The Direct Spectrophotometric Determination of Iron with Dibenzoylmethane in the Organic Phase

By Yoshimi UMEZAKI

(Received August 21, 1963)

In the preceding paper,[1] the author has described a spectrophotometric determination of uranium with dibenzoylmethane (DBM) in the organic phase. Since DBM reacts with iron (III) to form a colored complex, iron may be determined in a way similar to that used for uranium. Shigematsu and Tabushi[2] have reported a spectrophotometric determination ot iron with DBM after forming an iron-DBM complex in an aqueous solution and after extracting the complex into butyl acetate. This method, however, is too greatly subject to interference by diverse ions.

As the extraction of iron (III) with methyl isobutyl ketone (MIBK) in a hydrochloric acid solution is an excellent method for separating iron from interfering ions, this extraction method is, as a preliminary separation, employed in various methods of determination for iron.[3] Recently, Jackson and Phillips[4] have reported a spectrophotometric determination of iron with *o*-phenanthroline after the MIBK extraction. In this case, iron extracted in MIBK is stripped by an aqueous solution and reduced to iron (II), and then the color is developed.

This paper describes a simple, sensitive and selective spectrophotometric determination of iron (III) with DBM in the organic phase after the MIBK extraction.

Experimental

Apparatus.—Absorbance measurements were made with a Hitachi spectrophotometer, Model EPV-2A, using 1-cm. glass cells.

Reagents.—*Standard Iron Solution.*—A stock solution containing 100 μg. of iron (III) per ml. was prepared by dissolving iron (III) chloride in a 0.1 N hydrochloric acid solution. Standardization was made by titration with a 0.01 M EDTA solution.

Dibenzoylmethane Solution.—A 0.5% solution was prepared by dissolving 0.5 g. of dibenzoylmethane in 100 ml. of methanol.

Solutions of Diverse Ions.—Reagents grade salts, usually the chlorides, were used for testing the interference of cations. Anions were tested by the addition of sodium or potassium salts.

Traces of iron involved in the reagents were removed when necessary with an anion exchange resin column.

Procedure.—Transfer 5.0 ml. of a slightly acidic sample solution containing less than 40 μg., preferably 10 to 30 μg., of iron (III) to a 50 ml. separatory funnel. Add 5.0 ml. of concentrated hydrochloric acid and 3.0 ml. of MIBK. Shake vigorously for about 1 min. After the phases have separated, discard the aqueous layer. Run the organic phase through a small plug of filter paper* in the stem of the separatory funnel into a dried small vessel. Transfer 2.0 ml.** of the extract to a 10 ml. volumetric flask. Add 2.0 ml. of a 0.5% DBM solution and 0.5 ml. of pyridine, and dilute with methanol to the mark. Measure the absorbance at 410 mμ (or 425 mμ) against a blank.

Results and Discussion

Absorption Spectra.—The absorption spectra of the blank and the iron complex are shown in Fig. 1, together with those of copper, tin, vanadium and molybdenum. The maximum absorbance of the iron complex is observed at 410 mμ.

The Effect of the Diluent.—Since the iron-DBM complex is insoluble in methyl or ethyl alcohol, MIBK was primarily used as a diluent. In this case, however, an extremely large amount of DBM was necessary in order to ensure full color development, and this induced large blank values. In the study of the color reaction of the complex, it was found that the absorbance of the complex was markedly affected by the choice of diluent, as has been reported by Mann and White[5] for the *in situ* spectrophotometric determination of chromium with diphenylcarbazide. The comparison of some diluents, shown in Fig. 2, revealed that methanol is best for this purpose,

---

[1] Y. Umezaki, This Bulletin, **36**, 769 (1963).

[2] T. Shigematsu and M. Tabushi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 265 (1960).

[3] H. Goto and E. Sudo, *Japan Analyst* (*Bunseki Kagaku*), **9**, 213 (1960); N. Tajima and S. Kurobe, ibid., **9**, 399 (1960); N. Tajima and S. Kurobe, ibid., **9**, 798 (1960); N. Tajima and S. Kurobe, ibid., **10**, 528 (1961).

[4] H. Jackson and D. S. Phillips, *Analyst*, **87**, 712 (1962); H. Jackson and D. S. Phillips, ibid., **87**, 718 (1962).

* A one-eighth part of 11 cm. filter paper.

** When all the extracts are used for the color development, the effluent is collected directly in the volumetric flask, and the inside of the separatory funnel and the plug are washed with 1 ml. of MIBK.

