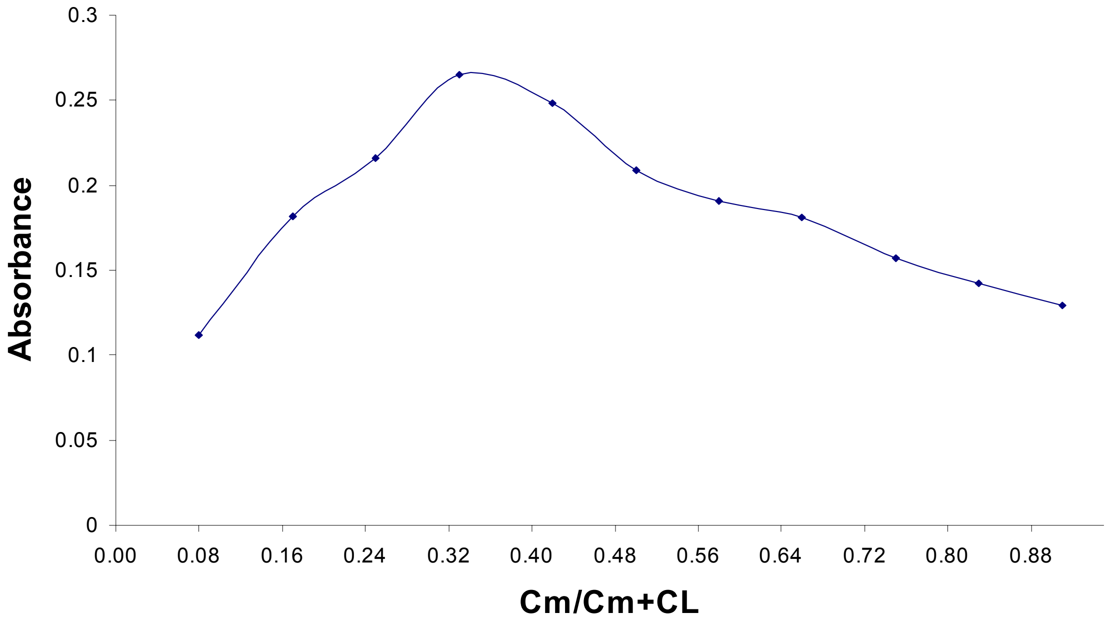
pH of the solutions were adjusted to 8.5. The resulting precipitate were extracted in chloroform. The volume of extract was made to 25 ml in volumetric flask. Absorbance were recorded at 450 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V and corresponding graph on page No. 62.

Ni(II) SB_I

Metal solution	: 0.005M
Ligand solutin	: 0.005M
Final volume of chloroform extract	: 25 ml
Wavelength	: 450 nm.
pH	: 8.5

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.112
2	10	0.17	0.182
3	9	0.25	0.216
4	8	0.33	0.265
5	7	0.42	0.248
6	6	0.50	0.209
7	5	0.58	0.191
8	4	0.66	0.181
9	3	0.75	0.157
10	2	0.83	0.142
11	1	0.91	0.129



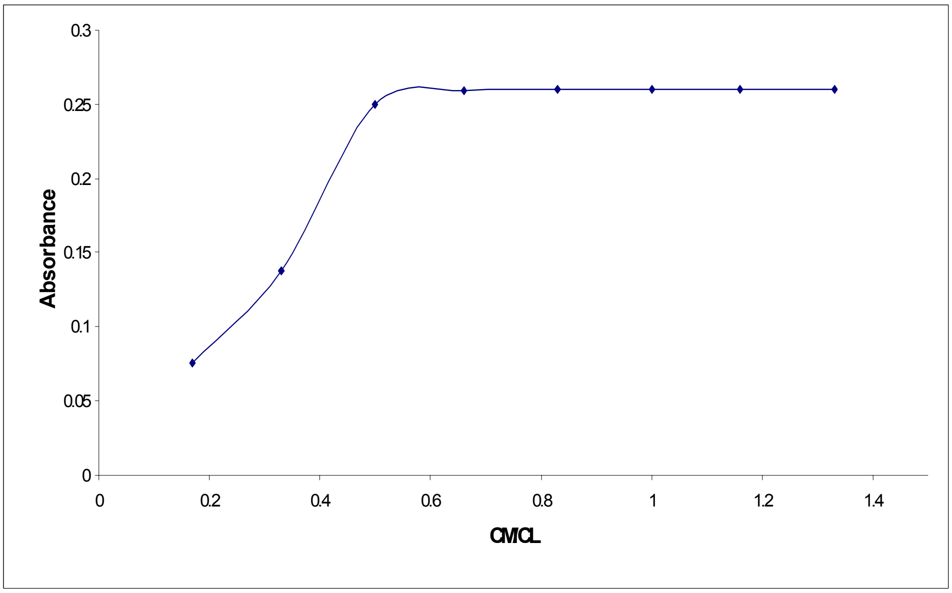
Composition of Ni(II) SB_I Complex of Job's method

Ni(II) SB$_I$

Metal solution	: 0.005M
Ligand solutin	: 0.005M (6.0 ml.)
Final volume of chloroform extract	: 25 ml
Wavelength	: 450 nm.
pH	: 8.5

TABLE-V

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	6	0.17	0.076
2	6	0.33	0.138
3	6	0.50	0.250
4	6	0.66	0.259
5	6	0.83	0.260
6	6	1.00	0.260
7	6	1.16	0.260
8	6	1.33	0.260



Composition of Ni(II) SB$_I$ Complex of mole-ratio method

It is evident from the graph that, absorbance gradually increases upto the molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

*** Evaluation of stability constant :**

$$MLn = M + nL$$

$$C(1-\alpha) \qquad C[n.c\alpha]^n$$

$$K_s = \frac{C(1-\alpha)}{C[n.c\alpha]^n}$$

taking n = 2 in this case the equation reduces to,

$$K_s = \frac{1-\alpha}{4\,\alpha^2 c^2}$$

$$\text{where} \qquad \alpha = \frac{E_m - E_s}{E_m}$$

E_m : Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines ;

E_s : absorbance at the stoichiometric molar ratio of the metal to reagent in complex

- Calculation of stability constant :

The stability constant is calculated from the above relation.

From mean K_s value, the standard free energy change ΔG^o for the formation reaction of complex has been calculated at 25^oC using the formula $\Delta G^o = - RTlnk$

Method	**E_m**	**E_s**	**α**	**K_s**
Job	0.27	0.26	0.0370	7.03×10^6
Mole ratio	0.26	0.25	0.0384	6.5×10^6

Mean K_s = 6.76×10^6

ΔG^o = -9.312 k.cal/mole

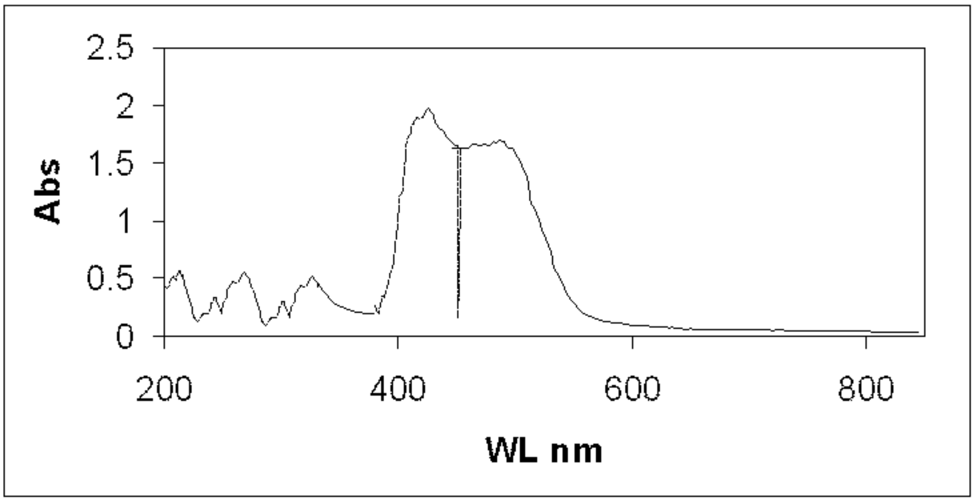
* Effect of diverse ions :

To study the effect of foreign ions on gravimetric determinations of Ni(II), 8-10 mg of various cations were added to a known amount of Ni(II) solution at pH 8.5 and gravimetric estimations were done. It was observed that Sr(II), Mg(II), Pd(II), Fe(III), Zn(II), Ba(II) do not interfere at this pH, but Cu(II), Mn(II) interfere seriously. Many common anions were not found to interfere.

* Estimation of Ni(II) as nickel oxide from its chelate :

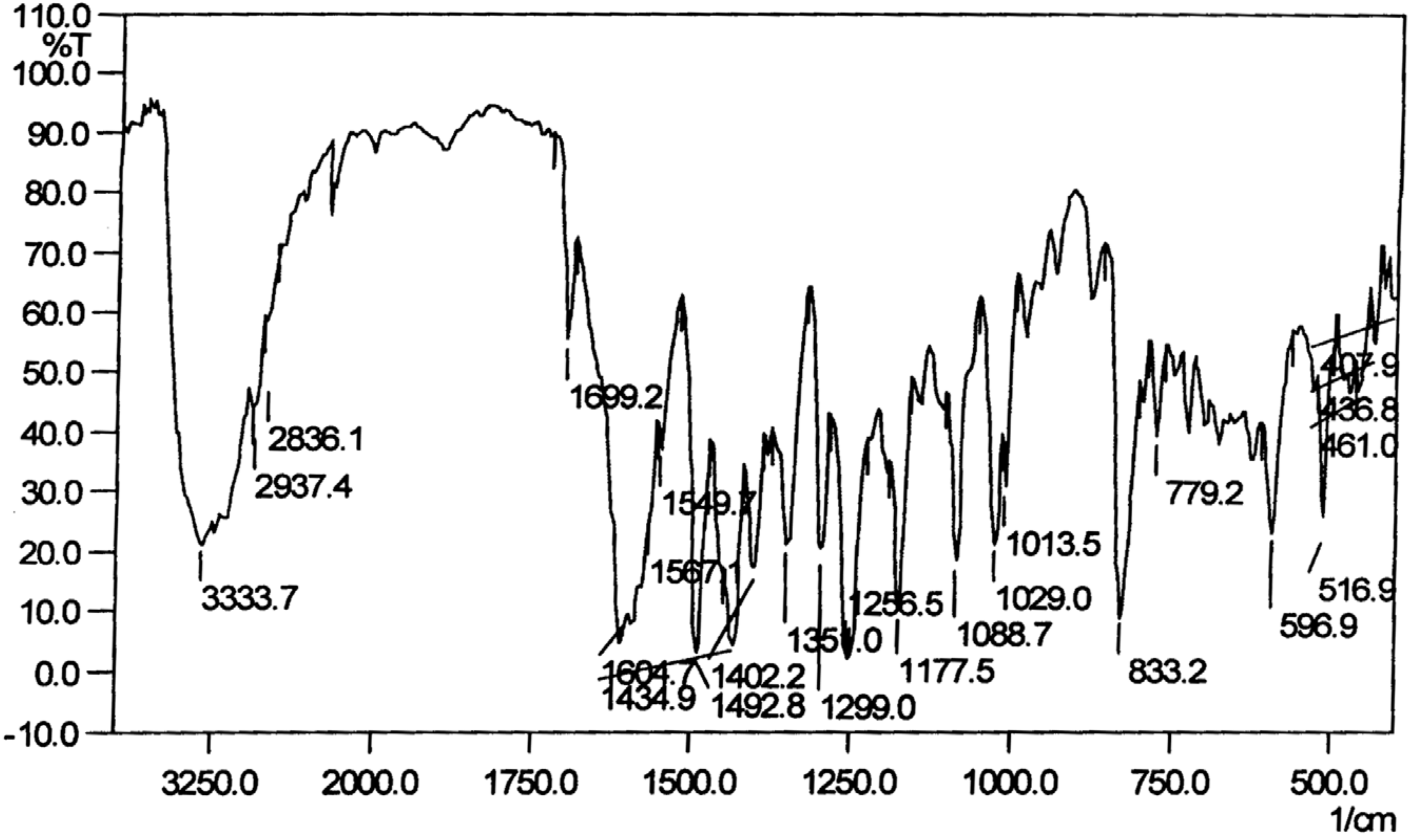
Ni(II) - SB$_I$ reagent (0.250 g) was ignited with the same method as used for copper chelate. It was cooled and weighed as nickel oxide. The results are tabulated below.

Chelate	Weight of chelate ignited in mg	Weight of NiO obtained in mg	Percentage of metal	
			Calc.	Found
Ni(I)I - SB$_I$	250	23.63	7.74	7.07



Absorption Spectra of Ni(II)-SB_I Complex

IR SPECTRA OF Ni(II)-SB_I COPMLEX



6.3 STUDY OF Mn(II) COMPLEX :

Preparation of standard solution of Manganese (II) :

Manganese sulphate 2.113 g was dissolved in little acid and double distilled water and diluted to 250 ml to get 0.05 M solution of Manganese (II). This solution was standardised volumetrically using EDTA[1-C]. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

*** Reaction of SB_I reagent with Mn(II) :**

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination.

*** Reaction of the ligand with Mn(II) at different pH values :**

5 ml of SB_I reagent solution was added to 2 ml of standard 0.05 M Manganese (II) solution at different pH. The results are Tabulated in Table-I.

*** Solubility of the chelate :**

Dark green Mn(II) chelate is insoluble in water and ethanol, while it is soluble in dioxane, chloroform, DMF, THF, acetone giving dark green solution. The solution of the chelate was stable and could be kept for long time without any decomposition.

*** Limit of identification and dilution limit :**

The limit of identification (X) was determined in a similar way as done for Mn(II)-SB_I using standard solution of manganese sulphate solution at pH 9.0. The limit of identification was found to be 6.875 γ/ml and corresponding dilution limits is 1:1, 4.5, 4.59

TABLE - I

pH	Buffer	Observation
7.0	NaOH + KH_2PO_4	Green opalescene
7.5	NaOH + KH_2PO_4	Green colouration
8.0	NH_3 + NH_4Cl	Dark green precipitate
8.5	NH_3 + NH_4Cl	Dark green precipitate
9.0	NH_3 + NH_4Cl	Dark green precipitate
9.5	NH_3 + NH_4Cl	Dark green precipitate
10.0	NH_3 + NH_4Cl	Dark green precipitate
10.5	NH_3 + NH_4Cl	Dark green precipitate

* Gravimetric determination of Mn(II) with SB_I reagent :

A 1.0 % solution of the reagent in dioxane was used.

Manganese sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water. A small excess of reagent SB_I was added to (1%, 14 ml). Then the pH was adjusted to pH 8.5 to 9.0 using NH_3 and NH_4Cl buffer. The dark green precipitate of manganese chelate formed were kept at room temperature for 24 hours. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by the dioxane to remove excess of reagent. The chelate was dried to constant weight at 80-85^{o}C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

*** Calculations :**

10 ml solution gave 0.4159 g of Manganese-SB_I complex

Found manganese = 0.02758 g

10 ml manganese sulphate contains = 0.02750 g

Error = 0.00008 g

= + 0.29 %

TABLE - II

Estimation of Mn(II) using SB_I Legand :

Mn(II) taken = 0.02750 g.

$MnSO_4.H_2O$ Drying temperature = 110 - 115°C

pH	Mn(II) complex in (g)	Mn(II) found in (g)	Error in (g)	Error %
7.5	0.4059	0.02684	-0.00066	-2.68
7.5	0.4076	0.02695	-0.00055	-2.28
8.0	0.4085	0.02701	-0.00049	-2.06
8.0	0.4102	0.02712	-0.00038	-1.66
8.5	0.4171	0.02758	+0.00008	+0.29
8.5	0.4183	0.02766	+0.00016	+0.58
9.0	0.4194	0.02773	+0.00023	+0.83
9.0	0.4205	0.02780	+0.0003	+1.087

*** Spectrophotometric study of Mn(II) complex :**

The Manganese chelate of SB_I reagent has been found to be soluble in chloroform, dioxane, DMF and THF. This enabled to verify the Beer's law and its application for spectrophotometric determination.

*** Absorption Spectra :**

To take the absorption spectra, 5 mg of chelate was dissolved in 100 ml of chloroform and the spectra was scanned in the region 340-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 520 nm and hence all the measurements were carried out at 520 nm. Absorption spectra of manganese SB_I reagent is shown on page No. 77.

*** Verification of Beer's Law :**

To 8 ml of solution (0.01 M) of the reagent SB_I chalcone, varying amount of metal solution (0.005 M) were added and the pH was adjusted to 9.0 using NH_3-NH_4Cl buffer. The insoluble complex precipitated was extracted in chloroform using three 5.0 ml portions of chloroform and the final volume of chloroform extract was adjusted to 25 ml in volumetric flask. The absorbance of these solutions were measured at 520 nm against chloroform as the blank.

Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 15.4 ppm of Mn(II). The standard graph thus obtained may be used for the determination of manganese in unknown solution using SB_I. The results are tabulated in Table-III. The graph is shown on page 71.

Molar absorptivity calculated from Beer's law plot was found to be 9.0×10^2 lit.mol^{-1} cm^{-1} for Mn(II)-SB_I complex at 520 nm.

*** Composition of Chelate :**

The composition of Mn(II) chelate with the schiff base SB_I has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

Verification of Beer's Law

Mn(II) SB_I

Varying amount of metal solution : 0.005M

Ligand solutin : 8.0 ml (0.01M)

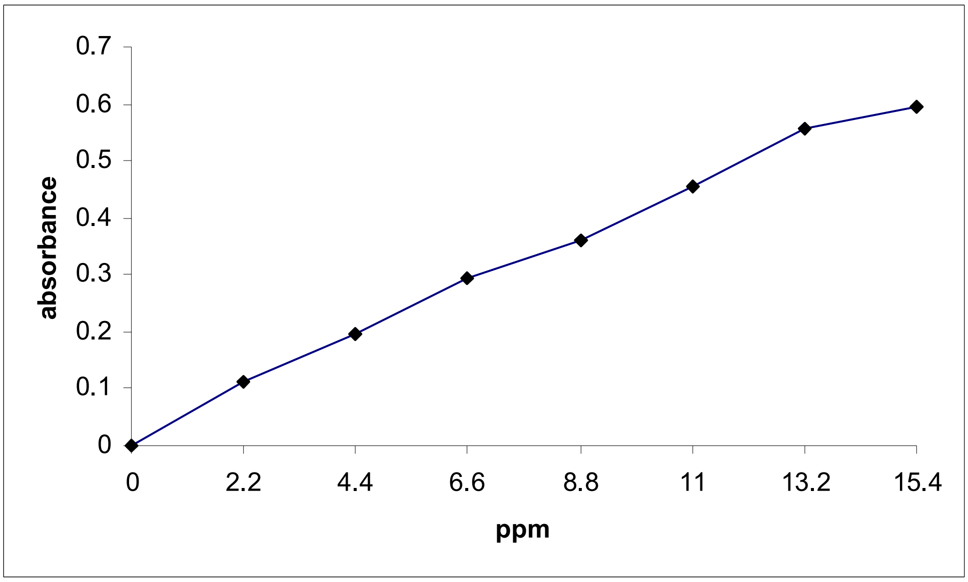
Final volume of chloroform extract : 25 ml

Wavelength : 520 nm.

pH : 9.0

TABLE-III

Mn(II) Solution taken in ml	Mn (II) Taken in ppm	Absorbance
0.3	2.2	0.112
0.6	4.4	0.195
0.9	6.6	0.293
1.2	8.8	0.362
1.5	11	0.454
1.8	13.2	0.558
2.1	15.4	0.594



Verificaiton of Beer's Law: Mn(II) SB_I Complex

(i) Composition of Mn(II)-SB$_I$ complex by Job's method of continuous variation :

A 0.001 M solution of Mn(II) was prepared by suitable dilution of the standard solution. The solution of the reagent (0.001 M) was prepared in absolute ethanol. The solution of the metal salt and the reagent were mixed in varying proportions as under :

Metal ion solution	:	0, 1, 2, 3, - - - - 11, 12 ml
Reagent solution	:	12, 11, 10, 9, - - - - 1, 0 ml

pH of the various solutions were adjusted to 9.0. The precipitated complex was extracted with three 5.0 ml portions of chloroform and final volume of chloroform extract was made to 25 ml in volumetric flasks. The absorbance of chloroform extracts were measured at 520 nm. The results are tabulated in Table-IV.

From the graph (page No. 73), it has been found that maximum occurs at 0.33 ratio of metal ion concentration to total concentration of metal and ligand indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In this method, equimolar solutions of the Mn(II) as well as the reagent (0.001 M) were used. A series of solutions were prepared keeping the reagent solution (6 ml) constant while varying the amount (from 1.0 to 9.0 ml) of 0.001 M metal solution. pH of the solutions were adjusted to 9.0. The resulting precipitate were extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 520 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V. The graph is shown on page No. 74.

It is evident from the graph that, absorbance gradually increases upto the molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

Mn(II) SB_I

Metal solution : 0.001M

Ligand solutin : 0.001M

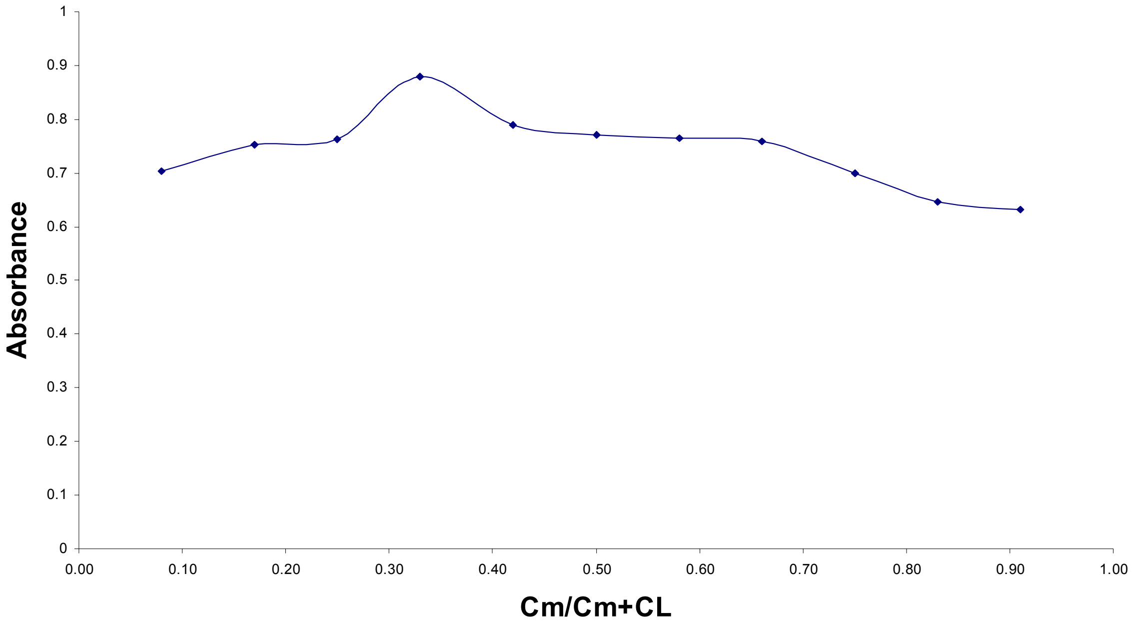
Final volume of chloroform extract : 25 ml

Wavelength : 520 nm.

pH : 9.0

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.703
2	10	0.17	0.753
3	9	0.25	0.762
4	8	0.33	0.880
5	7	0.42	0.790
6	6	0.50	0.770
7	5	0.58	0.764
8	4	0.66	0.758
9	3	0.75	0.699
10	2	0.83	0.674
11	1	0.91	0.632



Composition of Mn(II) SB_I Complex of job's method

Mn(II) SB_I

Metal solution : 0.001M (Varying amount)

Ligand solutin : 0.001M (6.0 ml.)

