CHAPTER - V

SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH 5-NITROSALICYLALDEHYDE THIOSEMICARRBAZONE

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Introduction :

The element iron is known from ancient times. Due to its abundance in nature, it ranks forth most element in the earth's crust. To a very small extent iron occurs in metallic state which is meteoric in origin. It is malleable, ductile, tough, silvery gray, and magnetic metal. Iron is the important constituent of red haemoglobin of blood. It is perhaps the most useful of all the metals. The iron pillar at Kutubminar near Delhi was erected at the beginning of the Christan era. Now a-days iron is used on large scale in the manufacture of structural steel, magnets, and dyes (e.g. inks, blue print paper and rough pigments). The variety of iron alloys are known and widely used. Many of the iron alloys have valuable properties and have industrial uses. The iron alloys find applications as magnetic alloy, electrical and heat corrosion resistance alloys and thermal expansion alloys etc.

The element iron is the 6th element of the first transition series. It belongs to VIII group of the periodic table. It occurs in two states as ferrous and ferric iron respectively.

Numerous reagents were reported in the literature for the determination of iron but few of them are well suited for the determination of traces of iron. Some reagents react with ferric iron and other with ferrous iron. Among those reagents which have been reported, the thiocyanate method is the most frequently employed reagent for the spectrophotometric determination of small amounts of iron.

But in this method the intensity of the colour in the iron thiocyanate solution depends upon various factors such as excess of thiocyanate, a kind of acid used and standing time. The spectrophotometric studies of iron with the reagent 1,10 phenanthroline[2-3], and its derivatives[4-7], have been also reported. However, the method is less sensitive and metal ions like W, Ni, Co, Cu, etc. show strong interference during the determination of iron.

Among the various reagents that have been proposed for the photometric determination of iron, the most recent are some derivatives of phenols and napthols[8], azoderivative of antipyrine, 2,6 pyridine diol[9], disodium 3-(2-pyridyl)-1, 2,4-triazine-5, 6-di(4'-phenyl sulphonate[10]), azoderivative of antipyrine[11], 2,4,6-tri(2'-pyridyl)-1,3,5 triazine[12], cacotheline[13], which is the nitrate derivative of bisdimethyl mono nitrobrucine hydrate. Besides these reagents, some of the promising analytical reagents investigated include 2-furylmethanethiol, 3-(2-furyl)-2-mercapto propenoic acid and 3,4,5,6-tetrahydro-2-mercapto-pyrimidine[14], hydrazinium hydrazine carbodithioate[15], di-2-pyridyl ketone thiosemicarbazone[16] 2-amino-5-nitro sopyrimidine 4,6 diol[17], 4 phenyl-3-TSC of biacetyl monomixe[18].

However these methods suffer from many disadvantages, e.g. with 2, 6-pyridine diol, heating for 30 min. is required and the complex dissociates within 20 minnutes while in case of 2,4,6-tri (2'-pyridyl)-1,3,5 triazine, the violet complex of iron is stable only for one hour. Besides many metal ions associated with iron interference seriously in the determination of iron.

Many reagents have been reported for photometric determination of iron in the literature. Some of those include Oximes:2-hydroxy-Hethoxy acetophenone oxime [19], 2-hydroxy-1-napthaldoxime [20], and 2,6 diacetyl pyride dioxime[21], Organic acids:thioglycolic acid [22], tannic acid[23], pyrazine-2-3 di-carboxylic acid [24], 1-(2-carboxy-5-sulphanatophenyl)-3-hydroxy-3-phenyltriazen [2-(3-hydroxy-3-phenyltriazen)-4-sulphobenzoic acid][25], N-m-sulphophenyl benzo hydroxamic acid [26], Ketones: For example thenoyltrifluoroacetone [27], 2,2'-dipyridyl-ketone amino ethylimine [28], naphthoxyacetyl-acetophenone [29], Thiosemicarbazones: di-2-pyridyl ketone thiosemicarbazone [30], 4-phenyl-3-thiosemicarbazone [18], 3-methoxy TSC [31], picolinaldehyde 4-phenyl 3-thiosemicarbazone[32]. . Coumarines 6,7-dihydroxy-4-methylcoumarin [33], substituted pyrimidines: 2-furylmethanethiol, 3-(2-furyl)-2-mercaptopropenoic acid and 3,4,5,6-trihydro-2-mercaptopyrimidine[14], 4-amino-5-nitroso-pyrimidine-2, 6-diol, 1,2,3,4-tetrahydro-6-hydroxy-5-nitroso-pyrimidine 2,5-dione[35], Substituted Phenols : 4-(4,5-dimethyl-2 thiazolylazo)-2-methyl-resorcinol [36], 4(4-methyl-2-thiazolylazo resorcinol[37], Hydrazones: 2,2'-dipyridyl [di-(2-pyridyl) Ketone]. 2-pyridylhydrazone[38]. These methods however, suffer from either low sensitivity or interference of many metal ions associated with iron e.g. in the photometric determination of iron. Cu and Zr(IV) interfere by forming precipitate with the reagent 2-hydroxy-1-naphaldoxime or low stability of the complex.

However, the proposed method for determination of iron is free from disadvantages mentioned above. The proposed reagents 5-NO_2 SAT reacts with iron in acidic medium to form green coloured complex which is stable for more than two days. The complex is measured at 560 nm, against reagent as a blank. Thus the present method, besides being highly sensitive, is very simple to carry out as no extraction and no multiplicity of solvents are required.

EXPERIMENTAL

Preparation of Standard Ion Solution :

A standard solution of iron(III) (1 mg|ml) was prepared by dissolving 2.156 gm of ferric ammonium sulphate (AR) in 250 ml of distilled water containing a few drops of concentrated sulphuric acid. The solution was standardised by the method described in Vogel. A 25 ml of the stock solution of iron is pipetted in a 250 ml conical flask and is made 5-6 N with respect to HCl. The solution is heated to 70-90^{o} C.

It is then reduceed by adding concentrated Stannous chloride solution dropwise from burette, with stirring until the yellow colour of the solution has disappeared. The solution is then rapidly cooled under the tap water to about 25°C. The slight excess of stannous chloride present is removed by adding saturated solution of mercuric chloride rapidly in one portion and with through mixing. A slight silky white precipitate of mercurous chloride should be obtained. If a heavy precipitate forms or grey or black precipitate is obtained, too much stannous chloride has been used. In this case it is better to discard the solution. The solution is diluted to 200 ml with 2.5% sulphuric acid. A 5 ml of syrupy phosphoric acid and 0.3 to 0.4 ml diphenylamine sulphonate indicator are added. The whole solution is titrated slowly and with constant stirring against standard 0.025 N potassium dichromate solution to the first permanent violet blue colouration. The determination is repeated with two other similar quantities of the stock solution. The stock solution was found to contain 1.02 mg of iron per ml.

