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SPECTRO PHOTOMETRIC DETERMINATION OF IRON (III) WITH 3, 3-DIMETHYL-1-(2-CARBOXYPHENYL) TRIAZENE

Shahid Masood Yousaf, Gulraze Shahnaz and Nasir Ahmad

Department of Chemistry, Quaid-i-Azam University Islamabad, Pakistan

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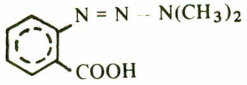
A new spectrophotometric method for the estimation of iron (III) is described. Ferric ions form a stable, water soluble, intense violet complex ion with 3, 3-dimethyl-1-(2-carboxylphenyl) triazene (DCPT) at pH 2.8. The complex ion has a broad absorption band centred at 520 nm. The complex with maximum colour intensity is formed when the metal ion and the ligand are present in 1:2 ratio. The coloured solution obeys Beer's law in the 0-20 ppm concentration range. A number of metal ions, if present below certain concentrations, do not interfere the determination of iron (III).

Key words: Spectrophotometoric, Determination, Iron (III).

INTRODUCTION

A number of spectrophotometric methods for determination of ferrous and ferric ions have been reported [1-8]. The commonly used reagents for developing colour in solutions containing iron ions include thiocyanate [9], 1, 10-phenanthroline [10], ethylenediamine-*bis*(sulphosalicylaldehyde) [11], 1-phenyl-3-quinolyl 2-thiourea [12] and some recently reported compounds as 8-hydrazinoquinoline hydrazone [13], ethyl α-ethylamino-2-hydroxy benzyl phosphonate [14], 3-aldehydosalicylidene cyanoacetylhydrazone [15] and 2-(5-chloro-2-pyridylazo)5-diethylaminophenol [16]. Many of these reagents not only produce colour with iron compounds but also interact with allied metals such as copper (II), nickel (II), cobalt (II), silver (I) or mercury (II) to give coloured species which interfere with the estimation. In some cases coloured species are extracted into organic liquids before measuring their absorbence [17-19]. The accuracy and precision of such methods depend upon the efficiency of the extraction procedure. In addition, some of the reagents themselves are coloured [20-22] and absorb in the visible region of the spectrum, thus introducing a limiting factor. In certain cases, the coloured species in the test solution are not stable, and undergo change in the colour intensity with time. This also affects the accuracy of the method.

The present work describes a new spectrophotometric method for the determination of iron (III) in solution. A colourless reagent, 3, 3-dimethyl-1-(2-carboxyphenyl) triazene (I) produces violet colour with ferric ion solution. Extraction of the coloured species into the organic phase is not necessary, as the ligand and its ferric complex are soluble in water at the working pH. The ligand produces an intense violet coloration in ferric ion solution at pH 2.8, which has its maximum absorbence at 520 nm. The colour is stable for an infinite period of time. This method is specific for iron (III) estimation at the working pH, as a number of other metal ions do not give any colour reaction with this ligand. The method is precise and very accurate. It measures ferric ions in the concentration range 0.1 – 20 ppm.



(I) DCPT

EXPERIMENTAL

Reagents. Analytical reagent grade compounds such as ferric ammonium sulphate, potassium hydrogen phthalate, hydrochloric acid (25 %) were used. The ligand, 3, 3-dimethyl-1-(2-carboxyphenyl) triazene, was obtained from Fluka, Switzerland and used without further purification. Other metal salts used in these studies were supplied either by BDH or E. Merck.

Instrumentation. The solution spectra were recorded on a Hitachi model 220-S recording spectrophotometer. A set of two glass cells of one cm thickness were used for the measurement of absorbence. The pH of the test solutions were measured on Schott and Gen, Maiz model CG 717 pH meter.

Solutions. (i) A stock solution of 3, 3-dimethyl-1-(2-carboxyphenyl) triazene (3×10^{-3} M) was prepared by dissolving accurately weighed 0.57961 g of the reagent in

distilled water and making the volume to one litre in a volumetric flask.

(ii) Metal ion solution was obtained by dissolving 0.48221 g of ferric ammonium sulphate in 3.0 ml of concentrated hydrochloric acid and diluting it to 1 litre in a volumetric flask. The solution thus obtained contained 56 μg/ml of iron (III) ion.