[5] C. K. Mann and J. C. White, *Anal. Chem.*, **30**, 989 (1958).

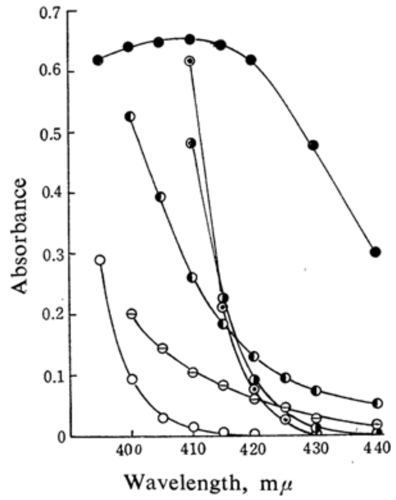

Fig. 1. Absorption spectra.

● Fe(III) 30 μg. ○ Blank, 0.5% DBM×2 ml.
⊖ Cu(II) 10 mg. ⊙ Sn(IV) 10 mg.
◑ Mo(VI) 200 μg. ◐ V(V) 200 μg.

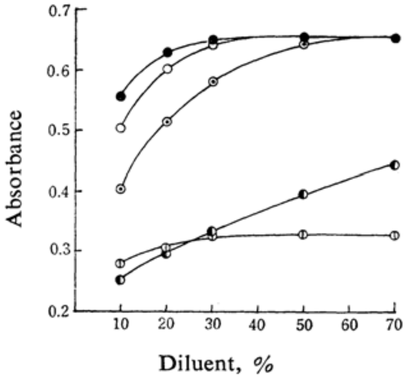

Fig. 2. Effect diluent.
30 μg. of Fe(III) present in aq. soln.

- ● Methyl alcohol, 0.5% DBM×2 ml., 2 ml. extract was used.
- ○ Ethyl alcohol, 1% DBM×2 ml., 2 ml. extract was used.
- ⊙ Ethyl alcohol, 0.5% DBM×2 ml., 2 ml. extract was used.
- ◐ Acetone, 0.5% DBM×2 ml., 2ml. extract was used.
- ⦶ Ethyl alcohol, 0.5% DBM×2 ml. 1 ml. extract was used.

while ethanol is barely satisfactory. No precipitation of the complex occurred in this combination of solvents (MIBK : pyridine : methanol = 2 : 0.5 : 7.5). The effect of diluents on the color development of the complex apparently parallels the magnitude of the dielectric constants of the solvents. If this assumption is true, water, which has the highest dielectric constant, should be most effective. In fact, the addition of water instead of methanol up to 2 ml. gave a light pink color even before the addition of pyridine, though its use is not adequate for the standard procedure because a large amount of water causes precipitation.

Pyridine Concentration.—Pyridine was chosen as a miscible base in order to neutralize the acid extracted simultaneously into the organic phase and in order to ensure the full color development of the complex. The role of pyridine is not clear; it is not certain whether it only neutralizes the acid or whether it forms some adducts with iron-DBM as in cobalt-TTA and pyridine.[6]

As Fig. 3 shows a very small amount of pyridine is sufficient for full color development; 0.5 ml. was used in practice.

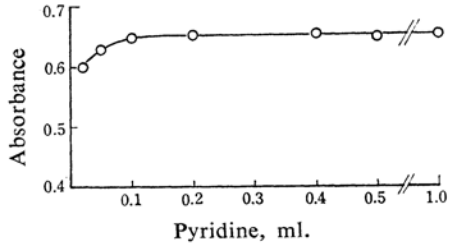

Fig. 3. Effect of pyridine.
30 μg. of Fe(III) present in aq. soln. 0.5% DBM×2 ml.

DBM Concentration.—As Fig. 4 shows, 2 ml. of a 0.5% DBM solution is sufficient in the methanol system.

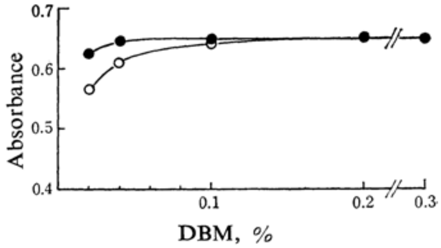

Fig. 4. DBM concentration.
30 μg. of Fe(III) present in aq. soln.; 1 ml. of pyridine was used.

- ● Methyl alcohol was used as diluent.
- ○ Ethyl alcohol was used as diluent.

