

# LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF IRON USING ACETOPHENONE 2',5'-DIHYDROXY THIOSEMICARBAZONE (ADHTS) AS A NEW ANALYTICAL REAGENT

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## ABSTRACT

Acetophenone 2',5'-dihydroxy thiosemicarbazone (ADHTS) is proposed as a new sensitive and selective reagent for the Spectrophotometric determination of trace amount of Iron. The optimum extraction conditions were evaluated by studying various parameters like pH, solvent, reagent concentration, equilibration time and stability of extracted complex. The reagent reacts with Iron to form a yellow colored 1:2 chelate, at the pH 3.6. The complex is extracted in n-Butanol. The absorption spectrum shows maxima at 430 nm. Beer's law is obeyed in the concentration range 1 to 8 ppm for Iron. The molar absorptivity is  $646.06 \text{ L mol}^{-1} \text{ cm}^{-1}$  and Sandell's sensitivity is  $0.0869 \mu\text{g cm}^{-2}$ . The Limit of Detection for the proposed method was found to be 0.561 ppm. The proposed method is highly sensitive, selective, simple, rapid, accurate, and has been satisfactorily applied for the determination of Iron in the synthetic mixtures, and real samples.

**Key words:** Iron, Spectrophotometric determination, n-Butanol, Acetophenone 2', 5'- dihydroxy thiosemicarbazone derivative

## INTRODUCTION

Literature survey reveal a number of reagents have been employed for the Spectrophotometric determination [1] of Fe (III), but suffer from limitations such as critical pH [2], requirement of masking agent [3] or other agents [4], requirement of heating [5], interference from some ions [6], less sensitive [7] etc. In this paper a new method has been developed using Acetophenone 2',5'-dihydroxy thiosemicarbazone (ADHTS) for extraction and Spectrophotometric determination of Iron, which is simple, selective and sensitive

## EXPERIMENTAL

A Shimadzu UV visible 2100 spectrophotometer with 1 cm quartz cell and a digital ELICO LI-120 pH meter were used for the absorbance and pH measurement respectively. The stock solution of Iron was prepared and standardized [8] and working solution of lower concentration was obtained by suitable dilution. The reagent, ADHTS was synthesized by the procedure reported in the literature. The reagent was confirmed by IR, NMR, Mass and elemental analysis. A 0.1% reagent solution of ADHTS in methanol was prepared and used for extraction studies.

## PROCEDURE

The extraction experiments were performed by shaking the appropriate organic and aqueous solution. The reagent ADHTS formed a yellow coloured complex with Iron which was transferred in a separating funnel. It was extracted into  $10 \text{ cm}^3$  n-Butanol and then transferred to 10mL volumetric flask by passing through some amount of anhydrous sodium sulphate in order to absorb trace amount of water. The amount of Iron present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 430 nm and that in the aqueous phase was determined by known method [9].

## RESULTS AND DISCUSSION

### Extraction as a function of pH

In order to obtain the optimum extraction condition for Iron, the extraction was carried out at various pH from 1 to 10 keeping the organic to aqueous volume ratio of 1:1. The extraction was found to be quantitative at the pH 3.6 and hence pH 3.6 was selected for further studies (fig.1).