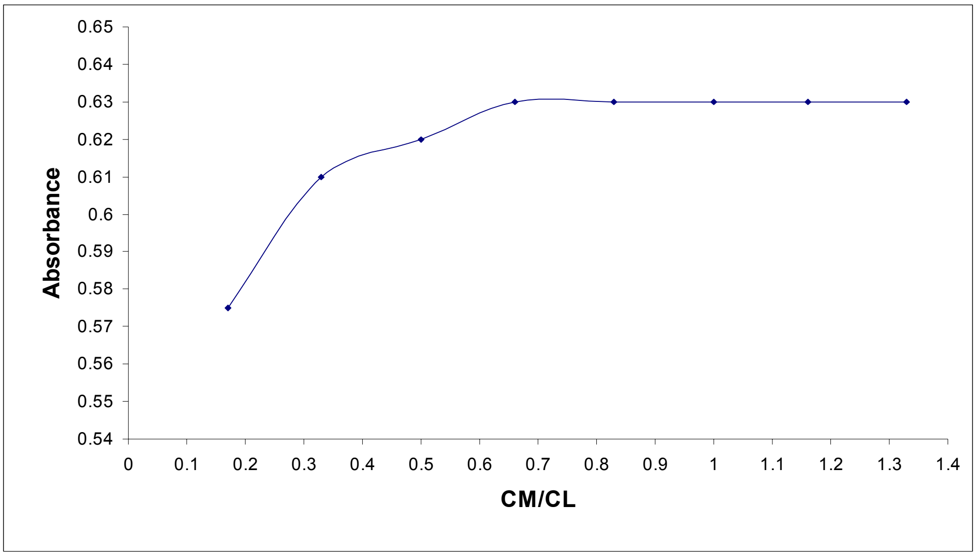
Final volume of chloroform extract : 25 ml

Wavelength : 520 nm.

pH : 9.0

TABLE-V

Metal ion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.575
2	6	0.33	0.61
3	6	0.50	0.62
4	6	0.66	0.63
5	6	0.83	0.63
6	6	1.00	0.63
7	6	1.16	0.63
8	6	1.33	0.63



Composition of Mn(II) SB_I Complex of mole-ratio method

* Evaluation of stability constant :

$$MLn = M + nL$$

$$K_s = \frac{C(1-\alpha)}{C[n.c\alpha]^n}$$

taking n = 2 in this case the equation reduces to,

$$K_s = \frac{1-\alpha}{4\alpha^2 c^2}$$

$$\text{where} \quad \alpha = \frac{E_m - E_s}{E_m}$$

E_m : Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines ;

E_s : absorbance at the stoichiometric molar ratio of the metal to reagent in complex

- Calculation of stability constant :

The stability constant is calculated from the above relation.

From mean K_s value, the standard free energy change ΔG^o for the formation reaction of complex has been calculated at 25^oC using the formula $\Delta G^o = - RT \ln k$

Method	**E_M**	**E_s**	**α**	**K_s**
Job	0.91	0.88	0.03296	8.9×10^6
Mole ratio	0.63	0.62	0.01587	39.0×10^6

Mean $K_s = 23.9 \times 10^6$

$\Delta G^o = -10.06$ k.cal/mole

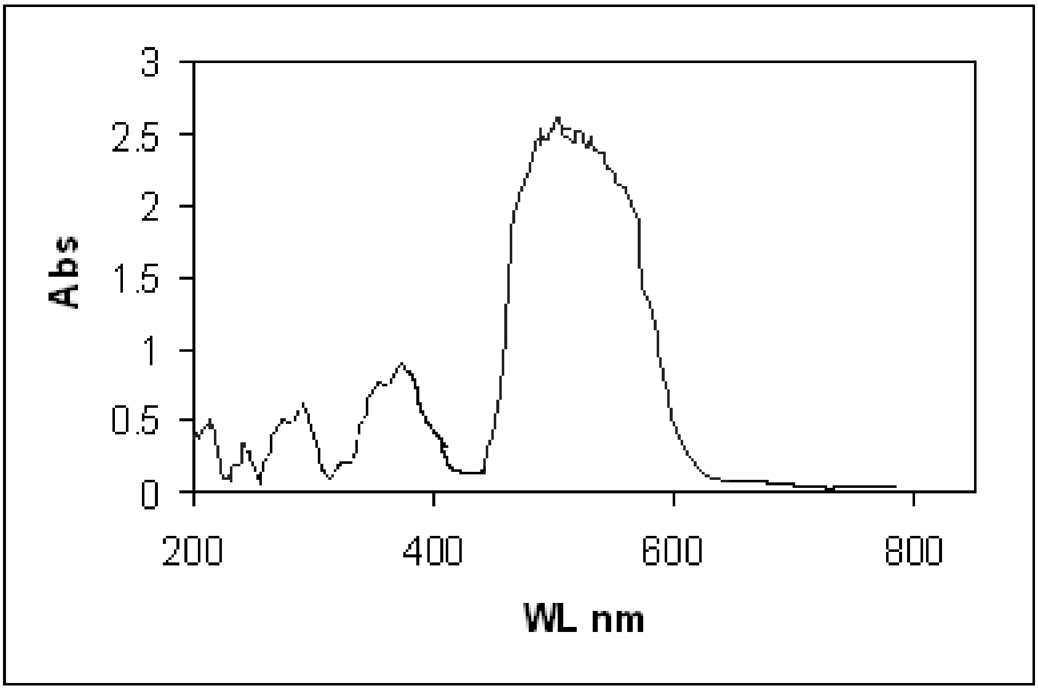
* Effect of diverse ions :

To study the effect of diverse ions on gravimetric determinations of Manganese, 8-10 mg of various cations were added to a known amount of Manganese(II) solution at pH = 9.0 and gravimetric estimations were done. It was observed that Ba(II), Ca(II), Sr(II), Mg(II), Zn(II), Fe(III), Pd(II) do not interfere at this pH, but Cu(II), Ni(II) interfere seriously. Many common anions like chloride, bromide, nitrite, nitrate, sulfate, iodide were not found to interfere.

* Estimation of Manganese as Manganese oxide from its chelate :

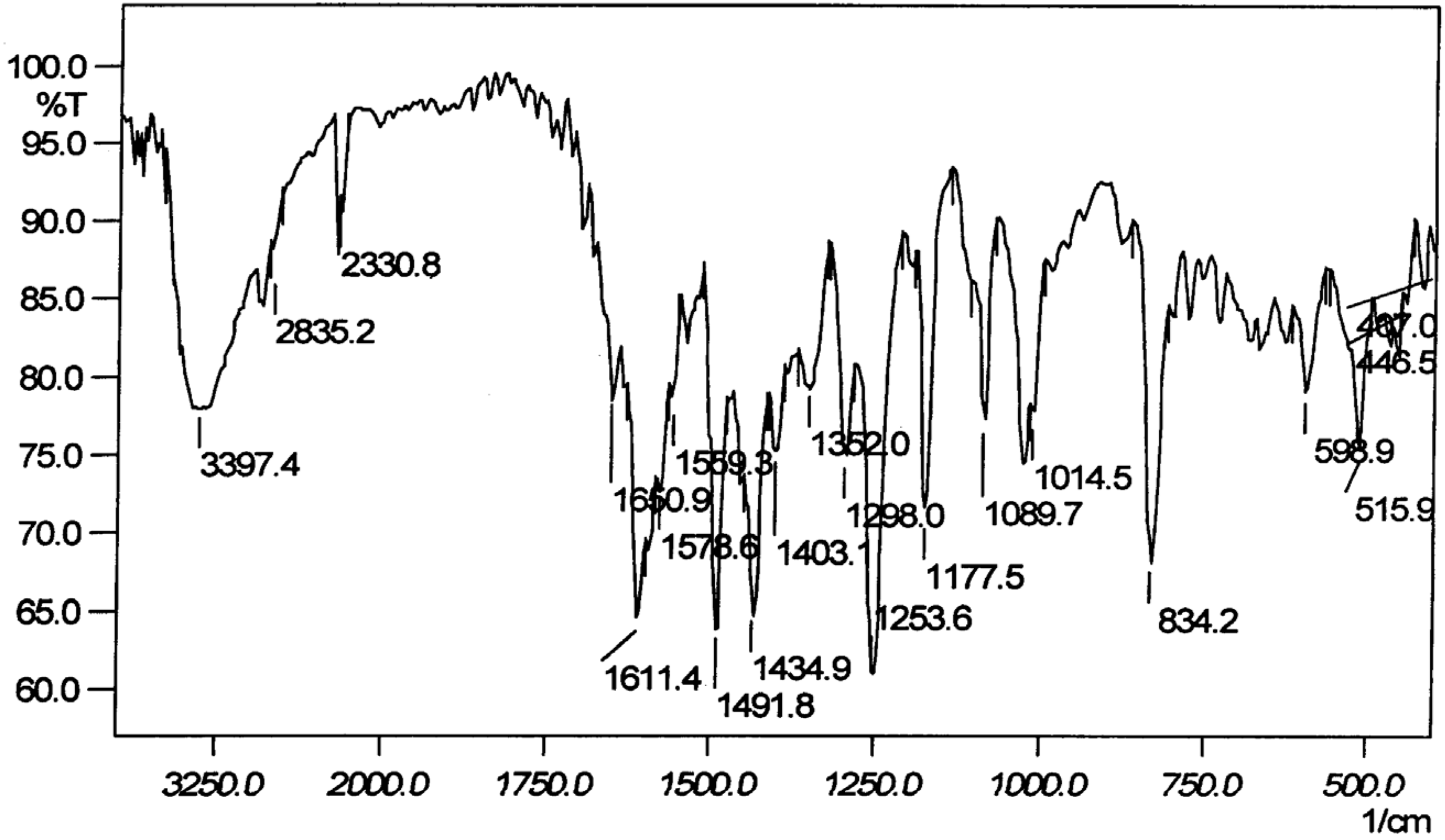
Manganese - SB_I schiff base (0.250 gm) was ignited with the same method as used for copper chelate. It was cooled and weighed as Mn_2O_3. The results are tabulated below.

Chelate	Weight of chelate ignited in mg	Weight of Mn_2O_3 obtained in mg	Percentage of metal	
			Calc.	Found
Mn(II) - SB_I	250	20.48	7.294	6.092



Absorption Spectra of Mn(II)-SB$_I$Complex

IR SPECTRA OF Mn(II)-SB$_I$ COPMLEX



6.4 STUDY OF Fe(III) COMPLEX :

*** Preparation of standard solution of Ferric Chloride ($FeCl_3$) :**

Ferric chloride (anhydrous) 2.0276 g was dissolved in double distilled water, containing a little free acid and was diluted to 250 ml to get 0.05 M stock solution of ferric chloride. This was standardised gravimetrically[1-D]. It was diluted to get 0.005 M solution.

*** Gravimetric determination of Fe(III) :**

1% solution of the schiff base in dioxane was used in all detection and gravimetric determination.

*** Absorption Spectra :**

To take the absorption spectra, 3 ml of 0.02 M solution of reagent and 1 ml of 0.005 M metal ion were taken into 25 ml volumetric flask. The pH of the solution was adjusted within the range where maximum colour develops. The coloured complex was soluble in water and ethanol medium. The exact pH range was decided after studying the pH effect. The solution was then made upto the mark keeping the concentration of alcohol 75% in final solution. The absorbance values were measured against the reagent blank in the wave length range 200 nm to 800 nm. Absorbance spectra is given on page No. 90. It was observed that the absorbance of the coloured solution of the chelate increases continuously towards the shorter wave length. The spectra shows a shoulder at 500 nm and hence all the measurements were donet at 500 nm.

*** Effect of pH :**

The study of the effect of pH, a series of solution were prepared by taking 1 ml (0.005 M) ferric chloride solution and 3 ml (0.02 M) reagent solution. pH of the solution were adjusted to 2.0, 2.5, 3.0 and 3.5 with sodium acetate - hydrochloric acid buffer. The coloured solution were then diluted to 25 ml keeping the final concentration of alcohol 75%. The absorbance spectra of each solution was obtained between 200 to 800 nm. It was observed that colour intensity is maximum at pH 2.5 indicating that maximum complex is formed at this pH. The results are tabulated in Table-I.

At any pH value between 2.0 to 3.5, the nature of the absorbance spectra remains the same. This suggested that under the conditions of the study, only one complex between Fe(III) and the reagent is formed.

TABLE - I

Absolute data of Fe-III - SB_I complex

Metal solution : 1 ml (0.005 M)
Ligand solution : 3 ml (0.02 M)
Final volume : 25 ml
Wave length : 500 nm

pH	Buffer	Observation
2.0	Na-acetate-hydrochloric acid	0.246
2.5	Na-acetate-hydrochloric acid	0.271
3.0	Na-acetate-hydrochloric acid	0.218
3.5	Na-acetate-hydrochloric acid	0.184

*** Limit of identification and dilution limit :**

The limit of identification (X) is the quantity of material in microgram (γ) per ml of the sample solution which is detectable by the particular technique and expressed in gram (γ/ml) (1γ : 1 microgram = 0.001 mg). The following simple relation exists between the dilution limit, the volume of the test solution and identification limit.

$$\text{Dilution Limit} = \frac{\text{1: Volume of the test solution in ml} \quad \times 10^6}{\text{Limit of identification in } \gamma/\text{ml}}$$

The limit of identification (X) was determined with the standard ferric chloride solution employing spot plate technique 1.0 ml of the metal ion solution of different concentration at pH 5.0 was treated with 5 ml of 0.05 M ethanolic solution of the reagent. The limit of identification was found to be 6.876 γ/ml and corresponding dilution limit is 1:1, 45, 458.

*** Gravimetric determination of Fe(III) with SB_I :**

A 1.0 % solution of the reagent in dioxane was used.

Ferric chloride solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 3.0 to 4.0 using sodium acetate - hydrochloric acid buffer. The solution was warmed at 60°C and small excess of reagent SB_I was added (1%, 30 ml). The precipitate obtained were digested on water bath for 60 minutes at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by 50% aqueous ethanol-dioxane to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-III.

*** Calculations :**

10 ml solution gave 0.4179 g of Fe(III) SB_I

Found Ferric chloride = 0.02806 g

10 ml Ferric chloride contains = 0.02800 g of Fe(III)

Error = 0.00006 g

= 0.21 %

TABLE - II

Estimation of Fe(II) using SB_I Legand :

Fe(III) taken = 0.02800 g.

$FeSO_4.6H_2O$ Drying temperature = 80 - 85°C

pH	Fe(III) complex in (g)	Fe(III) found in (g)	Error in (g)	Error %
2.5	0.4102	0.02754	-0.00046	-1.64
2.5	0.4126	0.02770	-0.00030	-1.07
3.0	0.4147	0.02784	-0.00016	-0.57
3.0	0.4157	0.02791	-0.00009	-0.32
3.5	0.4176	0.02804	+0.00004	-0.014
3.5	0.4182	0.02808	+0.00008	+0.028
4.0	0.4202	0.02821	+0.00021	+0.75
4.0	0.4227	0.02838	+0.00038	+1.35
4.5	0.4248	0.02852	+0.00052	+1.85
4.5	0.4266	0.02864	+0.00064	+2.28
5.0	0.4287	0.02878	+0.00078	+2.78
5.0	0.4307	0.02892	+0.00092	+3.28

Spectrophotometric study of Fe(III) complex :

The Fe(III) - SB_I chelate has been found to be soluble in chloroform, dioxane, DMF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

* Effect of the reagent concentration :

A series of solution were taken, keeping the concentration of ferric ion constant (0.005 M, 1 ml) while the amount of (0.05 M) reagent SB_I was varied. The absorbance of the solutions after the colour development as usual, were recorded at 520 nm. The absorbance was found to increase till addition of approximately 8 times excess of the reagent. Thus, about 8 times excess of the reagent found to be sufficient for the maximum complex formation.

* Effect of solvent and time :

Since the complex is easily soluble in dioxane, the volume of dioxane was kept same in all final solutions, prepared for absorbance measurements of Fe(III)-SB_I complex.

From the study of effect of time on absorbance, it was found that colour development is quite rapid and the absorbance of solution remains unchange for 2 hours and after 2 hours the colour fades and absorbance of solutions changes.

Verification of Beer's Law :

To 10 ml of solution (0.01 M) of the reagent solution in each of a set of 25 ml volumetric flask, 2 ml buffer solution (pH 2.5) were added. Varying amount of Fe(III) solution (0.005 M) were added and the contents were made upto the mark with ethanol and distilled water to make dioxane in final solutions were measured at 500 nm against reagent blank prepared in identical condition. Absorbance values were plotted against the Fe(III) content. A straight line passing through the origin, indicating the obeyance of the Beer's law was obtained upto 20.1 ppm of Fe(III). Standard graph thus obtained may be used for the determination of ferric in unknown solution using schiff base SB_I. The results are tabulated in Table III and graph is shown on page No. 85.

Molar absorptivity calculated from Beer's law plot was found to be 11 x 10^2 lit.mol^{-1} cm^{-1} for Fe(II)-SB_I reagent at 500 nm.

* Composition of the Chelate :

The composition of Fe(III) chelate with the reagent SB_I has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

Verification of Beer's Law

Fe(III) SB_I

Varying amount of metal solution : 0.005M

Ligand solutin : 10.0 ml (0.01M)

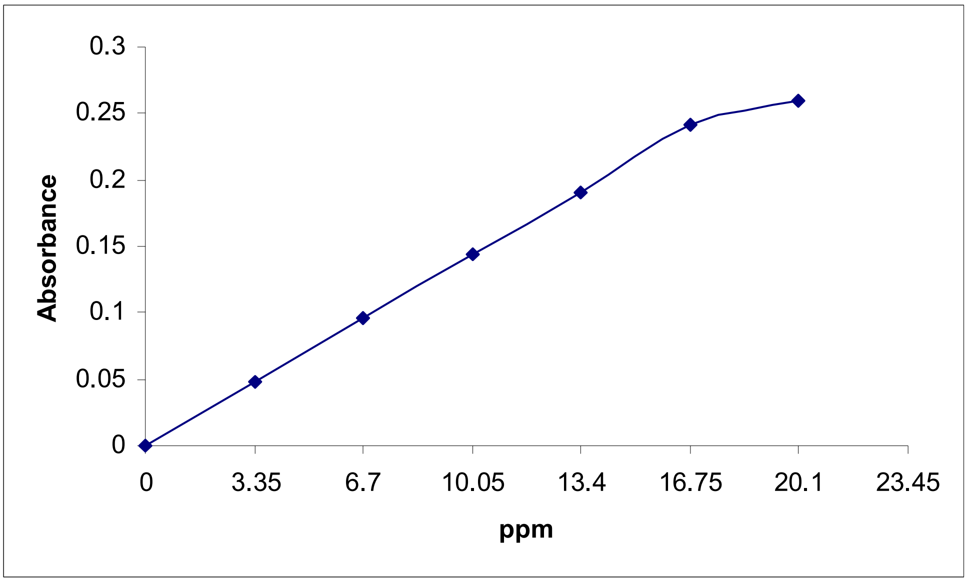
Final volume of chloroform extract : 25 ml

Wavelength : 500 nm.

pH : 2.5

TABLE-III

Fe(III) Solution taken in ml	Fe (III) Taken in ppm	Absorbance
0.3	3.35	0.048
0.6	6.7	0.096
0.9	10.05	0.144
1.2	13.4	0.19
1.5	16.75	0.241
1.8	20.1	0.259



Verificaiton of Beer's Law: Fe(III) SB_I Complex

(i) Job’s method of continuous variation :

A series of solution were prepared by mixing ‘X’ ml of 0.005 M (Fe III) solution. 12-X ml of 0.005 M reagent solution and 2 ml of buffer solution of pH = 2.5. These solutions were then made upto 25 ml keeping the final concentration of dioxane.

Absorbance of these solutions were recorded at 500 nm against metal ion blank. The results are tabulated in Table-IV and graph is shown on page No. 88.

From the graph, it has been found that maximum occurs at 0.33 ratio of metal ion concentration to total concentration of metal and reagent indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In the mole ratio method, equimolar solutions of the Fe (III) ion as well as the reagent (0.005 M) were used.

A series of solutions were prepared, keeping the concentration of reagent constant (6.0 ml, 0.005 M) while varying the metal ion concentration (from 1 to 9.0 ml, of 0.005 M) pH of these solutions were adjusted by the buffer solution at pH 2.5. These solutions were diluted to 25 ml in volumetric flasks. Absorbance of these solutions were then recorded at 500 nm as usual. Absorbance were plotted against the ratio of concentration of reagent to metal ion. The results are tabulated in Table-V and graph is shown on page No. 89.