The working solutions containing 10, 15, 20, 30, 40, ug/ml of iron(II) was prepared by dilution of the stock solution. Ferric iron is reduced to ferrous state by adding a few drops of saturated ascorbic acid solution.

Reagent Solution :

A 0.240 gm of the reagent 5-nitrosalicylaldehyde thiosemicarbazone was dissolved in 100 ml freshly purified and distilled dioxane to obtain 0.01 M reagent solution. The solution is quite stable towards light and heat. It is easily soluble in dioxane and can be kept over a week period. All solutions used in study of diverse ions were prepared from A.R. grade chemicals.

Apparatus :

A Carl-Zeiss (JENA) spectrophotometer (Spekol) equipped with 1 cm quartz cells was used for all the absorbance measurements.

Recommended procedure :

To an aliquot of sample solution containing upto 600 μg (24 ppm) of iron(II) solution, 3 ml of 1 x 10^{-2} m reagent solution in dioxane were added. The mixture was adjusted to 0.15 M with respect to HCl by rapid addition of HCl. The flask was briskly shaken and was made to 25 ml with distilled alcohol. The absorbance of the green complex was measured at 560 nm against reagent as a blank. The amount of iron(II) was calculated from the calibration curve.

RESULTS AND DISCUSSION

Spectral Characteristicis :

The absorption spectrum of Fe(II) 5-nitrosalicylaldehyde thiosemicarbazone complex using 24 ppm of iron(II) solution and 0.01 M reagent in dioxane is shown in Fig. 1. The solution of 5-nitrosalicylaldehyde thiosemicarbazone in

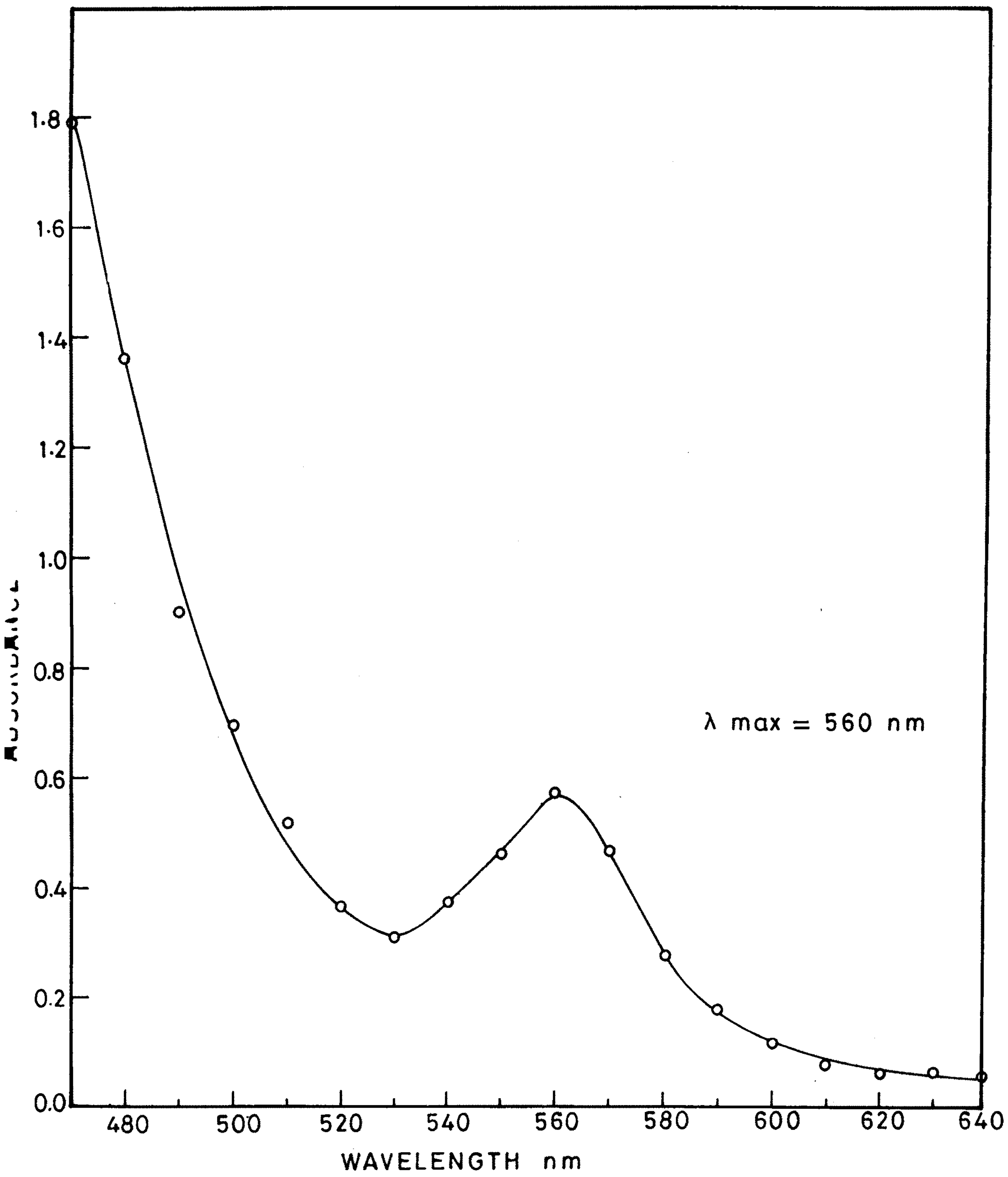


FIG. 1 - ABSORPTION SPECTRA OF 5-NITRO SAT Fe(II) COMPLEX.
Fe (II) — 24 ppm

dioxane is yellowish in colour and does not absorb significantly at 560 nm. Therefore all the absorption measurements reagent is used as blank. The absorption measurements were made in the region 450-700 nm. The Fe(II) 5-nitro SAT complex exhibits the absorption maxima at 560 nm. The molar extinction coefficient as determined from Beer's law plot 2267 L $mole^{-1}$ cm^{-1} and the Sandell's sensitivity was 24 $ng|cm^{-2}$ at 560 nm.