(iii) A buffer solution was prepared by mixing 289 ml of 0.1M HCl solution with 500 ml of 0.1M solution of potassium hydrogen phthalate and diluting to one litre. This solution after thorough mixing had pH 2.8.

(iv) A number of stock solutions of various interfering metal ions of 0.1M concentration were prepared by dissolving calculated amounts of their halides or nitrates in distilled water.

Development of colour in ferric ion solution. and intense violet coloration was obtained when equal volumes of the stock solutions of DCPT and ferric ion were mixed and pH maintained at 2.8 by suitable means. This solution was diluted to mark in a volumetric flask. The absorption spectrum of this solution (Fig. 1) consists of a broad band centred at 520 nm. Its extinction coefficient is 875 moles lit^{-1} cm^{-1}.

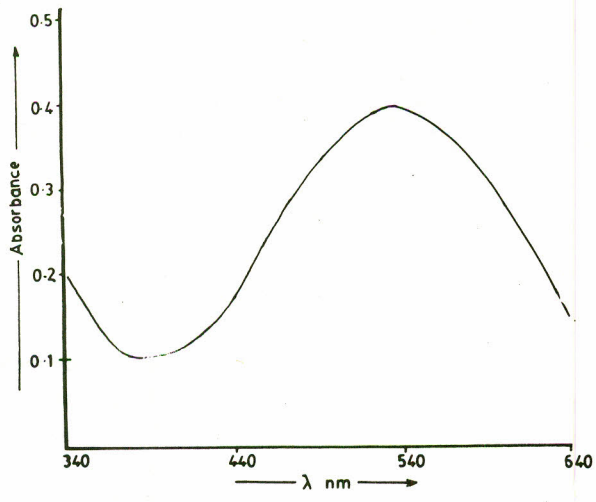


Fig. 1. Absorption specturm of Fe(III)-DCPT system in aqueous solution

Effects of pH and time on colour intensity. A number of coloured solutions were prepared by mixing excess of stock solution of the ligand with suitable volumes of ferric ion stock solutions. The pH of these solutions was varied over a wide range (2-12), particularly between 2.0-3.5. The solutions were diluted to mark in volumetric flasks, and their absorbence measured after thorough mixing. The complex ion had maximum absorbence at pH 2.8 as shown in Fig. 2.

The effect of time on colour intensity of a 1 x 10^{-3}M solution of the complex ion maintained at pH 2.8 was also observed for two days. The absorbence of the solution was measured after regular intervals. There was no change in the colour intensity of the solution even after 48 hr.

Determination of metal to ligand ratio. A number of solutions containing x ml of the stock solution of ligand and 10-x ml of the standard metal ion solution were prepared. Their pH was maintained at 2.8 by adding 10 ml of the buffer solution. The absorbence of these samples was measured at 520 nm and plotted as a function of the mole fraction of the metal ion. The maximum absorbence is observed at 1:2 metal ion to ligand ratio.

