

A Simple and Effective Spectrophotometric Method for the Determination of Iron(III) with Res-Acetophenone Guanylhydrazone (Rag)



Chemistry

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ABSTRACT

We report here a new simple effective spectrophotometric method for the determination of Iron(III) with Res-acetophenone guanylhydrazone [RAG]. A standard procedure of the absorption spectra of the reagent and the complex is recommended. The absorbance measurements are carried out at 520 nm [Molar extinction co-efficient is 0.4033×10^4 lit. mole cm^{-1}] at pH 7.6. Beer's law is valid up to 10.0 ppm. Sandell's sensitivity of the method is $0.1164 \mu\text{g}/\text{cm}^2$. The Job's variation and mole ratio method show that the composition of Fe(III) RAG complex is 1:2. The instability constant is 0.1289×10^{-8} . The method is applied for the determination of iron in cupranickel alloy and synthetic mixtures.

INTRODUCTION :

Numerous methods for the spectroscopic determination of Iron have been reported [1-6], but very few are in practice. Res-acetophenone guanylhydrazone (RAG) has been used as sensitive reagent for Fe(III). It forms a red colored complex with iron at pH 7.6, which leads to the development of a simple and rapid spectrophotometric method for the determination of iron at tracer level.

EXPERIMENTAL :

The spectral measurements were done on ELICO (CL-27) visible digital spectrophotometer, equipped with 10.01 mm matched pair of glass cuvettes. The pH measurements were done on ELICO (L1-120) digital pH meter, using glass calomel combination electrode. For standardization of pH meter, potassium hydrogen phthalate (pH = 4.01) and borax (pH = 9.18) buffers were used.

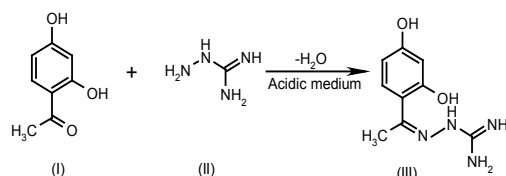
SYNTHESIS OF RAG :

For the synthesis of Res-acetophenone guanylhydrazone (RAG), aminoguanidine bicarbonate was used instead of amino guanidine dihydrochloride, which simplified and gave much better yield.

A solution of amino guanidine bicarbonate, 1.0g in 50% nitric acid and Res- acetophenone, 2.054g in 10ml absolute ethanol were mixed together. The mixture was kept in ice cold water for half an hour. The pale yellow colored product was separated by filtration and crystallized from absolute ethanol (2.0g) (percentage = 65.48 % ee) M.P. = $94^\circ \pm 1^\circ \text{C}$.

The molecular formula was confirmed on the basis of micro-elemental analysis as $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_2$. Calculated percentage of elements was C = 51.92%, H = 5.76% N = 26.92% and O = 15.38%. Experimental percentage of elements was found to be C = 51.37%, H = 5.59% and N = 27.13%. The reagent RAG is soluble in ethyl alcohol, methyl alcohol and acetone but insoluble in benzene, chloroform and carbon tetrachloride.

SCHEME:



Res-acetophenone Aminoguanidine (RAG)
Res-acetophenone guanylhydrazone

Materials and methods :

A standard solution of Fe(III) (1 mg/ml i.e. $1.7910 \times 10^{-2} \text{ M}$) was prepared by dissolving 0.308 g of A.R. grade Ferric ammonium

sulphate monohydrate in 100 ml distilled water containing a 2-3 drops of sulphuric acid. The solution was standardized with Volhard's method volumetrically. [7]

A stock solution of $0.5 \times 10^{-2} \text{ M}$ reagent (RAG) was prepared by dissolving 0.104 g of it in 100ml ethyl alcohol.

The buffer solutions were prepared by dissolving appropriate amounts of boric acid and sodium hydroxide.