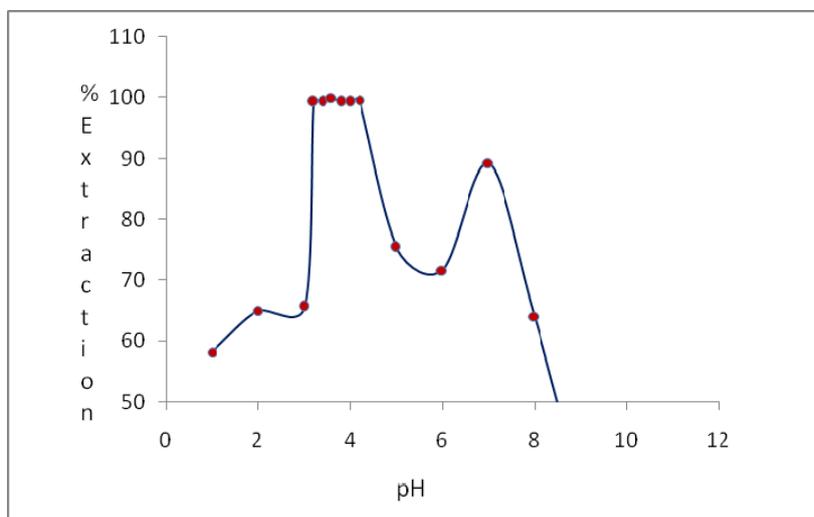


Fig. 1. The effect of pH on the extraction of Iron with ADHTS in n-Butanol.

### Absorption spectrum

The absorption spectrum of Fe (III): ADHTS in n-Butanol, shows an intense absorption peak at 430 nm. The absorption due to the reagent is negligible at this wavelength and hence, the absorption measurements were taken at this wavelength using a reagent blank.

### Effect of solvent

The suitability of various solvents was investigated using organic solvents such as n-Butanol, carbon tetrachloride, Ethyl acetate, Benzene, Xylene, Toluene, Iso-amyl alcohol, ether and pet ether etc. The extraction of Iron with ADHTS was found to be quantitative when both were dissolved in aqueous solution containing n-Butanol as a solvent. Therefore n-Butanol was used as a solvent as it gave better and quick phase separation.

### Effect of salting out agents

The presence of salt of alkali and alkaline earth metals do not show any improvement in the percentage extraction of Iron between n-Butanol and aqueous phase. Hence, these salts have not been added in the aqueous phase before extraction for subsequent studies.

### Effect of reagent

The effect of variation in concentration of ADHTS shows that 1 cm<sup>3</sup> of 0.1% methanolic solution of ADHTS is sufficient for colour development and extraction of 20.0 µg/cm<sup>3</sup> of Iron solution.

### Effect of equilibration Time

The study of change in absorbance with variation in equilibration time for the extraction of Iron shows that equilibration time of 1 minute is sufficient for the quantitative extraction of Fe (III).

### Stability of the complex with time

The stability of the colour of the extracted species with time shows that the absorbance of the extracted species is stable upto 35 hrs. Throughout the experiment, for the reason of practical convenience, the absorbance measurements have been carried out within one hour of the extraction of Iron.

### Beer's law and sensitivity

Calibration graph for Iron was constructed under optimum conditions (Fig.2). The graph obeys Beer's law in the range of 1 to 8 ppm for Iron. The molar absorptivity and sandell's sensitivity were calculated to be 646.06 L mol<sup>-1</sup>cm<sup>-1</sup> and 0.0869 µg cm<sup>-2</sup> respectively.

### Limit of detection (LOD)

LOD (Limit Of detection) of the present method was calculate at 98.3 % confidence level by analyzing blank solution with reference to solvent. Standard deviation of blank solution and slope of calibration curve use for calculating limit of detection is found to be 0.561 µg / mL.

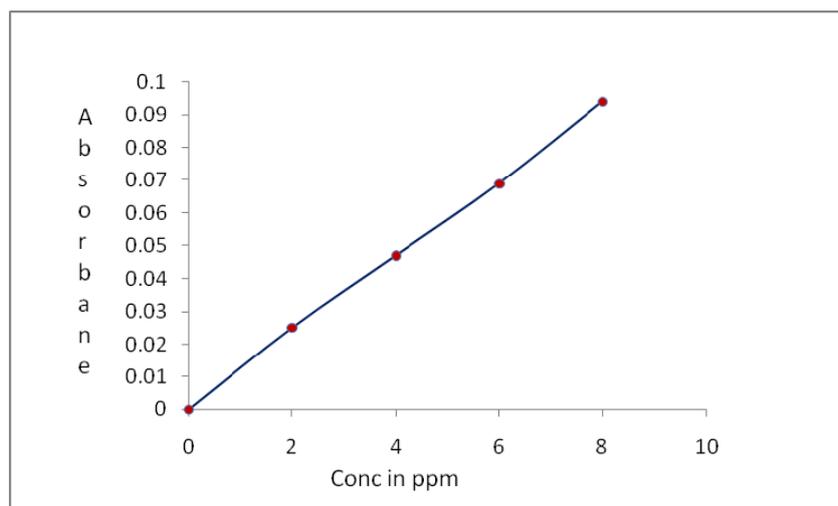


Fig. 2. Calibration plot of Fe(III): ADHTS

### 3.5 Composition of the extracted species

The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Fe(III): ADHTS complex is 1:2. (Fig. 3.)

