

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON (II) WITH [N - (O -METHOXY BENZALDEHYDE)- 2 - AMINO PHENOL]

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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 - methoxy benzaldehyde) 2 - aminophenol (NOMBAP) as an analytical reagent. NOMBAP has been synthesized and characterized by elemental and spectral analysis. NOMBAP extracts Fe (II) quantitatively (99.67%) into ethyl acetate from an aqueous solution of pH range 5.6 - 6.8. The ethyl acetate extract shows an intense peak at 470 nm (λ max). Beer's law is obeyed over the Fe (II) concentration range of 1 - 7 μ g/ml. The sandell's sensitivity and molar absorptivity for Fe - NOMBAP system is 0.0176 μ gcm⁻² and 3166 L mole⁻¹ cm⁻¹ respectively. The composition of extracted species is found to be 1:2 (Fe : NOMBAP) by Job's Continuous Variation and Mole Ratio Method. The average of 10 determination of 50 μ g of Fe (II) in 10cm³ of solution is 49.85 μ g which is varied between 49.61 μ g and 50.09 μ g at 95% confidence limit and standard deviation is ± 0.337 . Interference by various ions has been studied. The proposed method has been successfully applied for determination of Fe (II) in Ore and Pharmaceutical samples.

Keywords: Extractive Spectrophotometry, Iron (II), N (o - methoxy benzaldehyde) 2 - aminophenol (NOMBAP), Ore and Pharmaceutical Samples.

INTRODUCTION

Iron is transition element belongs to group VIII and period 4th of the periodic table. It is necessary trace element used by all living organisms and also a vital constituent of plant and animal life. It is key component of haemoglobin. 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 > 0.3 ppm in drinking water (U.S Public Health Service Drinking Water Standards). 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 versatility [1-2]. Solvent extraction as a separation technique with spectrophotometrically using different organic reagent have significant role in pharmaceutical science [3]. Literature survey reveals that various reagents [4-15] are available

for the spectrophotometric determination of iron. In the present communication, we describe the extractive spectrophotometric determination of Fe (II) with N-(o-methoxybenzaldehyde) 2-amino phenol (NOMBAP).

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.

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 gravimetrically [14-15]. 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.

General procedure for preparation of [N - (o - methoxy benzaldehyde) 2 - aminophenol] (NOMBAP)

The reagent NOMBAP was synthesized by refluxing equimolar amount of ethanolic solution of o - methoxy benzaldehyde with 2 - aminophenol for 4-5 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (yield 80%, m.p. 87^o - 88^o C) which was collected by filtration. The resulting NOMBAP was recrystallised using aqueous ethanol as the procedure recommended by Vogel [13].

The product obtained was characterized by elemental and spectral analysis. Its solution was prepared in Dimethylformamide (DMF).

Procedure for the Extraction and separation of Iron (II)

An aliquot of aqueous solution containing 500 μ g of Fe(II), 2ml of 5% hydroxylamine hydrochloride and 2 ml of 2% solution of NOMBAP prepared in DMF were mixed in 25 ml beaker. The pH of solution was adjusted to the desired value with dilute solution of HCl /NaOH, keeping the total volume to 10 ml with distilled water. The resulting

solution was then transferred into 125 ml separatory funnel. The beaker was then washed with 5 ml portion of organic solvent and each washing was added to the solution in 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 1-70 μ g of Fe (II), 2ml of 5% hydroxylamine hydrochloride, 2ml of buffer solution (sodium acetate and acetic acid) of pH 6.0 and 2ml of 2% solution of NOMBAP 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 470 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 (99.67%) by NOMBAP into ethyl acetate from an aqueous solution of pH 5.6 to 6.8 in presence of 2ml 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: NOMBAP complex showed an intense peak at 470 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 7.0 μ g/ml [Fig -IV]. The molar absorptivity of the extracted complex on the basis of Fe (II) content was calculated to be 3166 L mol⁻¹ cm⁻¹. It was found that 2 ml of 2.0% DMF solution of NOMBAP was sufficient to extract 70 μ g of Fe (II). The colour of the ethyl acetate extract was found to be stable at least 24 hrs. at room temperature.

