

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON (II) WITH [2(E)[(2,4-DICHLOROPHENYL) IMINO] METHYL} -6-METHOXY PHENOL] (DCPIMMP)

Nitin Kadam*¹ Ritika Makhijani¹

1. Department of Chemistry, Vivekanand Education Society's College of Arts, Science and Commerce, Mumbai-400071, INDIA

Abstract

Using 2-{(E)-[(2,4-dichlorophenyl) imino] methyl} -6- methoxyphenol (DCPIMMP) as an analytical reagent, a simple, fast, and sensitive spectrophotometric technique has been devised to measure Fe (II). The synthesis of and characterization of DCPIMMP using elemental and spectral analyses. DCPIMMP quantitatively extracts (98.26%) Fe (II) into ethyl acetate from an aqueous solution with a pH range of 5.5 to 6.5. At 484 nm (λ max), the ethyl acetate extract exhibits a strong peak. Over the Fe (II) concentration range of 1 to 8 μ g /ml, Beer's law is observed. For the Fe-DCPIMMP system, the Sandell's sensitivity and molar absorptivity are 0.0235 g cm^{-2} and 2373 $\text{L mole}^{-1} \text{ cm}^{-1}$, respectively. The Job's Continuous Variation and Mole Ratio Method is used to determine that the extracted species have a 1:2 composition (Fe: DCPIMMP). The standard deviation is 0.289, and the average of 10 measurements of 50 μ g of Fe (II) in 10 cm^3 of solution is 49.70 μ g, ranging between 49.41 μ g and 49.99 μ g at 95% confidence level. Different ions' interference has been investigated. Fe (II) in ore and pharmaceutical sample determination using the suggested method has been successful.

Keywords: Extractive Spectrophotometry, Iron (II), 2-{(E)-[(2,4-dichlorophenyl) imino] methyl} -6- methoxyphenol. [DCPIMMP], Ore and Pharmaceutical Samples.

Introduction

Iron is a chemical element with the symbol Fe and atomic number 26. It is a metal in the first row of transition metals and is the fourth most abundant element in the Earth's crust. Iron is essential for many biological processes, including the transport of oxygen in the blood, and is an important component of many enzymes and proteins.

Iron has a silvery-gray appearance and is malleable, ductile, and magnetic. It has a high melting point of 1,538°C and a boiling point of 2,862°C. Iron is also a good conductor of heat and electricity.

Iron is used extensively in the production of steel, which is a combination of iron and carbon. Steel is used in the construction of buildings, bridges, and other infrastructure, as well as in the manufacturing of machinery, vehicles, and appliances. Iron is also used in the production of other alloys, such as stainless steel, and in the manufacturing of iron oxide pigments, magnets, and electronics.

Iron deficiency can lead to anemia, a condition in which there are not enough red blood cells to carry oxygen to the body's tissues. Symptoms of anemia can include fatigue, weakness, shortness of breath, and headaches. Iron deficiency is especially common in pregnant women, young children, and individuals on a vegetarian or vegan diet.

On the other hand, excessive iron intake can be harmful to human health. High levels of iron in the body can cause damage to organs such as the liver, heart, and pancreas. People with a genetic disorder called hemochromatosis absorb too much iron from their diet, which can lead to iron overload and increase the risk of liver disease, heart disease, and diabetes.

Overall, it is important to maintain a balance of iron intake for optimal health. The recommended daily intake of iron varies depending on age and gender, with higher requirements for pregnant women and individuals with increased iron needs due to certain medical conditions.

In order to quantitatively determine iron at trace levels, extremely sensitive, accurate, and selective analytical procedures are required.

In chemistry, a solvent extraction is a significant separation process. Because of its ease, speed, and variety, it has developed into one of the most promising methods for separating metal ions at the trace level^[1-2]. In pharmaceutical research, solvent extraction plays a vital role as a separation procedure with spectrophotometrically employing various organic reagents^[3]. According to a literature review, there are many reagents^[4-14] that can be used to measure iron using spectrophotometry. We report the extractive spectrophotometric measurement of Fe (II) using 2-{(E)-[(2,4-dichlorophenyl) imino] methyl} -6-methoxyphenol. [DCPIMMP] in the current communication.

Materials And Methods

The optically matched quartz or glass cells of the ELICO - SL 159 spectrophotometer with a 1 cm path length were used to measure absorbance. For measuring pH, an ELICO LI 127 pH meter was used.