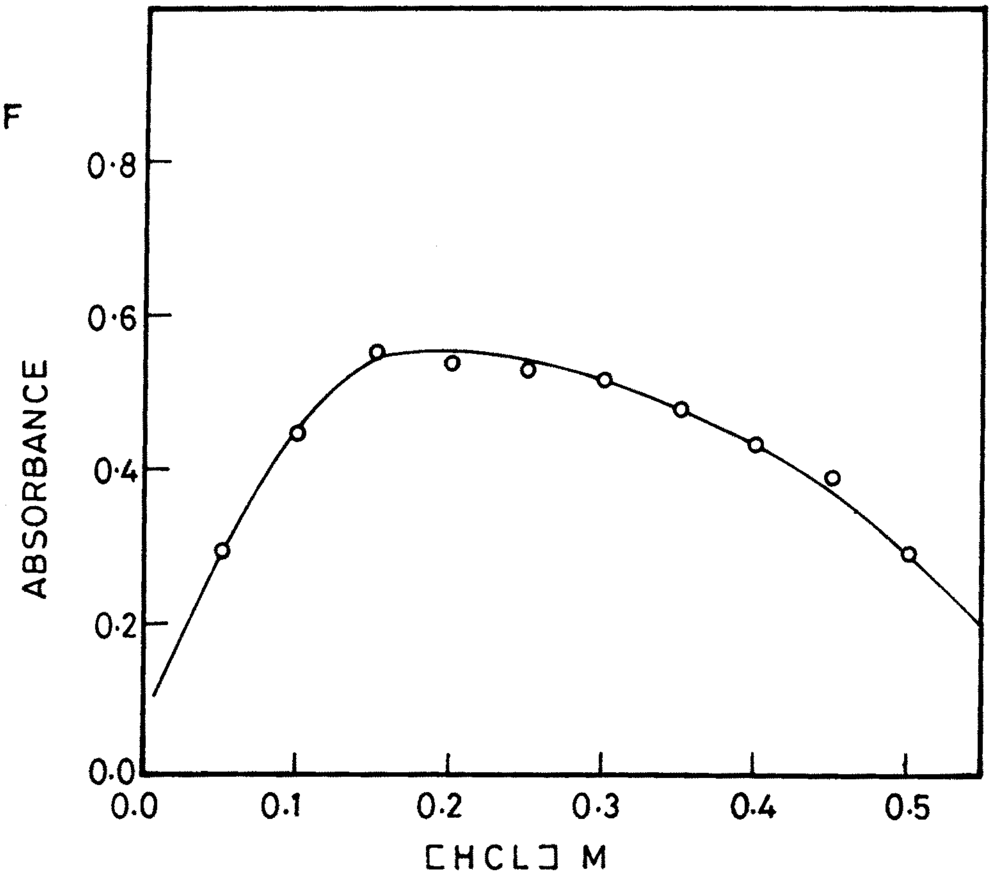
Effect of Acidity :

In order to find out the optimum concentration of hydrochloric acid required for the full colour development of Iron(II) complex as a means of acidification, hydrochloric acid was varied in the range of 0.1M to 1M. The curve in the Fig. 2 indicates that the absorbance of the complex at 560 nm, containing 24 ppm of Iron(II) and 1 x 10^{-2} M reagent was found maximum and constant between 0.15 M HCl. In addition, sulphuric acid, perchloric acid, nitric acid were also tested as a means of acidification with perchloric acid and nitric acid the absorbance decrease rapidly, hence must not be employed. However with sulphuric acid optimum concentration range was found to be same as with HCl. Hence 0.15 M HCl has been recommended as the means of acidification for further studies.

Effect of Reagent Concentration :

Solutions containing the same amount of Iron(II) (24 ppm) and different amounts of the reagent from 0.5 to 8 ml of 1 x 10^{-2} M reagent solution were prepared. The colour

FIG. 2
EFFECT OF
ACIDITY



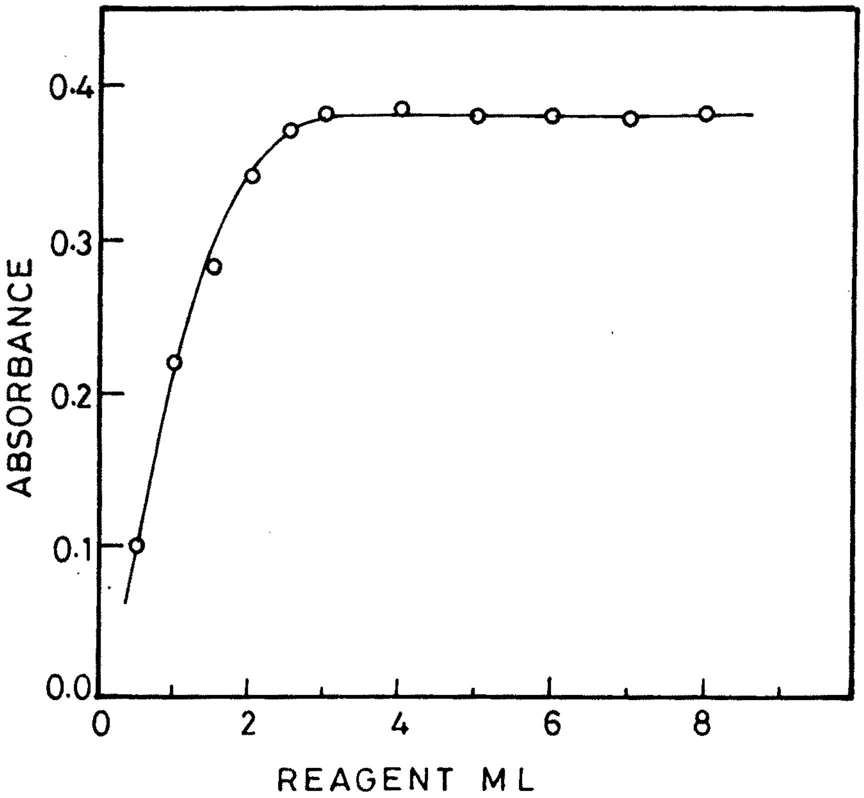


FIG. 3
EFFECT OF REAGENT
CONCENTRATION
Fe(II) 5-NO_2 SAT
COMPLEX.

was developed as outlined in the general procedure and the absorbance of the complex was measured at 560 nm. The results of studies as shown in fig. 3 indicates that 24 ppm of iron(II) required minimum of 1 ml reagent. At this concentration, the metal to reagent ratio in terms of moles is 1:5. However, 3 ml of 0.01M (15 fold molar excess) reagent was employed for further studies to ensure maximum colour intensity of Iron complex. At higher reagent concentration there was insignificant decrease in absorption.

Effect of Alcohol :

In order to find out the amount of alcohol needed during the complexation of Fe(II) -5nitrosalicylaldehyde thiosemicarbazone complex. The amount of alcohol was varied between 30% to 76%. It was found from the curve that the amount of alcohol required for full colour development of Fe(II) complex is in the range 76 to 70% (Fig. 5). At less than 30% alcohol precipitation occurs where as decrease in absorbance occured at greater than 76% alcohol. Hence for all the subsequent measurements 70% alcohol was recommended.