It is evident from the graph that, the absorbance gradually increases upto molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

*** Evaluation of stability constant :**

The stability constant is calculated from the above relation :

$$K_S = \frac{(1-\alpha)}{4C^2\alpha^2} \qquad \alpha = \frac{E_m - E_s}{E_m}$$

From means K_S value, the standard free energy change ΔG^o for the complex formation reaction has been calculated using the formula, $\Delta G^o = - RT \ln k$

Method	**E_M**	**E_s**	**α**	**K_s**
Job	0.215	0.200	0.06976	1.9×10^6
Mole ratio	0.242	0.227	0.06198	2.4×10^6
	Means K_S = 3.9×10^6			
	ΔG^o = -8.986 k.cal/mole			

*** Effect of diverse ions :**

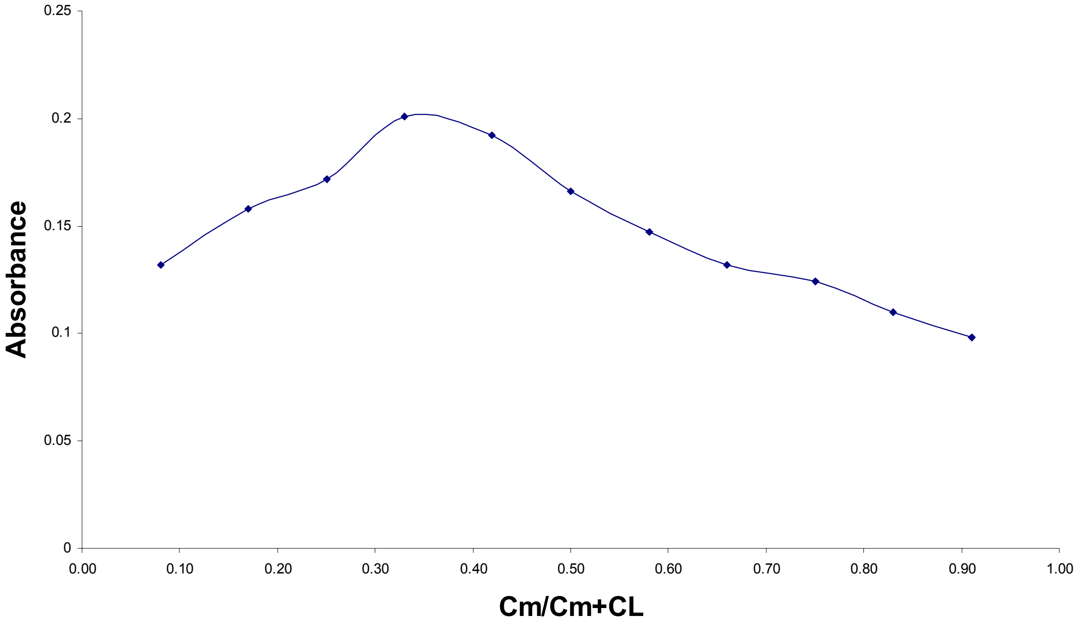
In determinations of 15 ppm Fe(III), at pH 2.5, the cations Zn(II), Mg(II), Sr(II) did not interfere even when present in 10-fold excess. Cu(II) and Pd(II) interfere seriously. Many common anions were not found to interfere.

Fe(III) SB_I

Metal solution	: 0.005M
Ligand solutin	: 0.005M
Final volume of chloroform extract	: 25 ml
Wavelength	: 500 nm.
pH	: 2.5

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.132
2	10	0.17	0.158
3	9	0.25	0.172
4	8	0.33	0.201
5	7	0.42	0.192
6	6	0.50	0.166
7	5	0.58	0.147
8	4	0.66	0.132
9	3	0.75	0.124
10	2	0.83	0.110
11	1	0.91	0.098



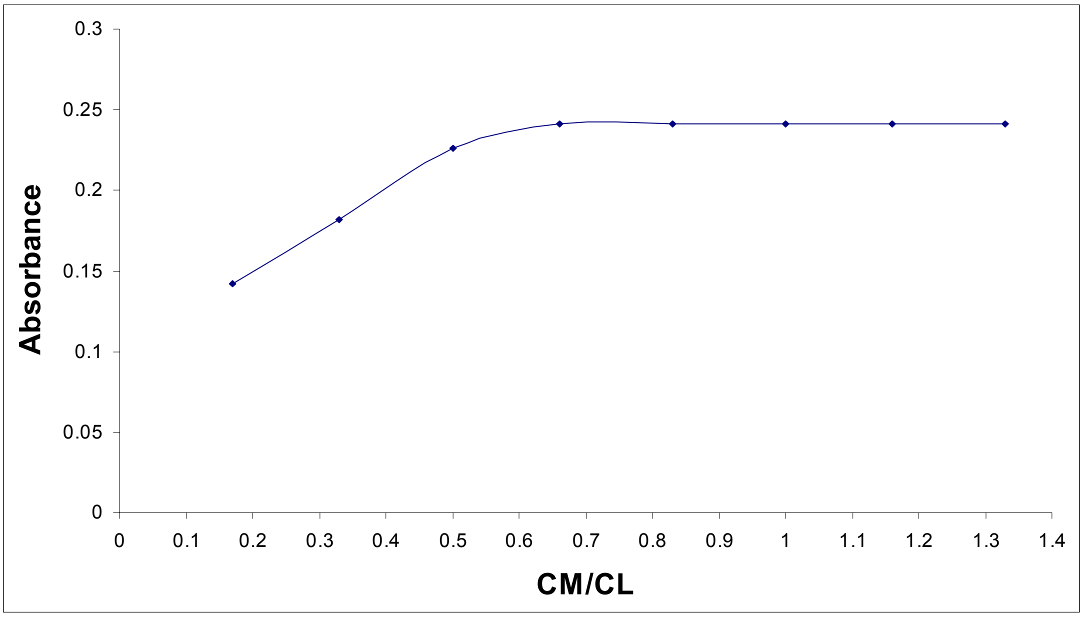
Composition of Fe(III) SB_I Complex of job's method

Fe(III) SB$_I$

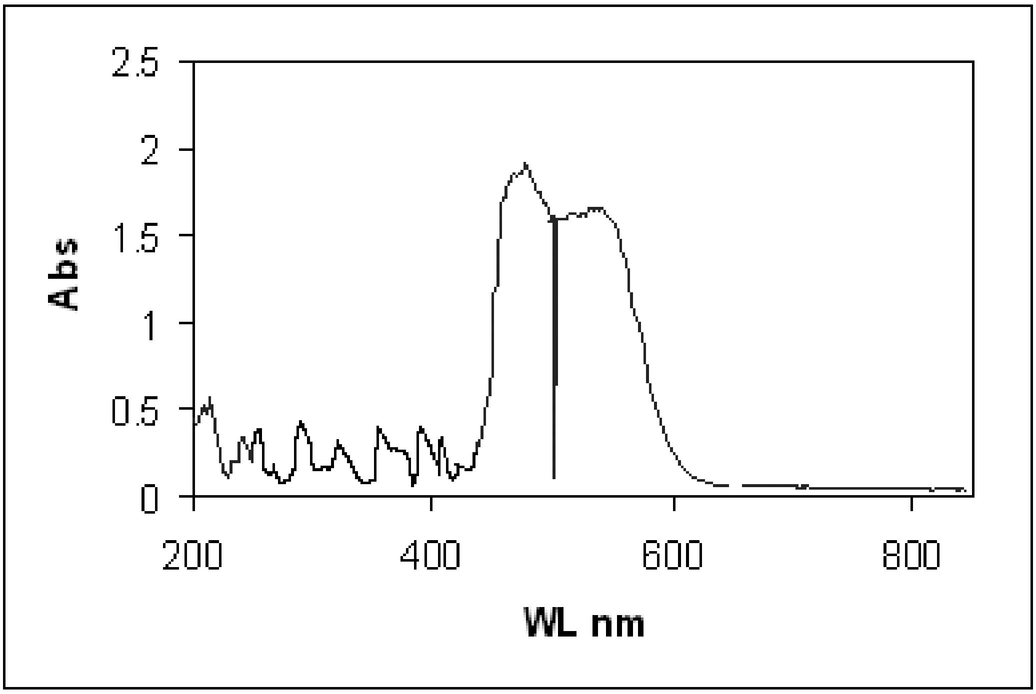
Metal solution	: 0.001M (Varying amount)
Ligand solutin	: 0.005M (6.0 ml.)
Final volume of chloroform extract	: 25 ml
Wavelength	: 500 nm.
pH	: 2.5

TABLE-V

Metalion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.142
2	6	0.33	0.182
3	6	0.50	0.226
4	6	0.66	0.241
5	6	0.83	0.241
6	6	1.00	0.241
7	6	1.16	0.241
8	6	1.33	0.241



Composition of Fe(III) SB$_I$ Complex of mole-ratio method



Absorption Spectra of Fe(III)-SB_I Complex

IR SPECTRA OF Fe(III)-SB_I COPMLEX

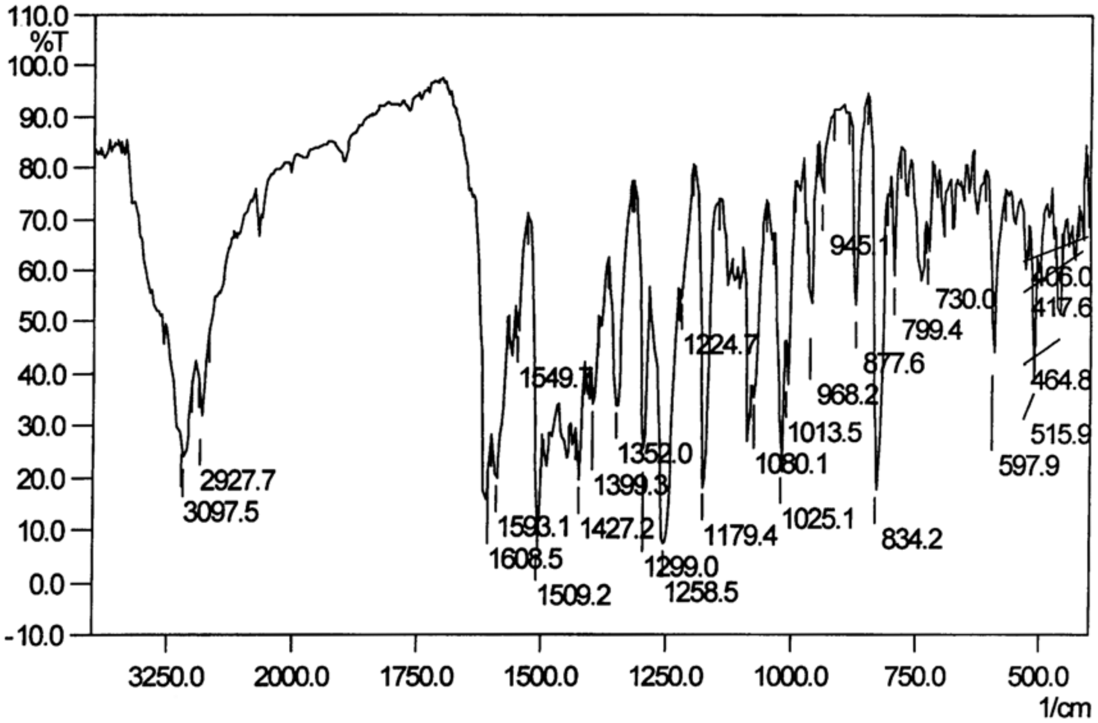


Table of IR spectral data of metal complexes.

Schiff Base	Cu(II)-SB_I	Ni(II)-SB_I	Mn(II)-SB_I	Fe(III)-SB_I	Assign.
1610	1599	1604	1611	1593	-C=N str
959	730	779	700	730	C=S/C-S
-	512	516	515	515	M-N
-	468	461	445	464	M-S

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1. A. A. I. Vogel; "*A Text book of Quantitative Inorgaince Analysis*", *Longamans, Green and Co., London, W.I.*, 4th Ed. (1978), p. 321.

   B. Idem; idib., p. 322

   C. Idem; idib., p. 330

   D. Idem; idib., p. 322

Chapter-VII

Spectrophotometric Determination of Ni(II), Mn(II), Fe(III) and Zn(II) with 5-(3-bromophenyl)-4-{[(1E)-(4-methylphenyl)methylene]amino}-4H-1,2,4-triazole-3-thiol (SB_{II})

7.1 STUDY OF Ni(II) COMPLEX :

Preparation of standard solution of Nickel (II) :

Stock solution of Ni(II) (0.05 M) was prepared by dissolving 3.208 g of $NiSO_4.5H_20$ in distilled water with little acid and diluting to 250 ml. This solution was standardised volumetrically using EDTA[1-B]. Experimental solutions of required concentration were prepared by suitable dilution of the above stock solution.

* Reaction of SB_{II} reagent with Ni(II) :

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination.

* Reaction of the ligand with Ni(II) at different pH values :

5 ml reagent (SB_{II}) was added to 2 ml of standard 0.05 M Ni(II) solution at different pH. The results are Tabulated in Table-I.

* Solubility of chelate :

The light green Ni(II) chelate is insoluble in water and ethanol, while it is soluble in chloroform, dioxan, DMF, THF, ethylacetate. The solution of the chelate was stable and could be kept for long time without any decomposition.

* Limit of identification of dilution limit :

The limit of identification (X) was determined in a similar way as done for Cu(II)-SB_{II} using the standard nickel sulphate solution at pH 8.5. The limit of identification was found to be 7.4063 γ/ml and corresponding dilution limits is 1:1, 3.5, 0.20

TABLE - I

pH	Buffer	Observation
7.0	NaOH + KH_2PO_4	Small amount of light green precipitate
7.5	NH_3 + NH_4Cl	Light green precipitate
8.0	NH_3 + NH_4Cl	Light green precipitate
8.5	NH_3 + NH_4Cl	Light green precipitate
9.0	NH_3 + NH_4Cl	Light green precipitate
9.5	NH_3 + NH_4Cl	Light green precipitate
10.0	NH_3 + NH_4Cl	Light green precipitate

* Gravimetric determination of Ni(II) with SB_{II} reagent :

A 1.0 % solution of the reagent in dioxane was used.

Nickel sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 7.5 to 8.0 by using NH_3-NH_4Cl buffer. The solution was warmed at 60°C and small excess of reagent SB_{II} was added (1%, 25 ml). A light green precipitate obtained were digested on water bath for 60 minutes at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by dioxane to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

* **Calculations :**

10 ml solution gave 0.4053 g of Ni(II)-SB_{II} reagent complex

Found nickel = 0.02961 g

10 ml nickel sulphate contains = 0.02950 g of Ni(II)

Error = 0.00011 g

= + 0.39 %

TABLE - II

Estimation of Ni(II) using SB_{II} Legand :

Ni(II) taken = 0.02950 g.

Drying temperature = 110 - 115°C

$NiSO_4.6H_2O$

pH	Ni(II) complex in (g)	Ni(II) found in (g)	Error in (g)	Error %
7.5	0.4001	0.02923	-0.00027	-0.91
7.5	0.4015	0.02933	-0.00017	-0.59
8.0	0.4027	0.02942	-0.00008	-0.23
8.0	0.4039	0.02951	+0.00001	-0.033
8.5	0.4046	0.02956	+0.00006	+0.20
8.5	0.4053	0.02961	+0.00011	+0.37
9.0	0.4062	0.02968	+0.00018	+0.61
9.0	0.4082	0.02982	+0.00032	+1.08
9.5	0.4090	0.02988	+0.00038	+1.28
9.5	0.4095	0.02992	+0.00042	+1.42
10.0	0.4108	0.03001	+0.00051	+1.72
10.0	0.4119	0.03009	+0.00059	+2.00

* Spectrophotometric study of Ni(II) complex :

The Ni(II) - SB_{II} chelate has been found to be soluble in chloroform, dioxane, DMF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

* Absorption Spectra :

To take the absorption spectra, 5 mg of chelate was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the region 350-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 450 nm and hence all the measurements were carried out at 450 nm.

* Verification of Beer's Law :

To 6 ml of solution (0.01 M) of the reagent SB_{II}, varying amount of Ni(II) solution (0.005 M) were added. The pH was adjusted to 8.5 using NH_3-NH_4Cl buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and the final volume of chloroform extract was diluted to 25 ml in volumetric flask. The absorption of these solutions were measured at 450 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 30.48 ppm of Ni(II). The standard graph thus prepared may be used for the determination of nickel in unknown solution using SB_{II} reagent. The results are tabulated in Table-III. The graph is shown on page 98.

Molar absorptivity calculated from Beer's law plot was found to be 2.1×10^2 lit.mol^{-1} cm^{-1} for Ni(II)-SB_{II} complex as 450 nm.

Verification of Beer's Law

Ni(II) SB_{II}

Varying amount of metal solution : 0.005M

Ligand solutin : 6.0 ml (0.01M)

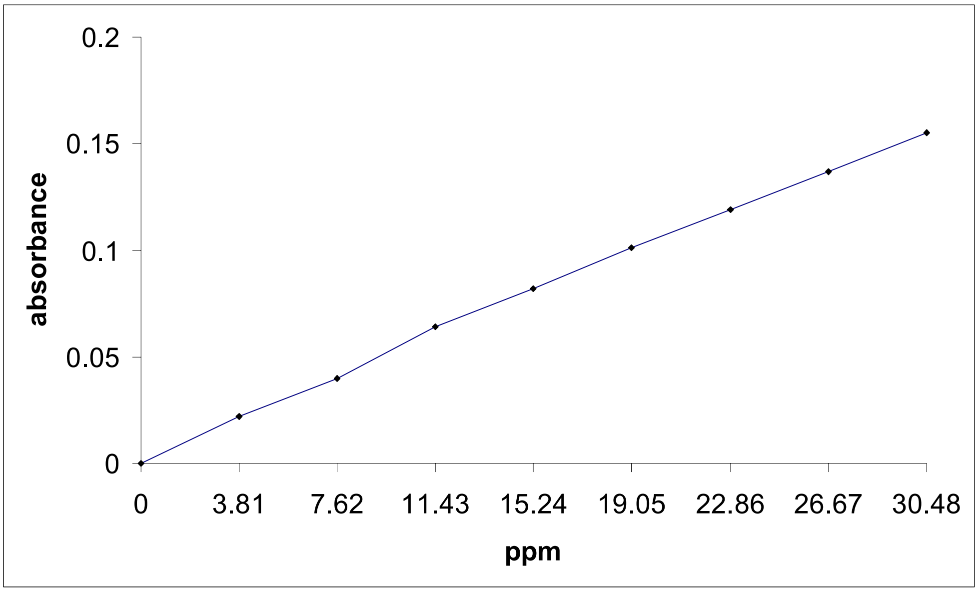
Final volume of chloroform extract : 25 ml

Wavelength : 450 nm.

pH : 8.5

TABLE-III

Ni(II) Solution taken in ml	Ni(II) Taken in ppm	Absorbance
0.3	3.81	0.022
0.6	7.62	0.04
0.9	11.42	0.064
1.2	15.24	0.082
1.5	19.05	0.0101
1.8	22.86	0.0119
2.1	26.67	0.137
2.4	30.48	0.155



Verificaiton of Beer's Law: Ni(II) SB_{II} Complex

* Composition of Chelate :

The composition of Ni(II) chelate with the reagent SB_{II} has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

(i) Composition of Ni(II)-SB_{II} complex by Job's method of continuous variation :

A 0.005 M solution of Ni(II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.005 M) was prepared in dioxane. The solution of metal salt and the reagent were mixed in varying proportions as under :

Metal ion solution : 1, 2, 3, - - - - 9, 10, 11 ml
Reagent solution : 11, 10, 9, - - - - 3, 2, 1 ml

pH of the solution was adjusted to 8.5. The precipitated complex was extracted with three 5 ml portions of chloroform. The volume of chloroform extract was adjusted to 25 ml in volumetric flask. The absorbance of chloroform extracts were tabulated in Table-IV.

From the graph (page No. 100), it has been found that maximum occurs at 0.33 ratio of metal ion concentration to the total metal and ligand concentration indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In this method, equimolar solutions of the nickel (II) as well as the reagent (0.005 M) were used. A series of solutions were prepared by keeping the reagent solution (6 ml) constant while varying the amount (from 1 to 8.0 ml) of 0.005 M metal solution.

pH of the solutions were adjusted to 8.5. The resulting precipitate were extracted in chloroform. The volume of extract was made to 25 ml in volumetric flask. Absorbance were recorded at 450 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V and corresponding graph on page No. 101.

It is evident from the graph that, absorbance gradually increases upto the molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

* Evaluation of stability constant :

$$\begin{array}{ll} MLn \;===\; & M + nL \\ C(1-\alpha) & C[n.c\alpha]^n \end{array}$$

$$K_s = \frac{C(1-\alpha)}{C[n.c\alpha]^n}$$

taking n = 2 in this case the equation reduces to,

$$K_s = \frac{1-\alpha}{4\,\alpha^2 c^2}$$

$$\text{where} \qquad \alpha = \frac{E_m - E_s}{E_m}$$

E_m : Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines ;

E_s : absorbance at the stoichiometric molar ratio of the metal to reagent in complex

- Calculation of stability constant :

The stability constant is calculated from the above relation.