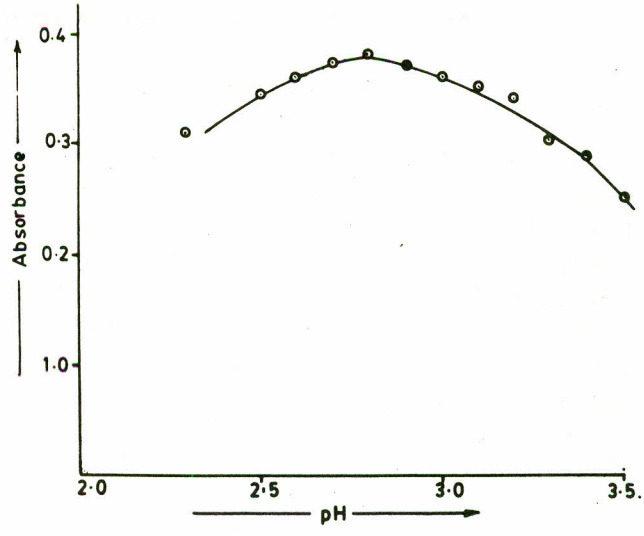


Fig. 2. Effect of pH on intensity of Fe(III)-DCPT complex ion solution

Preparation of calibration curve. Varying volumes (0.1-10 ml) of the metal ion solution were added separately to a number of 25 ml volumetric flasks each containing 8 ml of the ligand stock solution. The volume of the flasks were made upto mark with the buffer solution. The contents were thoroughly mixed and left in the dark for 15-20 min. The absorbance of each of the sample solution was measured and plotted as a function of concentration of the metal ion. A linear plot with origin at zero was obtained (Fig. 3). This calibration curve was used in subsequent determinations of the ferric ion in various samples. Upto 20 ppm concentration of ferric ion Beer's law is well obeyed.

Estimation of iron in presence of interfereing ions. The interference due to allied metal ions in the determination of iron (III) was studied with a view to ascertain the limitations of this method. The effect of other metal

ions on absorbance was studied under optimum conditions by mixing 50 ppm of each interfering metal ion with 5 ppm of iron (III) solution. The samples were stored in dark for 1 hr and later their absorbance was measured. The concentration of ferric ions in these samples was calculated from the calibration curve and compared with standard samples

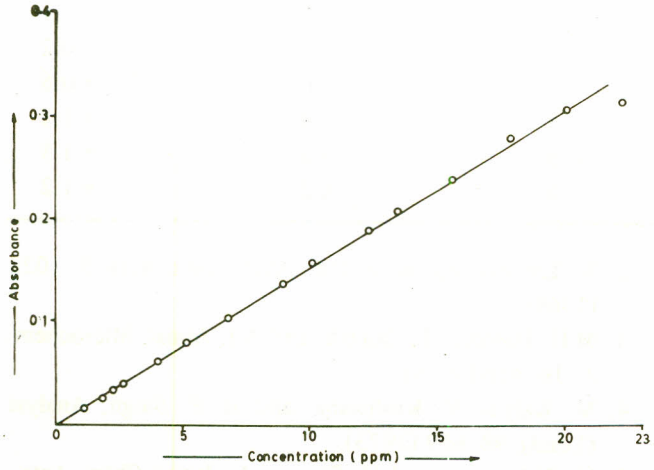


Fig. 3. Calibration curve for Fe(III)-DCPT complex ion solution

having no other allied metal ion. The results are reproduced in Table 1. The limit of tolerance for interfering metal ions (10, 50, 100 ppm) in the presence of 5 ppm of iron (III) was also determined (Table 2). A number of samples containing varying amounts of iron (III) were also studied separately with and without the presence of mixture of two or more interfering metal ions. These results are collected in Table 3.

DISCUSSION

The absorption spectrum of the violet coloration obtained by mixing aqueous solution of ferric ion and DCPT recorded between 340-650 nm, consists of a well defined broad band centered at 520 nm. The components of the coloured solution (i.e. Fe^{3+} and DCPT) individually do not absorb in this region of the spectrum. The molar concentration ratio of iron (III) ion to the ligand should be 1:2 for producing maximum absorption. The effect of pH on absorbence of the complex ion solution was studied between pH 2.0-12.0. The colour of the complex ion persisted in acidic medium but disappeared at higher pH values, perticularly obove 11 where brown precipitates of hydrated oxide appeared. The effect of pH on colour intensity in these systems was closely studied between the 2.0-3.5 range. Maximum absorbence was exhibited by the system at pH 2.8. However, these samples have comparable absorbance between pH 2.6-3.0 and measurements can efficiently be made within this range.

The effect of adverse metal ions upon the estimation of iron (III) by the present method was also investigated.

Table 1. Effect of diverse ions.