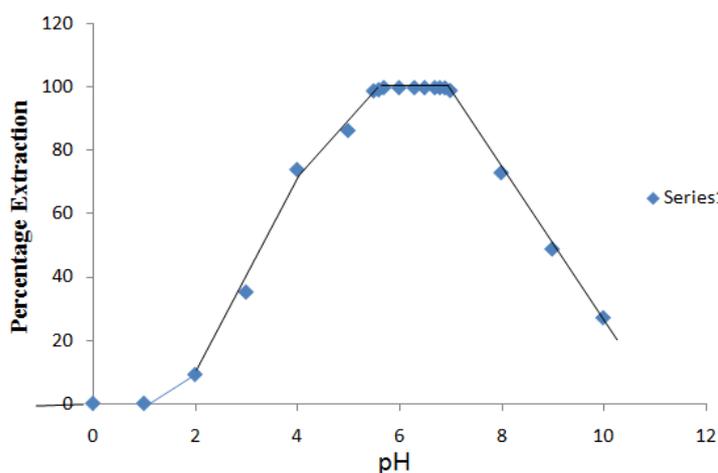


Fig. I

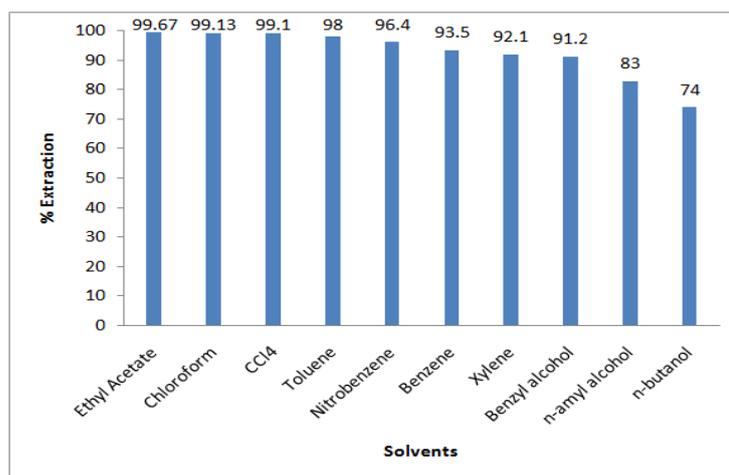
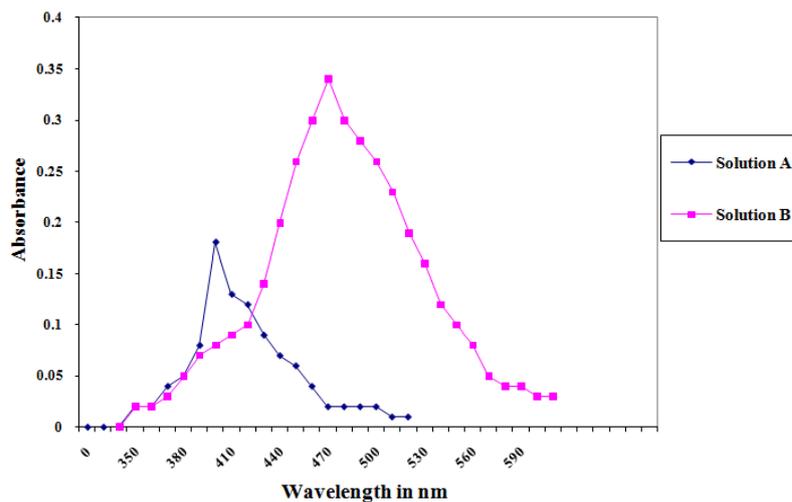


Fig. II:



Solution A: Absorbance spectra of NOMBAP
 Solution B: Absorbance spectra of Fe - NOMBAP complex

Fig. III:

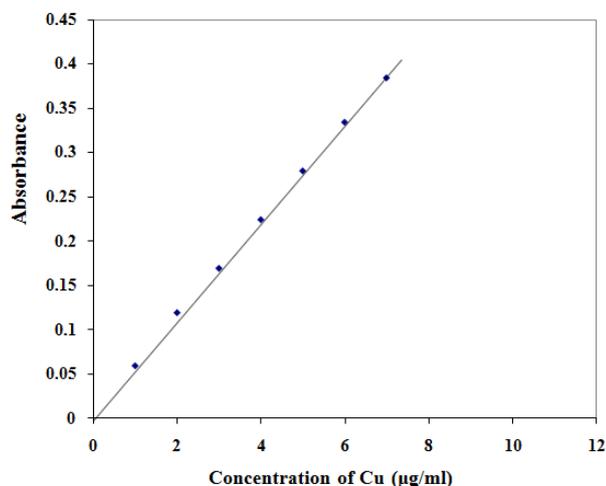


Fig. IV: Calibration Curve for Fe (II)

Effect of other ions on the absorbance of Fe: NOMBAP

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):

- a) 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).
- b) 2 mg each of Pb(II),Cd(II) and Zn(II),

c) 1 mg each of Pd (II), Pt(IV) and Hg(II),

d) 20 mg each of chloride, iodides, bromide, fluoride,, sulphate, nitrate, thiocyanate, phosphates, acetate, citrate, thiourea and tri ethyl amine.

Composition of the Extracted Complex

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

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

S. No.	Interfering Ions	Amount added in mg	Masking agent added 1ml of 0.5M solution	Absorbance
1.	Cu (II)	10	NaH ₂ PO ₄	0.81
2.	Ru(III) and Rh(III)	10	Thiourea	0.81
3.	Ag(I)	10	Potassium thiocyanate	0.81
4.	Mn (II)	10	Potassium thiocyanate	0.81
5.	Cr(III)	10	Tri ethanol amine	0.81
6.	V(V)	10	Tri ethanol amine	0.81
7.	Ni(II)	10	5 - sulphosalicylic acid	0.81
8.	Oxalate	10	Sodium molybdate	0.81

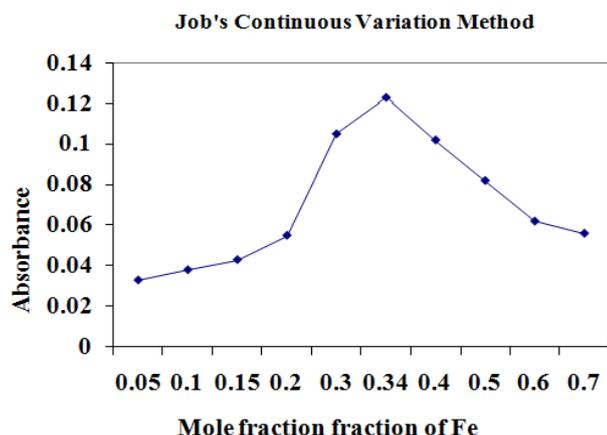


Fig. V: Job's Continuous Variation Method

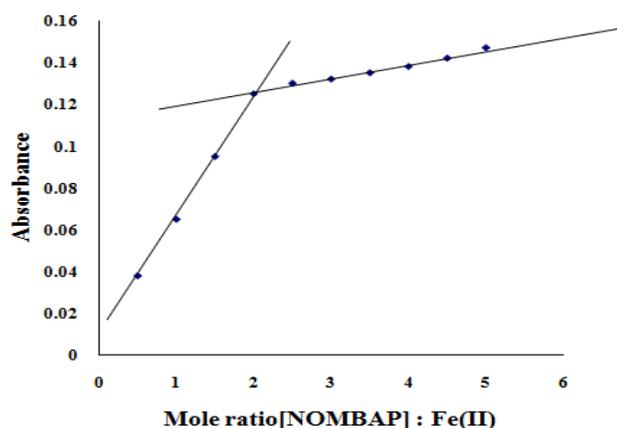


Fig. VI: Mole Ratio Methods

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 cm^3 solutions was 49.85 μg , which is varied between 49.61 and 50.09 at 95% confidence limit Standard deviation and Sandell's sensitivity of the extracted species is found to be ± 0.337 and $0.0176 \mu\text{gcm}^{-2}$ 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 method[15]for Fe (II) (Table - II).

Table II

Samples	Fe(II) found (mg) * Present method	1:10 Phenanthroline method [15]	Reported value (mg)
Pyrolusite	4.97%	4.993%	---
FerriumXT	99.95	99.96	100.00

*Average of three determinations

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