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The Coprecipitation and Spectrophotometric Determination of Iron as 8-Hydroxyquinolinate

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The coprecipitation and spectrophotometric method, which is likened to the solvent extraction and spectrophotometric method, was applied to the following system for the first time; ferric ion was coprecipitated as 8-hydroxyquinolinate with an organic coprecipitant, and was determined spectrophotometrically after the precipitate was dissolved with an organic solvent. The effect of the ligand concentration on the pH *vs.* absorbance curve in the present method was apparently similar to that for solvent extraction. A nearly constant absorbance was obtained above pH 4 at a ligand concentration of 4×10^{-3} M. Over 100 mg of *o*-phenylphenol, an almost quantitative coprceipitation was obtained, though the absorbance decreased gradually as the coprecipitant was increased. The effect of diverse ions was also examined. Titanium(IV), vanadium(V) and molybdenum(VI) interfered considerably, while others have little effect on the absorbance. The method was applied to the determination of trace amounts of iron in natural waters and reagent grade sodium chloride.

The coprecipitation method for trace metal ions with organic coprecipitants has been developed for the chemical separation of radioisotopes, and the chemical enrichment of trace elements in natural water and biological materials.[1-3] Compared with inorganic coprecipitants, such as ferric hydroxide, organic coprecipitants have several advantages such as they are easily eliminated from the precipitate by ashing. This fact is of use especially in the treatment of radioactive solutions, and they are very selective, free from trace elements, and easy to filter.

Kuznetsov[2] has studied several types of organic coprecipitation processes for over 35 elements, and compared them to extraction by solid extractants. Tappmeyer and Pickett[4] have investigated the coprecipitation mechanism of metal 8-hydroxyquinolinates with organic coprecipitants and indicated that the factors influencing the

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[1] H. V. Weiss and M. G. Lai, *Anal. Chem.*, **32**, 475 (1960); H. V. Weiss, M. G. Lai and A. Gillespie, *Anal. Chim. Acta*, **25**, 550 (1961); H. V. Weiss and M. G. Lai, *ibid.*, **28**, 242 (1963).

[2] V. I. Kuznetsov, in "Radioisotopes in Scientific Research," Vol. II (ed. R. C. Extermann), Pergamon Press, London (1958), pp. 264—283.

[3] S. Hirano, A. Mizuike and Y. Ujihira, *Bunseki Kagaku (Japan Analyst)*, **12**, 160 (1963); Y. Ujihira, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 642 (1963); *Bunseki Kagaku (Japan Analyst)*, **14**, 399 (1965); Y. Ujihira and E. Niki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 620 (1966).

[4] W. P. Tappmeyer and E. E. Picket, *Anal. Chem.*, **34**, 1709 (1962).

coprecipitation of these metal chelates with organic coprecipitants like β-naphthol and phenolphthalein were the same as those that influenced solvent extraction. They also noted a similarity between the plots calculated by employing the equilibrium considerations of solvent extraction, and the plots experimentally determined showed good agreement. In our previous paper,[5] the influence of organic coprecipitants on the coprecipitation efficiency of six metals was examined, and it was found that organic coprecipitants with hydroxyl groups such as *o*-phenylphenol or α-naphthol were excellent for coprecipitation. Also it was suggested that a metal ion could be determined spectrophotometrically if the precipitate containing the coprecipitated metal chelate was filtered and dissolved in a suitable organic solvent. This new method is likened to the "solvent extraction and spectrophotometric method." It is expected that the method has the advantages of easiness in chemical treatment, and of good selectivity on chemical separation, which are observed in the extraction method, and a high concentrating efficiency, which is observed in the coprecipitation method.

In the present work, the main object is to examine whether ferric ion is coprecipitated as 8-hydroxyquinolinate with such an organic coprecipitant as *o*-phenylphenol, and is determined spectrophotometrically after the precipitate is dissolved with a suitable organic solvent.

Experimental

Reagents. A standard stock solution of iron was prepared by dissolving the pure metal in 6 N perchloric acid, by adding a few drops of 30% hydrogen peroxide solution, by fuming with concentrated perchloric acid repeatedly and by diluting with deionized water. Reagent grade *o*-phenyplhenol was purified by reduced pressure distillation. 8-Hydroxyquinoline was dissolved in dilute hydrochloric acid.

The other chemicals were chemically pure or reagent grade materials.

