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The Spectrophotometric Determination of Iron(III) with Methylthymol Blue

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The reaction between iron(III) and methylthymol blue has been studied spectrophotometrically in an attempt to establish the optimum conditions for determining small amounts of iron. Depending on the acidities of a solution, iron(III) reacts with methylthymol blue to form one of two complexes. The 1-to-1 complex, which has its maximum absorbance in the acidity range from 0.07 to 1.00 M with respect to perchloric acid, has an absorption maximum at about 580 mμ against a reagent blank. The 1-to-2 (metal-reagent ratio) complex, which has its maximum absorbance in the pH range from 4.5 to 5.5, has an absorption maximum at about 520 mμ against a reagent blank. With either complex, Beer's law is obeyed over the range from 5 to 50 μg. of iron(III) in 25 ml. of complex. The apparent molar extinction coefficients of the two complexes at their absorption maxima were calculated to be 15000 and 14000 respectively (the former, at 0.08 M HClO; the latter, at pH 5). According to Sandell's notation, the sensitivities of the reactions are 0.004 μg. of iron(III) per cm^2 at 580 mμ and 0.005 μg. of iron(III) per cm^2 at 520 mμ respectively. The effect of diverse ions was examined with a solution containing iron(III) and 25 cations.

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Methylthymol blue was first prepared by Körbl et al.[1] It has since been widely used as a universal metallochromic indicator in complexometric titrations. The color reaction between this reagent and such metal cations as zirconium(IV),[2,3] yttrium(III),[4] lanthanum(III),[4] mercury(II),[5] thorium(IV),[6,7] and gallium(III)[8] has been studied spectrophotometrically in determining these cations.

It has been found that, depending on the acidity of a solution, iron(III) reacts with methylthymol blue to form two complexes, with metal-ligand ratios of 1 to 1 and 1 to 2, and that these reactions are applicable to the spectrophotometric determination of iron. The proposed metho dis very sensitive; it is comparable in sensitivity with the method using xylenol orange,[9] ferron,[10] hydrazinophthalazine,[11] or salicylaldoxime.[12]

Experimental

Reagents.—*The Standard Ferric Perchlorate Solution.*—This was prepared by dissolving the freshly-precipitated ferric hydroxide in hot 4.5 M perchloric acid and then diluting it with water to make the solution about 0.01 M with respect to iron. The solution was standardized by the complexometric titration[13] using α-pyridyl-β-azonaphthol as an indicator. Working solutions of iron were then prepared by diluting the standard solution with distilled water.

Methylthymol Blue Solution.—A 1×10^{-3} M methylthymol blue solution was prepared by dissolving the Dotite MTB reagent (disodium salt), which was used without further purification, in distilled water.

An acetate buffer solution and nitric acid were used for the adjustment of the pH values. Solutions of diverse ions were prepared by dissolving the respective compounds (all reagent-grade chemicals) in distilled water in appropriate concentrations.

Apparatus.—A Hitachi spectrophotometer, model EPV-2, was employed, with 1 cm. cells for all the absorbance measurements. A Hitachi glass-electrode pH meter, model EHP-1, was employed for all the pH determinations.

Results and Discussion

Absorption Curves.—The absorption curves of the solutions containing iron(III) and methylthymol blue at different acidities are shown in Figs. 1 and 2. These curves were obtained by measuring the absorbance of the colored solutions against a reagent blank which contained the same amount of methylthymol blue.

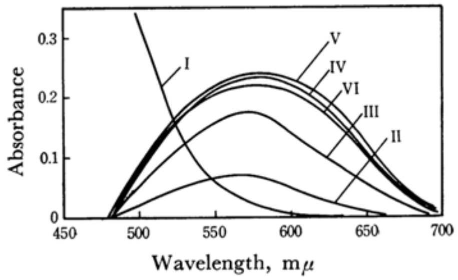

Fig. 1. Absorption curves of methylthymol blue and its iron complex at various acidities.
Iron: 26.8 μg.; MTB: 1.96×10^{-4} M
I: MTB vs. water at pH 0-6; II: Iron complex vs. a reagent blank
$HClO_4$ concn.: II 0.30 M; III 0.20 M; IV 0.15 M; V 0.08 M; VI 0.05 M

