



SOLVENT EXTRACTION COUPLED WITH SPECTROPHOTOMETRY FOR DETERMINATION OF IRON IN TABLET, ORE AND ALLOY

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Abstract

Reagent Acetophenone 2', 4'- dihydroxy semicarbazone, is proposed as a sensitive spectrophotometric reagent for Fe(III). It is synthesized and characterized by NMR, IR and elemental analysis. A selective spectrophotometric method is presented for the trace determination of Fe(III) using A24DHS as spectrophotometric reagent ($\lambda_{\max} = 350$ nm) in acidic aqueous solution (pH = 3.4). The Beer's law is obeyed in the concentration range from 1 to 5 ppm. The A24DHS forms a 1:2 violet coloured complex. The Sandell's Sensitivity is $0.01024 \mu\text{g cm}^{-2}$ with molar absorptivity $4048.0 \text{L mol}^{-1} \text{cm}^{-1}$. The proposed method has been successfully applied to the determination of Iron in tablet, ores & alloy.

Key words : Iron, Spectrophotometry, n-Butyl alcohol, Acetophenone 2', 4'-dihydroxy, semicarbazone derivative.

1. Introduction

Iron and its compounds are widely used in alloys and various biological samples. Trace concentrations of Iron can also affect the physical and mechanical properties of metal and alloys. Iron is essential to nearly all known organisms. Therefore, precise knowledge of the Iron present in a various samples is required, for which an accurate assessment of the Iron is need of analytical methods for determination at ppm level. Methods such as atomic emission and mass spectrometry^{1, 2} which require sophisticated instruments. Some of the reagents used for the spectrophotometric determination of Iron are Bathophenanthroline³, Mercap to pyridine-1-oxide⁴, Pyridazine-3,6-diol⁵, etc. However, most of these methods suffer from certain limitation, such as interference by number of ions^{6, 7}, of low sensitivity⁸.

2. Experimental

The pH measurements were made using a pH meter Elico, Model LI-129, India in conjugation with a combined glass and calomel electrode. Shimadzu UV-Visible 2100 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements.

3. Synthesis of the Reagent

Acetophenone 2', 4' - dihydroxy semicarbazone(A24DHS)

Synthesis of ADHS involves two steps.

- Conversion of Resorcinol to 2',4'-Dihydroxy acetophenone⁵.
- Synthesis of semicarbazone derivative of 2',4'- dihydroxy actophenone⁶.

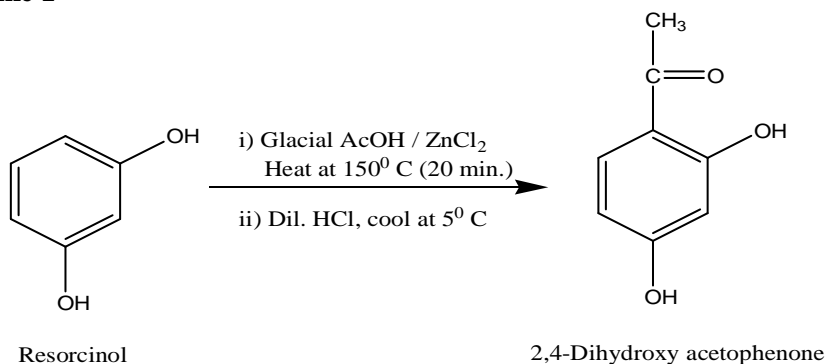
A) Conversion of Resorcinol to 2,4-Dihydroxy acetophenone

Freshly fused and powdered Zinc chloride (0.24 mole) is dissolved in glacial acetic acid (32 mL) by heating in a beaker on a sand bath. Dry Resorcinol (0.2 mole) is added with stirring to the mixture at 140⁰C. The solution is heated until it just begins to boil and kept for 20 min. At 150⁰C. Dilute Hydrochloric acid (1:1) is added to the mixture and solution cooled (5⁰C). The separate product is filtered and washed with dilute HCl (1:3). It is recrystallise from hot water containing little HCl. M.P. is 142⁰C (ref.⁷). Yield is 84.45 %. (Scheme 1)

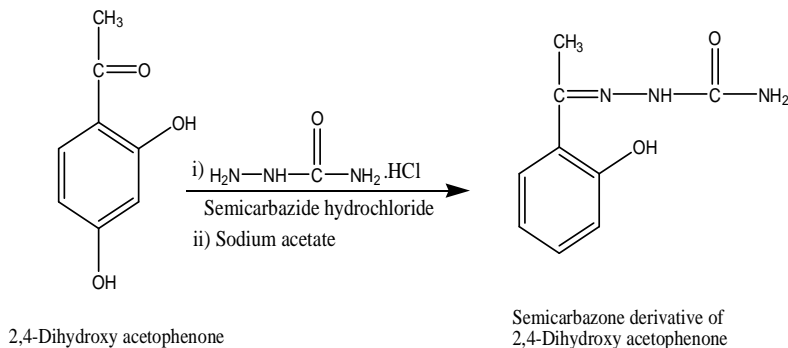
B) Synthesis of semicarbazone derivative of 2',5'- dihydroxy actophenone

Equimolar mixture of sodium acetate and semicarbazide hydrochloride is dissolved in minimum quantity of water and then it is added to methanolic solution of 2',4'-Dihydroxy acetophenone. After addition warm the solution and stir the solution about one hour. The pink coloured compound is precipitate out, which is washed and then recrystallised by using 50% ethyl alcohol as solvent.(Scheme 2)

Scheme 1



Scheme 2



Physical characteristics and Spectral interpretation (Table 1, 2& 3)

Table 1: The physical characteristics of A24DHS are shown in table.