Procedure :

A suitable aliquot of the solution containing 50 μg of Fe (III) was taken in a 10ml volumetric flask. To this, was added 2.5 ml of reagent (RAG) solution of concentration ($1.0 \times 10^{-2} \text{ M}$) and diluted to 2/3 volume of the flask. Then pH of the solution was adjusted to 7.6 by adding buffer solution and diluted to volume with distilled water. The absorbance of the Fe(III)-RAG complex was measured at 520 nm against reagent blank. The concentration of Fe(III) in an unknown solution was determined from a calibration curve obtained under identical conditions.

Applications:

The method was applied in the determination of Fe(III) in the analysis of Cupranickel alloy and synthetic mixtures.

1)Determination of Iron(III) in Cupronickel Alloy :

A 0.7g alloy sample is treated with 2.0 ml conc. HNO_3 when the reaction is almost over, the mixture is warmed on a hot plate to complete dissolution. After addition of 1.0ml conc. H_2SO_4 , the mixture is evaporated until white fumes appear; then cooled and diluted to about 100ml with 0.3ml HCl. The solution is heated almost to boiling and H_2S is passed through it to precipitate all the copper. The Copper sulphide is filtered off and washed. The filtrate is boiled to remove hydrogen sulphide then evaporated to about 50ml. To oxidize Fe(II) to Fe(III), 2.0ml of 30% hydrogen peroxide solution is added and the solution is boiled to decompose the excess of peroxide. The solution is then made up accurately to 100 ml with distilled water.

The aqueous solution was used for determination of iron(III) after elimination of Mn and Ni, as per recommended procedure. The results are given in table.1

Table.1: Determination of Iron(III) in Cupronickel Alloy

Sample	Composition %	Iron(III)		Relative standard deviation %
		Found %	X %	
Cupronickel Alloy	Cu(II) = 67.0	0.827	0.835	0.98
	Fe(III) = 0.83	0.835		
	Mn(II) = 0.80	0.841		
	Ni(II) = 31.2	0.838		

2) Determination of Iron(III) in synthetic mixtures :

The method has been tested on a number of synthetic mixture and the results are shown in table.2

Table.2 Determination of Iron(III) in synthetic mixtures**Iron (III) = 17.5 µg****Each ion added = 125.0 µg**

Ions added, µg	Iron (III), µg	
	Found	X
Mg(II), Zn(II), Ce(IV)	17.2, 17.7, 17.3	17.40
Bi(III), Sb(III), Al(III)	17.4, 17.5, 17.6	17.50
Ag(I), Th(IV), Pb(II)	17.7, 17.4, 17.2	17.43
Mo(VI), Cr(III), Pt(IV)	17.0, 17.6, 17.7	17.43
Hg(II), Cd(II), Ni(II)	17.8, 17.3, 17.5	27.53

RESULTS AND DISCUSSION:

The absorption spectrum of Fe(III)-RAG complex recorded at pH 7.6 shows a peak at 520 nm. At this wavelength, the molar extinction coefficient of the complex is 0.4033×10^4 lit. mole⁻¹. cm⁻¹ and of the reagent 0.0080×10^4 lit. mole⁻¹.cm⁻¹. About five-fold molar excess of the reagent concentration was sufficient for full color development of the complex. The Beer's law is valid up to 10.0 ppm of Fe (III). Sandell's sensitivity [8] of the method is 0.1164 µg/cm². The composition of the complex was determined by Job's continuous variation method [9] and mole ratio method.[10] These methods indicate the formation of a single complex having the composition 1:2 [Fe(III) : RAG]. The degree of dissociation was obtained by mole ratio method and was found to be 0.1049. The apparent instability constant[11] was found to be 0.1289×10^{-8} . To study the effect of diverse ions, Fe(III) was determined in presence of various cations and anions. It is evident that Fe(III), like ions such as Ba(II), Au(III), Ag(I), Bi(III), Co(II), EDTA⁻⁴ and citrate ions interfere seriously and can be tolerated in presence of appropriate masking agents.[12]

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