From mean K_s value, the standard free energy change ΔG^o for the formation reaction of complex has been calculated at 25^{o}C using the formula $\Delta G^o = -RTlnk$

Method	**E_M**	**E_s**	**α**	**K_s**
Job	0.90	0.87	0.03338	8.7×10^6
Mole ratio	0.61	0.59	0.03278	9.0×10^6

Mean K_s = 8.85×10^6

ΔG^o = -9.472 k.cal/mole

Ni(II) SB$_I$

Metal solution : 0.005M

Ligand solutin : 0.005M

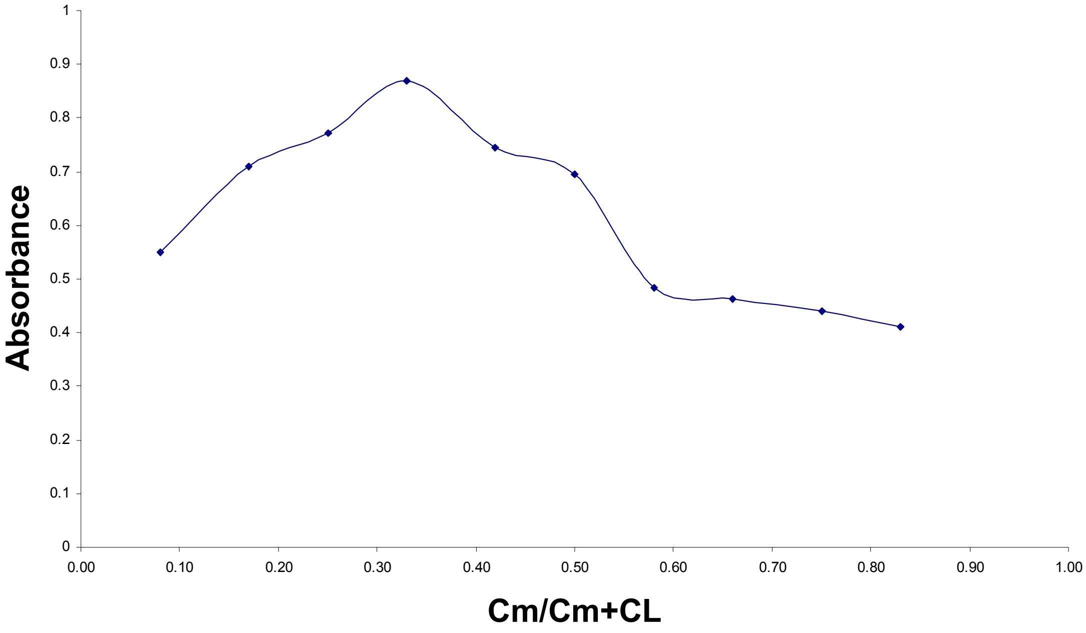
Final volume of chloroform extract : 25 ml

Wavelength : 450 nm.

pH : 8.5

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.550
2	10	0.17	0.710
3	9	0.25	0.772
4	8	0.33	0.870
5	7	0.42	0.745
6	6	0.50	0.695
7	5	0.58	0.484
8	4	0.66	0.463
9	3	0.75	0.440
10	2	0.83	0.410
11	1	0.91	0.405



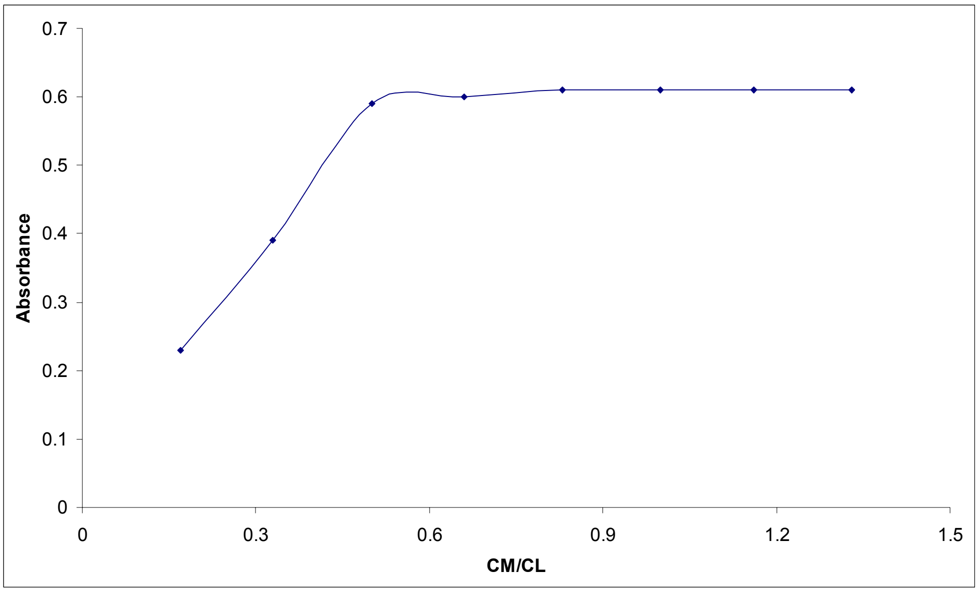
Composition of Ni(II) SB$_{II}$ Complex of Job's method

Ni(II) SB_I

Metal solution	: 0.005M (Varying amount)
Ligand solutin	: 0.005M (6.0 ml)
Final volume of chloroform extract	: 25 ml
Wavelength	: 450 nm.
pH	: 8.5

TABLE-V

Metal ion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.23
2	6	0.33	0.39
3	6	0.50	0.59
4	6	0.66	0.600
5	6	0.83	0.610
6	6	1.00	0.610
7	6	1.16	0.610
8	6	1.33	0.610



Composition of Ni(II) SB_{II} Complex of mole-ratio method

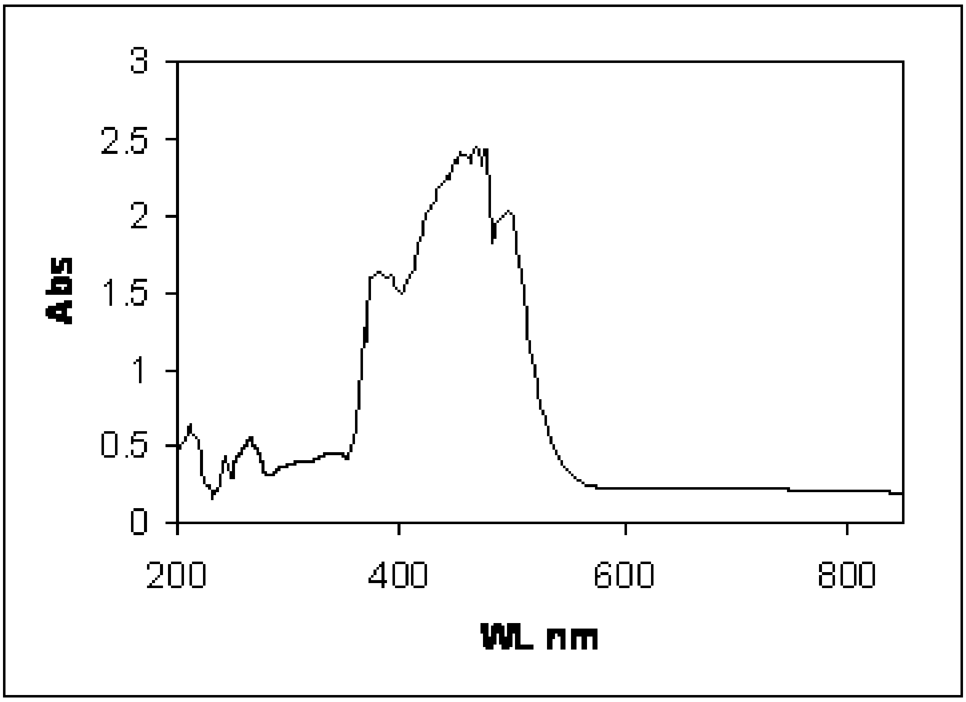
* Effect of diverse ions :

To study the effect of foreign ions on gravimetric determinations of Ni(II), 8-10 mg of various cations were added to a known amount of Ni(II) solution at pH 8.5 and gravimetric estimations were done. It was observed that Sr(II), Mg(II), Pd(II), Fe(III), Zn(II), Ba(II) do not interfere at this pH, but Cu(II), Mn(II) interfere seriously. Many common anions were not found to interfere.

* Estimation of Ni(II) as nickel oxide from its chelate :

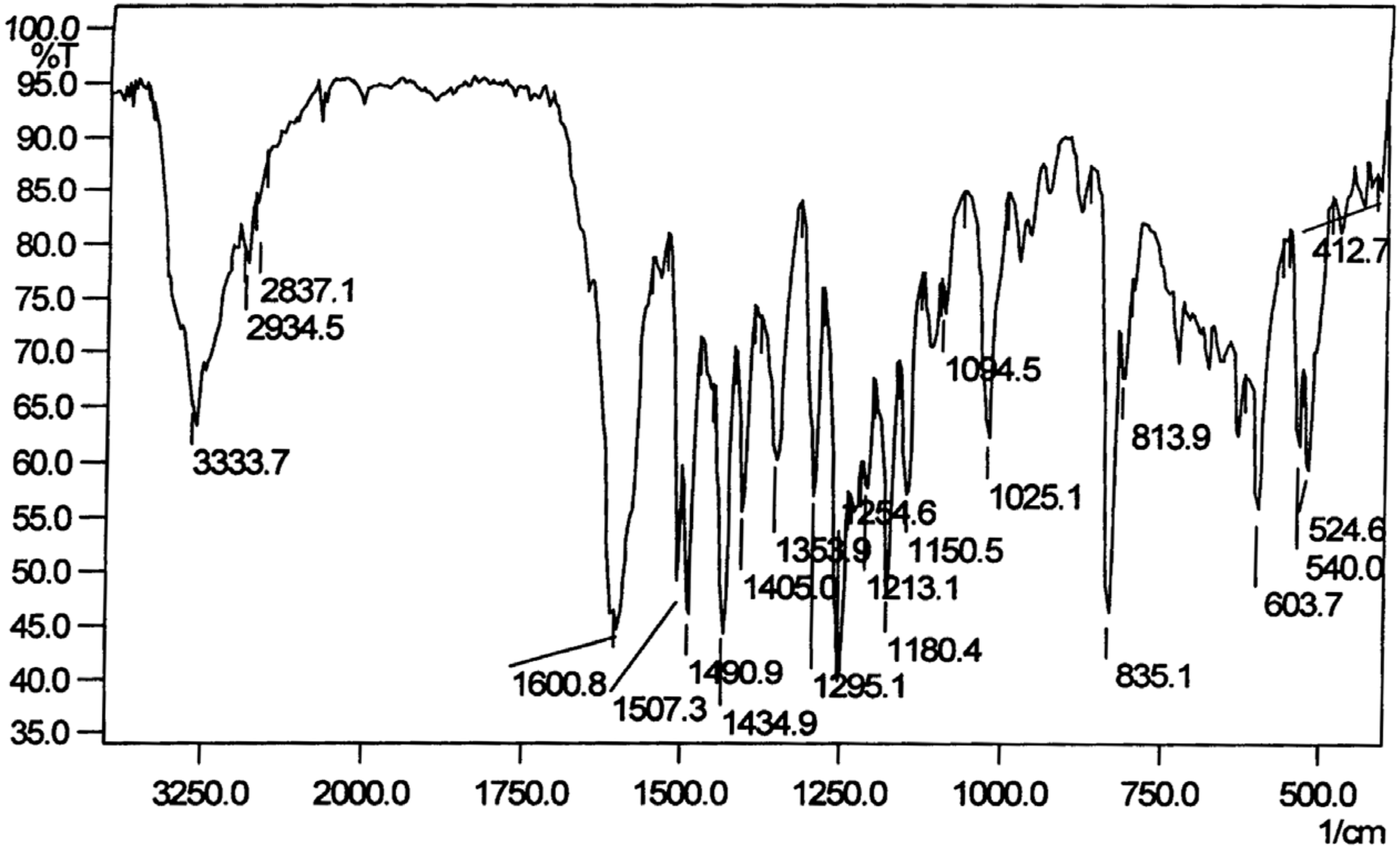
Ni(II) - SB_{II} reagent (0.250 g) was ignited with the same method as used for copper chelate. It was cooled and weighed as nickel oxide. The results are tabulated below.

Chelate	Weight of chelate ignited in mg	Weight of NiO obtained in mg	Percentage of metal	
			Calc.	Found
Ni(I)I - SB_{II}	250.0	23.10	8.139	7.919



Absorption Spectra of Ni(II)-SB_{II} Complex

IR SPECTRA OF Ni(II)-SB$_{II}$ COPMLEX



7.2 STUDY OF Mn(II) COMPLEX :

Preparation of standard solution of Manganese (II) :

Manganese sulphate 2.113 g was dissolved in little acid and double distilled water and diluted to 250 ml to get 0.05 M solution of Manganese (II). This solution was standardised volumetrically using EDTA[1-C]. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

* Reaction of SB_{II} reagent with Mn(II) :

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination.

* Reaction of the ligand with Mn(II) at different pH values :

5 ml of SB_{II} reagent solution was added to 2 ml of standard 0.05 M Manganese (II) solution at different pH. The results are Tabulated in Table-I.

* Solubility of the chelate :

Dark green Mn(II) chelate is insoluble in water and ethanol, while it is soluble in dioxane, chloroform, DMF, THF, acetone giving dark green solution. The solution of the chelate was stable and could be kept for long time without any decomposition.

* Limit of identification and dilution limit :

The limit of identification (X) was determined in a similar way as done for Ni(II)-SB_{II} using standard solution of manganese sulphate solution at pH 9.0. The limit of identification was found to be 6.875 γ/ml and corresponding dilution limits is 1:1, 4.5, 4.59

TABLE - I

pH	Buffer	Observation
7.0	NaOH + KH_2PO_4	Green opalescene
7.5	NaOH + KH_2PO_4	Green colouration
8.0	NH_3 + NH_4Cl	Dark green precipitate
8.5	NH_3 + NH_4Cl	Dark green precipitate
9.0	NH_3 + NH_4Cl	Dark green precipitate
9.5	NH_3 + NH_4Cl	Dark green precipitate
10.0	NH_3 + NH_4Cl	Dark green precipitate
10.5	NH_3 + NH_4Cl	Green opalescene

* Gravimetric determination of Mn(II) with SB_{II} reagent :

A 1.0 % solution of the reagent in dioxane was used.

Manganese sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water. A small excess of reagent SB_{II} was added to (1%, 14 ml). Then the pH was adjusted to pH 8.5 to 9.0 using NH_3 and NH_4Cl buffer. The dark green precipitate of manganese chelate formed were kept at room temperature for 24 hours. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by the dioxane to remove excess of reagent. The chelate was dried to constant weight at 80-85^{O}C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

*** Calculations :**

10 ml solution gave 0.4008 g of manganese-SB_{II} complex

Found manganese = 0.02756 g

10 ml manganese sulphate contains = 0.02750 g

Error = 0.00006 g

= + 0.21 %

TABLE - II

Estimation of Mn(II) using SB_{II} Legand :

Mn(II) taken = 0.02750 g.

$MnSO_4.H_2O$ Drying temperature = 80 - 85^{O}C

pH	**Mn(II) complex in (g)**	**Mn(II) found in (g)**	**Error**	
			in (g)	**%**
7.5	0.3913	0.02691	-0.00059	-2.14
7.5	0.3932	0.02704	-0.00046	-1.67
8.0	0.3950	0.02716	-0.00034	-1.23
8.0	0.3973	0.02732	-0.00018	-0.65
8.5	0.3996	0.02748	+0.00002	-0.07
8.5	0.4008	0.02756	+0.00006	+0.21
9.0	0.4025	0.02768	+0.00018	+0.65
9.0	0.4046	0.02782	+0.00032	+1.16
9.5	0.4069	0.02798	+0.00048	+1.74
9.5	0.4092	0.02814	+0.00064	+2.32
10.0	0.4117	0.02831	+0.00081	+2.94
10.0	0.4134	0.02843	+0.00093	+3.38

*** Spectrophotometric study of Mn(II) complex :**

The Manganese chelate of SB_{II} reagent has been found to be soluble in chloroform, dioxane, DMF, THF. This enabled to verify the Beer’s law and its application for spectrophotometric determination.

*** Absorption Spectra :**

To take the absorption spectra, 5 mg of chelate was dissolved in 100 ml of chloroform and the spectra was scanned in the region 350-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 520 nm and hence all the measurements were carried out at 520 nm. Absorption spectra of manganese SB_{II} reagent is shown on page No. 115.

*** Verification of Beer's Law :**

To 8 ml of solution (0.005 M) of the schiff base SB_{II}, varying amount of metal solution (0.001 M) were added and the pH was adjusted to 9.0 using NH_3-NH_4Cl buffer. The insoluble complex precipitated was extracted in chloroform using three 5.0 ml portions of chloroform and the final volume of chloroform extract was adjusted to 25 ml in volumetric flask. The absorbance of these solutions were measured at 520 nm against chloroform as the blank.

Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 13.2 ppm of Mn(II). The standard graph thus obtained may be used for the determination of manganese in unknown solution using SB_{II} chalcone. The results are tabulated in Table-III. The graph is shown on page 110.

Molar absorptivity calculated from Beer's law plot was found to be 14×10^2 lit.mol^{-1} cm^{-1} for Mn(II)-SB_{II} complex at 520 nm.

*** Composition of Chelate :**

The composition of Mn(II) chelate with the reagent SB_{II} chalcone has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

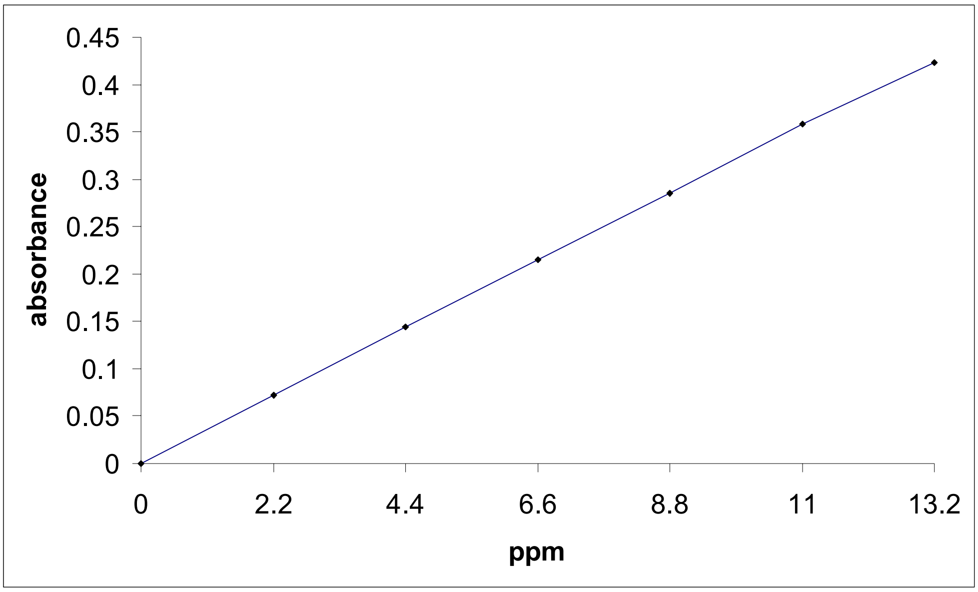
Verification of Beer's Law

Mn(II) SB_{II}

Varying amount of metal solution	: 0.001M
Ligand solutin	: 8.0 ml (0.005M)
Final volume of chloroform extract	: 25 ml
Wavelength	: 520 nm.
pH	: 9.0

TABLE-III

Mn(II) Solution taken in ml	Mn (II) Taken in ppm	Absorbance
0.3	2.2	0.072
0.6	4.4	0.144
0.9	6.6	0.215
1.2	8.8	0.285
1.5	11.0	0.358
1.8	13.2	0.423



Verificaiton of Beer's Law: Mn(II) SB_{II} Complex

(i) Composition of Mn(II)-SB$_{II}$ complex by Job's method of continuous variation :

A 0.001 M solution of Mn(II) was prepared by suitable dilution of the standard solution. The solution of the reagent (0.001 M) was prepared in absolute ethanol. The solution of the metal salt and the reagent were mixed in varying proportions as under :

Metal ion solution : 0, 1, 2, 3, - - - - 11, 12 ml
Reagent solution : 12, 11, 10, - - - - 2, 1, 0 ml

pH of the various solutions were adjusted to 9.0. The precipitated complex was extracted with three 5.0 ml portions of chloroform and final volume of chloroform extract was made to 25 ml in volumetric flasks. The absorbance of chloroform extracts were measured at 520 nm. The results are tabulated in Table-IV.

From the graph (page No.112), it has been found that maximum occurs at 0.33 ratio of metal ion concentration to total concentration of metal and ligand indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In this method, equimolar solutions of the Mn(II) as well as the reagent (0.001 M) were used. A series of solutions were prepared keeping the reagent solution (5 ml) constant while varying the amount (from 1.0 to 9.0 ml) of 0.001 M metal solution. pH of the solutions were adjusted to 9.0. The resulting precipitate were extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 520 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V. The graph is shown on page No. 113.

It is evident from the graph that, absorbance gradually increases upto the molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

* Evaluation of stability constant :

$$MLn === M + nL$$

$$K_S = \frac{C(1-\alpha)}{C[n.c\alpha]^n}$$

taking n = 1 in this case the equation reduces to,

$$K_S = \frac{1-\alpha}{4\alpha^2 c^2}$$

$$\text{where} \qquad \alpha = \frac{E_m - E_s}{E_m}$$

E_m : Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines ;

E_s : absorbance at the stoichiometric molar ratio of the metal to reagent in complex

- Calculation of stability constant :

The stability constant is calculated from the above relation.

From mean K_S value, the standard free energy change ΔG^o for the formation reaction of complex has been calculated at 25°C using the formula $\Delta G^o = - RT \ln k$

Method	**E_M**	**E_s**	**α**	**K_s**
Job	0.97	0.94	0.03092	10.0×10^6
Mole ratio	1.71	1.65	0.03508	7.8×10^6
Mean $K_S = 8.95 \times 10^6$ ΔG^o = - 9.478 k.cal/mole				

Mn(II) SB$_{II}$

Metal solution : 0.001M

Ligand solutin : 0.001M

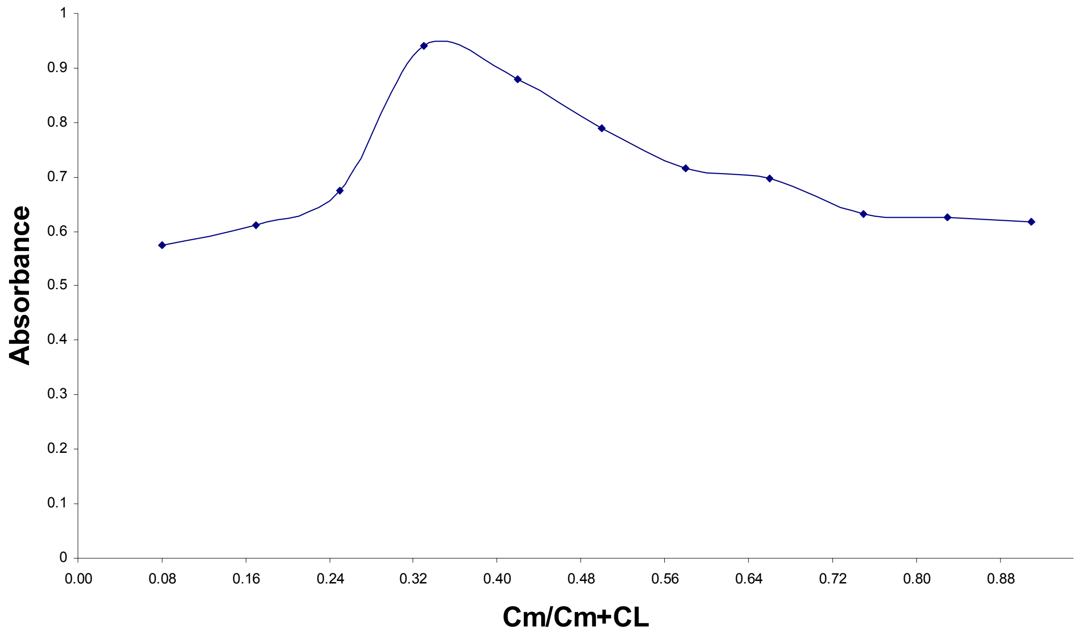
Final volume of chloroform extract : 25 ml

Wavelength : 520 nm.

pH : 9.0

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.575
2	10	0.17	0.612
3	9	0.25	0.674
4	8	0.33	0.940
5	7	0.42	0.88
6	6	0.50	0.79
7	5	0.58	0.715
8	4	0.66	0.698
9	3	0.75	0.632
10	2	0.83	0.625
11	1	0.91	0.617



Composition of Mn(II) SB$_{II}$ Complex of Job’s method

Mn(II) SB_{II}

Metal solution : 0.001M (Varying amount)

Ligand solutin : 0.001M (6.0 ml.)