Ammonium ferrous sulphate that had been precisely weighed was dissolved in water that contained sulphuric acid to create a stock solution of Fe (II), which was then gravimetrically calibrated^[1-14]. Fe (II) 3 working solutions were created by diluted the stock solution to the proper concentration. All other reagents used were of the AR grade, and doubly distilled water was utilized to prepare all solutions.

General procedure for preparation of [2-{(E)-[(2,4-dichlorophenyl) imino] methyl} -6-methoxyphenol. [DCPIMMP]

The reagent DCPIMMP was synthesized by refluxing equimolar amount of ethanolic solution of 2-Hydroxy-3-methoxybenzaldehyde and 2,4-Dichloroaniline for 3-4 hours. On cooling the reaction mixture, a sharp orange crystal product separated out which was collected by filtration. The resulting DCPIMMP was recrystallized using aqueous ethanol as the procedure recommended by Vogel^[12].

Procedure for the Extraction and separation of Iron (II)

An aliquot of aqueous solution containing 500 µg of Fe(II), 2ml of 5% hydroxylamine hydrochloride and 2 ml of 0.5 % solution of DCPIMMP prepared in DMF were mixed in 25 ml beaker. In order to keep the total volume at 10 ml with distilled water, the pH of the solution was adjusted to the necessary value with a diluted solution of HCl/NaOH. In a 125 ml separatory funnel, the resultant solution was then transferred. A 5 ml amount of an organic solvent was used to wash the beaker, and after each wash, the solution was added to the separatory funnel.

The two phases were equilibrated for 1 minute and allowed to separate. After the separation of two phases, pH of the equilibrated aqueous phase was measured and iron content in each phase was estimated by 1, 10 -phenanthroline method^[14]. The extraction was carried out with different solvents to find out the best extracting solvent. On the basis of iron content in aqueous and organic phase extraction coefficient and percentage extraction was calculated.

Extractive Spectrophotometric Determination of Fe (II):

To an aliquot of aqueous solution containing 1-80µg of Fe (II), 2 ml of 5% hydroxylamine hydrochloride, 2 ml of buffer solution (sodium acetate and acetic acid) of pH 6.0 and 2 ml of 2% solution of DCPIMMP prepared in DMF were added. The volume of solution was made up to 10 ml with distilled water. The solution was then equilibrated for one minute with 10

ml of ethyl acetate and the phases were allowed to separate. The ethyl acetate extract was collected in a 10 ml measuring flask and made up to mark with ethyl acetate, if necessary. The absorbance of ethyl acetate extract was measured at 484 nm against a reagent blank prepared under identical conditions. The measured absorbance was used to compute the amount of Fe (II) present in the sample solution from predetermined calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH.

Procedure for the Determination of Fe(II) in Pyrolusite ore Sample :

0.1 – 0.2 gm of ore sample was dissolved in boiling with 10 ml of aquaregia. The resulting solution was evaporated to dryness and the residue was dissolved in 10 ml of dilute HCl filter, if required. The resulting solution was diluted to 250 ml of distilled water. 1ml aliquot of this solution was analyzed for Fe (II) by the procedure as described earlier.

Procedure for the Determination of Fe (II) in Pharmaceutical Sample

0.5-1.0 gm sample of pharmaceutical product was dissolved in boiling with 10 ml of aquaregia. The resulting solution was evaporated to dryness and the residue was dissolved in 10 ml of 6N HCl filter, if required. The resulting solution was diluted to 250 ml of distilled water. 1ml aliquot of this solution was analyzed for Fe (II) by the procedure as described earlier.

Results And Discussion:

Fe (II) could be extracted quantitatively (98.26%) by DCPIMMP into ethyl acetate from an aqueous solution of pH 5.5 to 6.5 in presence of 2 ml of 5% hydroxylamine hydrochloride [Fig I]. Organic solvents used for extraction of Fe (II) can be arranged on the basis of their extraction coefficient values as ethyl acetate > chloroform > carbon tetrachloride > toluene > nitrobenzene > benzene > xylene > benzyl alcohol > n-amyl alcohol > n-butanol [Fig II]. Ethyl acetate was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. The ethyl acetate extract of Fe: DCPIMMP complex showed an intense peak at 484 nm [Fig - III]. The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to Beer's law at this wavelength over a Fe (II) concentration range of 0.1 to 8.0 $\mu\text{g/ml}$ [Fig -IV]. The molar absorptivity of the extracted complex on the basis of Fe (II) content was calculated to be $2373 \text{ L mol}^{-1} \text{ cm}^{-1}$. It was found that 2 ml of 2.0% DMF solution of DCPIMMP was sufficient to extract

80 μg of Fe (II). The colour of the ethyl acetate extract was found to be stable at least 24 hrs. at room temperature.

