

DEVELOPMENT OF EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON (II) WITH [N - (O - HYDROXY BENZYLIDENE) PYRIDINE - 2 - AMINE]

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ABSTRACT

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Fe (II) by using N - (o - hydroxy benzylidene) pyridine - 2 - amine (NOHBPA) as an analytical reagent. NOHBPA has been synthesized and characterized by elemental and spectral analysis. NOHBPA extracts Fe (II) quantitatively (99.60%) into benzene from an aqueous solution of pH range 5.6 - 6.5. The benzene extract shows an intense peak at 530 nm (λ max). Beer's law is obeyed over the Fe (II) concentration range of 0.1 - 12 μ g/ml. The sandell's sensitivity and molar absorptivity for Fe - NOHBPA system is 0.0125 μ gcm⁻² and 4469.27 L mole⁻¹cm⁻¹ respectively. The composition of extracted species is found to be 1:2 (Fe: NOHBPA) by Job's Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method has been successfully applied for determination of Fe (II) in Pharmaceutical samples.

Keywords: Extractive Spectrophotometry, Iron (II), N - (o - hydroxy benzylidene) pyridine -2- amine (NOHBPA), Pharmaceutical Samples.

INTRODUCTION

Iron is an essential element that is required for human life. Much of the iron in the body is found in red blood cells and carries oxygen to every cell in the body. Extra iron is stored in the liver, bone marrow, spleen, and muscles. Though iron is one of the most essential micronutrients for human beings yet it is toxic when its concentration is > 0.3ppm in drinking water (U.S Public Health Service Drinking Water Standards). Iron is also a vital constituent of plant and animal life with the key component of hemoglobin and plays a vital role in variety of biochemical process. Lack of iron causes anemia in human being while excess of iron in the body causes Haemochromatosis (liver and kidney damage). According to the World Health Organization (WHO), iron deficiency is the number one nutritional disorder in the world. Up to 80% of the world's population may be iron deficient and 30% may have iron deficiency anemia. Hence, it is necessary to seek highly sensitive, accurate and selective analytical methods for quantitative determination of iron at trace levels.

A solvent extraction is becoming important separation technique in chemistry. It has grown into one of the most promising method in the separation of metal ions at trace level because of its simplicity, rapidity and versatility¹⁻². Solvent extraction as a separation

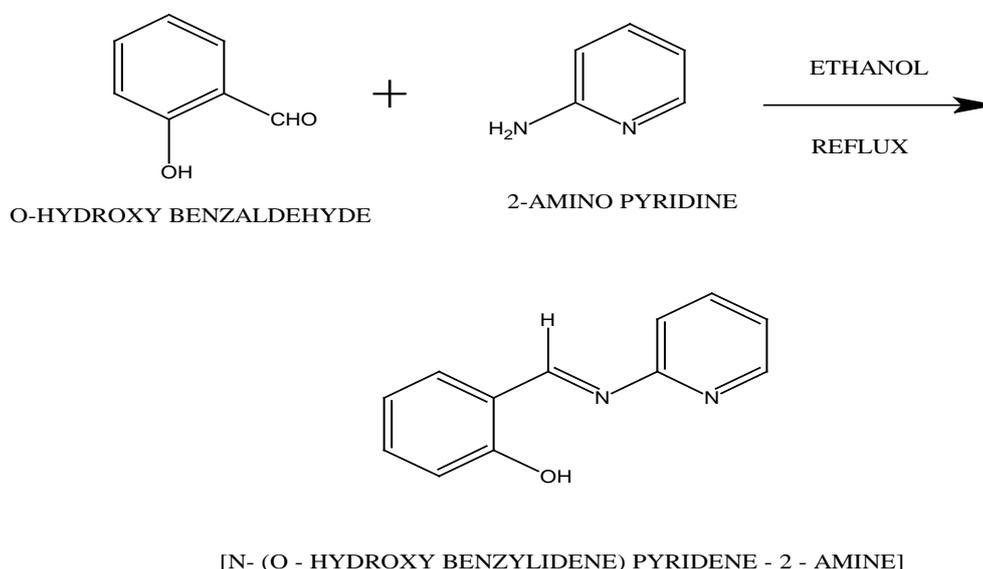
technique with spectrophotometrically using different organic reagent have significant role in pharmaceutical science³. Literature survey reveals that various reagents⁴⁻¹² are available for the spectrophotometric determination of iron. In the present communication, we describe the extractive spectrophotometric determination of Fe (II) with [N - (o - hydroxy benzylidene) pyridine - 2 - amine]

MATERIALS AND METHODS

ELICO - SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length was used for absorbance measurement. An ELICO LI 127 pH meter was employed for pH measurements.