Compound	Color	Yield (%)	Molecular Formula	M. P (°C)	Mol Weight
A24DHS	Light Pink	75.25	C ₉ H ₁₁ N ₃ O ₃	222-224	209.202

Table 2: IR - Spectral data of A24DHS (Elico Infra-Red Spectrophotometer)

Frequency (cm ⁻¹)	Functional group	Frequency (cm ⁻¹)	Functional group
3483	v _(O-H) stretching	1284	C-N stretching
3095	v _(CH) aromatic stretching	1375, 1173, 1155, 1116	In plane bonds due to aromatic substituted benzene ring
1593	v _(C=N) stretching	854	Substituted benzene ring
1520	v _(C=C) stretching	758	v _(C-H) stretching due to substituted benzene ring
1680	v _(C=S) stretching	538	Benzene ring deformation
1458	C-O-H bending	1375	(CH ₃ -C) bending
1323	Ph-C-O stretching		

Table 3: H¹- NMR Spectral data of A24DHS (Bruker NMR spectrophotometer)

The chemical shifts were reported in δ relative to TMS used as an internal standard for NMR.

Solvent	No. of protons	δ in ppm	Assignment
d ⁶ -DMSO	s, 3H	3.39	CH ₃ -C=N
	s, 2H	2.14	-NH ₂
	s, 1H	2.48	-NH-
	two d, 2H	6.1 to 7.3	Aromatic Proton
	d, 2H	12.98	-OH



Conclusion from spectra : The spectral interpretation confirms the structure of A24DHS.

4. Procedure for the Extraction:

1 mL of aqueous Iron metal solution containing 5 µg of Iron was added to 2 mL of reagent in 10 mL standard volumetric flask. The pH of the solution adjusted to 3.4 and final solution diluted to 10 mL. The solution was then transferred to 100 mL separating funnel. 10 mL n-Butyl alcohol was transferred to the same funnel. The funnel was shaken for two minutes and allowed to stand. Separated organic phase was passed through anhydrous Na₂SO₄ in order to absorb trace amount of water and then collected in 10 mL standard measuring flask diluted up to the mark with n-Butyl alcohol. The amount of Iron present in the organic phase determined quantitatively by spectrophotometric method at 350 nm and that in the aqueous phase was determined by thiocyanate method.

Fe (III) standard solutions

It was prepared by dissolving exact weighed amount of ammonium ferric sulphate in distilled water containing few drops of sulphuric acid.

5. Research & Development of Method:

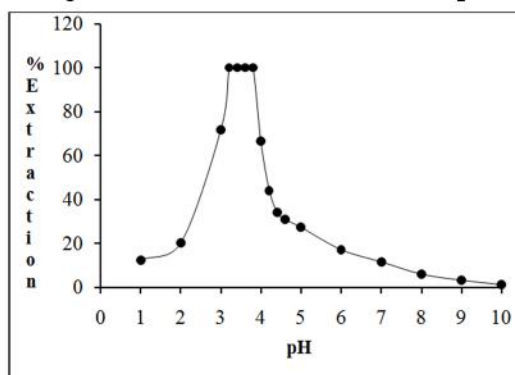
The results of various studies are discussed below.

5.1 Extraction as a function of pH:

The extraction of Iron with Acetophenone 2',4'-dihydroxy semicarbazone has been studied over the pH range 1-10 and was observed that percentage extraction of Fe (III) is maximum at pH range 3.2-3.8. Hence, further extraction and determination carried out at pH 3.4.

(Figure 1)

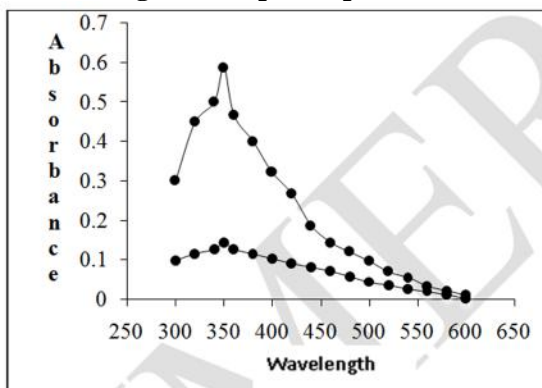
Fig 1: Extraction as a function of pH



5.2 Absorption spectrum:

The absorption spectrum of Fe (III): A24DHS in n-Butyl alcohol shows the maximum absorption at 350 nm. The absorption due to reagent at 350 nm is almost negligible. Hence all measurements were carried out at 350nm. (Figure2)

Fig 2:Absorption spectrum



5.3 Influence of diluents:

Extraction was carried out in various organic solvents and it was found that extraction of complex maximum in n-Butyl alcohol. Hence, n-Butyl alcohol was used for extraction of all other measurements.

