

## **Rapid, Economical and Selective Complexometric Determination of Iron (III) in its synthetic alloys using 3 hydroxy-3 phenyl-1-(2,4,6-tribromophenyl) triazene.**

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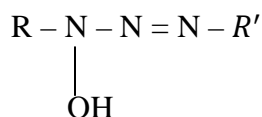
### **Abstract**

The present study describes a simple, selective, rapid and economical method for the determination of iron (III) in its synthetic alloys using 3-hydroxy-3-phenyl-1-(2,4,6-tribromophenyl) triazene as metallochromic indicator in the  $P^H$  and temperature range of 2.5-3.0 and 20 – 60<sup>o</sup>c respectively. The colour and shape of the synthesized indicator was light yellow shining needles having melting point of 59<sup>o</sup>c. It was crystallized from ethanol. The results of elemental study showed that, the values of C, H, N obtained experimentally agrees very well with those obtained theoretically. The colour at the end point changes from violet to light yellow using EDTA as a titrant. There is no interference in either determination from common metal and anion ions other than Pb(II), Cr(II), Mo(VI), Mn(II), U(vI), Cu(II), Cd(II),  $F^-$ ,  $PO_4^{3-}$ ,  $C_2O_4^{2-}$ ,  $HPO_4^{2-}$ . Reproducible and accurate results are obtained for 5.59 -1.12mg of Iron with relative error less than  $\pm 1.79\%$  and standard deviation not more than 0.10%. The results of the test method and reference method (Atomic absorption spectrophotometric) showed that, there is no statistical difference in the results by the two methods.

**Index terms** – Hydroxytriazenes, Metallochromic indicator, Complexmetric titration, Iron (III), EDTA, Foreign ions, Selective.

## 1.0 INTRODUCTION

Hydroxytriazenes have the general structure



Where R and R' is alkyl or aryl group [1], [2]. Hydroxytriazenes are widely used as ligands to coordinate different transition or inner transition metal ions due to their good solubility of their complexes [3]. They coordinate with the metal ions via the N-OH and the –N=N=N- group [4]. For example it was reported that complexometric determination of Zn(II) using three hydroxytriazenes as metallochromic indicators in three medicines-zivinal-CD, Becozine, and Vinyneral Z [5].

Complexometry is a very useful method for the determination of major quantities of metals present in various combinations [6], [7], [8]. The indicators used in complexometric titrations are as follows; Mordant black II, Eriochrome black T, Solochrome black T (Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg), Murexide, Ammonium Purpurate (Ca, Cu, Co), Catechol-Violet (Mn, Mg, Fe, Co, Pb), Methyl blue, Thymol blue (Pb, Zn, Cd, Hg), Alizarin (Pb, Zn, Co, Mg, Cu), Sodium Alizarin Sulphonate (Al, Th), Xylenol Orange (Bi, Th, Pb, Zn, Cd, Hg) [9]. In all these procedures the quantity of the element determined is hampered by the presence of some cations and anions [10]. For example, Cu, Ni, Co, Cr, Al, even in traces, must be absent when conducting titration of Iron (III) with EDTA using Eriochrome black T as indicator [11].

In the present study the possibility of using hydroxytriazenes as indicators for Iron (III) - EDTA titration has been extensively explored. The effects of foreign ions are studied and application of the method in the determination of iron (III) in its synthetic alloys is also reported in this paper.

## 2.0 MATERIALS AND METHODS

All chemicals used in the analysis were of analytical reagent grade (merk) and used without further purification and in all of the steps redistilled water was used. The atomic absorption spectrophotometer (Varian spect-AA-10-model) was used for measurements.

## **2.1 PREPARATION OF HYDROXYTRIAZENE.**

The synthesis of the new hydroxytriazene described in this study proceeded as follows:

### **2.1.1 Preparation of aryl hydroxylamine**

Nitrobenzene (0.25mol), ammonium chloride (15g), water (400ml) and rectified spirit (100ml) were mixed and stirred mechanically at 40°C zinc dust (40g) was subsequently added in small quantities until the temperature reached 60°C and maintained for 15 minutes. The resultant mixture was filtered at the pump and the residue washed with 100ml of warm water (40°C). The filtrate was left to cool in a freezer at 0°C.

### **2.1.2 Preparation of aryldiazonium salts.**

Aromatic primary amine (0.2ml) was dissolved in a warm mixture of concentrated  $H_2SO_4$  (60ml) and water (10ml) with vigorous stirring. It was then kept in freezer to cool. In a separate beaker sodium nitrite (13.9g) was dissolved in water (40ml) and left in the same freezer. After three hours the aromatic amine Sulphate solution was transferred to an ice bath and the sodium nitrite solution slowly added with stirring. The temperature of the reaction mixture was maintained at well below 5°C, which favoured the formation of the aryldiazonium salt.