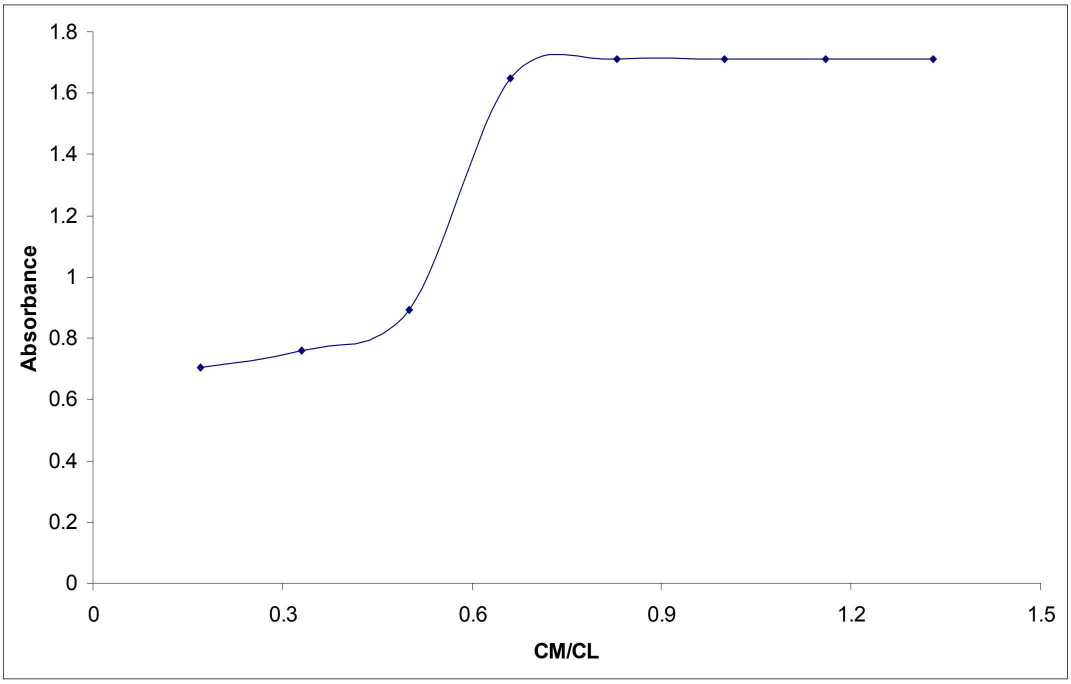
Final volume of chloroform extract : 25 ml

Wavelength : 520 nm.

pH : 9.0

TABLE-V

Metal ion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.705
2	6	0.33	0.761
3	6	0.50	0.892
4	6	0.66	1.65
5	6	0.83	1.71
6	6	1.00	1.71
7	6	1.16	1.71
8	6	1.33	1.71



Composition of Mn(II) SB_{II} Complex of mole-ratio method

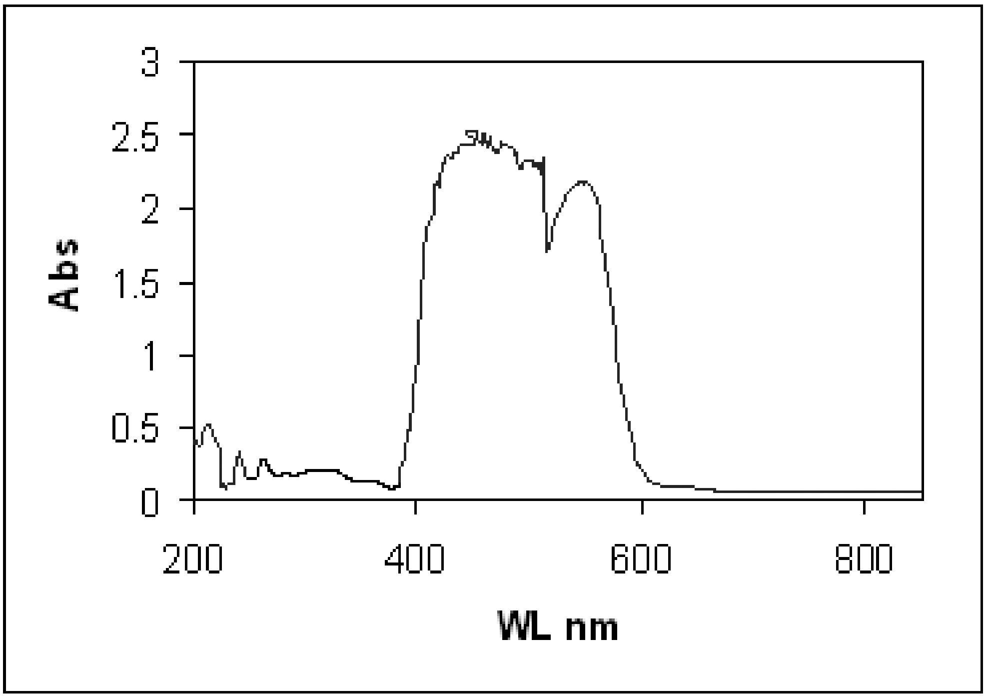
*** Effect of diverse ions :**

To study the effect of diverse ions on gravimetric determinations of Manganese, 8-10 mg of various cations were added to a known amount of Manganese(II) solution at pH = 9.0 and gravimetric estimations were done. It was observed that Ba(II), Ca(II), Sr(II), Mg(II), Zn(II), Fe(III), Pd(II) do not interfere at this pH, but Cu(II), Ni(II) interfere seriously. Many common anions like chloride, bromide, nitrite, nitrate, sulfate, iodide were not found to interfere.

*** Estimation of Manganese as nickel oxide from its chelate :**

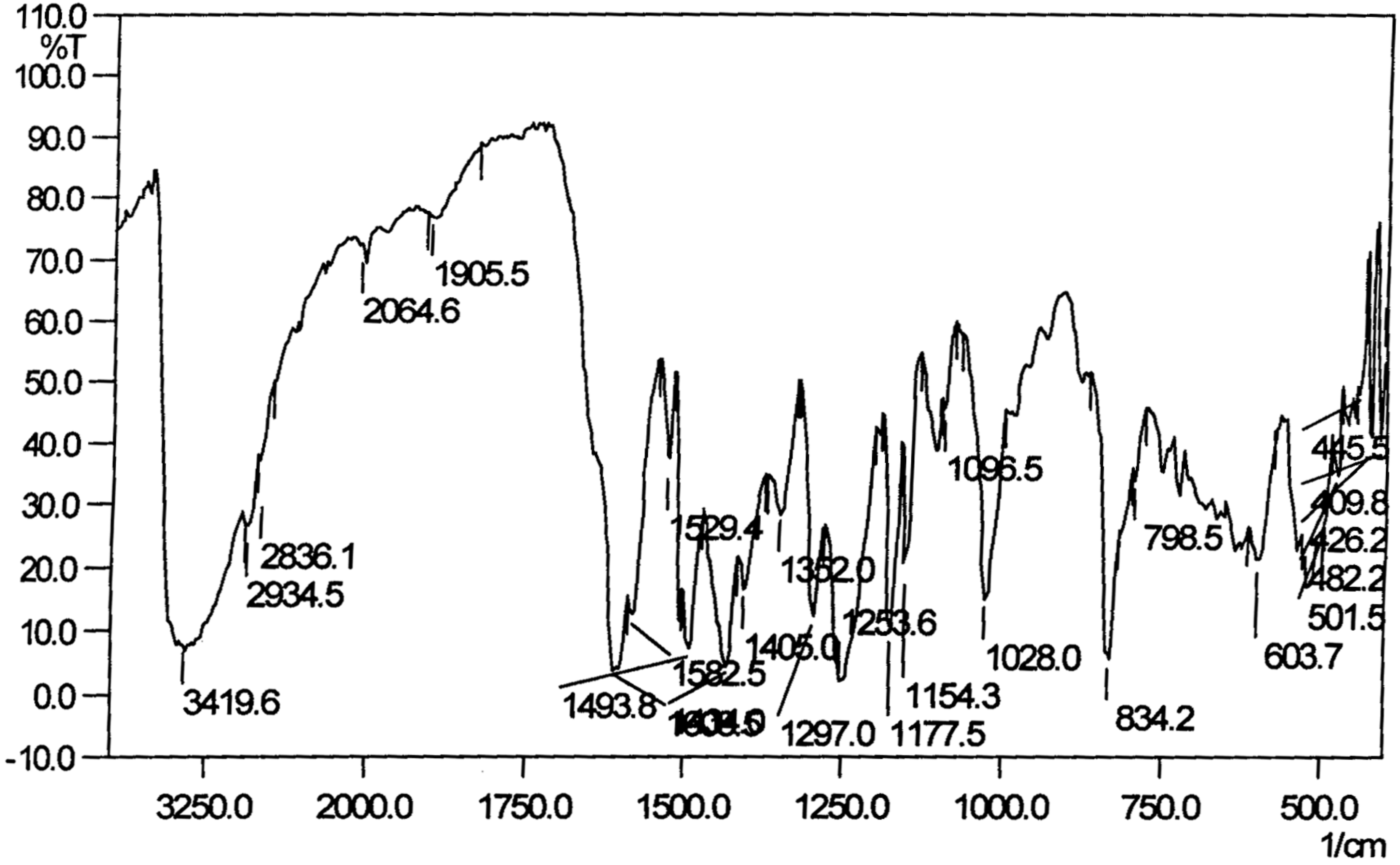
Manganese - SB_{II} reagent (0.250 gm) was ignited with the same method as used for copper chelate. It was cooled and weighed as Mn_2O_3. The results are tabulated below.

Chelate	Weight of chelate ignited in mg	Weight of Mn_2O_3 obtained in mg	Percentage of metal	
			Calc.	Found
Mn(II) - SB_{II}	250	21.06	7.68	6.92



Absorption Spectra of Mn(II)-SB_{II} Complex

IR SPECTRA OF Mn(II)-SB$_{II}$ COPMLEX



7.3 STUDY OF Fe(III) COMPLEX :

* Preparation of standard solution of Ferric Chloride ($FeCl_3$) :

Ferric chloride (anhydrous) 2.0276 g was dissolved in double distilled water, containing a little free acid and was diluted to 250 ml to get 0.05 M stock solution of ferric chloride. This was standardised gravimetrically[1-D]. It was diluted to get 0.005 M solution.

* Gravimetric determination of Fe(III) :

Gravimetric determination of Fe(III) using SB_{II} could not be done, as Fe(III) forms water soluble purple coloured complex with the reagent at pH = 2.5.

* Absorption Spectra :

To take the absorption spectra, 3.0 ml of 0.02 M solution of reagent and 1 ml of 0.005 M metal ion were taken into 25 ml volumetric flask. The pH of the solution was adjusted within the range where maximum colour develops. The coloured complex was soluble in water and ethanol medium. The exact pH range was decided after studying the pH effect. The solution was then made upto the mark keeping the concentration of alcohol 75% in final solution. The absorbance values were measured against the reagent blank in the wave length range 200 nm to 800 nm. Absorbance spectra is given on page No. 131. It was observed that the absorbance of the coloured solution of the chelate increases continuously towards the shorter wave length. The spectra shows a shoulder at 500 nm and hence all the measurements were noted at 500 nm.

* Effect of pH :

To study of the effect of pH, a series of solution were prepared by taking 1 ml (0.005 M) ferric chloride solution and 3 ml (0.02 M) reagent solution. pH of the solution were adjusted to 2.0, 2.5, 3.0 and 3.5 with sodium acetate - hydrochloric acid buffer. The coloured solution were then diluted to 25 ml keeping the final concentration of dioxane. The absorbance spectra of each solution was obtained between 200 nm to 800 nm. It was observed that colour intensity is maximum at pH 2.5 indicating that maximum complex is formed at this pH. The results are tabulated in Table-I.

At any pH value between 2.0 to 3.5, the nature of the absorbance spectra remains the same. This suggested that under the conditions of the study, only one complex between Fe(III) and the reagent is formed.

TABLE - I

Absorbance data of Fe-III - SB_{II} complex

Metal solution	:	1 ml (0.005 M)
Ligand solution	:	3 ml (0.02 M)
Final volume	:	25 ml
Wave length	:	500 nm

pH	Buffer	Observation
2.0	Na-acetate-hydrochloric acid	0.236
2.5	Na-acetate-hydrochloric acid	0.259
3.0	Na-acetate-hydrochloric acid	0.214
3.5	Na-acetate-hydrochloric acid	0.193

* Limit of identification and dilution limit :

The limit of identification (X) is the quantity of material in microgram (γ) per ml of the sample solution which is detectable by the particular technique and expressed in gram (γ/ml) (1γ : 1 microgram = 0.001 mg). The following simple relation exists between the dilution limit, the volume of the test solution and identification limit.

$$\text{Dilution Limit} = \frac{\text{1: Volume of the test solution in ml} \times 10^{6}}{\text{Limit of identification in } \gamma/\text{ml}}$$

The limit of identification (X) was determined with the standard ferric chloride solution employing spot plate technique 1.0 ml of the metal ion solution of different concentration at pH 5.0 was treated with 5 ml of 0.05 M ethanolic solution of the reagent. The limit of identification was found to be 6.876 γ/ml and corresponding dilution limit is 1:1, 45, 458.

*** Gravimetric determination of Fe(III) with SB_{II} :**

A 1.0 % solution of the reagent in dioxane was used.

Ferric chloride solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 3.0 to 4.0 using sodium acetate - hydrochloric acid buffer. The solution was warmed at $60^{o}C$ and small excess of reagent SB_{II} was added (1%, 30 ml). A buff precipitate obtained were digested on water bath for 60 minutes at $60^{o}C$. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by 50% aqueous ethanol-dioxane to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-$115^{o}C$ in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

* **Calculations :**

10 ml solution gave 0.4021 g of Fe(III) SB_{II}

Found Iron = 0.02808 g

10 ml Ferric contains = 0.02800 g of Fe(III)

Error = 0.00008 g

= 0.028 %

TABLE - II

Estimation of Fe(III) using SB_{II} Legand :

Fe(III) taken = 0.02800 g.

$FeSO_4.6H_2O$ Drying temperature = 80 - 85°C

pH	Fe(III) complex in (g)	Fe(III) found in (g)	Error	
			in (g)	%
2.5	0.3944	0.02754	-0.00046	-1.64
2.5	0.3967	0.02770	-0.00030	-1.07
3.0	0.3987	0.02784	-0.00016	-0.57
3.0	0.3997	0.02791	-0.00009	-0.32
3.5	0.4016	0.02804	+0.00004	-0.014
3.5	0.4021	0.02808	+0.00008	+0.028
4.0	0.4040	0.02821	+0.00021	+0.75
4.0	0.4064	0.02838	+0.00038	+1.35
4.5	0.4084	0.02852	+0.00052	+1.85
4.5	0.4102	0.02864	+0.00064	+2.28
5.0	0.4122	0.02878	+0.00078	+2.78
5.0	0.4142	0.02892	+0.00092	+3.28

Spectrophotometric study of Fe(III) complex :

The Fe(III) - SB_{II} chelate has been found to be soluble in chloroform, benzene, carbon tetrachloride, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

* Effect of the reagent concentration :

A series of solution were taken, keeping the concentration of ferric ion constant (0.005 M, 1 ml) while the amount of (0.05 M) reagent SB_{II} was varied. The absorbance of the solutions after the colour development as usual, were recorded at 500 nm. The absorbance was found to increase till addition of approximately 8 times excess of the reagent. Thus, about 8 times excess of the reagent found to be sufficient for the maximum complex formation.

* Effect of solvent and time :

Since the complex is easily soluble in dioxane, the concentration of ethanol was kept 75% in all final solutions, prepared for absorbance measurements of Fe(III)-SB_{II} complex.

From the study of effect of time on absorbance, it was found that colour development is quite rapid and the absorbance of solution remains unchange for 2 hours and after 2 hours the colour fades and absorbance of solutions changes.

Verification of Beer's Law :

To 10 ml of solution (0.01 M) of the reagent solution in each of a set of 25 ml volumetric flask, 2 ml buffer solution (pH 2.5) were added. Varying amount of Fe(III) solution (0.005 M) were added and the contents were made upto the mark with ethanol and distilled water to make dioxane in final solutions were measured at 500 nm against reagent blank prepared in identical condition. Absorbance values were plotted against the Fe(III) content. A straight line passing through the origin, indicating the obeyance of the Beer's law was obtained upto 20.1 ppm of Fe(III). Standard graph thus obtained may be used for the determination of ferric in unknown solution using schiff base SB_{II}. The results are tabulated in Table III and graph is shown on pageNo. 124.

Molar absorptivity calculated from Beer's law plot was found to be 14.02 x 10^2 lit.mol^{-1} cm^{-1} for Fe(III)-SB_{II} reagent at 500 nm.

*** Composition of the Chelate :**

The composition of Cu(II) chelate with the reagent SB_{II} has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

(i) Job's method of continuous variation :

A series of solution were prepared by mixing 'X' ml of 0.005 M (Fe III) solution. 12-X ml of 0.005 M reagent solution and 2 ml of buffer solution of pH = 2.5. These solutions were then made upto 25 ml keeping the final concentration of dioxane.

Absorbance of these solutions were recorded at 500 nm against metal ion blank. The results are tabulated in Table-IV and graph is shown on page No. 125.

From the graph, it has been found that maximum occurs at 0.33 ratio of metal ion concentration to total concentration of metal and reagent indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In the mole ratio method, equimolar solutions of the Fe (III) ion as well as the reagent (0.005 M) were used.

A series of solutions were prepared, keeping the concentration of reagent constant (6.0 ml, 0.005 M) while varying the metal ion concentration (from 1 to 9.0 ml, of 0.005 M) pH of these solutions were adjusted by the buffer solution at pH 2.5. These solutions were diluted to 25 ml in volumetric flasks. Absorbance of these solutions were then recorded at 500 nm as usual. Absorbance were plotted against the ratio of concentration of reagent to metal ion. The results are tabulated in Table-V and graph is shown on page No. 126.

It is evident from the graph that, the absorbance gradually increases upto certain molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

* Evaluation of stability constant :

The stability constant is calculated from the above relation :

$$K_S = \frac{(1-\alpha)}{4\alpha^2 C^2} \qquad \alpha = \frac{E_m - E_s}{E_m}$$

From mean K_S value, the standard free energy change ΔG^o for the complex formation reaction has been calculated using the formula, $\Delta G^o = - RT \ln k$

Method	E_M	E_s	α	K_s
Job	0.310	0.295	0.04838	4.1×10^6
Mole ratio	0.322	0.308	0.04387	5.1×10^6

Mean K_S = 4.6×10^6

G^o = - 9.084 k.cal/mole

Verification of Beer's Law

Fe(III) SB_{II}

Varying amount of metal solution : 0.005M

Ligand solutin : 10.0 ml (0.01M)

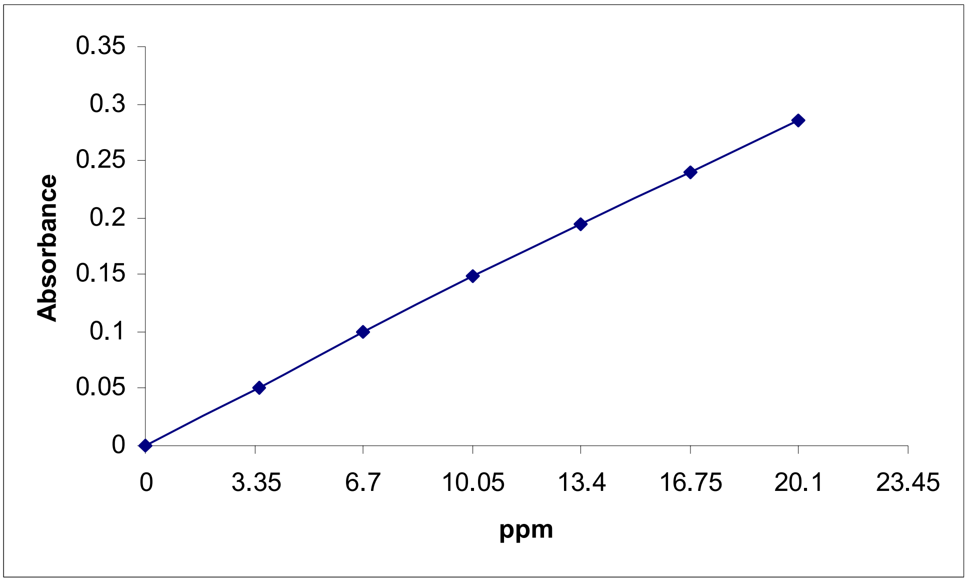
Final volume of chloroform extract : 25 ml

Wavelength : 500 nm.

pH : 2.5

TABLE-III

Fe(III) Solution taken in ml	Fe (III) Taken in ppm	Absorbance
0.3	3.35	0.05
0.6	6.7	0.1
0.9	10.05	0.148
1.2	13.4	0.195
1.5	16.75	0.24
1.8	20.1	0.286



Verificaiton of Beer's Law: Fe(III) SB_{II} Complex

Fe(III) SB$_{II}$

Metal solution : 0.005M

Ligand solutin : 0.005M

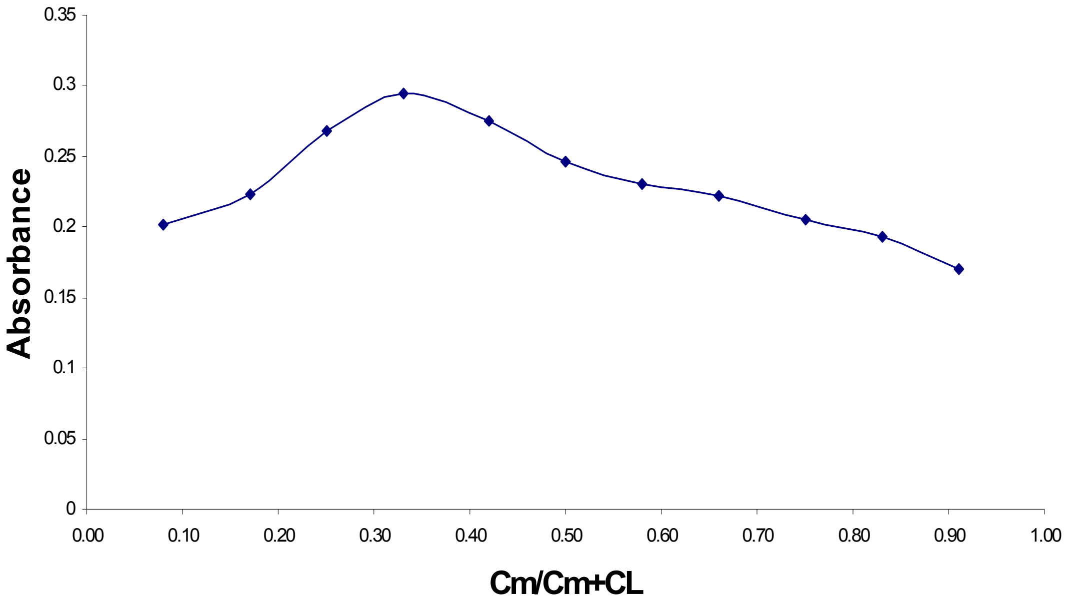
Final volume of chloroform extract : 25 ml

