NOTES

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Spectrophotometric Determination of Iron(III) with Rhodamine B and Confirmation of the Composition of Its Complex[*1]

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Rhodamine B (RHCl) has been used in the spectrophotometric determination of gallium(III), gold(III), thallium(III), and antimony(V), forming a complex which can be extracted with organic solvents. Iron(III) also forms a complex with rhodamine B. Consequently, iron(III) in a sample solution interferes with the determination of the above metals.[1–3] It is reported that the iron complex could not be extracted from a 1 N hydrochloric acid solution with benzene by Snell and Snell,[4] or from a 6 N hydrochloric acid solution with isopropyl ether by Onishi and Sandell.[5] However, when a certain organic solvent was used, this complex could be extracted under satisfactory conditions. For these reasons, the spectrophotometric determination of iron(III) based on this color reaction was attempted in a previous work by extraction from a 6 N hydrochloric acid solution with benzene,[6] but this method was not satisfactory because of the lower sensitivity.

The purpose of the present work is to study the determination of a trace of iron(III) with high sensitivity by improving the procedure reported in the previous paper,[6] and to confirm the composition of this complex by employing the method of continuous variation, and that of Molland.

Experimental

Reagents. *Standard Iron(III) Solution.* The stock solution of iron(III) was prepared by dissolving about 3 g of a reagent-grade iron(III) chloride in 250 m*l* of 1 N hydrochloric acid. The concentration of iron in this solution was determined by the oxine method.[7]

Rhodamine B Solution. The solution was prepared by dissolving 0.3 g of RHCl (JIS special grade) dried at 110°C for about 3 hr in 100 m*l* of distilled water.

Extracting Agents. The organic solvents were used after they had been purified by the usual method.[8]

Butyl Cellosolve (BC) Solution. This solution was prepared by dissolving 100 m*l* of ethylene glycol monobutyl ether (butyl cellosolve of Wako Pure Chemicals) in 200 m*l* of distilled water.

Apparatus. A Hitachi photometric photometer, model FPW-4, and an Ito spectrophotometer, model QU-3, were empolyed for all the absorbance measurements, using a 1 cm glass cell.

Standard Procedure for the Determination. A given amount of RHCl, a small amount of BC, and a desired amount of hydrochloric acid were added to a 50 m*l* volumetric flask containing an iron(III) solution, and then mixture was diluted to the mark with water. A 25 m*l* portion of this solution pipetted in a 250 m*l* separating funnel was shaken vigorously with 10 m*l* of an adequate organic solvent for 2 min. The organic layer containing this complex was then completely separated from the aqueous layer by centrifugation. The absorbance of the colored organic layer was measured at 550 mμ or 562 mμ (absorption maximum) against a reference organic solvent treated by the same procedure.

Results and Discussion

The Effects of Extracting Agents. The rhodamine B-iron(III) complex can be extracted from a 6 N hydrochloric acid solution with benzene. The absorption maximum of the colored complex has been known to appear at 558 mμ.[6] If this

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[*1] This work was presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y. (1959), p. 276.

2) L. Luck, *Anal. Chem.*, **31**, 1680 (1959).

3) F. Feigl, "Spot Test in Inorganic Analysis," Elsevier Publishing Company, Amsterdam, London, New York, Princeton (1958), p. 106.

4) F. D. Snell and C. T. Snell, "Colorimetric Method of Analysis," Vol. IIA, D. van Nostrand Co., Toront, New York, London (1959), p. 125.

5) H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, **13**, 159 (1955).

6) H. Imai, *Tech. Reps. of Kansai Univ.*, **4**, 59 (1962).

7) R. Berg, *Z. Anal. Chem.*, **76**, 197 (1929).

8) K. Hata, N. Sugiyama, S. Kobayashi, M. Ota and M. Ōki, "Kagaku Jikken Ho," Kagaku Zokan 6, Kagaku Dojin, Tokyo (1961), pp. 16, 31, 39, 41, 43, 50.

9) H. Imai and K. Nakayama, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 1187 (1966).