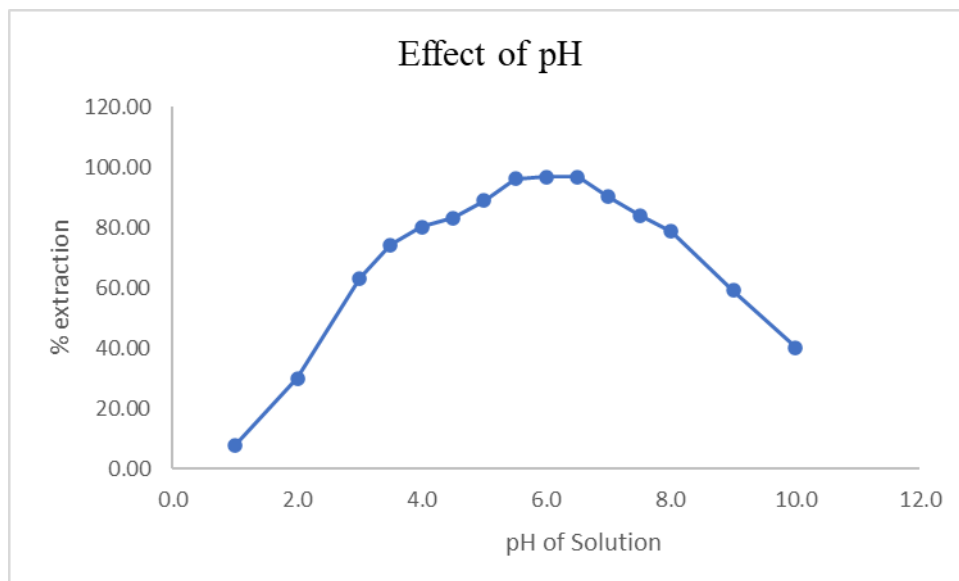


Fig. I Effect of pH

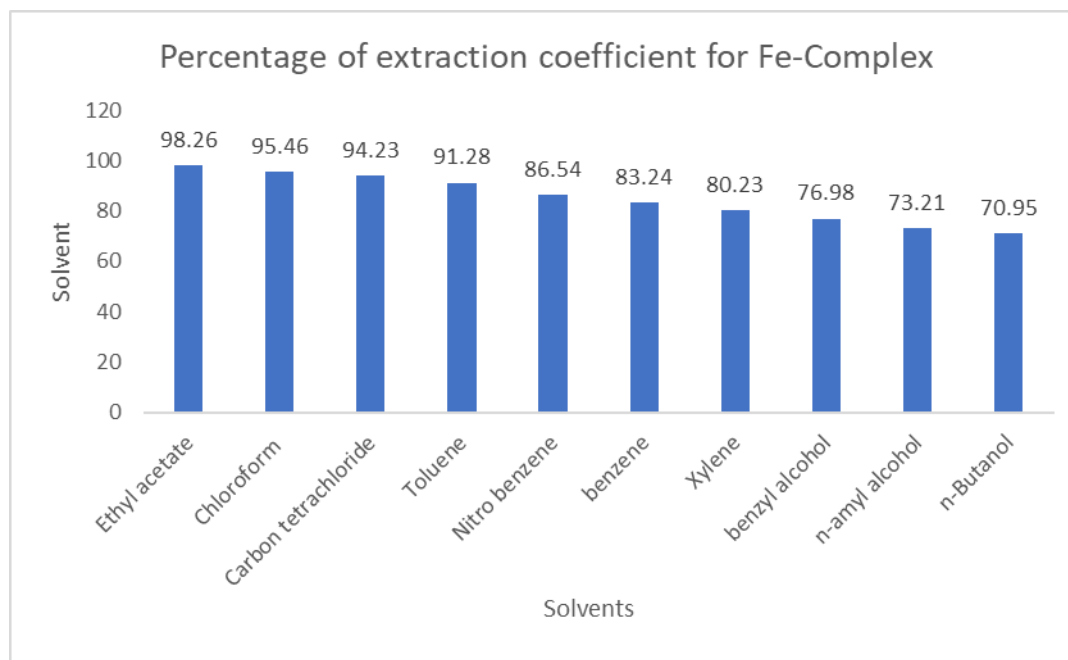
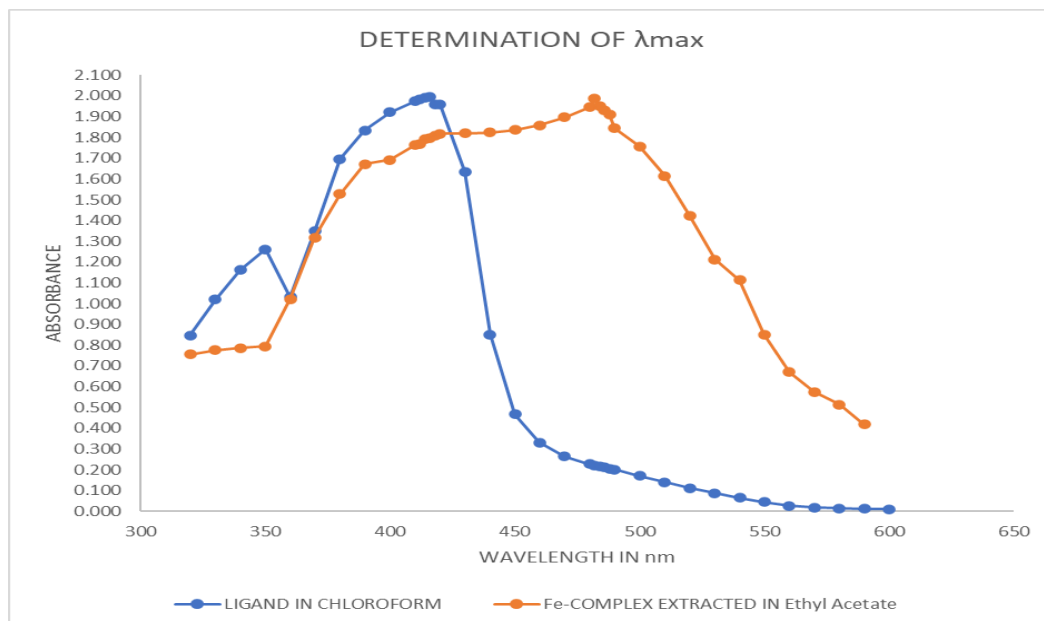


Fig. II: Effect of Solvents