The Effect of the Volume of the Aqueous Solution.—Since MIBK dissolves in water to some extent and vice versa, any change of the volume ratio of the two phases should be avoided as much as possible. In the recommended procedure, 3 ml. of MIBK decreases its volume to 2.1 to 2.2 ml. after passing through the filter paper plug. The effect of the volume of the aqueous solution was ex-

---

[6] J. P. Fackler, *Inorg. Chem.*, **2**, 266 (1963).

TABLE I. EFFECT OF VOLUME OF AQUEOUS SOLUTION (20 μg. of iron(III) present)

Volume of aq. soln. ml.	Absorbance
8.0	0.429
9.0	0.436
10.0	0.437
11.0	0.437
12.0	0.441

amined with varying volumes of the sample solution using 3 ml. of MIBK. As Table I shows, a variation of the volume by ±1 ml. for 10 ml. of the sample solution does not yield any appreciable error.

The Effect of the Acidity of the Aqueous Solution.—Since the volume of the extract decreases with the increasing acidity of the aqueous solution, a relatively severe control of the acidity is desired. As is shown in Table II, the range of permissible variation in the acidity is narrow; i. e., about ±0.15 N corresponds to a 1% error.

TABLE II. EFFECT OF ACIDITY OF AQUEOUS SOLUTION (20 μg. of iron(III) present)

Acidity of aq. soln. N	Absorbance	
	2 ml. extract	Whole extract
5.3	0.422	0.524
5.9	0.437	0.523
6.5	0.456	0.527
7.1	—a)	0.511
7.7	—a)	0.487

a) Volume of extract was less than 2 ml.

When the adjustment of the acidity is rather difficult, the use of the entire extract instead of a 2 ml. portion is preferable.

Stability and Sensitivity.—The color develops almost instantaneously on the addition of the reagent and pyridine, and it is stable for a long time provided the container is sealed.

The sensitivity of this reaction is 0.0046 μg. Fe/cm^2 for $-\log T=0.001$ (2 ml. extract) and 0.0038 μg. Fe/cm^2 (whole extract).

Beer's Law.—Beer's law is obeyed up to 40 μg. of iron in an aqueous solution in the recommended procedure, as Fig. 5 shows.

The Mole Ratio.—The mole ratio of the complex was studied by the method of continuous variations; it is clear that, in the lower concentration of DBM, the ratio of iron to the reagent is 1 : 2, as is shown in Fig. 6. How-

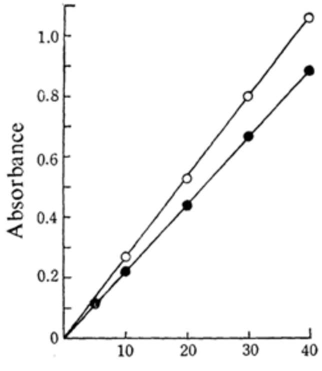

Fig. 5. Calibration curve.

● 2 ml. extract was used.
○ Whole extract was used.

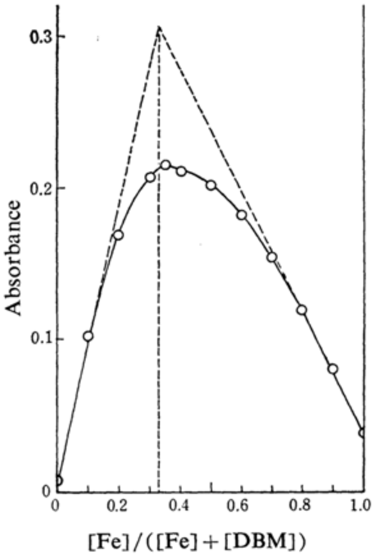

Fig. 6. Continuous variation method.
Wavelength: 410 mμ
$[\text{Fe}]+[\text{DBM}]=8.0\times10^{-5}$ M

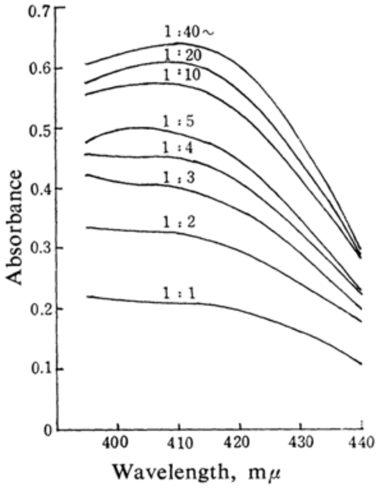

Fig. 7. Absorption spectra of iron-DBM complexes.
$[\text{Fe}]=4\times10^{-5}$ M
Ratios in the figure indicate [Fe]/[DBM].