Wavelength : 500 nm.

pH : 2.5

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.201
2	10	0.17	0.223
3	9	0.25	0.268
4	8	0.33	0.295
5	7	0.42	0.275
6	6	0.50	0.246
7	5	0.58	0.23
8	4	0.66	0.222
9	3	0.75	0.205
10	2	0.83	0.193
11	1	0.91	0.17



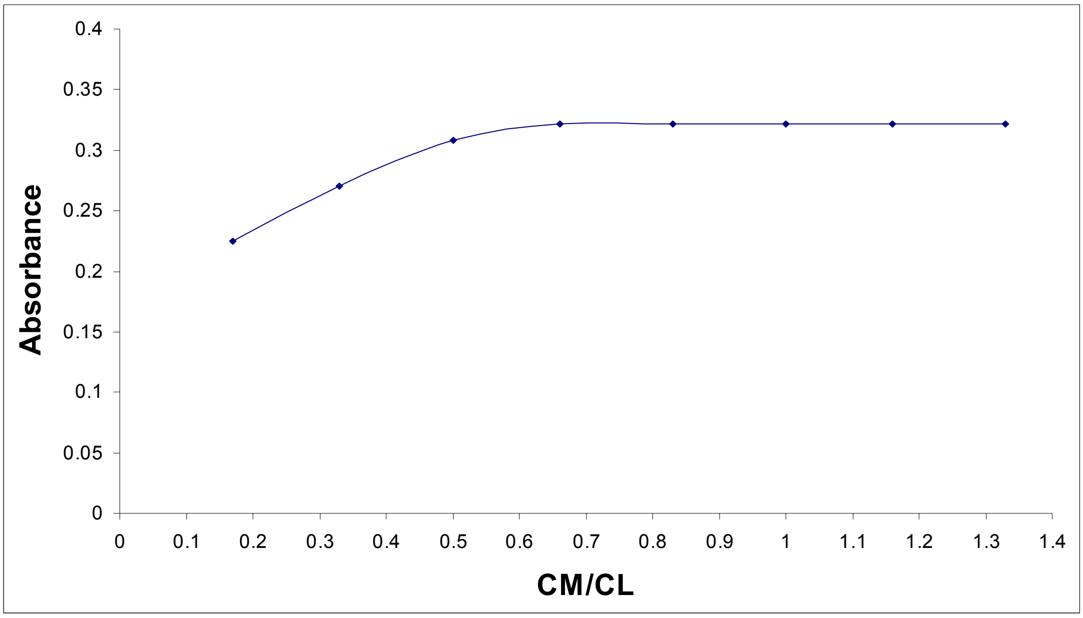
Composition of Fe(III) SB$_{II}$ Complex of job's method

Fe(III) SB_{II}

Metal solution	: 0.005M
Ligand solutin	: 0.005M (6.0 ml.)
Final volume of chloroform extract	: 25 ml
Wavelength	: 500 nm.
pH	: 2.5

TABLE-V

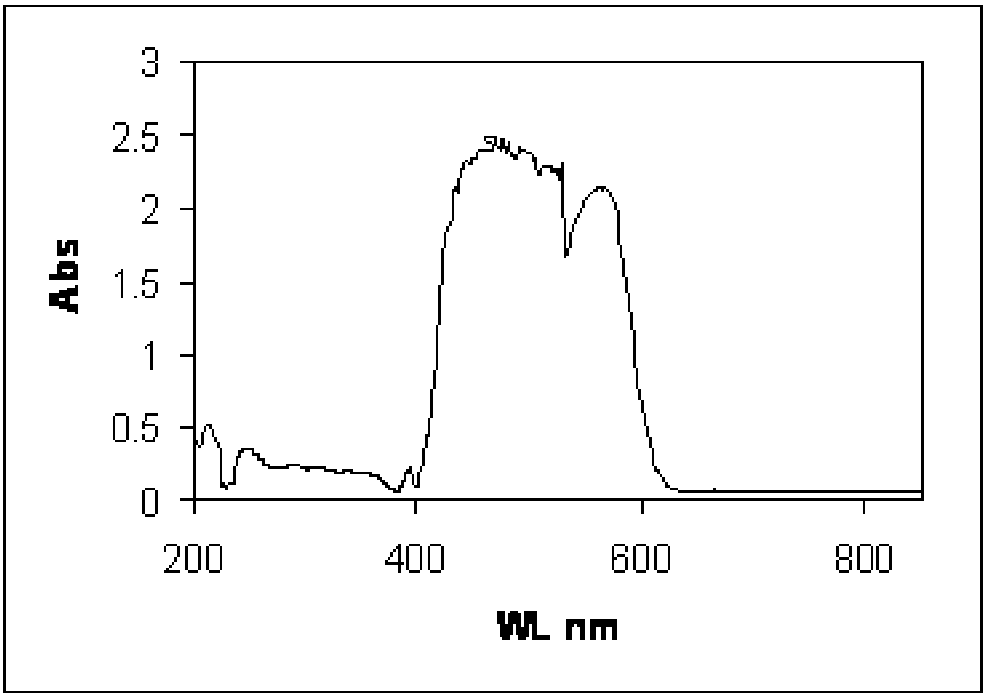
Metal ion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.255
2	6	0.33	0.27
3	6	0.50	0.308
4	6	0.66	0.322
5	6	0.83	0.322
6	6	1.00	0.322
7	6	1.16	0.322
8	6	1.33	0.322



Composition of Fe(III) SB_{II} Complex of mole-ratio method

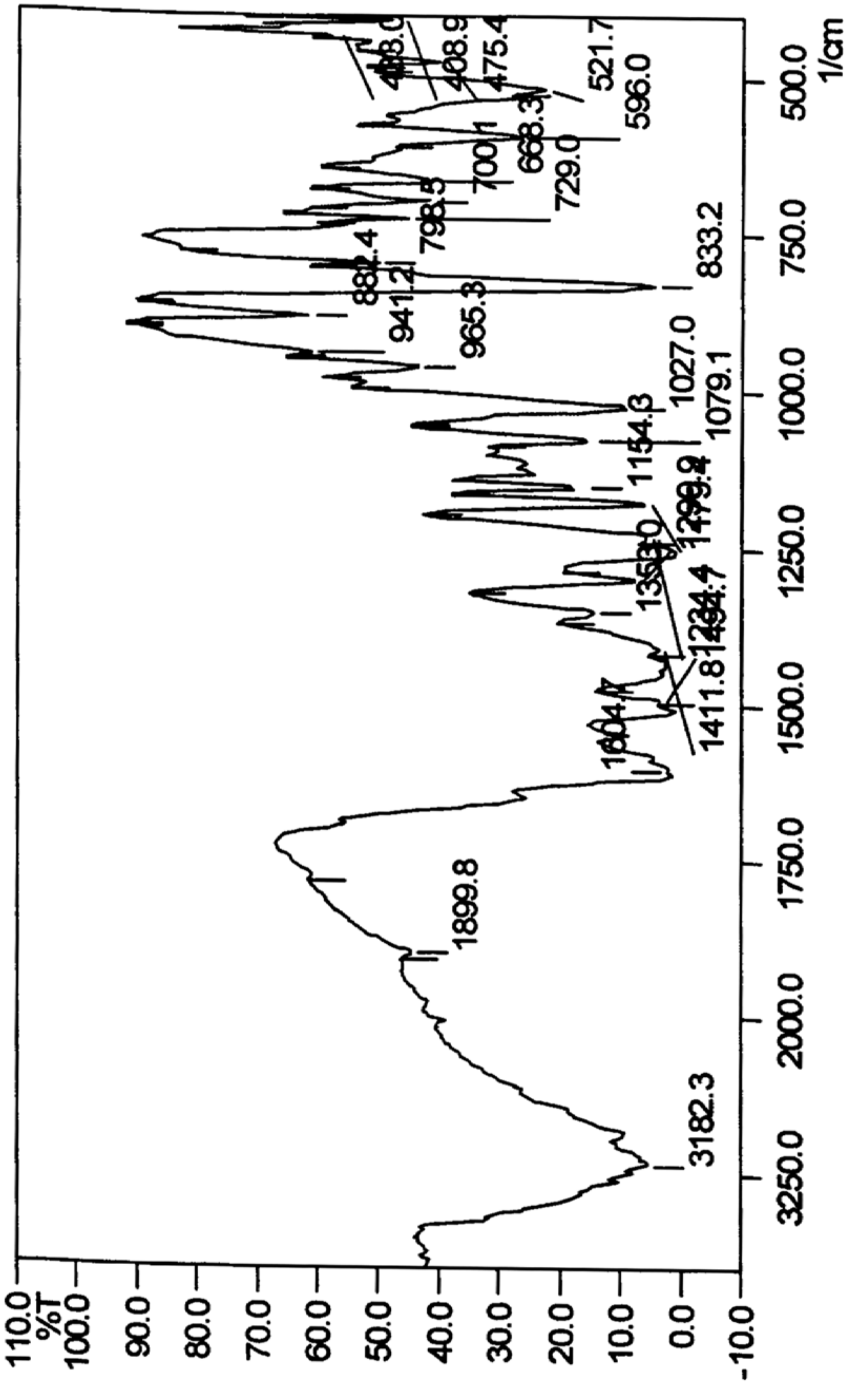
*** Effect of diverse ions :**

In determinations of 15 ppm Fe(III), at pH 2.5, the cations Zn(II), Mg(II), Sr(II) did not interfere even when present in 10-fold excess. Cu(II) and Pd(II) interfere seriously. Many common anions were not found to interfere.



Absorption Spectra of Fe(III)-SB$_{II}$ Complex

IR SPECTRA OF Fe(III)-SB$_{II}$ COPMLEX



7.4 STUDY OF Zn(II) SB_{II} COMPLEX :

Preparation of standard solution of Zinc(II) :

Stock solution of (0.05 M) of Zn(II) was prepared by dissolving 3.594 g of $ZnSO_4.7H_20$ in distilled water and little acid and diluting it to 250 ml. This solution was standardised volumetrically using EDTA[1-A]. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

* Reaction of SB_{II} with Zn(II) :

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination.

* Reaction with Zn(II) at different pH values :

5 ml SB_{II} solution was added to 2 ml of standard 0.05 M Zn(II) solution at different pH. The results are Tabulated in Table-I.

* Stability of chelate :

The buff colour Zn(II) chelate is insoluble in water and ethanol, while it is soluble in chloroform, dioxan, DMF, THF, ethyl acetate. The solution of the chelate was stable and could be kept for long time without any decomposition.

* Limit of identification and dilution limit :

The limit of identification (X) is the quantity of material in microgram (γ) per ml of the sample solution which is detectable by the particular technique and expressed in gram (γ/ml) (1γ : 1 microgram = 0.001 mg). The following simple relation exists between the dilution limit, the volume of the test solution and identification limit.

$$\text{Dilution Limit} = \frac{1 : \text{Volume of the test solution in ml} \times 10^6}{\text{Limit of identification in } \gamma/\text{ml}}$$

The limit of identification (X) was determined with the standard copper sulphate solution employing spot plate technique 1.0 ml of the metal ion solution of different concentration at pH 5.0 was treated with 5 ml of 0.05 M ethanolic solution of the reagent. The limit of identification was found to be 6.876 γ/ml and corresponding dilution limit is 1:1, 45, 458.

TABLE - I

pH	Buffer	Observation
2.0	HCl + CH_3COOH	Colouration
2.5	HCl + CH_3COONa	Buff precipitate
3.0	HCl + CH_3COONa	Buff precipitate
4.0	CH_3COOH + CH_3COONa	Buff precipitate
5.0	CH_3COOH + CH_3COONa	Buff precipitate
6.0	CH_3COOH + CH_3COONa	Buff precipitate
7.0	NaOH + KH_2PO_4	Buff precipitate
8.0	NH_3 + NH_4Cl	Buff precipitate
9.0	NH_3 + NH_4Cl	Buff precipitate
10.0	NH_3 + NH_4Cl	Buff precipitate

*** Gravimetric determination of Zn(II) with SB_{II} :**

A 1.0 % solution of the reagent in dioxane was used.

Zinc solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 3.0 to 4.0 using sodium acetate - hydrochloric acid buffer. The solution was warmed at 60^{o}C and small excess of reagent SB_{II} was added (1%, 30 ml). A buff precipitate obtained were digested on water bath for 60 minutes at 60^{o}C. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by dioxane to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115^{o}C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in table-II.

*** Calculations :**

10 ml solution gave 0.4051 g of Zn(II) SB_{II} complex

Found Zinc = 0.03273 g

10 ml Zinc solution contains = 0.03270 g of Zn(II)

Error = 0.00003 g

= 0.09 %

TABLE - II

Estimation of Zn(II) using SB_{II} Legand :

Zn(II) taken = 0.03270 g

Drying temperature = 110 - 115^{O}C

pH	**Zn(II) complex in (g)**	**Zn(II) found in (g)**	**Error**	
			in (g)	**%**
2.5	0.3960	0.03199	-0.00071	-2.21
2.5	0.3982	0.03217	-0.00053	-1.65
3.0	0.4001	0.03232	-0.00038	-1.18
3.0	0.4018	0.03246	-0.00024	-0.75
3.5	0.4035	0.03260	-0.00010	-0.31
3.5	0.4044	0.03267	-0.00003	-0.093
4.0	0.4071	0.03289	+0.00019	+0.59
4.0	0.4088	0.03303	+0.00033	+1.03
4.5	0.4111	0.03321	+0.00051	+1.59
4.5	0.4132	0.03338	+0.00068	+2.12
5.0	0.4151	0.03354	+0.00084	+2.62
5.0	0.4171	0.03370	+0.001	+3.12

* Spectrophotometric study of Zn(II) complex :

The Zn(II) - SB_{II} chelate has been found to be soluble in chloroform, dioxane, DMF, THF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

Absorption Spectra :

To take the absorption spectra, 5 mg of chelate was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the range of 350-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 410 nm and hence all the measurements were carried out at 410 nm. Absorption spectra is given on page No 140.

Verification of Beer's Law :

To 5 ml of solution (0.01 M) of the reagent SB_{II}, varying amounts of the metal ion solution (0.005 M) were added and the pH was adjusted to 5 using CH_3COONa + CH_3COOH buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and final volume of the chloroform extract was adjusted to 25 ml. The absorbance of these solutions were measured at 410 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained upto 18.72 ppm of Zn(II). The standard graph thus obtained may be used for the determination of zinc in a unknown solution using SB_{II} reagent. The results are tabulated in Table-III. The graph is shown on page 134.

Molar absorptivity calculated from Beer's law plot was found to be 10.01×10^2 $lit.mol^{-1}$ cm^{-1} for Zn(II)-SB_{II} reagent at 410 nm.

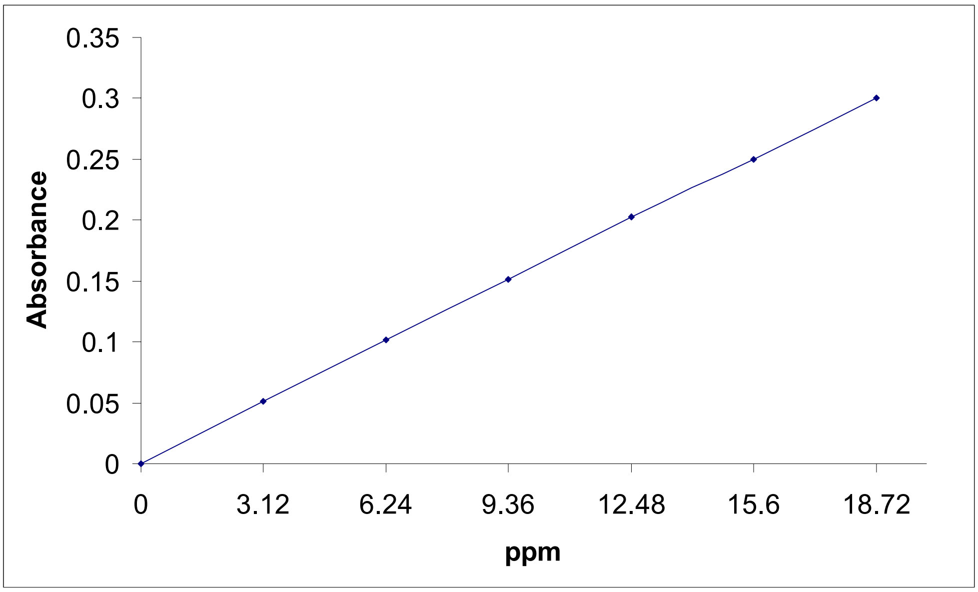
Verification of Beer’s Law

Zn(II) SB_{II}

Varying amount of metal solution : 0.005M
Ligand solutin : 5.0 ml (0.01M)
Final volume of chloroform extract : 25 ml
Wavelength : 410 nm.
pH : 5.0

TABLE-III

Zn(II) Solution taken in ml	Zn (II) Taken in ppm	Absorbance
0.3	3.12	0.051
0.6	6.24	0.102
0.9	9.36	0.151
1.2	12.48	0.230
1.5	15.6	0.25
1.8	18.72	0.3



Verificaiton of Beer’s Law: Zn(III) SB_{II} Complex

Composition of Chelate :

The composition of Zn(II) chelate with the reagent SB_{II} has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ration method.

(i) Composition of Zn(II)-SB_{II} complex by Job's method of continuous variation :

A 0.005 M solution of Zn(II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.005 M) was prepared in absolute ethanol. The solution of metal salt and the reagent were mixed in varying proportions as under :

Metal ion solution : 0, 1, 2, 3, - - - - 11, 12 ml
Reagent solution : 12, 11, 10, 9, - - - - 1, 0 ml

pH of the solution was adjusted to 5.0. The precipitated complex was extracted with three 5 ml portions of chloroform and final volume of chloroform extract was adjusted to 25 ml. The absorbance of chloroform extracts were measured at 410 nm. The results are tabulated in Table-IV.

From the graph (page No. 137), it has been found that maximum occurs at 0.4 ratio of metal ion concentration to the total metal and ligand concentration indicating the formation of 1:2 (M:L) complex.

(ii) Yoe and Jones mole ratio method :

In this method, equimolar solutions of the Zinc (II) as well as the reagent (0.005 M) were used. A series of solutions were prepared, keeping the reagent solution (6.0 ml) constant while varying the amount (from 1 to 8.0 ml) of 0.005 M metal solution.

pH of the solutions were adjusted to 5.0. The resulting precipitate were extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 410 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V. Graph on page No. 138.