Solution A: Absorbance spectra of DCPIMMP

Solution B: Absorbance spectra of Fe - DCPIMMP complex

Fig. III: Determination of λ_{max}

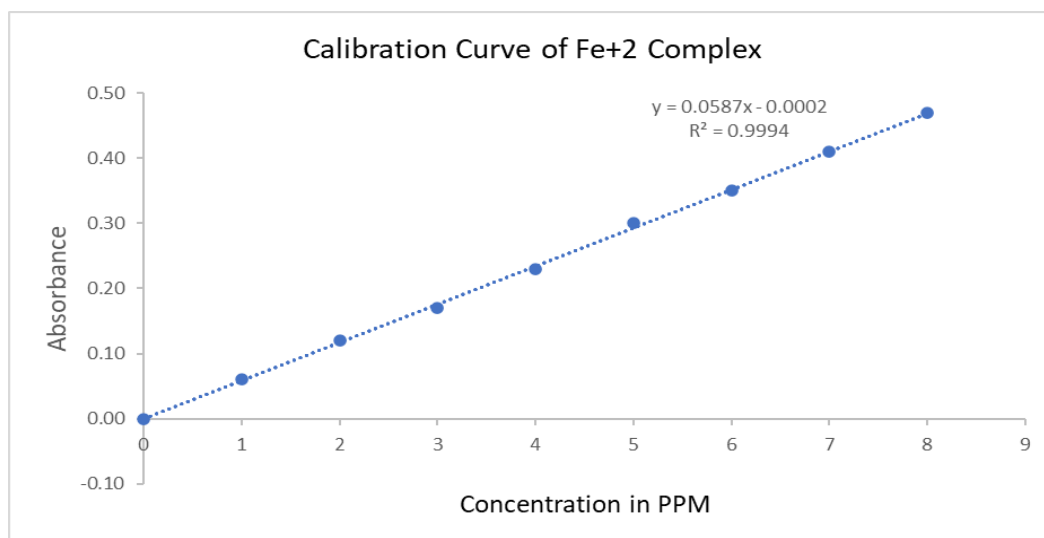


Fig. IV: Calibration Curve for Fe (II)