TABLE 1. EFFECT OF EXTRACTING AGENT

Fe(III): 41.63 μg/50 m*l*, HCl: 6 N, BC: 2 m*l*/50 m*l*. Extracting solvent: 10 m*l*/Sample soln. 25 m*l*. Wavelength: 550 mμ

0.3% RHCl (m*l*/50 m*l*)	Solvent (m*l*)	Absorbance	0.3% RHCl (m*l*/50 m*l*)	Solvent (m*l*)	Absorbance
15	Bn:MIBK=9.5:0.5	0.442	2	Bn:DON=9.5:0.5	0.038
15	Bn:MIBK=9.0:1.0	0.866	2	Bn:DON=9.0:1.0	0.041
15	Bn:MIBK=8.5:1.5	1.31	2	Bn:EA=9.5:0.5	0.043
5	Bn:MIBK=9.5:0.5	0.208	2	Bn:EA=9.0:1.0	0.078
5	Bn:MIBK=9.0:1.0	0.502	2	Bn:IAA=9.5:0.5	0.037
5	Bn:MIBK=8.5:1.5	0.814	2	Bn:IAA=9.0:1.0	0.064
2	Bn:MIBK=9.5:0.5	0.091	2	Bn:Ac=9.5:0.5	0.033
2	Bn:MIBK=9.0:1.0	0.230	2	Bn:Ac=9.0:1.0	0.086

Bn: Benzene, MIBK: Methyl isobutyl ketone, DON: Dioxane, EA: Ethyl acetate,
IAA: Isoamyl acetate, Ac: Acetone

complex was extracted with benzene only, the sensitivity of determination was relatively low compared the case with other methods. Then, the investigation of adding several mixed solvents to benzene was attempted, while varying the absorbance. The results are shown in Table 1.

The maximum degree of extraction of the complex formed in the aqueous solution was obtained by using the mixed solvent of benzene-MIBK. The reference solvent, when treated with the same procedure, gradually colored, while the MIBK concentration increased. As it is best for the color of the reference solvent to be colorless for the spectrophotometric determination, this complex was extracted with benzene containing 10 per cent MIBK by volume.

Effect of Hydrochloric Acid Concentration on the Extraction. The effect of acid concentration on the extraction was examined by using the above solvent.

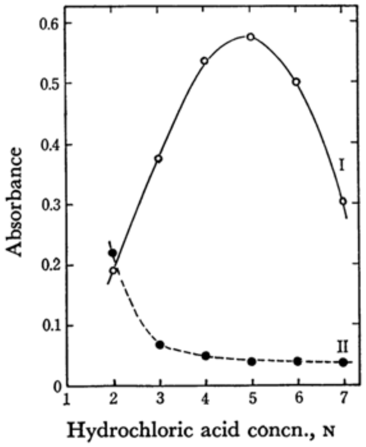

Fig. 1. Effect of acid concentration on absorbance. Fe(III): 41.63 μg/50 m*l*, BC: 2 m*l*/50 m*l*, 0.3% RHCl: 5 m*l*/50 m*l*. Extracting solvent: Bn 9 m*l*+ MIBK 1 m*l*/Sample soln. 25 m*l*. Wavelength: 550 mμ
I: Absorbance of this complex in the solvent
II: Absorbance of the reference solvent

From the curves shown in Fig. 1, it can be seen that the maximum absorbance is obtained when this complex was extracted from 5 N hydrochloric acid solution.

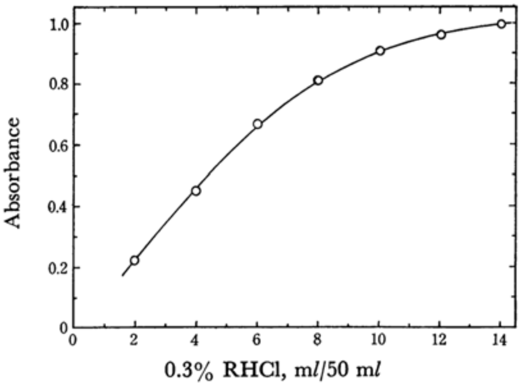

Fig. 2. Effect of RHCl concentration. Fe(III): 41.63 μg/50 m*l*, HCl: 5 N, BC: 2 m*l*/50 m*l*. Extracting solvent: Bn 9 m*l*+MIBK 1 m*l*/Sample soln. 25 m*l*. Wavelength: 550 mμ

Effects of the Amounts of RHCl and BC. The effect of adding the RHCl concentration to the aqueous layer on the absorbance was also investigated.

As is shown in Fig. 2, the absorbance depends on the concentration of RHCl. The reference solvent was observed to color gradually with an increase in the RHCl concentration. In view of the color of the reference solvent, we used 10 m*l* of 0.3% RHCl in one further experiments.

The effect of the amount of BC on the absorbance was studied. The results are shown in Fig. 3.

The absorbance increased with an increase in the amount of BC. When more than 2.5 m*l* of BC was added, the reference solvent colored considerably, this color intensity was observed to change gradually, when the solvent was permitted to stand.