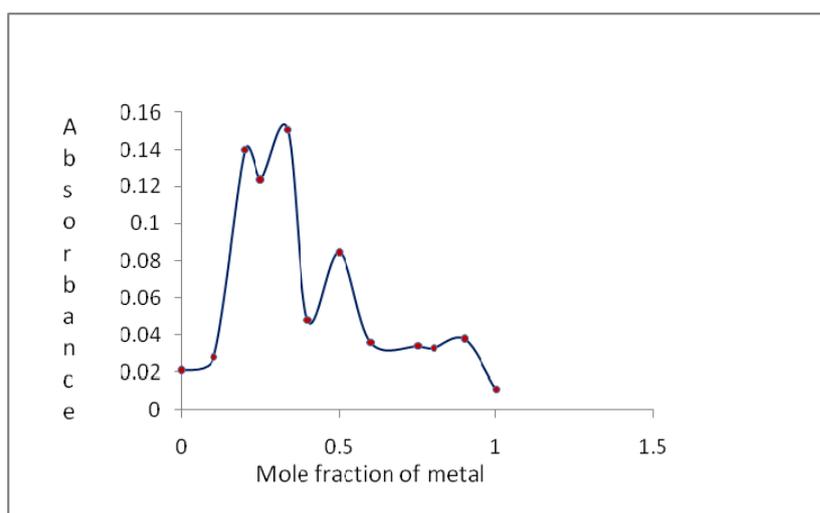


Fig. 3 Job's continuous variation plot

### Effect of foreign ions.

The tolerance limit of different metal ions was studied by carrying out determinations of 5  $\mu\text{g}$  of Fe(III) in presence of large number of foreign ions. It shows no interference with most of the foreign ions on the extraction of Iron. The interference of some metal ions are masked by using appropriate masking agents.(Table.1)

Table no. 1. Masking agents used

Sr. No.	Interfering Ion	Masking agent
1	Co(II)	Sodium cyanide
2	Ni(II)	DMG
3	Cu (II)	Sodium thiosulphate
4	V (V)	Thiourea

**Precision and accuracy**

The precision and accuracy of the method were studied by analyzing a series of solutions containing 5 µg of Iron. The average of 10 replicate analyses for Iron was 4.9989 µg which varies between  $4.9989 \pm 0.00528$  at 95% confidence limit. The standard deviation was 0.1008 and the variance was 0.01016064.

**APPLICATION**

The present method was applied to the determination of Iron in various synthetic mixtures. The results are shown in (Table.2)

**Determination of Iron in alloy**

About 0.5 g of sample (alloy) was dissolved in 15 cm<sup>3</sup> of aqua-regia. The solution was evaporated to dryness and the residue was treated with Conc. HNO<sub>3</sub> and diluted to 100 cm<sup>3</sup>. An aliquot of diluted solution was used for the extraction and spectrophotometric determination of Fe (III) by present method (Table.2)

Table. 2. Applications of proposed method

Sr. No.	Sample	Standard method (ppm)	Present method (ppm)
<b>Synthetic mixtures</b>			
1	Fe (5)+Mn (10)	5	4.95
2	Fe (5) + Zr (10)	4.98	4.96
<b>Iron alloys</b>			
1	Carbon steel	25	24.9
2	Steel	55	54.8

**CONCLUSION**

The proposed method is more highly sensitive and selective than the reported methods for the extractive Spectrophotometric determination of microgram amounts of Iron. It offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and suffers from less interference. It has been successfully applied to the determination of Iron at trace level in synthetic mixtures and alloys.

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