It is evident from the graph that absorbance gradually increases upto molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

- Evaluation of stability constant :

$$ML\eta \quad === \quad M + nL$$

$$C(1-\alpha) \qquad C[n.c\alpha]^{\eta}$$

$$K_S = \frac{C(1-\alpha)}{C[n.c\alpha]^{\eta}}$$

taking n = 2 in this case the equation reduce to,

$$K_S = \frac{(1-\alpha)}{4\alpha^2 C^2}$$

$$\text{where} \quad \alpha = \frac{E_m - E_s}{E_m}$$

E_m : Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines ;

E_s : absorbance at the stoichiometric molar ratio of the metal to reagent in complex

*** Calculation of stability constant :**

The stability constant is calculated from the above relation :

From means K_S value, the standard free energy change ΔG^O for the formation reaction of complex has been calculated at 25^{O}C using the formula $\Delta G^O = - RTlnk$

Zn(III) SB_{II}

Metal solution : 0.005M

Ligand solutin : 0.005M

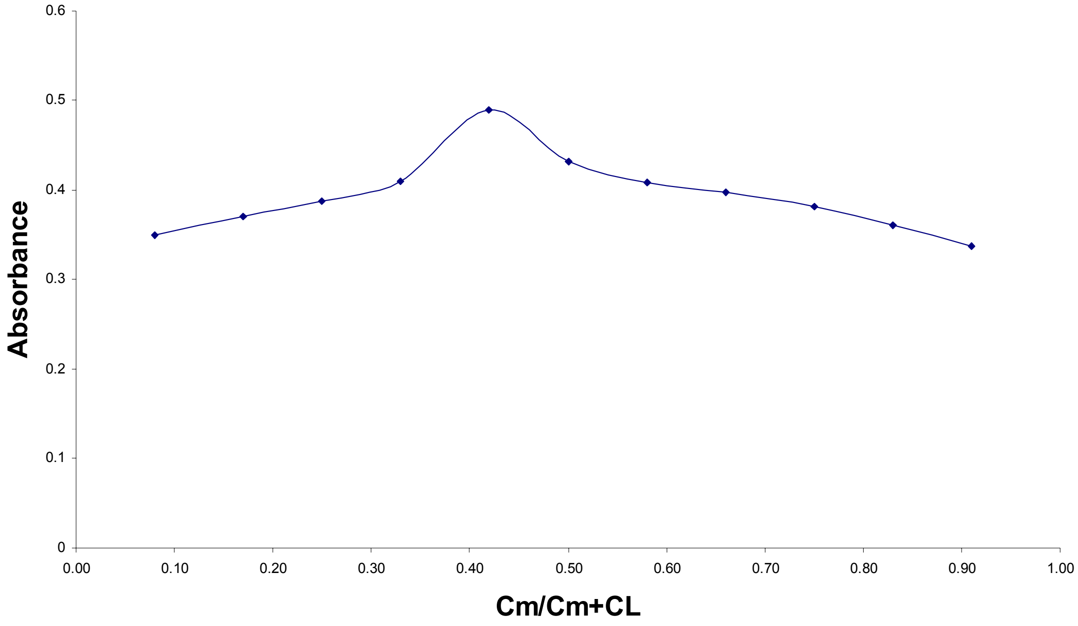
Final volume of chloroform extract : 25 ml

Wavelength : 410 nm.

pH : 5.0

TABLE-IV

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absrobance
1	11	0.08	0.35
2	10	0.17	0.371
3	9	0.25	0.388
4	8	0.33	0.41
5	7	0.42	0.49
6	6	0.50	0.432
7	5	0.58	0.408
8	4	0.66	0.397
9	3	0.75	0.382
10	2	0.83	0.361
11	1	0.91	0.338



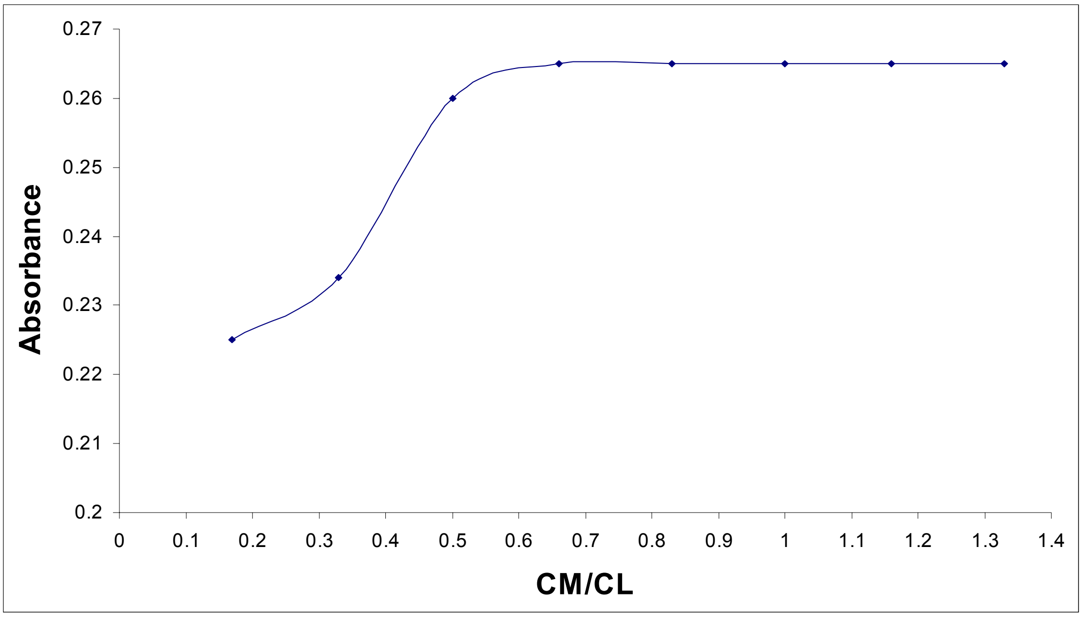
Composition of Zn(III) SB_{II} Complex of job's method

Zn(III) SB$_{II}$

Metal solution : 0.005M
Ligand solutin : 0.005M
Final volume of chloroform extract : 25 ml
Wavelength : 410 nm.
pH : 5.0

TABLE-V

Metal ion solution ml	Ligand solution ml	Cm/CL	Absrobance
1	6	0.17	0.225
2	6	0.33	0.234
3	6	0.50	0.260
4	6	0.66	0.265
5	6	0.83	0.265
6	6	1.00	0.265
7	6	1.16	0.265
8	6	1.33	0.265



Composition of Zn(II) SB$_{II}$ Complex of mole-ratio method

Method	E_M	E_S	α	K_S
Job	0.490	0.471	0.0387	6.4×10^6
Mole ratio	0.265	0.260	0.0188	27.8×10^6
	Means K_S =	17.1×10^6		
	ΔG^o =	-9.861 k.cal/mole		

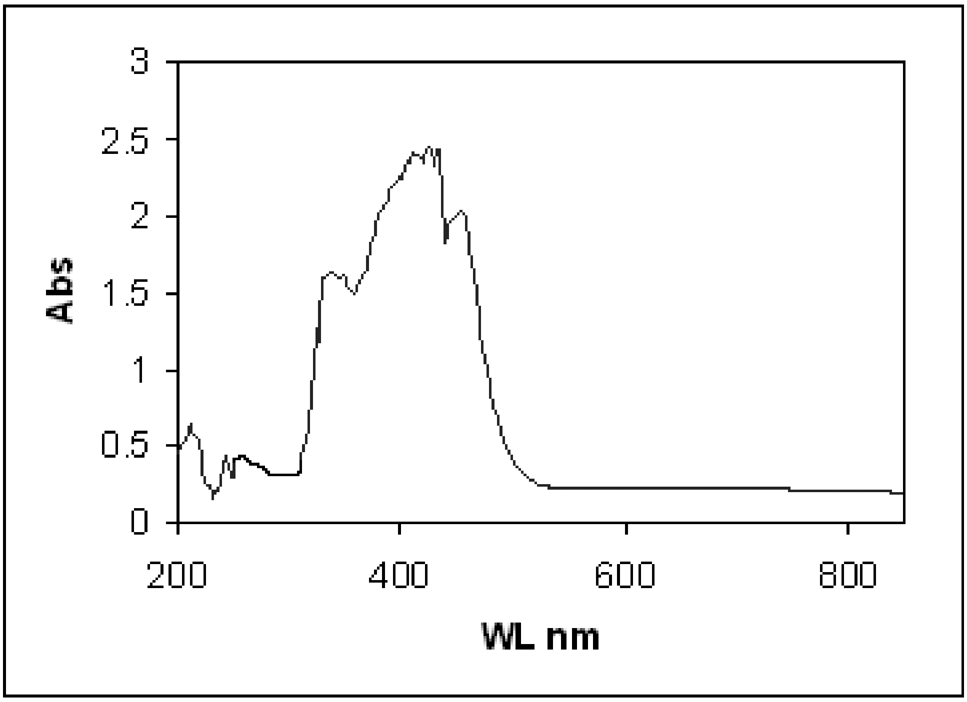
*** Effect of diverse ions :**

To study the effect of foreign ions on gravimetric determinations of Zn(II), 8-10 mg of various cations were added to a known amount of Zn(II) solution at pH 5.0 and gravimetric estimations were done. It was observed that Cu(II), Br(II), Sr(II), Mg(II), Mn(II), Ni(II) do not interfere at this pH, but Fe(III), Co(II), Pd(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

*** Estimation of zinc and zinc oxide from its chelate :**

Zinc (II) - SB_{II} (0.250 g) was ignited in a covered crucible. The ignited mass was then treated with a drop of concentrated nitric acid and then excess of acid was evaporated by heating the crucible over low flame. The temperature was gradually raised to a dull red heat to ensure complete conversion to zinc oxide. It was cooled and weighed as zinc oxide. The results are tabulated below.

Chelate	Weight of chelate ignited in mg.	Weight of ZnO obtained in mg.	Percentage of metal	
			Calc.	Found
Zn II - SB_{II}	250	23.88	8.94	7.74



Absorption Spectra of Zn(II)-SB_{II} Complex

IR SPECTRA OF Zn(II)-SB$_{II}$ COPMLEX

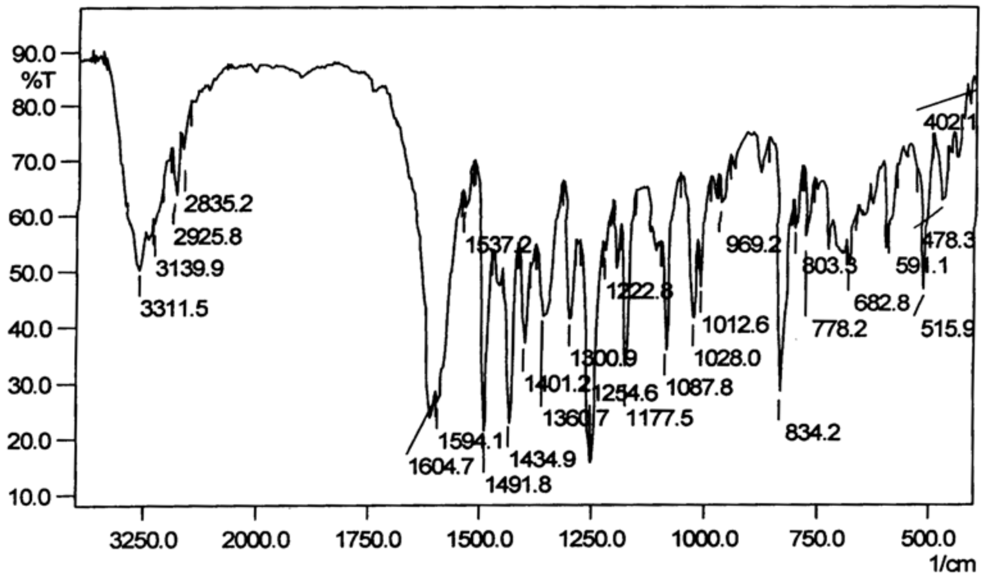


Table of IR spectral data of metal complexes.

Schiff Base	Ni(II)-SB$_{II}$	Mn(II)-SB$_{II}$	Fe(III)-SB$_{II}$	Zn(II)-SB$_{II}$	Assign.
1618	1600	1600	1604	1604	-C=N str
983	740	720	729	682	C=S/C-S
-	540	501	521	515	M-N
-	524	482	475	478	M-S

REFERENCES

1. A. A. I. Vogel; *“A Text book of Quantitative Inorgaince Analysis”, Longamans, Green and Co., London, W.I.*, 4th Ed. (1978), p. 321.

   B. Idem; idib., p. 322

   C. Idem; idib., p. 330

   D. Idem; idib., p. 322

[B] Corrosion Inhibition Activity of Schiff Bases

(SB_I and SB_{II})

Corrosion causes huge losses to buildings, automobiles industries and their services and is possibly the greatest consumer of metals today. The quantity of metals lost each day through corrosion is enormous, but if one includes all expenses from finding an ore to production of finished good, the cost of corrosion is devastating. Synthetic plastics and polymers have made monstrous stride recently but metals will never be replaced because of their unique properties of malleability, ductility, electrical conductance, thermal resistance, etc.

Beside the direct losses certain indirect economic cost is also associated with corrosion. These include loss of material, loss of production due to structure failure and consequent shut down of plants, loss due to adulteration of the main product, loss of efficiency of machinery and over design which should be included considering future corrosion of a system.

A great deal of study has been devoted to corrosion in multidisciplinary field of chemistry, engineering and metallurgy. Immense efforts have been made to understand the mechanism through which metals corrode in different environments and to minimize it by adopting various preventive measures. Methods to reduce corrosion include application of protective coatings, cathodic and anodic protection, alloying and use of different class of inhibitors alone or in combinations.

Corrosion may follow any one of several general patterns. Basically stated, corrosion results from the instability of a construction material with the environment in which the material is placed. All materials, both organic and inorganic, can react with their environments and may eventually lose their usefulness for a given application. Some non metals tend to decompose, usually as the result of chemical interaction with some component of their environment.

Corrosion can be defined as the destructive result of chemical reaction between a metal or metal alloy and its environmetn[1]. It is probably the commonest electrochemical phenomenon experienced in day to day life. Metal atoms are found in nature in the form of minerals. The same amount of energy needed to extract metals from their minerals emitted during the chemical reactions that produces corrosion. Thus corrosion has been called extractive metallurgy in reverse[2].

Mild steel is widely used as an engineering material and its corrosion in acidic medium is of great economic importance. The effect of various additives on corrosion of mild steel has extensively been studied[3-10]. It has been reported[11-16] that addition of certain organic compounds bearing hetero atoms, retards the corrosion of mild steel in acidic environments. Recently considerable interest has been generated in the use of nitrogen, oxygen and sulphur containing organic compounds as corrosion inhibitors for mild steel in different acids[17-18]. Vishwanathan et al[19] and others[20-22] have studied the effect of same aniline compounds on corrosion of mild steel in acidic solutions; pyrrole and its derivatives[23] have also been studied as corrosion inhibitor for mild steel in different acidic media. Pyridyl substituted triazoles have also been studied fro their effectiveness to reduce corrosion of mild steel in hydrochloric acid solution[24], certain aldehydes[25] have also been tested to reduce corrosion of mild steel in acid solutions. Fatty acid oxazoles[26] have also been studied to inhibit corrosion of mild steel. Querishi et al[27] have studied tetramethyl-dithiaoctaazacyclotetradeca hexane as corrosion inhibitor for mild steel in acid solutions. Coatings containing poly-pyrrole has been applied on mild steel to inhibit corrosion[28].

In the present study an attempt has been made to study the influence of varying concentrations of Schiff's bases derived from 4-methoxybenzaldehyde and 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol (SB_I) and 4-methylbenzaldehyde and 4-amino-5-(3-bromophenyl)-4*H*-1,2,4-triazole-3-thiol (SB_{II}), on corrosion of mild steel in different concentrations of hydrochloric acid and sulphuric acid employing mass loss technique.

The corrosion rate affecting by these factros

The most probably factor that the corrosion rate is greatly affected by relative corporation of cathodic and anodic areas and already reported[29] that there is a small anodic area with a large cathodic area. When a protective coating breaks at a few points intense corrosion at the anodic area takes place also and already been explained that inspite of the rates of corrosion action being predictable and now a day predict the rate of corrosion is not possible.

One of the factors that greatly affect the corrosion rate is the relative proportion of anodic and cathodic areas. It has been reported that if there is a large cathodic area with only a small anodic area, intense corrosion at the anodic area takes place e.g. when a protective coating breaks at a few points.

The corrosion reactions involves H^+ and OH^- ions, hence the effect of pH is obvious. Pourbiax[30] and other workers have studied the effect of pH in detail. As a general rule, acids are more corrosive than neutral or alkaline solutions. Most of the metals exhibit slight inhibition in alkaline solution and corrosion gradually increases as acidity increase and become rapid when the pH value is below 4.0.

Detailed study[31-36] has been carried out to study the effect of oxidizing agents n corrosion rate. Systems handling water, viz. boilers, heat exchangers etc. have been examined extensively as they face serious problem due to dissolved oxygen. The oxidizing agents, oxidize metals and are themselves reduced at cathodes and there by support cathodic reaction and promote corrosion.

The effect of temperature on the corrosion rate is complicated because of the fact that it affects various factors in different ways. The rate of chemical reaction increases with the rise in temperature but the solubility of the gases, like oxygen, which affects corrosion, decrease. Temperature may also affect the protective coatings in different ways. In general, the rate of corrosion due to oxygen or oxidizing agents is decreased with the rise in temperature but with increase in the rate of hydrogen evolution, corrosion is increased[37-39].

Liquids flowing with high velocity on the metal surfaces reduce the tendency to form a protective film and may even remove films already formed. It may even cause erosion. Consequently, at higher velocities, the corrosion rates are higher.

Heart treatment, differential aeration, concentration difference and microbiological effects are few other factors, which affect the rate of corrosion in specific environment and should be given emphasis in study of such systems.

Different Types of Corrosion

There are different forms of corrosion under following points

Pitting Corrosion

Pitting depends on differential aeration and easy explain on basis of differential araton38-40 pitting is localized attack on a corrosion resistant. It becomes anodic and corrodes as corrosion proceeds. Firstly a cavity or pit created, becomes deeper, and bottom becomes still less accessible oxygen and make more anodic it used to formation of pinholes, pits and cavities in metals, serious pitting may result from various grain boundary effects such as presence of cavities in the metal surfaces precipitation of another phase hawing a higher anodic potential.

Galvanic Corrosion

If coupled the tow dissimilar metals and placed in conducting solution or corrosive. Between the two metals due to potential difference electrons flow take place. The metals behave like opposite more resistant as cathodic and less resistant behave as anodic the dissolution of anodic metals take place leaving behind the cathodic metal this type of corrosion is termed as galvanic corrosion in this flow of electric current and dissimilar metals is involved.

Uniform Corrosion

When the regular removal of metal from the surface is observed as uniform corrosion. It represent the greatest instruction of metal on tonnage basis the uniformity in metal structure and composition and corrosion environments are prerequisite for such type of corrosion and its suitable example of uniform attack includ atmosphere corrosion and corrosion of metal in acid solutions.

Crevice Corrosion

Crevice corrosion occurs within crevice and other shielded areas on metal surface exposed to corrosives[39]. A very general term, which normally includes all observations of accelerated attack observed at the junction between tow metals exposed to corrosive environment. From an engineering point of view, crevice corrosion is considered important because it causes high torque or complete scizure in bearing and mechanical linkages in relatively short period of time.

Environmentally Induced Cracking (EIC)

We differentiate in three types and defined as brittle fracture of normally ductile alloy in the presence of an environment.

a. Stress Corrosion Cracking (SCC)

When surrounded by specific environmental conditions the stress corrosion cracking is exhibited by alloys having static tensile strength in presence of passive surface film under oxidizing condition and low corrosion rates are prerequisite for SCC to occur but pure metals are comparatively resistant to SCC.

b. Corrosion Fatigue Cracking (CFC)

The pure metal and alloy are equally susceptible for CFC and presence of corrosive environment usually increase the susceptibility and rate of fatigue cracking without corrosion and no required specific environment the cyclic stress under corrosive environment, results in corrosion fatigue cracking.

c. Hydrogen Induced Cracking (HIC)

Hydrogen Induced Cracking is the reaction of hydrogen with carbides often present as impurity to form methane. In decarbonization voids and surface blisters when atomic hydrogen migrates voids are formed from the internal defects and inclusions, where molecular hydrogen gas can nucleate generating sufficient internal pressure to deform and rupture the metal locally the hydrogen cracks and hydrogen blasters became evident.

Erosion Corrosion

Attack on a metal of increases in rate deterioration because of relative movement between a corrosive fluid and metal surface dissolved ions and it forms solid corrosion products these are removed from metal surface many opens of corrosive media could cause erosion corrosion.

Parting of Alloy or Dezincification

Use the corrosion process and removal of one element from a solid alloy is termed as dezincification. When the dezincification of brass zinc is preferentially corroded or parted from the alloy to leave a porous copper rich region which results in reduction in mechanical strength of the alloy a example selective to parting of alloy is removal of zinc in brass alloys.

Electrochemical Theory

Almost all-metallic corrosion process involves transfer to electronic charge in solutions. The electrochemical theory of corrosion was originated in way back 18th century, when Davy[41] proposed the electrochemical nature of corrosion. This was later on confirmed by many other workers[42-44]. However, Wagner and Traud[45] propounded the first systematic approach to the electrochemical theory of corrosion with their mixed potential theory. Certain controversies were also raised by many workers[45-49] against this theory but it was supported, throughout the 19th century and further formalized by large number of publications[50-58]. Many workers[59-67] have used this theory to study the corrosion behavior of different systems and others[68-74] has used it to assess the effectiveness of various preventive measures adopted to combat corrosion.

The mixed potential theroy along with Nernst and Tafel equations from the basis of modern electrochemical theory of corrosion[75]. It has now been accepted that most of the cases of corrosion can be explained on the basis of this theory. According to this theory, all corrosion reactions can be divided into two or more partial reactions[76]. One is the oxidation or de-electronation of metal and termed as anodic reactions.

Its general form can be written as follows-

$$M \longrightarrow M^{+n} + ne^- \qquad (1)$$

These one is the oxidation or de-electronation of metal and termed as anodic reaction and second reaction is the electron consuming and is termed as cathodic which can be several types depending on the nature of media surrounding the metal. The most common are-

Hydrogen evolution $2H^+ + 2e^- \longrightarrow H_2$ (2)

Oxygen reduction $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (3)

In acidic solution

Oxygen reduction $O_2 + 2H_2O + 4e^- \longrightarrow 4\ OH-$ (4)

In neutral solution of boric solution

Metal ion reduction $M^{3+} + e^- \longrightarrow M^{2+}$ (5)

Metal deposition $M^+ + e^- \longrightarrow M$ (6)

The common cathodic reaction is Hydrogen evolution since acid or acidic media and frequently encountered oxygen are frequently encountered oxygen reduction (3) and (4), is very common as any aqueous solution in contact with is capable of producing this reaction metal ion reduction (5) and deposition (6) are less common reaction in aerated acidic solution two cathodic reactions are possible more than one oxidation and reduction reaction may be occur during corrosion process. The reduction of oxygen and evolution of Hydrogen thus aerated solutions are more corrosive.

Consider the anodic reaction is the dissolution of iron in aerated solution.

$Fe \longrightarrow Fe^{2+} + 2e^-$ (7)

At cathodic site the reaction occurring are-

$2H^+ + 2e^- \longrightarrow H_2\ (g)$ (8)

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (9)

By the equation (7) depicts a single ferrous ion passing in to solution and leaving two electrons on the metal surface this separation of charge the electrical double layer gives rise to a characteristic potential for the Fe/Fe^{+2} couple half-cell. The half cell consist of a chemical species in a reduced state Fe (metal) and oxidized state Fe^{+2} similar half cell relationships. $O_2/OH^-$and H_2/H^+ exists for equation (8) and (9).

Dissolution of the metal under non-standard condition leaves accumulation of a negative charge on the surface. Between the metal and the solution produces a potential difference the electrode potential. By the equation (7) change in potential tends to retard the deposition of dissolved metal ions from the solution into the metal deposition of metal ion and continuation of the dissolution would result in the metal reaching a stable potential such that the rate of dissolation becomes equal to the rate of deposition. Now can be expressed by the nearest equation that in equilibrium state there will be $Fe_{ia} = Fe_{ic}$ because partial anodic current Fe_{ia} for metal dissolution and a balancing cathodic current Fe_{ic} foe the reduction of Fe^{2+} ion to Fe (metal) and the potential termed as the reversible potential (Er) with the standard potential Eo and a value dependent on the concentration of the dissolve metal ions. And can be expressed by the Nernst equation-

$$E = E_o + \frac{RT}{ZF}\frac{a(oxidesed)}{a(reduction)}$$

Where Z is the number of electrons involved in the reaction.

Corrosion Prevention

Prevent corrosion the techniques adopted can be classified under following heads.

Electrochemical Protection

Anodic and cathodic protection

Anodic Protection

The technique was developed using electrode kinetics principles and involves advance concept of electrochemical theory. At first it was suggested by Edeleance in 1954.

This technique is applicable for metals like Ni, Cr, Fe, Ti, Zn and alloys anodic protection converts the entire surface to anodic state with respect to external cathode in particular environment its exhibit active-passive transition.

Even under extreme corrosive conditions the current requirement is much less therefore its application becomes feasible maintenance of an enert barrier of coating on metal surface and anodic current involves formation the primary advantages of anodic protection are its applicability in extremely corrosive environment and low currents requirements.

Cathodic Protection

An external source D.C. is supplied in cathodic protection. So as to polarize the entire surface to the open circuit mode potential this results in the equi-potentiality of the anodic and cathodic regions all over the surface and the flow of corrosion current ceases. It using a rectifier and insoluble anode and external power supply a direct current is impressed on the system. By concling positive terminal to insoluble anode and connecting negative terminal to structure intended for cathodic protection. For higher corrosive media cathodic protection is very often not feasible because of the large requirement of current. A steady flow of current required for cathodic protection depends on the corrosive of the environments.