General procedure for preparation of [N - (o - hydroxy benzylidene) pyridine - 2 - amine] (NOHBPA)

The reagent NOHBPA was synthesized by refluxing equimolar amount of ethanolic solution of o - hydroxy benzaldehyde with 2 - amino pyridine for 6 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (yield 80%, m.p.70^o-71^oC) which was collected by filtration. The resulting NOHBPA was recrystallised using aqueous ethanol as the procedure recommended by Vogel¹³.



[N - (O - HYDROXY BENZYLIDENE) PYRIDINE - 2 - AMINE]

The purity of product was checked by TLC and characterized by elemental and spectral analysis. Its solution was prepared in Dimethylformamide (DMF). A stock solution of Fe (II) was prepared by dissolving accurately weighed ammonium ferrous sulphate in water containing sulphuric acid and it was standardized by gravimetrically¹⁴. Working solutions of Fe (II) were made by diluting the stock solution to an appropriate volume. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

Extractive Spectrophotometric Determination of Fe (II)

To an aliquot of aqueous solution containing 1-120 μ g of Fe (II), 1ml of 2M sodium thiosulphate, 2ml of buffer solution (sodium acetate and acetic acid) of pH 6.0 and 2 ml of 2% solution of NOHBPA prepared in DMF were added. The volume of solution was made up to 10 ml with distilled water. The solution was then equilibrated for 30 seconds with 10 ml of benzene and the phases were allowed to separate. The benzene extract was collected in a 10 ml measuring flask and made up to mark with benzene, if necessary. The absorbance of benzene extract was measured at 530 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 or acidity.

Determination of Fe (II) in Pharmaceutical Samples

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 1N HCl filter, if required and solution was diluted to 100 ml with doubly distilled water. The working solution was prepared by appropriate dilution of stock solution. To an aliquot of this solution 1ml was analyzed for Fe (II) by the procedure as described earlier.

RESULTS AND DISCUSSION

Fe(II) could be extracted quantitatively (99.60%) by NOHBPA into benzene from an aqueous solution of pH 5.6 to 6.5 in the presence of 1ml of 2M sodium thiosulphate. Organic solvents used for extraction of Fe (II) can be arranged on the basis of their extraction coefficient values as benzene > ethyl acetate > n-amyl alcohol > toluene > chloroform > carbon tetrachloride > xylene > benzyl alcohol > n-butanol > nitrobenzene. Benzene was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. The benzene extract of Fe: NOHBPA complex showed an intense peak at 530 nm [Fig - I]. 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 12 μ g/ml [Fig - II]. The molar absorptivity of the extracted complex on the basis of Fe (II) content was calculated to be 4469.27 L mol⁻¹ cm⁻¹. It was found that 2 ml of 2.0% DMF solution of NOHBPA was sufficient to extract 120 μ g of Fe (II). The colour of the Benzene extract was found to be stable at least 24 hrs. at room temperature.

