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Spectrophotometric and Derivative Spectrophotometric Determination of Iron(III) with 3-Hydroxy-2-Picolinamide

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3-Hydroxy-2-picolinamide gives a colour reaction with iron(III) which has been developed into a method for spectrophotometric determination of iron(III) in both derivative as well as normal modes. Molar absorptivity and Sandell's sensitivity of the complex at its λ_{max} (475 nm) have been found to be 2.244×10^3 l mol^{-1}cm^{-1} and 0.0248 μg cm^{-2} respectively. Beer's law is followed from 0.2 mM to 0.8 mM of iron(III). Interference due to the presence of a number of cations and anions has been studied and the method successfully applied to determine iron contents of iron formulations and a cement sample.

INTRODUCTION

Biochemical, physiological and industrial importance of iron is well established. This necessitates[1–5] development of methods for determining iron at various concentration levels in diverse matrices[6–8]. Spectrophotometric methods based on the use of thiocyanate[9–12], 1,10-phenanthroline[13–17] and ferron[18,19] are among the most frequently opted. In the present communication a chromogenic reaction between 3-hydroxy-2-picolinamide (Fig. 1) and

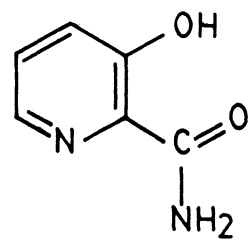

Fig. 1 3-Hydroxy-2-picolinamide

iron(III) has been investigated and a spectrophotometric method for the determination of iron(III) developed. The reagent is used to estimate iron content of a number of drugs and a cement sample. The results are comparable to those obtained by phenanthroline method.

EXPERIMENTAL

3-Hydroxy-2-picolinamide and the surfactant, Triton X-100, were procured from Fluka (Switzerland). Ferrous ammonium sulphate and other chemicals used were of analytical grade purity. Samples of iron containing drugs, namely, Idiglobin, Iberol and Imferon manufactured by Indian Drug and Pharmaceuticals Ltd., Gurgaon, Abbott Laboratories (India) Pvt. Ltd., Bombay and Rallis India Ltd., Konnagar, respectively, were used. Cement sample used was manufactured by Cement Corporation of India, Badarpur.

Ultraviolet-visible spectra were recorded on a Shimadzu UV-260 recording spectrophotometer with matched quartz cells and a bandwidth of 1 nm. First order derivative was recorded with $\Delta\lambda = 2$ nm. Elemental analysis of the isolated complex was carried out on Heraeus C H N Rapid Automatic Elemental Analyser. EC digital pH meter (Model 5651) was used for pH measurements.

Preparation of bulk solutions

Iron (III) solution (10 mM) was prepared by dissolving 0.3921 gm ferrous ammonium sulphate in water oxidising with nitric acid and making the solution to 100 ml. Centimolar (100 ml) ligand solution was made by dissolving appropriate amount of the ligand in 0.5 ml 1 : 1 sulphuric acid followed by 2 gm Triton X-100 and dilution of the content with water.

Preparation of working solutions

(i) To investigate the effect of varying hydrogen ion concentration on the complex formation, two sets of solutions, one with 0.5 ml of 1×10^{-2} M metal ion and other without it were prepared in the pH range 1.0 to 5.5. Each solution of either set contained 5 ml of 1×10^{-2} M ligand. Volume of the solutions were made up to 10 ml maintaining the pH at the desired value.

(ii) To see the effect of reagent concentration on the absorption spectrum of the system, a set of solutions containing increasing amount of the reagent in presence of a fixed amount of the metal ion at optimum pH was prepared.

(iii) To investigate the effect of varying metal ion concentration on the absorption spectrum of the complex, a set of solutions containing increasing amount of the metal ion in presence of excess of the ligand was prepared at pH 3.10 i.e. the pH of maximum complex formation.

Dissolution/digestion of samples for analysis

Mineralisation of pharamaceutical formulations was considered by treating the sample with conc. HNO_3 and evaporating it to dryness. It was repeated twice, and the residue finally taken up in the minimum amount of dil. HNO_3. The cement sample was digested similarly with conc. HCl and the residue taken up in dil. HCl.