ever, the absorption spectrum of this species is slightly different, there being no peak at 410 mμ, from that of the species obtained in a higher concentration of the reagent, which presumably has a mole ratio of 1 : 3, judging from its close resemblance to the absorption spectrum of iron-DBM in butyl acetate reported by Shigematsu and Tabushi.[2] The absorption spectra of these species change gradually with an increasing concentration of DBM ; the change is hardly observed when this ratio exceeds 1 : 40, as Fig. 7 shows.

The Effect of Diverse Ions.—The effect of diverse ions on the determination of iron is summarized in Table III.

TABLE III. EFFECT OF DIVERSE IONS
(20 μg. of iron(III) present)

Ion	Added mg.	Fe recovered μg.
As(III)	20	20.5, 20.5
Sb(V)	2	20.4, 20.3
Se(IV)	2	21.2, 21.0
Te(IV)	2	—[a]
	0.2	18.8, 18.5
Ge(IV)	2	20.8, 19.9
Sn(IV)	2	32.2, 33.2
	1	20.8,[b] 20.6[b]
V(V)	0.2	29.9
	0.04	20.8,[b] 21.0[b]
Cr(VI)	0.2	29.4
Cr(III)	20	20.4, 20.7
Mo(VI)	20	—[a]
	0.2	45.3
	0.2	22.2,[b] 22.0[b]
Cu(II)	20	24.2
	1	20.4, 20.5
Co(II)	20	19.7, 20.9
Ni(II)	20	19.7, 20.2
Mn(II)	20	20.4, 19.4
Zn(II)	20	20.7, 20.2
Hg(II)	20	20.5, 20.5
Be(II)	10	19.7, 20.4
Ce(III)	10	19.6, 20.2
Bi(III)	10	20.8, 20.1
Th(IV)	20	19.5, 20.2
Ti(IV)	2	20.2, 20.4
W(VI)	0.2	19.1, 19.4
U(VI)	20	90.7
	0.2	20.0, 20.7
NO_3^-	20	18.4, 18.1
	2	19.8, 20.0
SO_4^{2-}	20	19.0, 19.7
CH_3COO^-	20	19.5, 20.2
F^-	20	17.5, 17.1
PO_4^{3-}	20	19.8, 19.5

a) Precipitate was produced in the organic phase.
b) Measured at 425 mμ.

Goto et al.[7] reported that antimony(III, V), arsenic(III, V), tin(IV), selenium(IV), tellurium(IV), germanium(IV), chromium(VI), vanadium(V) and molybdenum(VI) are also extracted, more or less, with MIBK from a hydrochloric acid solution. Of these ions, arsenic, antimony, selenium and germanium do not interfere with the determination of iron, whereas tellurium, vanadium, chromium, molybdenum and tin do cause interference more or less. However, these interferences are reduced or eliminated by reduction (for chromium, chromium(VI) to chromium(III)) or by the measurement of the absorbance at a longer wavelength, where the absorbances due to these elements decrease rapidly, as Fig. 1 shows.

Among the ions which are not extractable, copper(II), uranium(VI) and tungsten(VI) interfere more or less. However, the interference with these ions is not so serious that the presence of 10- (for uranium and tungsten) to 50-fold (for copper) is permissible. Of the cations tested, the interference with vanadium is the most serious.

Sulfate, acetate and phosphate do not interfere, whereas nitrate interferes, especially in its higher concentration, where both the volume of the MIBK extract and the amount of the co-extracted acid become larger ; this spoils the experimental conditions.

Summary

A method has been described for the direct spectrophotometric determination of up to 40 μg. of iron(III) with DBM in the organic phase.

An orange complex, which is formed with the addition of DBM and pyridine to the MIBK extract of iron, has a maximum absorbance at 410 mμ. The effect of the diluent on the color reaction has been studied ; methanol has been selected as the best diluent of those tried. The color reaction conforms to Beer's law and has a sensitivity of 0.0046 μg. Fe/cm^2 for $-\log T = 0.001$. The effects of diverse ions on the determination of iron have been studied ; it has been found that this method is simple and is sensitive and selective to iron.

Resources Research Institute
Kawaguchi, Saitama

---

[7] H. Goto, Y. Kakita and K. Furukawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1513 (1958).