Effect of Dioxane Concentration :

To study the effect of dioxane concentration a series of solutions were prepared containing fixed amount of Fe(II), (24 ppm) and different amounts of the dioxane, varying from 0.5 to 5 ml of dioxane. The colour of Fe(II) complex was

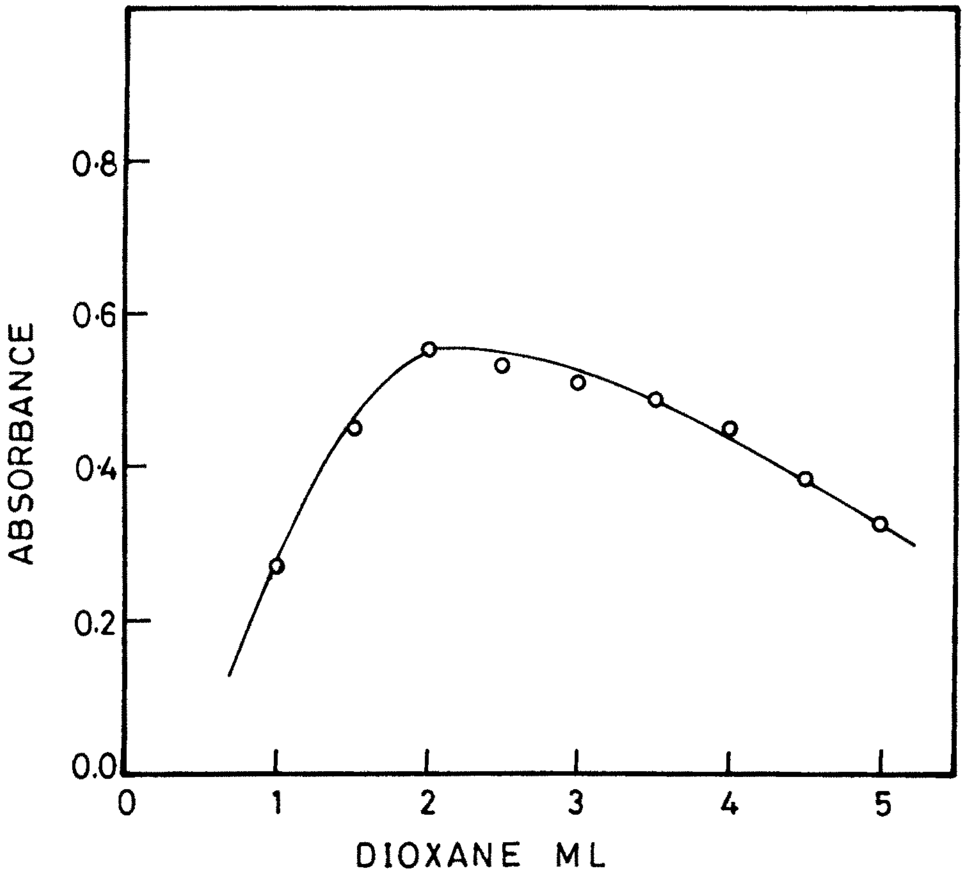
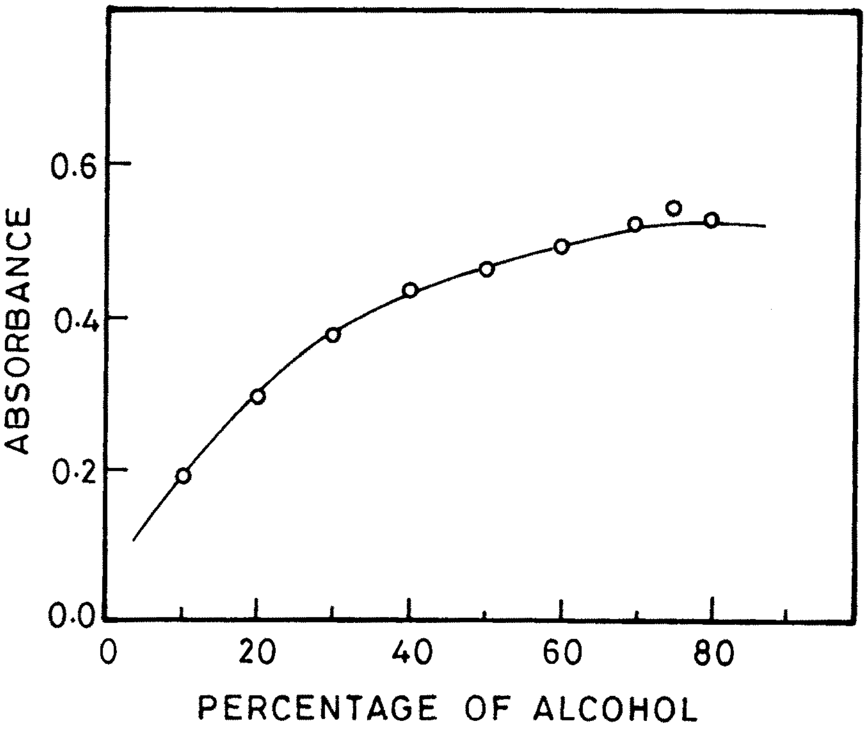


FIG. 4
EFFECT OF
DIOXANE
CONCENTRATION.

FIG. 5
EFFECT OF
PERCENTAGE
COMPOSITION OF
ALCOHOL.



developed as per the general procedure and absorbance was measured at 560 nm against reagent as a blank. The results of studies are shown in fig. 4 which indicate that 2 ml of dioxane is sufficient for full colour development. But for all subsequent measurements 3 ml of dioxane solution was used.

Effect of Ascorbic Acid Concentration :

The working solutions containing 10, 20, 30 µg/ml of iron(II) was prepared by dilution of stock solution. It is then reduced from ferric to ferrous state by adding a few drops of saturated ascorbic acid solution.

Just a few drops of ascorbic acid is sufficient to keep iron in ferrous state. When excess of ascorbic acid is added it effects colouring of the complex.

Validity of Beer's Law :

For the study of the validity of Beer's Law, the solutions containing different amounts of iron upto 50 ppm and the fixed amount of reagent (0.01M) were used. The colour of the complex was deveoped by following the recommended procedure. The absorption measurement of each solutions was made at 560 nm against reagent as a blank. The absorbance of the green complex of iron was plotted versus ppm of iron taken. (Fig. 6) From Fig. 6 it was found that the Beer's law is valid upto 40 ppm of iron.