### **2.1.3 Coupling and crystallization**

To aryl hydroxylamine (step I) in an ice bath was slowly added till aryldiazonium salt (step II) in small portions with continuous stirring. The  $P^H$  was maintained at 5-6 using sodium acetate and temperature at  $\leq 5^\circ C$ . Fifteen minutes later the resultant mixture was filtered at the pump, and the residue washed with ice cold water. The crude hydroxytriazene product was treated with activated charcoal and crystallized from ethanol.

## **2.2 REAGENTS**

### **2.2.1 EDTA solution**

A stock solution (0.01M) of disodium salt of EDTA was prepared by dissolving requisite quantity of the salt in water and standardized against zinc sulphate solution (0.01M) using xylenol orange as indicator at  $P^H$  6-7 [12].

### **2.2.2 Zinc sulphate solution**

Prepared by dissolving a known amount of zinc sulphate in water and standardize gravimetrically by oxinate method [13], [14].

### **2.2.3 Solution of diverse ions**

Solution of various cations and anions were prepared by dissolving calculated amount of appropriate salts in water or in suitable dilute acid and making up to a known volume.

### **2.2.4 Xylenol orange indicator (0.5%)**

A freshly prepared solution of xylenol orange in water was used [15].

### **2.2.5 Iron (III) stock solution (0.01m)**

Prepared by dissolving 1.2055g of ammonium iron (III) sulphate dodecahydrate in water containing concentrated sulphuric acid (5ml) in a calibrated flask [16].

## **2.3 PROCEDURE FOR COMPLEXOMETRIC TITRATION**

All the freshly prepared hydroxytriazene (0.1% in ethanol) solutions were screened as metallochromic indicators for iron (III) determination. Iron (III) solution ( $5.0 \times 10^{-3}M$ ) was titrated in the  $P^H$  range 2.0- 4.0.

## **2.4 EFFECT OF $P^H$ AND TEMPARATURE**

$P^H$  metric studies were carried out by performing the titration of iron (III) using a 1.0% sodium acetate-acetic buffer in the presence of a 1.0% perchloric acid solution. For synthesized hydroxytriazene the optimal  $P^H$  (2.5 – 3.0) and temperature (20 -60°C) ranges were determined in which the colour change at the end point was sharp and most perceptible. Interference by 35 different ions was also investigated.

## 2.5 TITRATION PROCEDURE.

A general titration procedure for ion (III) using hydroxytriazene as indicator was developed. Iron (III) solution (10ml) was diluted to 30ml with an ethanol-water mixture. Five to six drops of hydroxyzene were added, which usually resulted in instantaneous development of a blue colouration. The solution was at this point titrated very slowly with equimolar EDTA solution. The point where there was a sharp yellow colour change was taken as the end point in all the cases. The results were further augmented by atomic absorption spectrophotometry.

## 3.0 RESULTS AND DISCUSSION

The physical characteristics, crystalline shape, colour, melting point etc, for the synthesized hydroxytriazene are displayed in table 1, together with the crystallization solvent and the elemental analyses.

**Table 1: Physical characteristic and elemental analysis of 3-hydroxy-3-phenyl-1- (2, 4, 6-tribromophenyl) triazene.**

Physical characteristics		Elemental Analysis		Molecular Formula
		Th	Exp	
Colour and sharp of crystals	Light yellow shining needle	21.66	21.47	C <sub>12</sub> H <sub>8</sub> N <sub>3</sub> OBr <sub>3</sub>
Crystallized from	Ethanol	1.55	1.08	
M.P	59	10.83	11.07	

The titration of iron (III) in the concentration range of 0.002-0.010 mol/L (1.12-5.59mg) was carried out under optimized experimental conditions. These results are presented in table 2.

The results indicates that the relative error ranges between +1.19% to -1.79% and the standard deviation ranges from 0.02 to 0.10. These results revealed that iron (III) could be accurately

determined using this hydroxytriazene down to values as low as 0.002M. Further, the tabulated t value (2.365) at the 95% confidence level exceeds the calculated t value (0.036) and this shows that, there is no significant difference between the amount taken and that which was found. Hence the proposed method is precise and accurate.

**Table 2: Determination of iron in iron (III) nitrate solution (n=5)**

$P^H$  range = 2.5 -3.0

Temperature range = 20-60°C

End point: violet to light yellow

Iron/mg		Relative error %	Standard deviation	+ value at 95% confidence level
Taken	Found*			
5.59	5.62	+0.54	0.06	Calculated = 0.036 Tabulated = 2.365
5.03	5.06	+0.60	0.07	
4.47	4.50	+0.67	0.10	
3.91	3.93	+0.51	0.03	
3.35	3.34	-0.30	0.03	
2.80	2.81	+0.36	0.04	
1.68	1.70	+1.19	0.03	
1.12	1.10	-1.79	0.02	