Apparatus. A SV 50 Shimadzu automatic recording spectrophotometer was used for the measurement of absorption spectra. For quantitative measurement, a Model 139, Hitachi manual spectrometer was used with absorption cells having a path length of 1.00 cm. pH measurements were performed with a Hitachi-Horiba Model M-3 pH meter.

Procedure. An aliquot of a ferric perchlorate solution containing 11.2 μg of iron per m*l* was taken. Then 2 m*l* of 0.1 M 8-hydroxyquinoline and 5 m*l* of buffered solution (1.0 M NaAc-HAc) were added to the solution. The pH of the solution was then adjusted to the desired pH by the addition of 1 M hydrochloric acid, or 1 M sodium hydroxide. The aqueous phase was finally diluted to 50 m*l* with water. The solution after the pH adjustment was transferred to a 100 m*l* Erlenmeyer flask. Then 0.25 g of *o*-phenylphenol which was ground with the same quantity of sodium chloride in an agate mortar was added to it. After the flask was properly stoppered, it was shaken for 30 min and the solution allowed to settle. The solid phase was carefully filtered with a glass filter and dissolved with a suitable organic solvent, followed by dilution to 10 m*l*. After the solution was filtered through filter paper, the absorbance was measured against a blank solution.

Results and Discussion

Choice of Organic Coprecipitant and Organic Solvent. *o*-Phenylphenol was selected as an organic coprecipitant because it is more stable toward color change over long periods and in alkaline solution than α-naphthol; that is, color change hinders the measurement of absorbance. There are a few methods of treatment for *o*-phenylphenol to increase its efficiency of coprecipitation. The first is the method of crushing the coprecipitant in an agate mortar. The second is that of crushing it together with the same quantity of sodium chloride in the mortar. The third is that of dissolving it in an alkaline solution, followed by fine recrystallization in an acidic solution. In this study, the second method was chosen because of high efficiency, good reproducibility, and an easy method of coprecipitation.

Several kinds of organic solvents were tested in order to examine the easiness of dissolving the precipitate into them, and the final absorbance. The absorbance was measured at 0.620, 0.612, 0.597, 0.510 and 0.470 for benzene, methylisobutylketone, cyclohexane, amylalcohol and benzylalcohol, respectively. Benzene and methylisobutylketone are better than the others in both absorbance and solubility. Methylisobutylketone was used for the present purpose as it is more nonvolatile than benzene. As the chelate reagent does not coprecipitate in the present system, methylisobutylketone containing 2×10^{-3} M of 8-hydroxyquinoline was used to make the 8-hydroxyquinolinate stable.

Absorption Spectra. The absorption spectra for the methylisobutylketone solutions of ferric 8-hydroxyquinolinate containing 0.2, and 5 g of *o*-phenylphenol are compared in Fig. 1. The spectra have their maximum absorptions at 465, and 580 mμ, and as described later, they are slightly affected by the amount of coprecipitant. As the reagent and coprecipitant blank at 465 mμ shows scarcely any absorbance, the absorbance was measured throughout the experiment at that wavelength.

The Effect of pH and the Concentration of Reagent. To establish the optimum pH value of the aqueous phase for the coprecipitation of iron, the dependence of the absorbance of the organic phase on the pH values was studied. In Fig. 2, the absorbance of the organic phase measured at

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[5] M. Matsui, M. Munakata and T. Shigematsu, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 273 (1967).

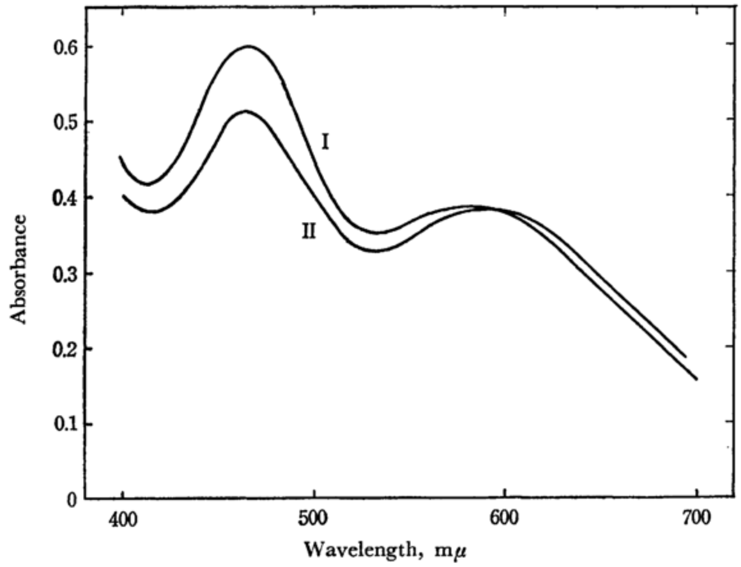

Fig. 1. Absorption spectra of ferric oxinate in methylisobutylketone. *o*-Phenylphenol: I 250 mg, II 5 g, 8-Hydroxyquinoline: 4×10^{-3} M Fe(III): 2×10^{-5} M in aqueous phase, Volume: aqueous phase 50 m*l*, organic phase 10 m*l*, pH: 4.50.

