

ANALYTICAL APPLICATION OF *p*-BROMOPHENYLAZO-BIS-ACETOXIME IN THE SPECTROPHOTOMETRIC DETERMINATION OF IRON (III)

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ABSTRACT

Spectrophotometric determination of iron (III) has been done using *p*-Bromophenylazo-bis-acetoxime at 370nm, keeping the pH in the range 3.5-4.5. The molar absorptivity and Sandell's sensitivity values are 1,030 dm³ mol⁻¹ cm⁻¹ and 54.22 ng cm⁻², respectively. The Beer's law is obeyed in the range (1 to 6) x10⁻⁵ M.

Keywords: Arylazo-bis-acetoxime, Spectrophotometric determination, Iron (III)

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INTRODUCTION

A number of arylazo-bis-acetoximes which are homologues of hydroxytriazenes have been synthesized and developed as reagents for the determination of transition metals¹⁻². We report here application of a similar compound, *p*-bromophenylazo-bis-acetoxime (*p*-BPABA) for spectrophotometric determination of iron (III).

EXPERIMENTAL

The *p*-Bromophenylazo-bis-acetoxime was prepared by method reported in literature³.

Stock Solution

A 1.0x 10⁻² M ferric nitrate nonahydrate (BDH) was prepared in distilled water. Few drops of (1 M) concentrated nitric acid were added to prevent hydrolysis. The solution was standardized with EDTA solution using sulphosalicylic acid as indicator. A 1x 10⁻² M solution of the reagent *p*-bromophenylazo-bis-acetoxime was prepared in acetone. Tris-buffer (2%, w/v) was prepared. Systronic 108 UV/VIS Spectrophotometer and a Systronic 324 pH meter were used respectively for absorption measurement and pH measurement.

Method

Spectrum of *p*-bromophenylazo-bis-acetoxime was measured in the wavelength region 360 – 430nm against solvent blank. Iron and *p*-Bromophenylazo-bis-acetoxime solutions were taken in 1:5 ratio and the spectrum of iron complex was recorded against reagent blank in the range 360-430 nm. The working wavelength was found to be 370 nm. A set of solutions containing Fe (III) and *p*-BPABA reagent in ratio 1:5 was prepared and pH was varied between 2 to 6. The pH range of constant maximum absorbance was found to be between 3.5 to 4.5. Composition of the complex was determined by Job's method and moles ratio method of Yoe and Jones. The study revealed that composition of iron (III) complex is 1:2 (M: R). Absorbance of set of six solutions containing Fe (III) to *p*-BPABA in ratio 1:5 was measured at corresponding working wavelength against reagent blank. Beer's law was obeyed in concentration range 1x10⁻⁵ to 6x10⁻⁵ M. Interference of 23 cations and anions in the determination of iron were studied. To the set of solutions containing iron to reagent 1:5 ratio, 10 ppm of different foreign ions were added and absorbance was measured against reagent blank under optimum conditions. Those ions, which did not interfere at 10 ppm level their interference was again studied at 50 ppm level. In case no or little change

in absorbance was seen as compared to the absorbance without any foreign ion, then for those ions interference was studied again at 100 ppm level. However tolerance of still higher concentration was not studied.

RESULTS AND DISCUSSIONS

Iron (III) was found to form 1:2 complex with *p*-bromophenylazo-bis-acetoxime.

Table-1: Value of log β and ΔG respectively by two different methods

Name of methods	Name of Reagents	Composition of complex	Concentration of complex (M)	E_m	E_s	α	$K_{inst.}$	B	Log β	ΔG at 27°C k.cal/mol
Harvey & Manning's method	<i>p</i> -bromo phenyl azo-bis-acetoxime	1:2	2.5×10^{-4}	0.265	0.184	0.306	1.035×10^{-8}	9.68×10^7	7.98	-10.95
Purohit's method	<i>p</i> -bromo phenyl azo-bis-acetoxime	1:2	1×10^{-3}	1.012	0.747	0.262	9.74×10^{-8}	1.03×10^7	7.01	-9.62
		1:2	5×10^{-4}	0.506	0.375	0.259	2.34×10^{-8}	4.27×10^7	7.63	-10.47

Stability constants

Harvey and Manning's method⁴ and Purohit's method⁵ have been used to determine the stability constants. Validity of the methods can be confirmed from the value of log β obtained from both the methods. The log β values agree quite well. Further the precision studies were carried out by measuring the absorbance of 10 sets of solution containing 27.92 ppm of iron (III), and *p*-BPABA in ratio of 1:5, under optimum conditions. The absorbance was measured against reagent blank at working wavelength (370 nm). Thus can be iron was successfully determined at ppm level with good precision.

Interference of several cations and anions in the determination of iron was studied at 10, 50 and 100 ppm level. Interference was studied using following 23 cations and anions viz. Na^+ , K^+ , NH_4^+ , Ba^{2+} , Cr^{3+} , Co^{2+} , Pb^{2+} , Ca^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , F^- , Cl^- , Br^- , I^- , NO_2^- , SO_4^{2-} , CO_3^{2-} , $C_2O_4^{2-}$, SO_3^{2-} , PO_4^{3-} . It was found that Na^+ , K^+ , NH_4^+ , Ba^{2+} , Pb^{2+} , Ca^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Cl^- , Br^- , I^- did not interfere even at 100 ppm level. However Na^+ , K^+ , NH_4^+ , Ba^{2+} , Pb^{2+} , Ca^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Cl^- , Br^- , I^- , NO_2^- , CO_3^{2-} , $C_2O_4^{2-}$ ions could be tolerated only upto 50 ppm and Na^+ , K^+ , NH_4^+ , Ba^{2+} , Cr^{3+} , Co^{2+} , Pb^{2+} , Ca^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , F^- , Cl^- , Br^- , I^- , NO_2^- , SO_4^{2-} , CO_3^{2-} , $C_2O_4^{2-}$, SO_3^{2-} , PO_4^{3-} ions only upto 10 ppm. However tolerance of any ion at higher concentration than 100 ppm was not studied. Thus it can be seen that iron (III) can be determined even in presence of number of ions present at 100 ppm level. Thus, from the above studies it can be concluded that *p*-bromophenylazo-bis-acetoxime can be used successfully for spectrophotometric determination of iron (III).

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