\* Average of five determination

In order to establish the possibility of using the proposed method for the quantitative determination of iron (III), the effect of diverse ions was studied. This was done by adding different amounts of diverse ions to a solution containing 2-80 mg of iron (III). The tolerance levels of the non interfering diverse ions are summarized in table 3. An error of less than +2% in the recovery was

considered to be tolerable. The diverse ions such as Pb (II)(51.80mg), Mo (VI)(95.94mg), Mn(II)(13.74mg), U(VI)(59.51mg), Cu(II)(15.89mg), Cd(II)(28.10mg), Cr(III)(13.00mg),  $F^-$ (4.75mg),  $PO_4^{3-}$  (23.74mg),  $C_2O_4^{2-}$ (22.05mg),  $HPO_4^{2-}$ (23.99mg), do interfere with the determination of iron (III). The results of interferences shows that, cation interfere causes positive error while anion causes negative error. The positive error might be contributed due to iron(III) and interference species competing for EDTA during titration while negative error might be due to interfering species forming a very stable complex with iron (III) leaving a small amount of uncomplex iron(III) for titration with EDTA. The interference of Cr (III) and Cu (III) is mainly due to the deep purple and blue colour of their EDTA complex respectively which makes the detection of their end point rather difficult. The interference of Ni(II) and Co(II) can be obviated by the addition of excess potassium cyanide prior to EDTA complexation as masking agent.

**Table3: Determination of iron (III) in presence of diverse metal ions**

**(Iron taken in solution =2.80mg)**

Diverse ion	Diverse ion taken /mg	Iron found* (mg)	Relative error %
Na(I)	5.75	2.79	-0.36
K(I)	9.78	2.78	-0.71
Mg(II)	6.08	2.76	-1.42
Ca(II)	10.02	2.82	+0.71
Ba(II)	34.34	2.75	-1.79
Sn(II)	29.67	2.76	-1.42
Zr(IV)	22.81	2.81	+0.36
Th (IV)	58.01	2.78	-0.71
W(VI)	45.96	2.81	+0.36
Zn(II)	16.34	2.75	-1.79
Co(II) <sup>s</sup>	14.73	2.77	-1.07
Hg(II)	50.15	2.77	-1.07
Ni(II) <sup>s</sup>	14.78	2.82	+0.71
NH <sub>4</sub> <sup>+</sup>	4.51	2.79	-0.36
S <sup>2-</sup>	8.02	2.76	-1.42

SO <sub>4</sub> <sup>2-</sup>	24.02	2.76	-1.42
SO <sub>3</sub> <sup>2-</sup>	20.02	2.78	-0.71
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	28.03	2.75	-1.79
Cl <sup>-</sup>	8.86	2.84	+1.43
I <sup>-</sup>	31.73	2.77	-1.07
NO <sub>2</sub> <sup>-</sup>	11.50	2.81	+0.36
NO <sub>3</sub> <sup>-</sup>	15.50	2.85	+1.79
CO <sub>3</sub> <sup>2-</sup>	15.00	2.83	+1.07
CH <sub>3</sub> COO <sup>-</sup>	14.76	2.78	-0.71

\*- Average of the five determination

S -Pre masked with potassium cyanide

The utility of the proposed method was explored in the determination of iron (III) in its synthetic mixture of iron (III) with alloy compositions. The analytical results are given in table 4. The calculated F value (1.020) is less than the tabulated value (9.28), so the two methods have comparable standard deviations. Further, the tabulated t for ( $N_1 + N_2 - 2$ ) at the 95% confidence level is 2.447 and the calculated t value is 0.008, so there is no statistical difference in the results by the test and reference method. This indicates that, the test method would be effective for the analysis of alloy samples of similar complexity.

**Table 4: Determination of iron (III) in synthetic mixture with alloy composition.**

Mixture	Composition %	Test method			Reference method		
		Iron found* %	Standard Deviation	Relative error %	Iron found* %	Standard Deviation	Relative error%
Fe+Ni	58+42	58.65	0.02	+1.12	58.20	0.74	+0.34
Fe +Si+Ca	8+90+2	7.85	0.02	-1.88	8.05	0.03	+0.63
Fe +Ni+Co	54+29+17	53.86	0.04	-0.26	53.98	0.53	-0.04
Fe +Co	60+40	60.51	0.04	+0.85	60.08	0.81	+0.13

\*Average of five determinations

#### 4.0 CONCLUSION



A new metallochromic indicator for direct complexometric determination of iron (III) have been introduced. The results obtained by the hydroxytriazene are comparable to those using atomic absorption spectrophotometric method. Interference studies have shown that direct complexometric determination of iron (III) can be satisfactorily performed in the presence of a number of cations and anions. This reveals that the method may be suitable for the determination of iron (III) in its alloys. Readily prepared and in higher yields, hydroxytriazene exhibit obvious advantages over some other metallochromic indicators such as Eriochrome black T, solochrome black T, murexid, etc.

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