RESULTS AND DISCUSSION

Absorption spectrum and effect of pH on the complex formation

Visible spectra between 200–700 nm of the solutions of 3-hydroxy-2-picolinamide and Fe(III)-3-hydroxy-2-picolinamide in the pH range 1.0 to 5.5 were recorded against water. The complex shows an absorption maximum at 475 nm. The relative increase in absorbance of the solutions containing metal ion was calculated and plotted against pH of the solutions. The maximum of this plot is observed at pH 3.10, which has been taken as the pH of maximum complex formation.

Effect of reagent concentration on the absorbance of the system

Absorbance (at λ_{max} of the complex) of the solutions containing increasing amount of the lignd in presence of a fixed amount of Fe(III), increased with increase in ligand concentration. It is found to increase sharply with increase in ligand to metal ratio up to 8.0, and becomes practically constant above 22.5. In all subsequent studies the reagent concentration was kept *ca.* 30 times that of the metal.

Effect of metal ion concentration on the absorbance of the system

Spectra of solutions containing increasing amount of the metal ion and fixed amount of the ligand from 300 nm to 700 nm are shown in Fig. 2. Absorbance of the solution at 475 nm (λ_{max} of the complex) was plotted against the metal ion concentration in order to evaluate the range over which absorbance is linearly proportional to the metal ion concentration. Regression analysis shows following relationship between absorbance and concentration with a correlation coefficient of 0.998.

$$A = 181.66 \times C + 4.25 \times 10^{-3}$$

Positive intercept, though very small in magnitude, is due to the absorption of the ligand at λ_{max} of the complex. The system follows Beer's law from 0.2 mM to 0.8 mM of Fe(III). Molar absorption coefficient with respect to Fe(III) and Sandell's sensitivity of the complex in the system have been found to be 2.244×10^3 *l* $mol^{-1}cm^{-1}$ and 0.0248 μg cm^2 respectively.

Relationship between metal ion concentration and absorbance at 475 nm, at fixed (1 : 30) metal to ligand ratio was also investigated. This, however, is not of much practical importance as in most of the cases iron content of the sample is not expected to be known to maintain the ratio.

Derivative spectra were recorded to ascertain the λ_{max} and minimise the error in absorbance due to contribution of the uncomplexed ligand at λ_{max} of the complex. The ligand gives no minimum/maximum on either side of the wavelength corresponding to λ_{max} position in derivative mode.

First derivative spectrum (Fig. 3) shows a trough at 530 nm, a crossover point

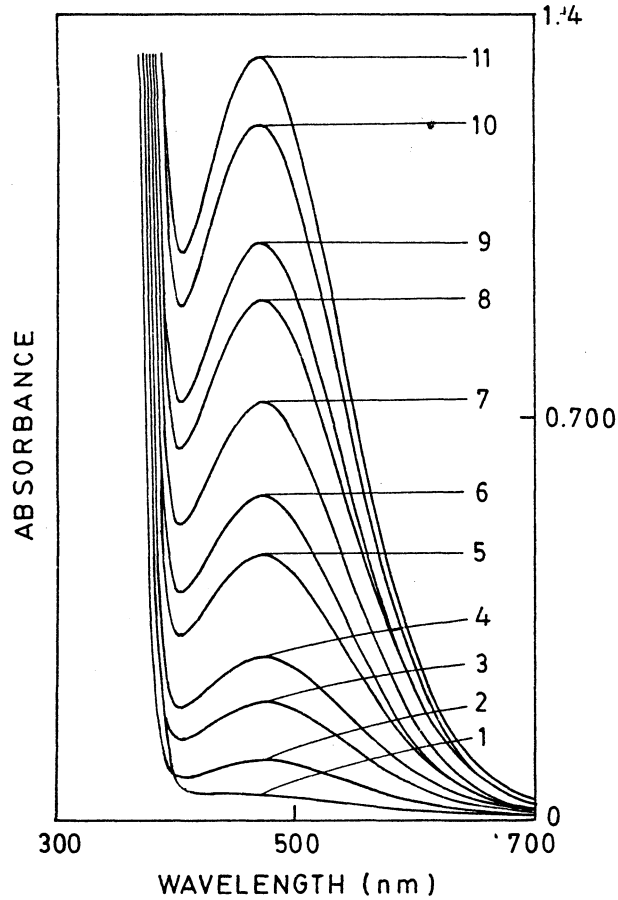

Fig. 2 Spectra of the solutions having metal ion concentration 0.1 to 1.0 x 10^{-3} mM at pH 3.1