Composition of the Extracted Complex

The composition of the extracted complex was found to be 1:2 (Fe: DCPIMMP) by Job's continuous variation [Fig - V] and Mole ratio methods. [Fig - VI]

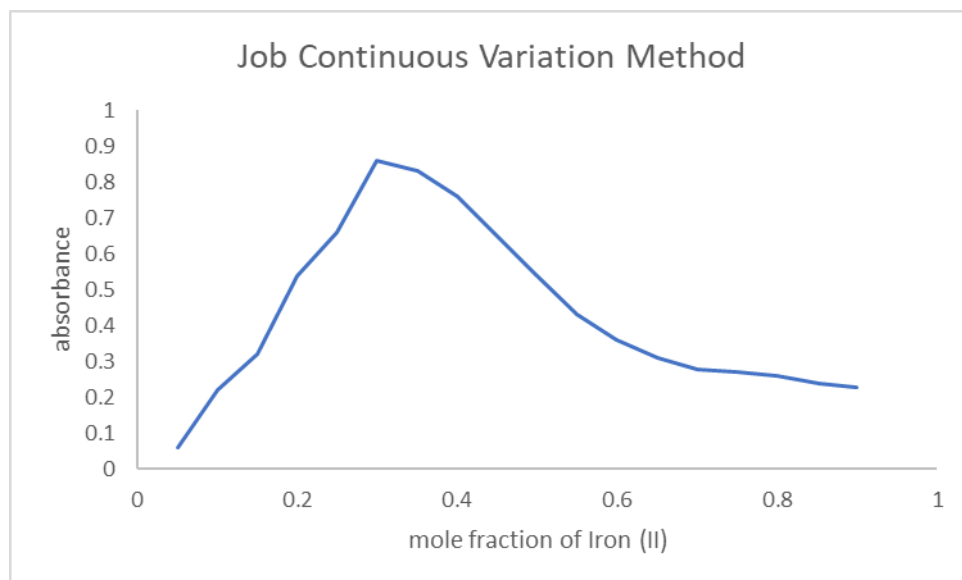


Fig. V: Job's Continuous Variation Method

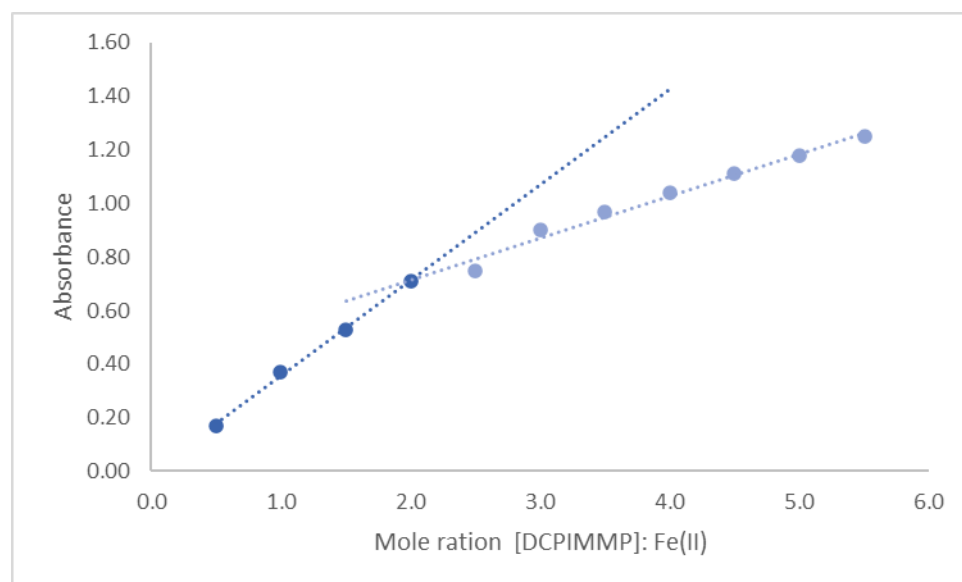


Fig. VI: Mole Ratio Methods

Effect of other ions on the absorbance of Fe: DCPIMMP

Fe (II) (40 µg) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Fe (II) (40µg):

- 10 mg each of Li(I), Be(II), Mg(II), Ca(II), Sr (II), Ba(II), Sn(II), Bi(III), Mo(VI), W(VI), Ce(IV), Th(IV) and Zr(IV).
- 2 mg each of Pb(II), Cd(II) and Zn(II),
- 1 mg each of Pd (II), Pt(IV) and Hg(II),
- 20 mg each of chloride, iodides, bromide, fluoride, sulphate, nitrate, thiocyanate, phosphates, acetate, citrate, thiourea and tri ethyl amine.