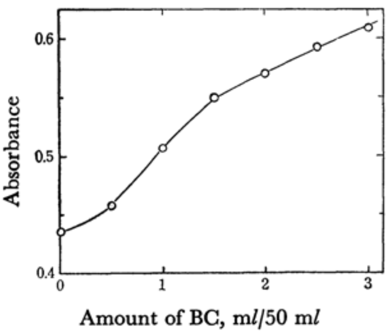

Fig. 3. Effect of the amount of BC on absorbance. Fe(III): 23.75 μg/50 m*l*, HCl: 5 N, 0.3% RHCl: 10 m*l*/50 m*l*. Extracting solvent: Bn 9 m*l*+MIBK 1 m*l*/Sample soln. 25 m*l*. Wavelength: 550 mμ

Therefore, in further experiments, 2 m*l* of BC were used.

Effect of Time of Standing. The stability of the color intensity of the complex present in the mixed solvent was determined by measuring the absorbance of the organic layer after known periods of time. In such measurements, the absorbance remained almost constant for about 1.5 hr after extraction.

Absorption Spectra and Calibration Curve for Iron(III). Figure 4 shows the absorption spectra of the complex which was extracted from the solution prepared by the addition of varying amounts of 0.3% RHCl to a given amount of iron(III).

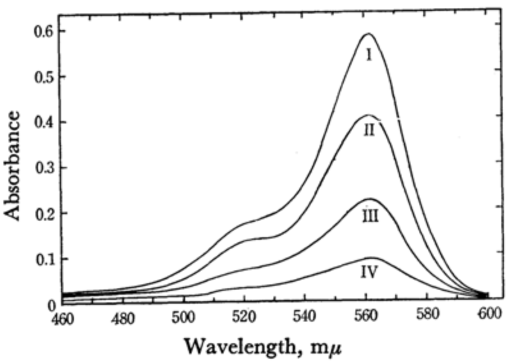

Fig. 4. Absorption spectra of complex. Fe(III): 23.75 μg/50 ml, HCl: 5 N, BC: 2 m*l*/50 m*l*. Extracting solvent: Bn 9 ml+MIBK 1 m*l*/Sample soln. 25 m*l*, 0.3% RHCl (m*l*/50 m*l*): I, 6.0; II, 4.0; III, 2.0; IV, 0.8

The maximum absorption wavelength in the range of RHCl concentration investigated was found at 562 mμ, this result indicated the presence of only one form of the complex.

The calibration curve for the iron(III) determination was prepared at the wavelengths of 550 mμ and 562 mμ in the manner described above.

In all the curves shown in Fig. 5, linear relationships between the absorbance and the concentration are found to be held up to 14 μg of iron(III) in 25 m*l* of the sample solution. The sensitivities of the determination at 562 mμ and 550 mμ were 0.0016 μg and 0.0021 μg iron(III) respectively per cm^2 for $\log(I_0/I)=0.001$. The determination at 562 mμ gives an approximately five-fold increase in the sensitivity compared with the previous investigation.[6]

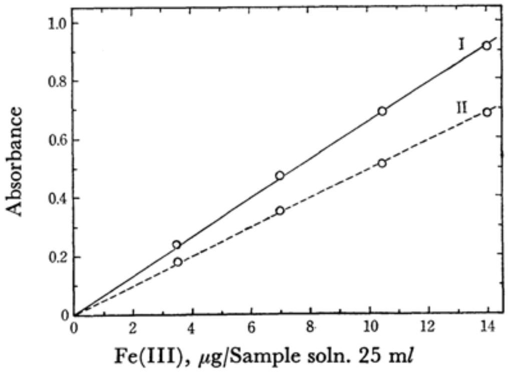

Fig. 5. Calibration curves. HCl: 5 N, BC: 2 m*l*/50 m*l*, 0.3% RHCl: 10 m*l*/50 m*l*. Extracting solvent: Bn 9 m*l*+MIBK 1 m*l*/Sample soln. 25 m*l*. Wavelength: I, 562 mμ; II, 550 mμ

The Effect of Diverse Ions. The interference of diverse metallic ions reacting with RHCl in the determination of iron(III) was studied under the conditions used in the proposed procedure. The results are summarized in Table 2.

It was found that gallium(III), gold(III), and thallium(III) interfered even in the smallest concentrations examined, while antimony(V) (in concentrations of more than about 7 μg/25 m*l*). Mercury(II), bismuth(III), and tin(IV) did not do so markedly.

The Composition of the Complex. The composition of the rhodamine B-iron(III) complex was determined by the two methods used in the determination of the compositions of rhodamine B-gold(III)[9] and -gallium(III) complex.[10]

The Method of Continuous Variation. The absorbance of the complex extracted from the aqueous layer, in which the total concentration of iron (III) and RHCl was 79.89×10^{-5} mol/*l* or 39.91×10^{-5} mol/*l* throughout, was plotted against [Fe]/([Fe]+[RHCl]).