at 475 nm and a peak at 430 nm which is the characteristic feature of the complex. As expected, the crossover point, observed at 475 nm, coincides with λ_{max} of the complex in the zero order spectrum. The trough depth (TD), measured from the ligand base, is found to be proportional to the metal ion concentration. Linear regression of concentration on trough depth (TD) gave the following relationship with a residue square of 0.998.

$$TD = 1.549 \times 10^4 \times C - 0.36$$

Though both through depth (TD) and absorbance (A) are linearly proportional to concentration C, the slope of the straight line obtained suggests that TD is more sensitive to concentration changes than the absorbance. However, either of these may be used for estimation using 3-hydroxy-2-picolinamide.

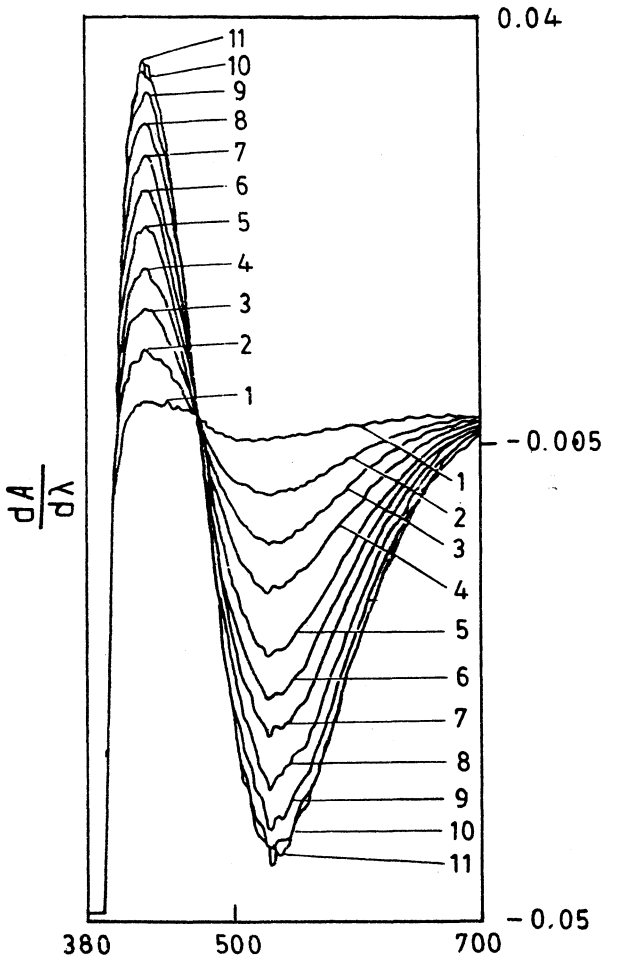

Fig. 3 Derivative spectra of the solutions described in Fig. 2

Influence of foreign ions on the determination of iron (III)

Effect of the presence of foreign ions on the determination of microgram amounts of iron by this method has been studied. The cations investigated are Fe^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, VO^{2+}, Cr^{3+}, Mn^{3+}, Pb^{2+}, Ti^{3+}, Mg^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+} The anions complexing ligands studied are Br^-, Cl^-, I^-, acetate, BO_3^{3-}, ascorbic acid, citrate, EDTA, tartrate and phosphate. Citrate, tartrate, EDTA, ascorbic acid and phosphate interfered seriously at tenfold excess (4.0×10^{-4} M) to that of the metal ion.