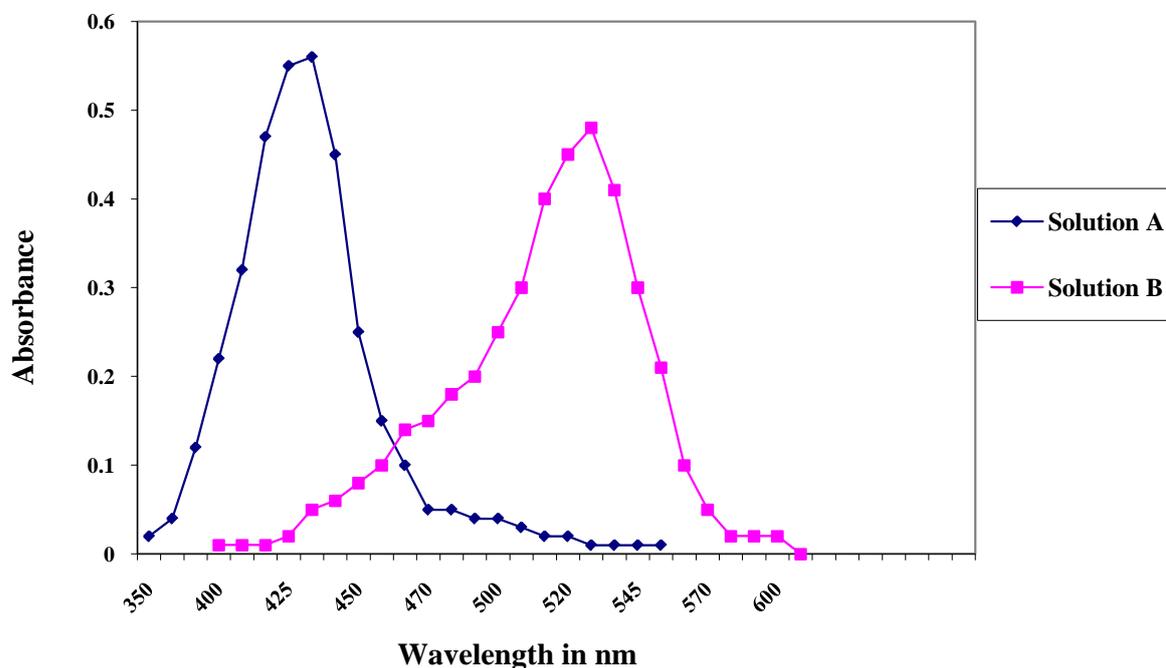


Fig. 1: Solution A: Absorbance spectra of NOHBPA; Solution B: Absorbance spectra of Fe - NOHBPA complex

Effect of Other Ions

Fe (II) (40 μ g) 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) (40 μ g): 10 mg each of Mg(II), Ca(II), V(V), Ni(II), Cu(II), Co(II), Zn(II), Mo(VI), Ce(IV), Be(II), Ba(II), Bi(III), Li(I), Zr(IV), Pd(II), Pt(IV), Ce(IV), Sn(II), Th(IV), W(VI) and 1mg of Cr(III); 20 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, carbonate, sulphate, thiocyanate, phosphates, acetate, persulphate and thiosulphate and 1mg of oxalate. Interference by the various ions were removed by using appropriate masking agent (Table - I).

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 40 μ g of Fe (II) in 10 cm³ solutions was 40.20 μ g, which is varied between 40.65 and 39.75 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be ± 0.632 and 0.0125 μ gcm⁻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 method¹⁵ for Fe (II) (Table - II).

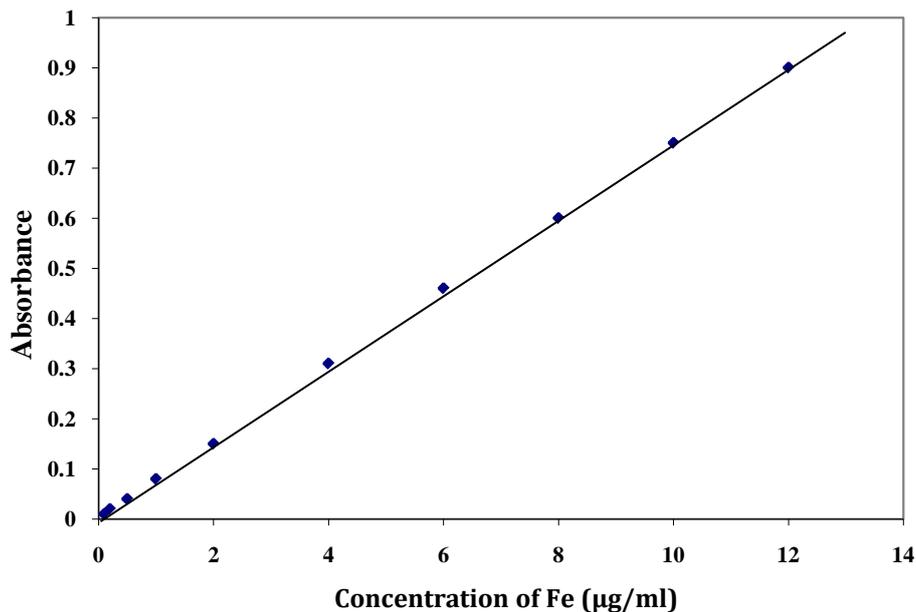


Fig. II: Calibration Curve for Fe (II)

Table I: Composition of the Extracted Complex

Interfering ion	Amount added in mg	Masking agent 2ml of 0.5M solution
Hg(II)	10	Potassium Iodide
Ag(I), Cd(II), Ru(III) and Rh(III)	10	Thiourea
Pb(II)	10	Sodium thiosulphate
Mn(II)	10	Thiocyanate
Citrate and EDTA	10	Copper sulphate