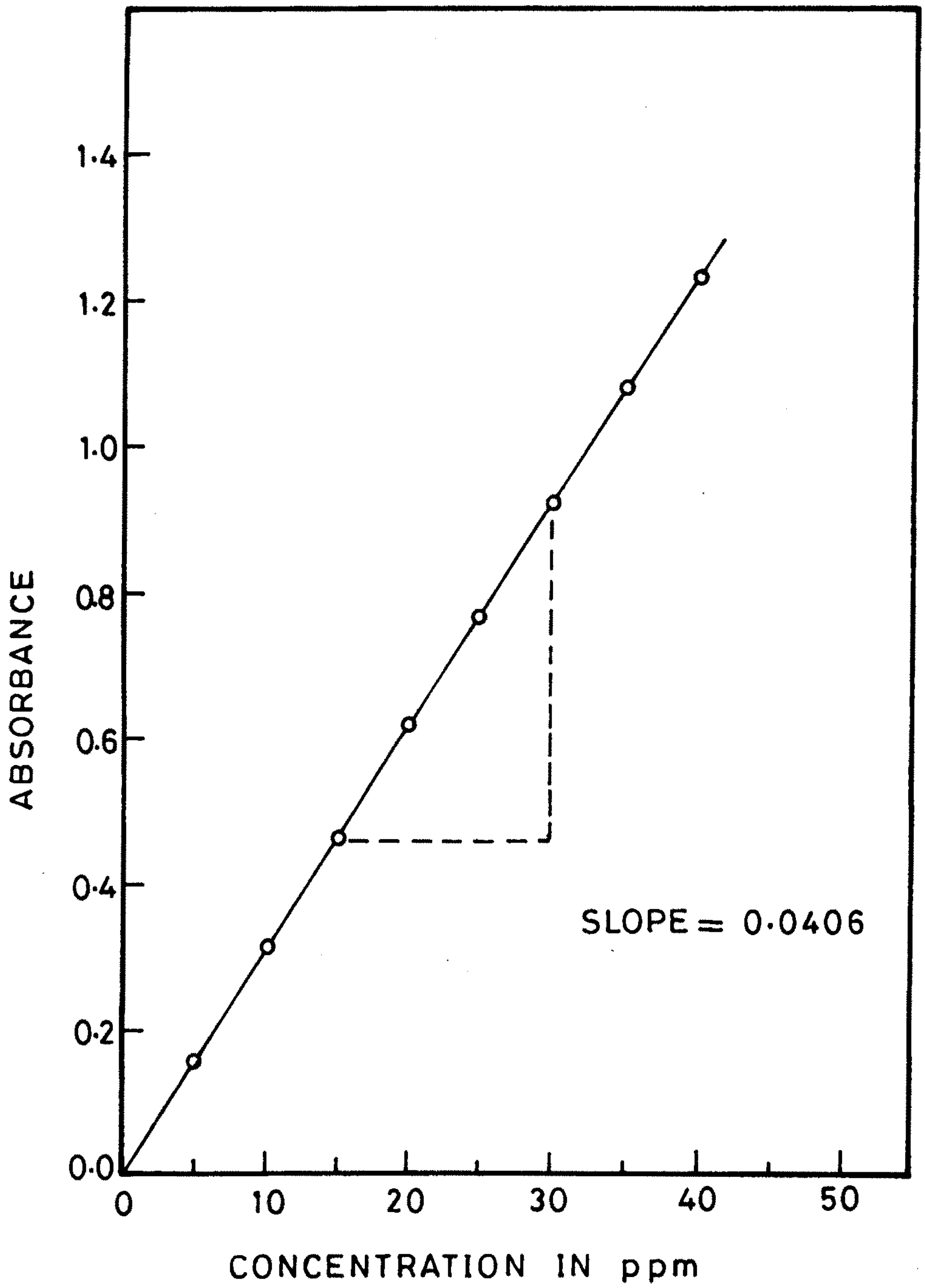


FIG. 6 - VALIDITY OF BEERS LAW FOR IRON (II) COMPLEX.

Composition of the complex :

In order to establish the composition of the complex, the equimolar solutions of metal and ligand (1.785 x 10^{-3} M) were used. The Job's and mole ratio method were used for determining the composition of the complex. A series of solutions were prepared in which mole fraction of reagent varied from 1 ml to 9 ml. Acidity of solution was adjusted to 0.15M with HCl and the colour of the complex was developed as per recommended procedure and the absorbances of the solutions were measured at 560 nm against reagent as a blank. The plot of absorbance versus the mole fraction of the ligand indicates that the Iron(II) forms 1:3 complex with the ligand 5-nitrosalicylaldehyde thiosemicarbazone Fig. 7.

The composition of the complex was verified by mole ratio method. For this method equimolar solutions at metal and ligand were used (1.785 x 10^{-3}). A series of solutions containing fixed volume of reagent and different amounts of iron were prepared. The 0.15M acidity was maintained by adding hydrochloric acid and the colour of the complex was developed as per the recommended procedure. The absorbance of solutions were measured at 560 nm against reagent as a blank. The plot of absorbance versus the reagent to metal ratio (Fig. 8) confirms the results obtained by application of Job's method.

Reproducibility, Accuracy and Sensitivity data :