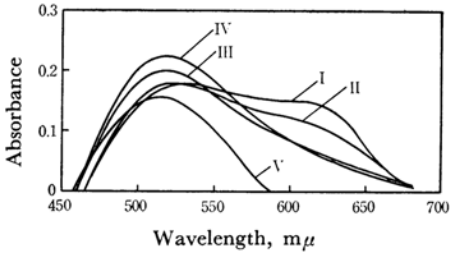

Fig. 2. Absorption curves of the iron-methylthymol blue mixture at various acidities.
Iron: 26.8 μg., Reference: a reagent blank
pH value: I 2.5; II 3.0; III 4.0; IV 4.5—5.5; V 6.5

When the concentration of perchloric acid is 0.05 to 0.20 M, the solutions give essentially identical absorption curves, with an absorption maximum at about 580 mμ. Above pH 2, the position of the maximum absorption shifts toward shorter wavelengths with the increase in the pH value. The curves obtained at pH 2.5 and 3.0 have a shoulder at about 610 mμ. Between pH 3.5 and 6.5, however, the solutions give absorption curves with an absorption maximum at about 520 mμ. Therefore, it may be concluded that, in the presence of an excess of methylthymol blue, two complexes are formed between iron(III) and the reagent.

The Effect of the Acidity.—The effect of the acidity on the absorbance of the solution was examined by measuring, at two wavelengths, 580 and 520 mμ, the absorbance of a solution containing 26.8 μg. of iron and a 5- to 10-fold excess of methylthymol blue. From the curves shown

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[1] J. Körbl and R. Pribil, *Collection Czech. Chem. Commun.*, **23**, 873 (1958).

[2] V. F. Lukyanov and E. M. Knyazeva, *Zavodsk. Lab.*, **26**, 263 (1960).

[3] A. K. Babko and V. D. Vasilenko, *Ukrain. Khim. Zhur.*, **26**, 514 (1960).

[4] H. Okada, K. Kaneko and S. Goseki, *Japan Analyst*, **12**, 822 (1963).

[5] N. Iritani and T. Miyahara, ibid., **12**, 1182 (1963).

[6] M. Otomo, ibid., **14**, 229 (1965).

[7] V. D. Vasilenko and M. V. Shanya, *Zh. Analit. Khim.*, **20**, 636 (1965).

[8] K. Tonosaki and K. Sakai, *Japan Analyst*, **14**, 495 (1965).

[9] M. Otomo, This Bulletin, **38**, 624 (1965).

[10] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd Ed., Van Nostrand Co., New York (1953), p. 324.

[11] R. Raggieri, *Anal. Chim. Acta*, **16**, 242 (1957).

[12] D. E. Howe and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **12**, 448 (1940).

[13] K. Ueno, "Kireto Tekitei (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 257.

in Fig. 3, it may be seen that the maximum absorbance is obtained in the acidity range from 0.07 to 0.1 M with respect to perchloric acid when measured at 580 mμ, and in the pH range from 4.5 to 5.5 when measured at 520 mμ.

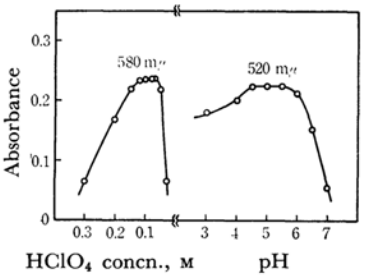

Fig. 3. Effect of acidity.
Iron: 26.8 μg.; MTB: 1.96×10^{-4} M
Reference: a reagent blank

The Stability of the Color.—The color development between iron(III) and the reagent occurs instantaneously at room temperature. The color intensity of the solution remained almost constant for at least 4 hr. after preparation, either at the acidity of 0.08 M or at pH 5.0.

Calibration Curves.—From the foregoing results, two optimum conditions for determining iron were found. The procedure for preparing the calibration curves for iron was as follows: An aliquot of the standard iron(III) solution was pipetted into a 25-ml. volumetric flask. The acidity of the solution was then adjusted to 0.08 M in the final concentration with perchloric acid or to pH 5.0 with an acetate buffer. To the solution, 2.5 to 3.5 ml. of a 1×10^{-3} M methylthymol blue solution was added, and the resulting solution was diluted with water to the mark. After about 30 min., the absorbance of the solution was measured at 580 or 520 mμ against the reagent blank.

The results shown in Fig. 4 indicate that Beer's law is followed by solutions containing up to at least 50 μg. of iron. The sensitivities of the methods are 0.004 μg. of iron per cm^2 at 580 mμ and 0.005 μg. of iron per cm^2 at 520 mμ.