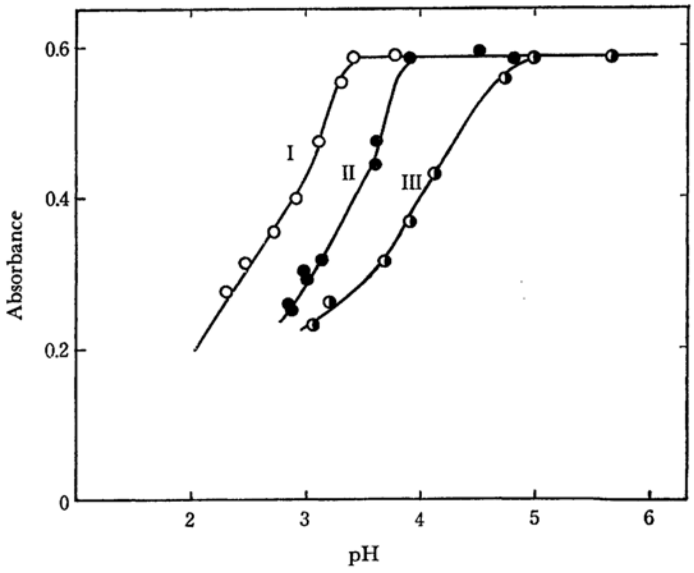

Fig. 2. Effect of pH and reagnet concentration. 8-Hydroxyquinoline: I 1×10^{-2} M, II 4×10^{-3} M, III 4×10^{-4} M. Others are same to in Fig. 1.

465 mμ was plotted against pH. The effect of the concentration of 8-hydroxyquinoline on the pH *vs.* the absorbance curve in the coprecipitation was similar to that in solvent extraction. That is, the chelate coprecipitated in the more acidic range of the solution as the concentration of the reagent became high. However, the shapes of the pH *vs.* absorbance curves of the present work were not so ideal as those of the solvent extraction. This fact shows that in the present system it is difficult to reach a state of true thermodynamic equilibrium. A nearly constant absorbance was obtained above pH 4 when the concentration of the reagent was 4×10^{-3} M. The pH value and reagent concentration were kept at 4.50, and 4×10^{-3} M, respectively, throughout the experiments.

The Effect of the Amount of Coprecipitant. The effect of the amount of *o*-phenylphenol on the

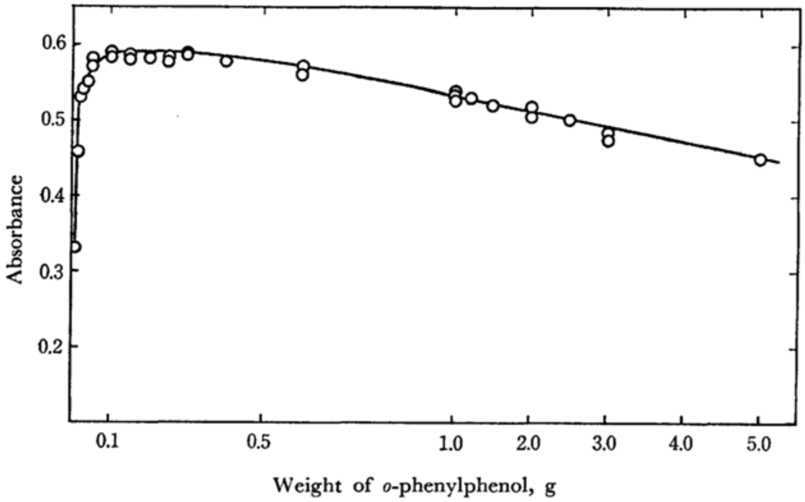

Fig. 3. Effect of *o*-phenylphenol.