S. No.	Interfering Ions	Amount added in mg	Masking agent added 1ml of 0.5M solution
1.	Cu (II)	10	NaH ₂ PO ₄
2.	Ru(III) and Rh(III)	10	Thiourea
3.	Ag(I)	10	Potassium thiocyanate
4.	Mn (II)	10	Potassium thiocyanate
5.	Cr(III)	10	Tri ethanol amine
6.	V(V)	10	Tri ethanol amine
7.	Ni(II)	10	5 - sulphosalicylic acid
8.	Oxalate	10	Sodium molybdate

Table I: Interference by the various ions was removed by using appropriate masking agent.

Precision, Accuracy, Sensitivity and Applications of Method

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Fe (II) following the recommended procedure. The average of 10 determination of 50 µg of Fe (II) in 10 cm³ solutions was 48

.70 µg, which is varied between

49.41 µg and 49.99 µg at 95% confidence limit Standard deviation and Sandell's sensitivity of the extracted species is found to be ±0.298 and 0.0235µgcm⁻² respectively. The proposed method has been applied for the determination of Fe (II) in pharmaceutical samples.

The results of the analysis of the samples were comparable with those obtained by the

standard method [14] for Fe (II) (Table - II).

Table II

Samples	Fe(II) found (mg) * Present method	1:10 Phenanthroline method [14]	Reported value (mg)
Pyrolusite	4.967%	4.993%	---
Ferium XT	99.91	99.96	100.00

*Average of three determinations

Acknowledgement

Authors are thankful to the Principal Dr. (Mrs.) Anita Kanwar, V.E. S. College of Arts, Science and Commerce, Sindhi Society, Chembur, Mumbai - 71 for providing necessary research facilities.

References

1. Khopkar S.M and Chalmers R.A, Solvent Extraction of Metals, Van Nostrad Reinhold Co. London, (1970) Feig F, Chemistry of specific, selective and sensitive Reactions, English Ed. By.Oesper R.E. Academic press, New York, (1949).
2. Mirzaeva KA, Akhmedove M..S, Ramazanov A, Akhmedov SA, Extraction and Spectrophotometric Determination of Dimedrol and Papavarine in Pharmaceutical Dosage Forms, J. Analytical Chem., (2004);59 (1): 215 - 218
3. Singh R.B, Garg BS, and Singh RP, Talanta,(1979); 26(2): 525 - 526
4. Karthikeyan J, Naik P.P, Shetty AN, Environ Monit. Assess, (2011); 176(1 - 4): 419
5. Amer SM, El-Saharty YS, Metwally FH, Younes KM, Spectrophotometric study of Etodolac complexes with copper (II) and iron (II), J Agric Food Chem;(2005); 53(14):5492-5498
6. Lingayat SK, Development of New Spectrophotometric Method for the Determination of Some Metal Ions from Transition Metals. Ph. D. Thesis, University of Mumbai, (2006)
7. Bhaskare CK, Kawatkar SG, Extractive photometric simultaneous determination of Iron (II) and copper (II) with syn-phenyl- α -pyridyl ketoxime and analysis of ferrites,

Talanta,(1975); 22(2): 189-193

8. Mahajan HA and Patil MR, Chim Anal, (1992); 37: 239
9. Lokhande RS, Makhijani Mamta and Barhate V D, Indian J.Chem, (2003); 15 (1): 535-537
10. Khambekar AM and Sawant AD, J. Indian Chem. Soc. (1997); 36A (5): 459 - 460
11. Nath R, Nantial SC and Singh H, Labdev, Part-A, (1974);12A (2):53- 58
12. Vogel AI, Practical Organic chemistry, 5th Ed. Longman group limited London,(1989)
13. Vogel AI, Text Book of Quantitative Inorganic Analysis Longman Green and Co.Ltd. London;(1978)
14. Sandell EB, Colorimetric Determination of Traces of Metals 3rd Edn, Interscience, NY;(1965); 414