Metal salts	Amount of ion (ppm)	Fe^{3+} present (ppm)	Fe^{3+} found (ppm)	Difference (ppm)
$CuCl_2 . 2H_2O$	50	5	5.2	+0.2
$CoCl_2 . 6H_2O$	50	5	5.2	+0.2
$NiSO_4 . 6H_2O$	50	5	5.0	0.0
$Pb(NO_3)_2$	50	5	5.4	+0.4
$AlCl_3 . 6H_2O$	50	5	5.5	+0.5
$ZnSO_4 . 7H_2O$	50	5	4.9	−0.1
$Hg(CH_3COO)_2$	50	5	5.5	+0.5
$CdCl_2 . H_2O$	50	5	5.75	+0.75
$CaCl_2 . H_2O$	50	5	6.0	+1.0
$CrCl_3 . 6H_2O$	50	5	4.5	−0.5
$MnCl_2 . 4H_2O$	50	5	4.85	−0.15

Table 2. Limits of tolerance for interfering metal ions.

Interfering ion	Amount (ppm)	Fe^{3+} present (ppm)	Fe^{3+} found (ppm.)	Difference (ppm)
$CrCl_3 . 6H_2O$	10	5	5.15	+0.15
	50	5	4.5	−0.5
	100	5	5.65	+0.65
$MnCl_2 . 4H_2O$	10	5	5.0	0.0
	50	5	4.85	−0.15
	100	5	5.3	+0.3
$CoCl_2 . 6H_2O$	10	5	5.5	+0.5
	50	5	5.2	+0.2
	100	5	5.85	+0.85
$NiSO_4 . 6H_2O$	10	5	5.5	+0.5
	50	5	5.0	0.0
	100	5	5.3	+0.3
$CuCl_2 . 2H_2O$	10	5	4.85	−0.15
	50	5	5.2	+0.2
	100	5	5.05	+0.05
$Pb(NO_3)_2$	10	5	5.3	+0.3
	50	5	5.4	+0.4
	100	5	5.5	+0.5
$ZnSO_4 . 7H_2O$	10	5	5.0	0.0
	50	5	4.9	−0.1
	100	5	5.5	+0.5

Table 3. Analysis of unknown mixtures.

Unknown sample	Amount of interfering ions (ppm)	Fe^{3+} present (ppm)	Fe^{3+} found (ppm)	Difference (ppm)
$FeCl_3$	–	10	9.9	– 0.1
$Fe(NO_3)_3 9H_2O$	–	10	9.8	– 0.2
$FeNH_4(SO_4)212H_2O$	Cu^{2+}, Zn^{2+}, Mn_2^{2+}(150)	5	5.6	+ 0.6
"	Ni^{2+}, Co^{2+}, Mn^{2+}(150)	5	6.4	+ 1.4
"	Mg^{2+}, Cu^{2+}, Mn^{2+}(150)	5	6.5	+ 1.5
"	Cr^{3+}, Al^{3+} (100)	5	6.2	+ 1.2

The concentration of various allied metal ions in test solutions were gradually increased and their absorbence measured. It was found that nickel(II), manganese(II), copper (II), cabalt (II) and zinc (II) do not interfere in the estimation of iron (III) even if present in excessive amounts (i.e. 1:20 mole ratio). Their limit of tolerence at 100 ppm of these ions in the presence of 5 ppm of iron (III) is in the range 0.05-0.5 ppm. However, other ions such as Ca (II), Cr (III), Pb (II), Al (III), Cd (II) and Hg (II) interfere and absorbence gradually increases with increasing concentration of these ions in iron (III) solution. The estimation of iron (III) is seriously affected in the presence of mixtures of two or more diverse ions such as Cu^{2+}, Zn^{2+}, Mn^{2+} or Ni^{2+}, Co^{2+}, Mn^{2+} etc. These ions introduce 12-30 % error when their total concentration is maintained at higher levels (i.e. 30:1) in the measuring solutions. In such cases, it becomes necessary to extract the ferric ion into a non-aqueous phase and measure its absorbence. However, the presence of relatively low concentrations of mixtures of these ions in test solution have no measurable effect on the estimation of iron and the error is within limits.

It is concluded from the preceding discussion that iron (III) in the presence of a number of allied metal ions in relatively low concentrations can be efficiently measured by this method. This method is superior to many others, e.g the thiocyanate method. It is selective for iron (III) at working pH; the colour is stable for more than 48 hrs. at room temperature, and a number of allied metals do not interfere to any appreciable extent in the estimation.

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