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

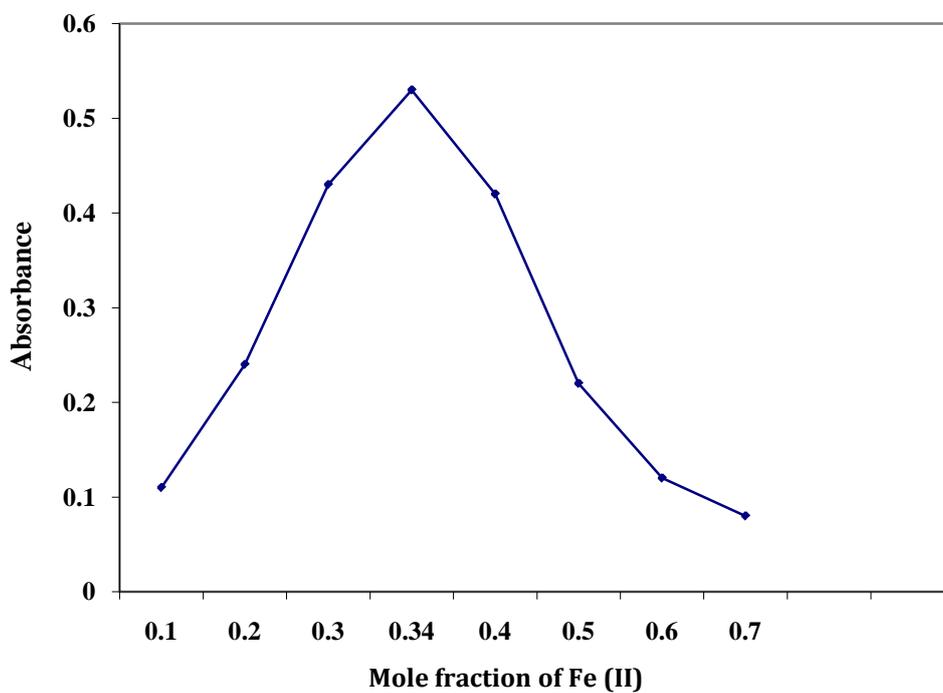


Fig. III: Job's Continuous Variation Method

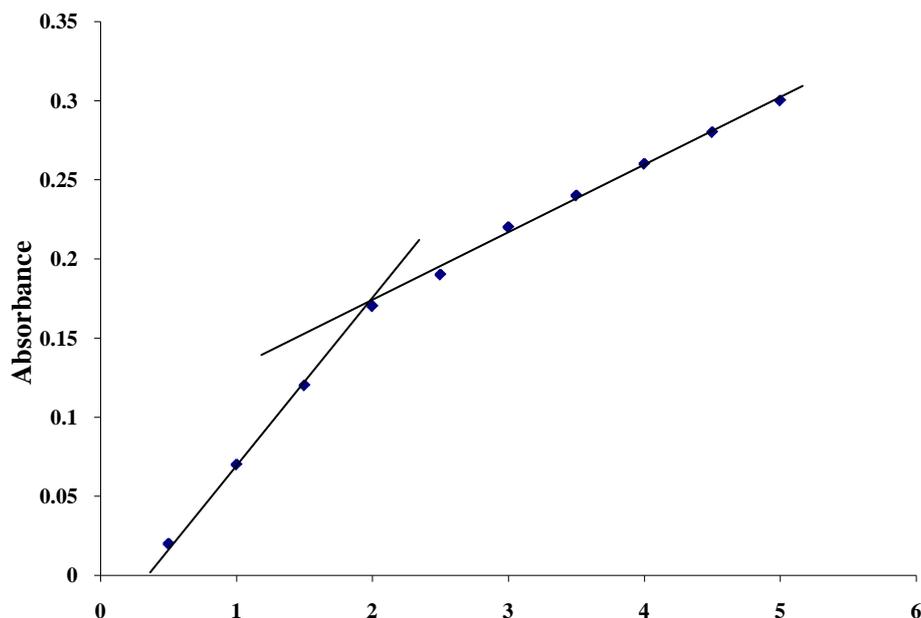


Fig. IV: Mole Ratio Methods
Mole ratio [NOHBPA] / Fe (II)

Table II: Determination of Fe (II) in Pharmaceutical Samples

Samples	Fe (II) found (mg) * Present method	Standard method (mg)	Reported value (mg)
Dexorange capsule	32.70	32.75	32.80
Autrin capsule	98.48	98.50	98.60

*Average of three determinations

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