For the study of reproducibility and accuracy

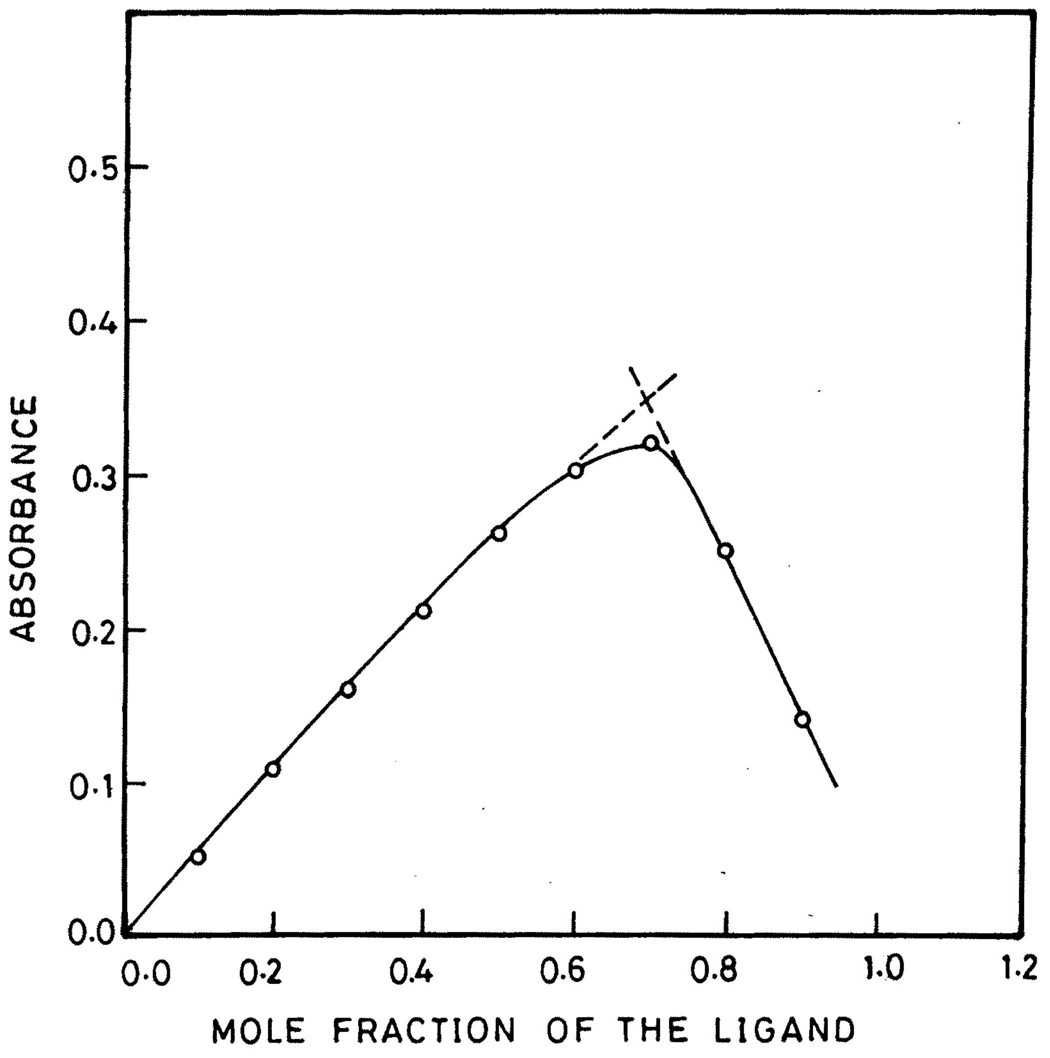


FIG. 7 – JOB'S PLOT.

$[M] = (1{\cdot}785 \times 10^{-3}$ M)

$[L] = (1{\cdot}785 \times 10^{-3}$)M

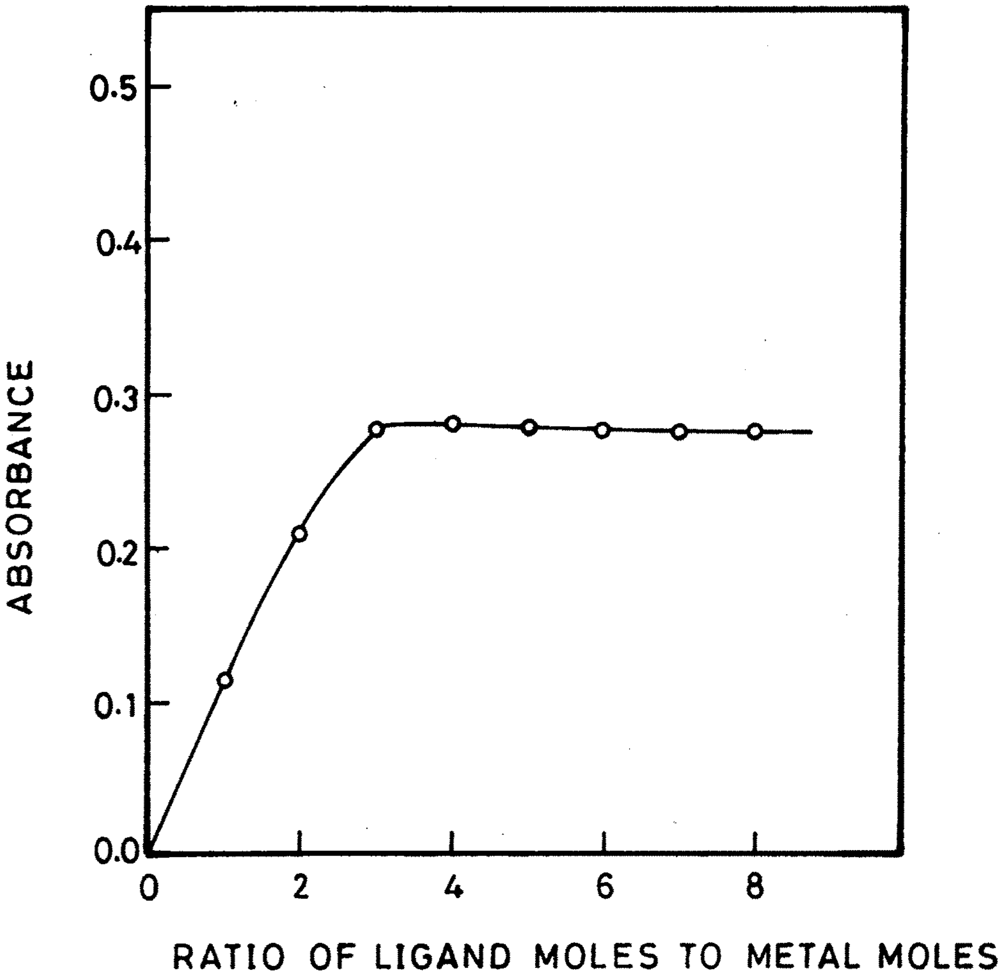


FIG. 8- MOLE RATIO PLOT FOR IRON(II) COMPLEX.
$[M] = [L] = 1{\cdot}785 \times 10^{-3}$ M

of the method, absorbance measurements with ten different identical solutions containing 24 ppm of Fe(II) were performed as outlined in the procedure and concentration determined using calibration curve. The results are shown in table No. 1.It is observed that there is an excellent agreement in the experimental valves. The method has high precision and accuracy.

Average of the ten readings are calculated. Deviation from these average readings was found out in each case and then standard deviation was calculated. From the standard deviation, reproducibility of the results with 95% confidence limit was calculated. The sandell sensitivity of the reaction as calculated from Beer's plot was found to be 24.0 $ng|cm^{-2}$.

Table No. 1 : Precision and Accuracy of the Method :

Amount of Fe(II) taken = 24 ppm

λ max = 560 nm

Concentration of reagent taken = 1 x 10 M

Acidity = 0.15M HCl

Sr. No.	Absorbance observed	ppm of Fe(II) found (X)	$X - \bar{X}$	$(X - \bar{X})^2$
1	.556	24.0	0.01	0.0001
2	.556	24.0	0.01	0.0001
3	.550	23.9	0.11	0.0121
4	.560	24.1	0.09	0.0081
5	.556	24.0	0.01	0.0001
6	.560	24.1	0.09	0.0081
7	.556	24.0	0.01	0.0001
8	.560	24.1	0.09	0.0081
9	.550	23.9	0.11	0.0121
10	.556	24.0	0.10	0.0001
	Total	240.1		0.0490

$$\text{Average value } (\bar{X}) = \frac{240.1}{10}$$

$$= 24.01$$

Standard deviation (δ)

$$\delta = \sqrt{\frac{(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \text{------} (X_n - \bar{X})^2}{(n - 1)}}$$

$$= \sqrt{\frac{0.0490}{10 - 1}}$$

$$= \sqrt{\frac{0.0490}{9}}$$

$$\delta = 0.073786$$

Error (E)