Composition and stability constant of the complex

From the plot of Job's method of continuous variations, at pH 3.1, the metal to ligand ratio in the complex is found to be 1 : 2. The complex is, therefore, represented as ML_2 where L stands for 3-hydroxy-2-picolinamide. Conditional stability constant[20] of the complex has been calculated after taking due care of the simultaneously existing equilibria.

$$Fe(CH_3COO)_3 + 2L \rightleftarrows FeL_2(CH_3COO) + 2CH_3COOH$$

The average of four values is found to be 1.98 with a covariance of 5%.

Isolation of Fe(III)-3-hydroxy-2-picolinamide complex

10 Ml of decimolar aqueous solution of iron (III) was mixed with an acidic solution containing about 500 mg of 3-hydroxy-2-picolinamide. On adjusting the pH to 3.10, a dark brown solid separated out. It was filtered, washed and dried in vacuum over P_2O_5. The complex is insoluble in acetone, methanol, chloroform, benzene and DMF and does not melt even at 320°C; yield 72%. Elemental analysis of the complex gave the following results: (in per cent: the figures in parentheses are theoretical values): C 34.19 (33.65), H 3.25 (2.81), N 13.62 (13.08). The analysis corresponds to a 1 : 2 stoichiometry of complex.

APPLICATIONS

Iron content of a number of commercially available pharmaceutical iron formulations and a cement sample was determined using 3-hydroxy-2-picolinamide.

A pharmaceutical and a cement sample have been mineralized as below:

(i) *Pharmaceutical sample:* A suitable amount of the drug (tab./cap./inj.) was treated with 5 ml HNO_3 and content digested to a paste. The process was repeated with one more addition of 5 ml HNO_3 and content baked for *ca.* 1 hr. The residue was moistened with $HCl + H_2SO_4$ and heated to dense white fumes; the paste obtained was taken in dil. H_2SO_4 and made up to the required volume depending upon the iron content.

(ii) *Cement:* This sample was also digested as above (i) except that HCl was used instead of HNO_3.

A suitable volume of the mineralised iron solution (10^{-2} M is Fe) was taken in a 10 ml volumetric flask and 5 ml of the reagent (3-hydroxy-2-picolinamide) solution containing surfactant was added. The pH of the solution was adjusted to 3.10 and content made up to the mark. Absorption spectrum of the solution was recorded after *ca.* $\frac{1}{2}$ hr. and iron content determined from the calibration graph. The results obtained are in agreement with phenanthroline method. The results are tabulated in Table 1.

TABLE 1
ANALYSIS RESULTS OF SOME OF THE IRON BEARING MATRICES WITH 1,10-PHENANTHROLINE AND THE DEVELOPED METHOD

S. No.	Sample	Iron content found (mM)				
		Theoretical	Experimental			
			1,10-Phenanthroline	% Error	3-hydroxy-2-picolinamide	% Error
1.	Idiglobin	0.1413	0.1410	0.21	0.1430	1.20
		0.2825	0.2820	0.17	0.2805	0.71
		0.4238	0.4244	0.14	0.4226	0.28
		0.5650	0.5640	0.14	0.5656	0.11
		0.7063	0.7072	0.12	0.7072	0.13
2.	Iberol	0.2766	0.2760	0.21	0.2760	0.22
		0.5532	0.5520	0.21	0.5526	0.11
		0.8297	0.8272	0.28	0.8270	0.32
		1.1063	1.1098	0.31	1.1104	0.38
		1.3829	1.3844	0.10	1.3846	0.12
3.	Imferon	0.1433	0.1428	0.35	0.1426	0.49
		0.2867	0.2872	0.17	0.2859	0.28
		0.4301	0.4308	0.16	0.4310	0.21
		0.5734	0.5724	0.17	0.5725	0.16
		0.7168	0.7176	0.11	0.7194	0.36
4.	Cement	0.2288	0.2280	0.34	0.2281	0.31
		0.4576	0.4570	0.13	0.4568	0.18
		0.6863	0.6878	0.21	0.6879	0.23
		0.9151	0.9140	0.12	0.9140	0.12
		1.1439	1.1468	0.25	1.1488	0.43

Conclusion

3-Hydroxy-2-picolinamide is a selective reagent for the determination of iron(III) in diverse matrices. Only one complex having 1 : 2 stoichiometry is formed. It is stable with time unlike the iron-thiocyanate complex.

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