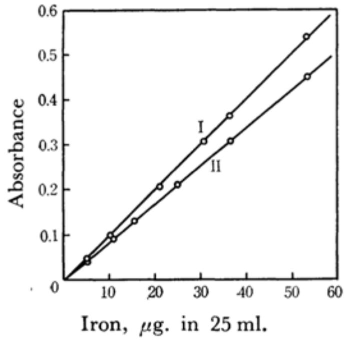

Fig. 4. Calibration curves.
I: MTB 1.15×10^{-4} M; $HClO_4$ 0.08 M; 580 mμ
II: MTB 1.37×10^{-4} M; pH 5.0; 520 mμ

The Effect of Diverse Ions.—The effect of diverse ions was examined with a solution containing 26.8 μg. of iron and diverse ions. The acid concentration of the solution was adjusted to 0.08 M with perchloric acid. Of the 25 cations tested, such ter- or quadrivalent cations as bismuth, gallium, indium, thallium, thorium, uranium, vanadium, and zirconium gave a positive error, while common divalent cations and some rare earth elements did not interfere. The following anions did not interfere under the conditions described: chloride, nitrate and sulfate up to at least 100 μmol., fluoride up to 5 μmol., tartrate and citrate up to 50 μmol. and phosphate up to 30 μmol. Oxalate, nitrilotriacetate and ethylenediaminetetraacetate, however, inhibit the formation of the complex, even when only trace amounts are present.

The Composition of the Complexes.—*The Complex with an Absorption Maximum at* 580 *mμ.* —The method described by Frank and Oswalt[14] was applied. This method is effective in the identification of a 1-to-1 complex with a formation constant of less than about 10^4.

An attempt was made with solutions with a given molar concentration of iron at a given perchloric acid concentration, but with varying methylthymol blue concentrations. If only a 1-to-1 complex is formed under the conditions, and if the absorbance of the solution, A, is measured against the reagent blank, the following relationship may be derived:

$$ab/A=(a+b)/(\varepsilon_C-(\varepsilon_O)_H)+1/(K_1')_H(\varepsilon_C-(\varepsilon_O)_H) \quad (1)$$

where a and b represent the total molar concentration of iron and that of the reagent respectively; ε_C is the molar extinction coefficient of the complex, and $(\varepsilon_O)_H$ is the apparent molar extinction coefficient of the reagent at a given acidity. $(K_1')_H$ is defined as:

$$(K_1')_H=x/(a-x)(b-x) \quad (2)$$

where x represents the equilibrium molar concentration of the complex at a given acidity.

In Fig. 5 ab/A is plotted against $(a+b)$ at 580 mμ. In these solutions, the concentration of iron was 1.92×10^{-5} M, while that of methylthymol blue varied from 1.0×10^{-4} to 1.2×10^{-3} M; the acidity was held constant at 0.02 M with respect to perchloric acid. The good linearity of the plots supports the assumption inherent in Eq. 1, indicating that only a 1-to-1 complex is found under the conditions investigated. The molar extinction coefficient was calculated to be 15000 at 580 mμ, and the value of $(K_1')_H$, to be 8.4×10^3.

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[14] H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

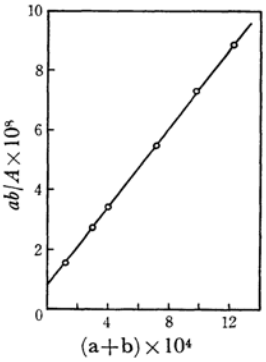

Fig. 5. Plot of ab/A vs. $(a+b)$ at 580 mμ.
a: 1.92×10^{-5} M; b: 1.0×10^{-4}—1.2×10^{-3} M
$HClO_4$: 0.20 M

The Complex with an Absorption Maximum at 520*m*μ. —The mole ratio of iron to the reagent was confirmed by the mole ratio method at pH 5.5. In this work, each solution was 1.02×10^{-4} M in the total concentration of methylthymol blue. The results are shown in Fig. 6, which indicates that probably a 1-to-2 complex is formed between iron and the reagent. The wavelengths, 540 and 550 mμ, were chosen because the reagent itself has too high an absorbance at 520 mμ. The molar extinction coefficient of this complex was calculated to be about 14000 at 520 mμ.

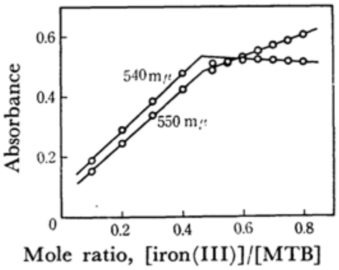

Fig. 6. Mole ratio method.
MTB: 1.02×10^{-4} M, pH: 5.5

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