EMPLOYING BARRIER TO ENVIRONMENTS

Changing Process Conditions

The most corrosion methods employed to reduce corrosion by changing process conditions of any service equipment or industrial unit can be optimized to reduce corrosion.

Lowering Temperature

The effect of temperature, corrosion rate have been extensively studied[77-80]. This usually causes a remarkable decrease in corrosion rate. It has been reported[81-82] that decreases in temperature towers down the corrosion rate to a large extent. However, temperature cannot be varied beyond certain limits, as it is an essential parameter for most of the unit process.

Removing Oxygen or Oxidizers

This is a very old corrosion – control technique. In modern practice, this is accomplished by vaccum treatment, inert gas spraying or through the use of oxygen scavengers. Although deaeration finds widespread application, it is not recommended for alloys. These materials required oxidizers to form and maintain their protective oxide films.

Decreasing Velocity

The practical method for corrosion control is used decreasing velocity, particularly erosion corrosion. Velocity generally increases corrosive attack, although there are some important exceptions. Very high velocity should be always avoided wherever possible to minimize corrosion.

Changing Concentration

In many process the presence of corrosive is accidental. For example eliminating chloride ions reduces corrosion by water coolant in nuclear reactors. Decreasing corrosive concentration is usually effective. Thus reduction in concentration is not a versatile mode to combat corrosion. Many acids such as sulphuric and phosphoric acids are virtually inert at high concentrations.

Proper Designing

For reduce corrosion proper designing of the process equipment also allow us certain geometrical configuration that facilitates corrosive concentrations are –

a. Designs that lead to heterogenetics in the metal (differences in thermal treatment or in the environment differences in temperature velocity).
b. Designs that result in inaccessible areas that cannot be reprotected e.g. by painting.
c. Features that trap, dust, moisture and water.
d. Crevices and situations where deposits can form on the metal surface.
e. Designs that leads to erosion – corrosion or to cavitatic on damage.

There should limitations have been imposed on this method of combating corrosion by unavoidable shape and size of the process equipment. These types of corrosion can be prevented by avoiding, the above mode of management.

Metallic and Other Inorganic Coatings

A satisfactory barrier between metal and its environment can provide by coatings of metallic and inorganic materials. Metal coatings are applied by electro-deposition, flame spraying, cladding and hot dipping and vapour deposition. The chief function of such coating is to provide an effective barrier.

Organic Coatings

Painting is a universal corrosion control technique and applications over high and low temperatures, and immersed of atmospheric conditions of exposure. These involve a relatively thin barrier between substrate material and the environments. Extensive literature[83-87] has been available describing different paint immulssions studied as protective coatings in variety of corrosive environments. Special rubber paints are commercially available which act as an effective corrosion control measures. Lacquers, polishes and similar organic coating are also employed as barrier between metal and its corrosive environment.

Inhibition

The present study deals with this particular mode of combating corrosion and hence is discussed in more detail.

Any substance which when added in small amount to the corrosive media, effectively decreases the corrosion rate is termed as inhibitor[88]. Inhibitors have gained importance other the years, because of their applicability in large number of systems and their efficiency to drastically reduce corrosion even in highly corrosive environments.

The earliest use of corrosion inhibitors perhaps date back to 1872, when Maragoni and Steranelli[89] employed essential and fixed oils to inhibit the corrosion of zinc in acid solution. In 1900 Robinson and Sutherland[90] and in 1907 Laverty and Laverty[91] suggest use of starch, tars and oils. Since the several types of inhibitors have been reported[92-93] for the prevention of metallic corrosion.

Certain compounds reported earlier[94-95] is used to control corrosion caused by water. Use of sulphites and hydrazines as scavenger to control dissolved oxygen is also a common practice[96-97]. Oxidizing ions such as ferric salt and nitrates will induce passivity in active passive alloys[98]. Calcium added once through water system fosters the formation of protective surface films by adjustment of the saturation index[99]. Certain weak bases like ammonia and amine compounds are use to neutralize acidic boiler streams and thereby decrease corrosivity[100-101].

Classification of Inhibitors

Bergman[102] has divided inhibitors as type A to include film forming type and type B, which act by deactivating the medium.

Type A – inhibitors are those, which form an inhibiting layer of film on the metal or react with the metal (passivaters). This type of inhibitors can be further subdivided as:

a. Inhibitors that reduce the corrosion rate but do not completely prevent corrosion, e.g., pickling inhibition.
b. Inhibitors that delay (or incubate) the onset of corrosion for long periods, so that the metal has a temporary immunity to corrosion, e.g., benzotriazole for copper.
c. Passive inhibitors, which result in the formation of passive films on the metal surface, the films generally being an oxide or an insoluble salt of metal, e.g., $NaNO_2$, phosphates and chromates for steel, sulphates for lead.

Type B – includes substances, which reduce the aggressiveness of the environment. This type of inhibitors cane be further divided into:

a. Inhibitors, which retard the corrosion process usually out completely preventing it e.g. sodium sulphate or hydrazine is added to water to remove dissolved oxygen, urea can be added to nitric acid to remove nitrous acid.

b. Inhibitors, which incubate corrosion by reacting with substances that produce corrosion in a given environment, e.g., organic amines which neutralize organic acids in oils and emulsions.

However, there can also be mixed type of inhibitors, which can both react with the metal and reduce the aggressiveness of medium, although one character usually predominates. For example Type AB would be filming type of inhibitor with the secondary action of ameliorating the environment while Type BA inhibitor might raise the pH whilst promoting the formation of barrier films.

From the practical point of view inhibitors can be grouped into following categories –

a. Proton acceptor which pick up a proton as hydrogen ion and migrate to cathodic sites.
b. Electron acceptor which are anodic inhibitor and substances causing passivation of the metal surface.
c. Overvoltage modifiers which bring about changes in the over-voltage characteristics of the anode and cathode.
d. Barriers which include above substances, which are adsorbed on the metal surface.

Inhibitors can also be classified on the basis of their made of action as-

(a) Surface coverage, (b) Adsorption, (c) Diffusion

The first classes of inhibitors function by reacting chemically with the metal to form a non-penetrable layer over the metal surface.

Last class of inhibitor operates in a mechanical barrier fashion by increasing the viscosity of the corrosive medium to such an extent that it is effective in blocking the diffusion of corrosion reactants and products.

Adsorption inhibitors are generally organic compounds including substances of colloidal nature. They appear to form a film over the metal surface and interfere with the corrosive medium thereby acting as a barrier between the metal and the corrosive. These type of inhibitors may also act preferentially either at anodic or cathodic sites depending on their chemical constitution. The pickling inhibitors, however appear to attack especially at those cathodic regions which favors the hydrogen evolution.

Adsorption type inhibitors are the commonest and most of the recent studies have been devoted to develop such type of inhibitors. Considerable interest have been generated in the use of different class of compounds as adsorption inhibitors for different metals and alloys[103-113].

A substance, which acts as an inhibitor for a particular system, not necessarily be effective for other systems. Thiourea for example is good inhibitor for aluminium in acid whereas it accelerates the dissolution of cadmium. KCN is an inhibitor for aluminium but has no effect on cadmium, manganese and zinc. Thus the choice of an inhibitor to prevent or minimize the corrosion of particular metal will chiefly depend on the metal and the corrosive environment.

Search for efficient corrosion inhibitor continues to be important due to certain limitations associated with other methods employed for corrosion prevention. Large number and variety of organic compounds are evaluated as corrosion inhibitors for different metals and alloys in different corrosive environments[114-130]. Frignani et al[131] have studied the effect of certain acetylenic derivatives on corrosion of metals in acid solutions. Effect of some phenols on corrosion of aluminium and aluminium alloys has also been studeid[132]. Several nitrogen, oxygen and sulphur containing organic compounds have been investigated as corrosion inhibitors for a variety of metal and their alloys in variety of corrosive media[133-143]. Certain aromatic amines have also been evaluated for their ability to inhibit corrosion[144-147]. Pyrrole[148], imidazole[149] and triazole[150] derivatives have been reported as corrosion inhibitors of different metals and alloys. Desai[151] has studied the effect of anisaldehyde and ethylene diamine as corrosion inhibitor for the zinc in sulphamic acid. Vashi et al[152] stated that foludines are good inhibitors for zinc metal in acid solution.

Among the compounds to have received attention as corrosion inhibitors are Schiff bases derived from aromatic amines and aldehydes.

In the present investigation, the inhibitive effects have been evaluated for Schiff bases namely: 5-(3-bromophenyl)-4-{[(1*E*)-(4-methoxyphenyl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols (SB_I) and 5-(3-bromophenyl)-4-{[(1*E*)-(4-methylphenyl)methylene]amino}-4*H*-1,2,4-triazole-3-thiols (SB_{II}).

METHODOLOGY

Corrosion consists of reaction between a metal and its environment and hence it affected by both the phases. It is therefore necessary to consider and control both phases while performing any corrosion test. Corrosion test are required to give qualitative and quantitative results which include routine test to maintain the strength of metal, structure and quality of process fluid, selection of different metal or alloy for particular application, tests to determine optimum working conditions, to minimize corrosion and tests to assess efficiency of any additive used as inhibitor.

While selecting any particular corrosion test it is worthwhile to enumerate the factors, which have important effect on the rate of corrosion. The factor associated with metal are the electrode potential of the metal, the state of aggregation presence of any strains, compositions of the metal, the over-voltage etc. Factors related to the environment include nature and concentration of the ions present, the conductivity of the solution, the nature and foreign bodies. Beside these certain factors apply on both phases are temperature, geometry of the system and the state of agitation. Thus no single corrosion test can forecast the behaviour of metal in the possible corrosive conditions.

Extensive study has been undertaken[153-159] on the corrosion tests, which determine the effect of certain additives on the corrosion rate when added to the corrosive media. Uligh[160], Ailor[161], Champion[164], Evans[162] have discussed these methods in detail. Many other workers[163-165] have also studied the methods of measuring corrosion rates of various systems and today comprehensive details are available regarding such corrosion tests.

EXPERIMENT

Mass Loss Measurements

Mass loss tests are the commonest and are practically most feasible. During these tests the metal specimen is exposed to the corroding media, either partially or wholly and reduction in mass is recorded after pre-decided intervals. While performing such tests following points should be taken into consideration to obtain reliable results.

A. Dimensions and Shape of Specimen –

Preferably a specimen should have a large ratio of surface area to mass[166], typically square or circular specimens[167] of low thickness should be used. All specimens should be cut from the center of the sheet to avoid any edge defects. The intensity of the corrosion may be influenced; hence the surface area of the specimen should precisely known the area of the specimen. Micrometers and vernier calipers may be used to obtain necessary dimensions. IT has been reported[168] that area of specimen for such test should not be less than 10 cm^2.

B. Specimen Pre-treatment-

Surface preparation is of prime importance in weight loss measurements. To achieve uniform surface, a substantial thickness of metal surface (10-20 microns) should be removed by milling and turning by use of emery papers or by means of mechanical grinding[169]. Care must be taken during such operations so that specimen does not become hot and disturb the original characteristics of metal.

All specimens should be degreased[170] after mechanical treatment. Chemical treatment should be given to remove any oxide film of any other contamination as described for different set of metals[171]. Finally the specimen should be dried in warm air and stored in any uncontaminated atmosphere.

C. Exposure to Environment –

The vessel used for total immersion tests should be of adequate dimensions so that it can accommodate the specimen along with support. Bengough and Wormawell[172] recommended that in general, corrosion vessel should not be less than 10 cm in diameter and should not contain 250 mL of corrosive media for a specimen having surface area of 15 sq.m. Regarding support to the specimen, it is recommended[173] that the specimen should be vertically suspended by using glass of nylon books so that uniform conditions prevail on both the sides.

D. Duration of Exposure-

Corrosion rates largely depend on time. It has been reported that initial rate is higher and thereafter rate decreases. In laboratory tests, duration of immension may very from vary from 24 to 120 hours for low strength corrosives and from 2 to 8 hours for highly corrosive media[175]. The time of exposure can be decided approximately, if corrosion rate is known by using following rlation[176].

$$\text{Time (in hour)} = \frac{2000}{C.R.(mpy)}$$

E. Test condition –

Corrosion rates are highly sensitive to temperature, agitation and aeration of which temperature has most profound effect.

Elevation of the temperature will normally accelerate corrosion rates upto certain limit and then decreases owing to the decrease in oxygen solubility[177]. Hackerman[174] has studied the effect of temperature on corrosion of metals in detail. For most of the corrosion tests, control of the temperature to +_ 0.5°C is often adequate which can be easily achieved by placing test vessels in thermostats.

Aeration of the corrosive media can be controlled by bubbling pure air through dispersion tubes and if de-aeration is required some inert gas like hydrogen or nitrogen should be passed. Agitation can be provided, by using mechanical or electrical stirrers otherwise, shockproof platforms should be used to provide stagnant conditions.

F. Weighing –

Prior to weighing, care must be taken to remove corrosion products from the specimen. The actual cleaning process depends upon the type of metal and deposition[178] but loosely bound products can be removed by simply washing the specimen under running water. Strongly adherent corrosion products can be removed either by tarnishing or by treating with proper chemical or solvent[179]. After cleaning the specimen it should be air-dried and its final mass be recorded to determine the mass loss.

G. Calculations –

The percentage inhibition efficiencies can be calculated using following equation[180].

$$\text{Percentage inhibition} = \frac{M_u - M_1}{M_u} \times 100 \qquad (1)$$

Where, M_u is the mass loss in uninhibited solution and M_1 is the mass loss in inhibited solution.

Corrosion rate is determined from the loss in mass as follows[180].

$$\text{CR (mpy)} = \frac{534 \times M}{A \times D \times t} \quad (2)$$

Where, M is the loss in mg, A is the area of the specimen square inches, D is the density in g/cm^3 and 't' is the time in hours.

MASS LOSS MEASUREMENTS

Mild steel specimens of composition 0.12% C, 0.32% Mn, 0.05% S, 0.02% SiO2, 0.02% W and rest Fe of size $5.0 \times 2.5 \times 0.02$ cm were used. For the complete immersion test, buffing and rubbing with emery paper to obtain mirror like finish polished all specimens. Chemical treatment was given by immersing the specimen in ammonium citrate (20%) at 75 to 80°C for about 20 minutes[181]. The specimens were finally degreased using acetone. All chemicals used were of AR grade quality and solutions were prepared in double distilled water.

The concentration of acid under sturdy was taken as 0.1N, 0.5N 1N and 2N concentration of inhibitor was varied from 1μM and 20μM. A specimen suspended by glass hook was immersed completely in each beaker containing 250 mL of the solution at 25±0.1°C. The immersion duration was ranging from 3 hours to 72 hours in different acid concentrations as shown in Table 8.1 to 8.10 visual inspection of the specimen was done and after removal of corrosion products, mass loss measurements were made.

BASIS AND SCOPE OF THE PRESENT WORK

The importance of a corrosion study lies in the fact that corrosion causes great losses to our economy and is a major threat for human safety. A survey carried out by Central Electrochemical Research Institute, Karaikudi, estimated the annual cost of corrosion in India at Rs. 1500 million. According to recent estimates by the Batellite Institute, corrosion costs the U.S.A. almost $300 billion per year. This loss to the US economy is more then the entire cost of floods and fires in the U.S.A. in fact 40% of the country steel production goes to replace corroded parts and products. The government committee on corrosion on U.K. estimates that the total loss to the national economy was a staggering $1365 million which was about 3.5% of GNP. According to another estimates, the money spend in controlling corrosion comes to the order of Rs. 150 corers in India, Rs. 400 corers in U.K., Rs. 250 corers in Australia and Rs. 1250 corers in U.S.A. each year. The loss to economy due to corrosion in some countries is depecited. In fact in India corrosion problem is more serious than in the colder countries due to its tropical climate. The corrosion Advisory Bureau of Metal Research Committee C.S.I.R. is involved in assessing the loss due to corrosion and suggesting various preventive measures to combat corrosion.

Thus the importance of corrosion studies is three fold. The first is economic including the objective of reducing material losses resulting from the corrosion. The second area is improved safety of operating equipment which through corrosion may fail with catastrophic consequences. Third is conservation, applied primarily to metal resources of the world’s supply of these is limited and their wastage includes corresponding losses of energy and water reserves associated with the production and fabrication of metal and their structures.

The inhibitors evaluated in the present study offers excellent inhibition for industrially important metals like mild steel. The versatility of these inhibitors lies in the fact that these compounds effectively reduces the corrosion rates to a large extent for all the three metals in highly corrosive environments of sulfuric acid, nitric acid and hydrochloric acid even at concentration of 4.0 N. Thus these inhibitors can be further explored for their commercial applicability in various protective coatings as they are effective even at very low concentration of 5 mM.

Table 8.1: The Weight loss (gm) percentage inhibition efficiency of Iron in 0.1N HCl on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	**Mass Loss (gm)**	**% Inhibition efficiency**	**Corrosion Rate (mpy)**
Blank of uninhibited	0.0126		252.195
Inhibitor I (SB_I)			
0.2%	0.0019	84.92%	38.029
0.4%	0.0017	86.51%	34.026
0.8%	0.0009	92.86%	18.016
Blank of uninhibited	0.0126		252.195
Inhibitor II (SB_{II})			
0.2%	0.0016	87.30%	32.532
0.4%	0.0014	88.88%	28.466
0.8%	0.0012	90.48%	24.402

Table 8.2: The Weight loss (gm) percentage inhibition efficiency of Iron in 0.5N HCl on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0152		306.952
Inhibitor I (SB_I)			
0.2%	0.0025	83.55%	50.486
0.4%	0.0020	87.50%	40.389
0.8%	0.0014	90.79%	28.272
Blank of uninhibited	0.0152		306.952
Inhibitor II (SB_{II})			
0.2%	0.0033	78.29%	66.641
0.4%	0.0029	80.92%	58.563
0.8%	0.0023	84.86%	46.447

Table 8.3: The Weight loss (gm) percentage inhibition efficiency of Iron in 1N HCl on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0202		407.923
Inhibitor I (SB_I)			
0.2%	0.0053	73.76%	107.029
0.4%	0.0034	83.17%	68.660
0.8%	0.0023	88.61%	46.447
Blank of uninhibited	0.0202		407.923
Inhibitor II (SB_{II})			
0.2%	0.0018	91.09%	36.350
0.4%	0.0016	92.08%	32.311
0.8%	0.014	93.06%	28.272

Table 8.4: The Weight loss (gm) percentage inhibition efficiency of Iron in 2N HCl on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	**Mass Loss (gm)**	**% Inhibition efficiency**	**Corrosion Rate (mpy)**
Blank of uninhibited	0.0457		922.876
Inhibitor I (SB_I)			
0.2%	0.0069	84.90%	139.340
0.4%	0.0055	87.96%	111.068
0.8%	0.0047	89.72%	94.913
Blank of uninhibited	0.0457		922.876
Inhibitor II (SB_{II})			
0.2%	0.0036	92.12%	72.700
0.4%	0.0034	92.56%	68.667
0.8%	0.0032	93.00%	64.625

Table 8.5: The Weight loss (gm) percentage inhibition efficiency of Iron in 3N HCl on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	**Mass Loss (gm)**	**% Inhibition efficiency**	**Corrosion Rate (mpy)**
Blank of uninhibited	0.0590		1191.459
Inhibitor I (SB_I)			
0.2%	0.0057	90.34%	115.107
0.4%	0.0044	92.54%	88.855
0.8%	0.0033	94.40%	66.641
Blank of uninhibited	0.0590		1191.459
Inhibitor II (SB_{II})			
0.2%	0.0095	83.90%	191.845
0.4%	0.0088	85.08%	177.709
0.8%	0.0075	87.29%	151.457

Table 8.6: The Weight loss (gm) percentage inhibition efficiency of Iron in 4N HCl on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0777		1569.091
Inhibitor I (SB_I)			
0.2%	0.0052	93.31%	105.010
0.4%	0.0044	94.34%	88.855
0.8%	0.0032	95.88%	64.622
Blank of uninhibited	0.0777		1569.091
Inhibitor II (SB_{II})			
0.2%	0.0140	81.98%	282.719
0.4%	0.0125	83.91%	252.428
0.8%	0.0108	86.10%	218.098

Table 8.7: The Weight loss (gm) percentage inhibition efficiency of Iron in 1N H_2SO_4 on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0410		827.963
Inhibitor I (SB_I)			
0.2%	0.0036	91.22%	72.699
0.4%	0.0019	95.37%	38.369
0.8%	0.0014	96.59%	28.272
Blank of uninhibited	0.0410		827.963
Inhibitor II (SB_{II})			
0.2%	0.0039	90.19%	78.757
0.4%	0.0024	94.14%	48.466
0.8%	0.0020	95.12%	40.388

Table 8.8: The Weight loss (gm) percentage inhibition efficiency of Iron in 2N H_2SO_4 on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0412		832.002
Inhibitor I (SB_I)			
0.2%	0.0019	95.39%	38.369
0.4%	0.0017	95.87%	34.330
0.8%	0.0014	96.60%	28.272
Blank of uninhibited	0.0412		832.002
Inhibitor II (SB_{II})			
0.2%	0.0023	94.42%	46.447
0.4%	0.0021	95.90%	42.408
0.8%	0.0019	96.39%	38.369

Table 8.9: The Weight loss (gm) percentage inhibition efficiency of Iron in 3N H_2SO_4 on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0424		856.235
Inhibitor I (SB_I)			
0.2%	0.0020	95.28%	40.388
0.4%	0.0018	95.75%	36.350
0.8%	0.0017	95.99%	34.330
Blank of uninhibited	0.0424		856.235
Inhibitor II (SB_{II})			
0.2%	0.0027	93.63%	54.524
0.4%	0.0022	94.81%	44.427
0.8%	0.0018	95.57%	36.350

Table 8.10: The Weight loss (gm) percentage inhibition efficiency of Iron in 4N H_2SO_4 on different concentration of inhibitors

Temperature = 25 ± 0.1°C

Inhibitor and Concentration	Mass Loss (gm)	% Inhibition efficiency	Corrosion Rate (mpy)
Blank of uninhibited	0.0495		999.614
Inhibitor I (SB_I)			
0.2%	0.0031	93.74%	62.602
0.4%	0.0026	94.75%	52.505
0.8%	0.0021	95.76%	42.408
Blank of uninhibited	0.0495		999.614
Inhibitor II (SB_{II})			
0.2%	0.0037	92.52%	74.719
0.4%	0.0035	92.92%	70.680
0.8%	0.0033	93.33%	66.641

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