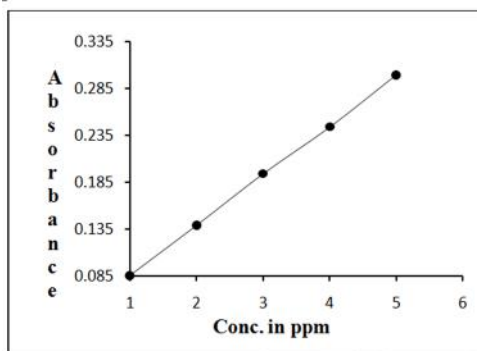
5.4 Effect of reagent concentration:

It was found that 2mL of 0.1% reagent is sufficient for the complex formation of the Iron in 10 mL of aqueous solution at pH 3.4

5.5 Calibration plot:

The Beer's law is obeyed in the range 1 to 5ppm. The molar absorptivity is $3899.2 \text{ L mol}^{-1}\text{cm}^{-1}$ and sandell's sensitivity $0.0288 \mu\text{g cm}^{-2}$ respectively. (Figure3)

Fig 3: Calibration plot





5.6 Limit of Detection :

LOD¹⁰ (Limit of Detection) of the present method was calculate at 98.3 % confidence level, it was 0.102 µg/mL.

5.7 Effect of divalent ions and foreign ions

The interference of various ions present in various amount is studied and it was indicated no interference in the spectrophotometric determination Iron. The ions which show interference in Iron determination were overcome by using appropriate masking agents. (Table 4)

Table 4:Effect of divalent ions and foreign ions

Sr. No.	Interfering Ion	Masking agent
1	V(V)	Thiourea
2	U (VI)	Oxine
3	Mo (VI)	Citrate
4	Cu (II)	Thiosulphate
5	Ti (IV)	Ascorbic acid

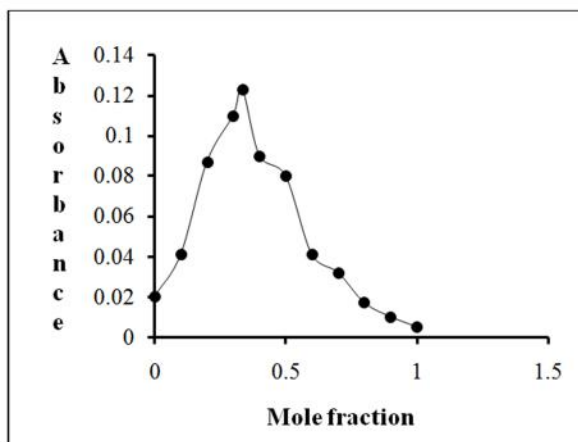
5.8 Precision and accuracy:

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 3µg of Iron in the aqueous phase. The average of ten determinations was 3.003 and variation from mean at 95% confidence limit was ± 0.00886.

5.9 Nature of extracted species:

Job's continuous variation method, Slope ratio method and Mole ratio method has been used for determination of composition of complex. It shows that the composition of complex is 1:2. (Figure4)

Fig 4:Nature of extracted species





6. Applications:

The proposed method was successfully applied for the determination of Iron from tablet, ores and alloys. (Table 7)

Table 5: Applications

Sr. No.	Samples	Amount of Fe (III)	
		Standard method	Present method
1.	Alloy/ Ore (0.3 g)		
a)	Hematite ore (53.06 % Fe)	0.159 µg	0.156 µg
b)	Elinver alloy (62.7 % Fe)	0.188 µg	0.186 µg
2.	Pharmaceutical sample		
	Supradyn (Multivitamin Tablet)	11.17 mg	11.18 mg

6.1 Determination of Fe (III) in alloys/ore

About 0.3 to 0.5 g sample (alloy/ore) was dissolved in 15 cm³ of aqua-regia. The solution was evaporated to dryness and the residue was treated with concentrated HNO₃ and diluted to 100 cm³. An aliquot of a diluted solution was used for the extraction and spectrophotometric determination of Fe (III) by present method.

6.2 Tablet

To the Supradyn, Multivitamin tablet 1.0 cm³ of concentrated HNO₃ was added and evaporated to dryness. It was treated with 5.0 cm³ of 30 % H₂O₂ every time, till solution become colourless. The colourless solution was then treated with dilute HCl and evaporated to dryness. The residue was dissolved in 10 cm³ distilled water and aliquot of this was used for Fe (III) analysis by the present method.

7. Conclusion

The developed method is compared with the thiocyanate method for the estimation Iron. The results are comparable with both the methods. The method is simple and does not required any sophisticated instruments.

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