Error (E) = Observed reading - Actual reading

E = O - A

= 24.01 - 24.0

= 0.01

Relative error

Percent (Accuracy)

$$= \frac{.01 \times 100}{24.0}$$

$$= 0.0416$$

Percentage coefficient of varivation :

$$\% \text{ C.V.} = \frac{\delta \times 100}{\bar{X}}$$

$$= \frac{.073786 \times 100}{24.01}$$

$$= 0.32736$$

Reproducibility with 95% percent confidence limit :

$$= \bar{X} \pm 2.26 \times \frac{\delta}{\overline{n}}$$

$$= 24.01 \pm 2.26 \times \frac{0.073786}{\sqrt{10}}$$

$$= 24.01 \pm 2.26 \times \frac{0.073786}{3.1622}$$

$$= 24.01 \pm 2.26 \times 0.23337$$

$$= 24.01 \pm 0.053733$$

Molar Extinction coefficient :

$$\varepsilon = \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{Atomic Weight}$$

$$= \text{Slope} \times 1000 \times \text{Atomic Weight}$$

$$= 0.0406 \times 1000 \times 55.847$$

$$= 2267.38 \text{ L Mole}^{-1} \text{ cm}^{-1}$$

$$\varepsilon = 2267.38 \text{ L Mole}^{-1} \text{cm}^{-1}$$

Sandell's Sensitivity (S) :

$$S = 10^3 \times \text{Atomic Weight} \times \text{Cmin}$$

$$\text{Where Cmin} = \frac{\text{Dmin}}{\varepsilon \times b}$$

$$= 10^3 \times 55.847 \times \frac{.001}{2.267 \times 1 \times 10^3}$$

$$= 10^3 \times 55.847 \times 0.004411$$

$$= 0.024 \ \mu g | cm^{-2}$$

$$= 24 \ ng | cm^{-2}$$

Effect of Diverse Ions :

The effect of diverse ions on the determination of 400 μg of Fe(II) with the reagent 5-nitrosalicylaldehyde thiosemicarbazone was investigated by following the recommended procedure. Initially foreign ion was added to the iron(II) solution in large excess fold for cations and 500 fold for anions. The tests were repeated with successively smaller amount of foreign ion when the interference of ion was intensive. An error of less than 2% in the absorbance of the complex at 560 nm was considered to be tolerable. In table No.2 the tolerance limits of various ions has been shown. These results show that relatively large amount of anions except EDTA, nitrite, citrate and tartrate could be tolerated in the determination of 400 μg of Fe(II).

Table No. 2 : Effect of Diverse Ions

Fe(II) = 40 μg

5-Nitro SAT = 0.01M in dioxane

Acidity = 0.15M HCl

λ max = 560 nm

FOREIGN ION	TOLERANCE LIMIT IN μg
Zr(II)	12000
Cr(III)	15000
Zn(II)	14000
Cd(II)	300
V(V)	3000
Ba(II)	20000
Sn(II)	4000
W(VI)	5000
Mn(VII)	1000
K(I)	5000
Mn(II)	3000
Pd(II)	1000
Ca(II)	20000
Se(II)	500
Ru(III)	none
Mo(VI)	5000
Cu(II)	none
Ni(II)	400

FOREIGN ION	TOLERANCE LIMIT IN µg
Pb(II)	none
Au(III)	200
Ag(I)	500
Ti(IV)	none
Os(VIII)	10000
Pt(IV)	none
Bi(III)	100
U(VI)	1000
Hg(II)	50
Tl(I)	500
Tortrate	2500
Po_4^{3-}	none
SCN	2500
Salicylate	1000
EDTA	none
$S_2O_3^{2-}$	2500
Thiourea	5000
F^-	1000
CN^-	none
Citrate	none

-: REFERENCES :-

1. Hacker, W., Zimmermann, A. and Rechmann, H. Anal. Chem., 1949, 104, 192.
2. Rao, V.P., Rao, K.V., and Sharma, B., Talanta, 1969, 16, 277.
3. Rao, V.P., and Sarma, B., Mikrochim. Acta, 1970, 4, 283.
4. UNY, G.; Mathieu, C. Tardif, J.P. and Dauk T.V., Anal. Chim. Acta, 1971, 53, 109.
5. Marezenko Z., Kasiura, K. and Mojski, M.; Chem.Anal. (Warsaw), 1971, 16, 203.
6. Kojne A.Z., Gesamte Inn. Med. Ihre, Grenzgeb, 1970, 25, 125.
7. Pustovar, P.V.A., Zh. Anal. Khim, 1979, 34, 511.
8. Toei, Kyoji, Motomizu, Shoji and Korenaga, Analyst, 1975, 100, 629.
9. Smaglyuk, N.G.; Talipov, Sh.T., Pivnenka, Z.A., Dzhiyanbaeva, R. Kh. and Khodzhaev, A.A., Zh. Analit. Khim., 1975, 30(9) 1680-1688.
10. Bansal, S.K., Suman Shrey, S.T.; and Sindhu, R.S., J.Indian Chem., Soc., 1989, 66, 917.
11. ZhouNan, Gu.,, Yuan-Xiang, Yao Xuzhang and Zhi-Ren; Talanta, 1989, 36(8), 855.
12. Krishnamurti G.S.R. and Huang P.M. Talanta, 1989, 37(7), 745.