Only one complex, 1 to 1, was recognized as being formed, because the average value of the intersecting points obtained from the curves shown in Fig. 6 was 0.51.

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[10] H. Imai, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*) **87**, 123 (1966).

Table 2. Effect of diverse ions

Fe(III) taken: 6.94 μg/25 ml. Condition: measured at same condition as in Fig. 5. Wavelength: 562 mμ

Diverse ions		Fe found	Deviation	Diverse ions		Fe found	Deviation
Kind	μg/25 ml	μg/25 ml	μg/25 ml	Kinds	μg/25 ml	μg/25 ml	μg/25 ml
Hg(II)	3694	6.85	+0.09	Tl(III)	5.38	12.76	+5.86
Ga(III)	1.08	7.82	+0.88	Bi(III)	1270	6.96	+0.02
Ga(III)	4.30	10.50	+3.56	Bi(III)	12700	7.88	+0.94
Au(III)	1.83	7.78	+0.84	Sn(IV)	1710	6.83	+0.11
Au(III)	3.65	10.14	+3.02	Sb(V)	7.33	6.80	−0.14
Tl(III)	2.69	8.76	+1.82	Sb(V)	14.66	8.02	+1.08

Deviation = Fe found − Fe taken

Table 3. Molland method

Condition: measured at same condition as in Fig. 5. Wavelength: 550 mμ

1			2			As_1/As_2
Fe(III) mol/l	RHCl mol/l	As_1	Fe(III) mol/l	RHCl mol/l	As_2	
9.94×10^{-5}	6.27×10^{-4}	0.380	6.27×10^{-4}	9.94×10^{-5}	0.436	1.15
9.94×10^{-5}	7.52×10^{-4}	0.415	7.52×10^{-4}	9.94×10^{-5}	0.508	1.22
9.94×10^{-5}	8.77×10^{-4}	0.485	8.77×10^{-4}	9.94×10^{-5}	0.588	1.21
9.94×10^{-5}	10.0×10^{-4}	0.550	10.0×10^{-4}	9.94×10^{-5}	0.650	1.18
9.94×10^{-5}	11.3×10^{-4}	0.610	11.3×10^{-4}	9.94×10^{-5}	0.711	1.17
9.94×10^{-5}	12.5×10^{-4}	0.660	12.5×10^{-4}	9.94×10^{-5}	0.792	1.20
					Average value	1.19

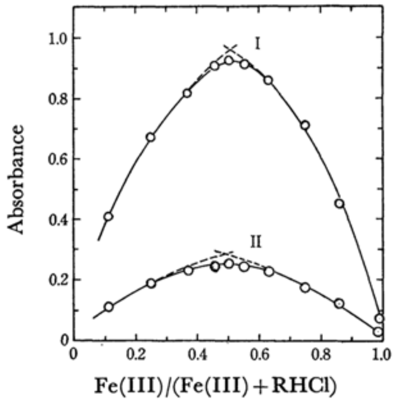

Fig. 6. Method of continuous variation.
Condition: measured at same condition as in Fig. 5. Wavelength: 550 mμ, [Fe]+[RHCl]: I, 79.89×10^{-5} mol/l, II, 39.91×10^{-5} mol/l

The Molland Method.[11] The formation of the rhodamine B-iron(III) complex can be represented by the following equation[12]:

$$n\mathrm{RH}^+ + m\mathrm{FeCl_4}^- \rightleftarrows (\mathrm{RH})_n\text{-}(\mathrm{FeCl_4})_m \qquad (1)$$

Therefore, the absorbance (As_1) of the complex extracted from the solution prepared by the addition of an RHCl solution (b mol/l) to a solution containing iron(III) (a mol/l) can be written:

$$As_1 = \varepsilon l x_1 \simeq \varepsilon l a/m \qquad (2)$$

where ε is the molar extinction coefficient of the complex, l, the thickness of the cell in cm, and x, the concentration of the complex formed.

On the contrary, the absorbance (As_2) obtained from the solution containing iron(III) (b mol/l) and RHCl (a mol/l) in the same manner as above can be given by:

$$As_2 = \varepsilon l x_2 \simeq \varepsilon l a/n \qquad (3)$$

The ratio of n to m may be determined by taking the ratio of the absorbance obtained from both solution:

$$As_1/As_2 = n/m \qquad (4)$$

The results obtained from this method are shown in Table 3.

Since the average value of the ratio of As_2 to As_1 obtained from Table 3 was 1.19, this complex was recognized as being 1 to 1.

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[11] J. Molland, *J. Am. Chem. Soc.*, **62**, 541 (1940).

[12] H. Imai, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **88**, 227 (1967).