13. Sarkar A., Paria P.K. and Majumdar S.K. J. Indian Chem., Soc., 1989 66, 428.

14. Izquiero, A. and Calmet J., Quim. Analit. Fac. Univ. Barcelona, Spain [A.A.1975, Vol. 28].

15. Byrko V.M., Busev, A.I., Tikhonova T.T., Baibakova N.V. and Shepel L.I., Zh. analit. Khim., 1975, 30(10), 1985.

16. Martinez M.P., Valcarcel, M. and Pino Perez, F., Analytica Chim. Acta, 1976, 81(1), 157.

17. Kundra S.K., Katyal, Mohan and Singh. R.P.,Sci., 1975, 44(5), 81.

18. Cano Pavon, J.M., Jimenez Sanchez, J.C. and Pino Perez F., Analytica Chim. 1975, 75(2), 335.

19. Desai, K.K., Mody M.F., Naik, N.B.; J.Inst. Chem. (India), 1983, 55(5), 175.

20. Santhalakshmi, K.S., Naidu, R.R. and Krishna, V.R., J. India, Chem. Soc., 1985, 62, 79.

21. Kato, Takeshi and Sasahara, Talsuya; Bunseki Kagaku, 1979, 28, 73.

22. Nemori, Akira, Sasaki, Hideyuki, Koro, Takatoshi, Bunseki Kagaku, 1983, 32(11), 706.

23. Chaudhary M.A., Javed, M. and Riaz, Ur-Rehman, Pakist., J. Scient. Ind. Res., 1973, 16(5), 172.

24. Sanyal, G.S. and Mookheria, S., Z. analty. Chem. 1975, 276(1) 71.

25. Chakraborti D., Analytica. Chim. Aca., 1974, 70(1), 207.

26. Mujumdar, A.K., Chakrbarthy, A.K. and Panigrahi S.K.; J.Ind. Chem. Soc., 1976, 53, 544.

27. Satake, M. and Shimizu, M.; Fukui Daigeku Kogakubu Kenkyh Hokoku, 1977, 25, 147.

28. Kato, Takeshi, Kano, Kiyoshi, Saski, Hiroaki, Bunseki Kagaka, 1987, 32(11), 659.

29. Deshmukh, M.B. Ambhore, D.P. and Joshi, A.P., J. Indian Chem. Soc., 1985, 62, 313.

30. Martinez, M.P., Valearcel, M. and Pino Perez F., Analytica Chim. Acta. 1976, 81(1), 157.

31. Goel, D.P., Gupta, S.N. and Banerjee, N.R. J.Indian Chem.Soc., 65, 607.

32. Jomey Ariza, J.L. Cano Pavon, J.M., and Pino Perez F., Afinidad, 1977, 34, 363.

33. Finkelsteinaite, M., Strechkite, G., and Panina.; Zh.V. Nauch Trudy Vyssh, Ucheb., Zaved, Lit., SSR, Khim Tekhnol, 1973 (15), 49; Refert, Zh., Khim, 19, GD, 1974, (3) Abstr. No. 3G 86.

34. Singh A.K., Katyal, M., Trikh, K.C. and Singh, R.P. J. Indian Chem. Soc., 1975, 52(9), 891.

35. Tsuchiya, Masaomi and Saski, Hirooki; Bunseki Kagaka, 1975, 24(14), 691.

36. Sanchez-Pedreno, C., Gareia Montelongo, F., Gonzatez Diaz, V., Depto Quim, 1975, 75(1), 79.

37. Weda, Kazumasa, Yoshimura, Osmamu, Yamamoto, Yoshikazu; analyst, 1983, 108, (1294), 1240.

38. Singh, R.B., Odashima, Tsugikatsu, Ishji, Hajime; Analyst, 1983, 108 (1290), 1120.

39. Alexaki Tzivanidou, H., Analytica Chim. Acta, 1975, 95(1), 231.

40. Xu, Qiheng, Hauxue Shiji, 1982, 4(4), 214.

41. Harvey, A.E. and Manning, D.L., J. Amer. Chem. Soc., 1950, 72, 4488.

42. Gerbeleu, Yu., Arion V.B., Leovae, V.M., Turta, K.I., Inorganic Chem. (Ammerican Chem. Soc.) 1992, 31, 3264-3268.

43. Silvio Decutins, Helmut W. Schmalle, J. Ammer. Chem. Soc., 1993, 32, 1888-1892.

44. Sinha, M.P., Singh, P.N., Verma, D.K., and Kamta Prasad Singh., J. Indian Chem. Soc., 1990, 67, 458.

45. Balakrishan and Aravindakshan K.K. J. Indian Chem. Soc., 1990, 68, 187.

46. Mousumi Bhattacharjee, Ashok Kumar and Seth D.S. J. Indian Chem. Soci., 1992, 69, 210.

47. James E.Bollinger and D. Max Roundhill J. Inorganic Chem. (Ammeri Chem. Soci.), 1993, 32, 2821-2826.

48. K. Balakrishnan and Aravindakshan, K.K., J. Indian Chem. Soci., 1990, 68, 187.

49. Chen L, Davies, J.A., Staples R., Inorganic Chem. Acta, 1989, 28, 163.

50. Fox, G.A., Piperpont C.G., J. Inorganic Chem., (Amme. Chem. Soci.) 1992, 31, 3718.

51. Dey K., Roy, S.B., Bhattacharya P.K. and Verma R.D., J. Indian Chem. Soc., 1985, 62, 809.

52. Dey K., Koner D., Bhattacharya P.K., Bhasin K.K. and Verma R.D., Polyhedron 5 (1986), 1201.

53. Nakamura M, Itoth, T., Okawa H. and Kida S., J. Inorg. N. Chem., 1981,43, 2281.

54. Biradar, N.S., and Kulkarni V.H., Inorganic Nuclear Chem. 1971, 33, 2481.

55. Fox, G.A., Bhattacharya, S. Piperpont C.G. Inorg. Chem. (Ammer Chem. Soci.) 1994, 30, 2895 .

56. Dey K, Sinha Roy, A.K., Bhasin K.K. and Verma R.D., Indian J. Chem. 26A, 1987, 230.

57. Sahni, S.K., Gupta S.P., Sangal S.K. and Rana, V.B., J. Inorganic nucl. Chem. 39, 1977, 1098.

58. Torihara N., Okawa H and Kida, S., Bull Chem. Soc., Japan 51, 1978, 3236.

59. Boucher L.J. and Herinifor D.R., J. Inorganic nucl. Chem., 1971, 33 4349.

60. Leovic V.M. Bielica, L.J., Jovanovic L.S. and Chundak Y.U., Polyhedron, 5, 1986, 983.

61. Iskander, M.F. and Saddeck, S., Inorganic Chim. Acta. 22, 1977, 141.

62. Golding R.M. and Jessop, K.J., Aust. J. Chem., 28, 1975, 179.

63. Dey K., Biswas A.K. and Sinha Roy A.K., Indian J. Chem. 20A, 1981, 848.

64. Cesarotti E., Grassi M. and Prati L., Polyhedron 9, 1990, 639.

65. S. Koch, G. Ackermann and Lindner Talanta 1992, 39, 693.

66. Suma, S., Sudarsankumar and Prabhakaran; Indian J. of Chem., 1994, 33A 1107.

67. Dhumwad, K.B., Gudasi and Goundar, T.R., Indian J. of Chem. 1994 33A, 320.

68. Hauptkorn S., Schneider G., Krivan., J. Anal. atom. Spectron, 9, 1994, 463-468.

69. Daryle H. Busch and Nathaniel W. Alcok., Chemical Reviews 1994, 94(3), 585.

70. Strauch, P., Dietzch L., Golic and Hoyer, E., J. Inorganic Chem. (Ammeri Chem. Soci.) 1995, 34, 763.

71. Kamalendu Dey, Prabir Kumar, Bhattacharya and Alok Kumar Mallick, Indian J. Chem. 1995, 34A, 529.