absorbance of the organic phase was studied. As shown in Fig. 3, the absorbance of the organic phase increased rapidly until 100 mg of coprecipitant, had a nearly constant value from 100 to 400 mg, and decreased gradually as more coprecipitant was added. The gradual decrease in the absorbance does not mean the lowering of coprecipitation efficiency, but rather the fall in the absorption coefficient of the chelate probably is due to the solvation effect of the polar coprecipitant. This may be seen from the following: The absorbances in the coprecipitation method were identical for any certain of coprecipitant above 250 mg with those in the extraction method (where the same quantity of coprecipitant was added into the methylisobutylketone phase), by which iron was extracted quantitatively. This showed the quantitative coprecipitation of any amount of coprecipitant. Also, the solvation effect was suggested from the absorption spectra in Fig. 1, where there was almost no change in absorption intensity but some change in energy at the longer wavelength, though the absorbance at 465 mμ decreased as precipitant increased. Thus, 250 mg of *o*-phenylphenol was used throughout the experiments.

The Effect of Standing and Shaking Time. The absorbance of the methylisobutylketone solution of ferric 8-hydroxyquinolinate was measured at 465 mμ at appropriate intervals of time to examine the effect of the standing and shaking time. As shown in Fig. 4, little influence of the standing time was observed upon the absorvance of the organic phase. Similarly, the absorbance was almost constant for 5 min and over of shaking time.

Coprecipitation of the Chelate Reagent. To examine the coprecipitation of the reagent with coprecipitant, the following procedure was adopted. Two milliliters of 0.1 M 8-hydroxyquinoline and 1 m*l* of buffer solution was taken in an Erlenmeyer flask. The solution was then adjusted to pH 4.50 and diluted to 50 m*l* with water. The absorbance of the solution was measured at 410 mμ. After the solution was treated according to the process used in this study, the absorbance of the filtrate was measured at the same wavelength, and the procedure was repeated. The corresponding absorbances were 0.591, 0.602 and 0.597. This result indicates that the reagent was scarcely coprecipitated with the coprecipitant.

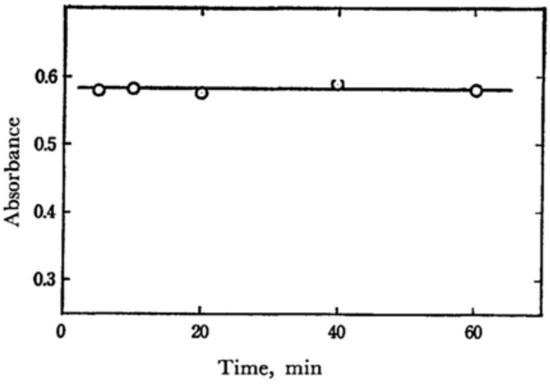

Fig. 4. Effect of shaking time.
pH: 4.5 Wavelength: 465 mμ

Calibration Curves. A calibration curve was made by coprecipitating different amounts of iron with 0.25 g of *o*-phenylphenol as a 8-hydroxyquinoline chelate. The absorbance of the solution at 465 mμ was measured against a blank. A good linear relationship was obtained by plotting the absorbance of the solution against the concentration of iron added in the aqueous solution, as shown in Fig. 5. The other curve in Fig. 5

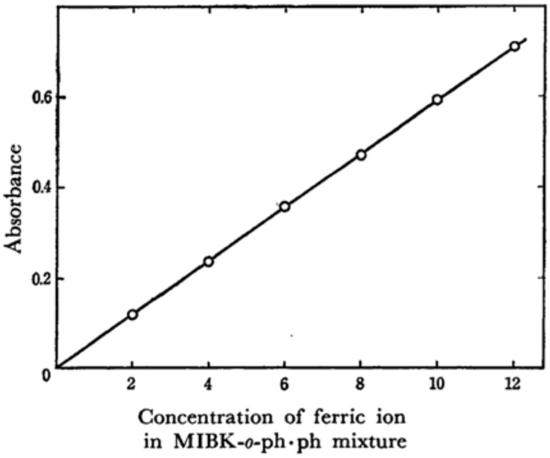

Fig. 5. Calibration curve of ferric oxinate.
pH: 4.5 Wavelength: 465 mμ

was made by extracting iron with 8-hydroxyquinoline into a 10 m*l* portion of methylisobutylketone with 0.25 g of the coprecipitant from 50 m*l* portions of the aqueous solution. As these calibration curves are in good agreement, it is considered that the coprecipitation of iron is almost quantitative.

TABLE 1. EFFECT OF DIVERSE IONS

Ion	Added, mg	Fe found,* μg
Al(III)	0.1	51
Ba(II)	10	50
Ca(II)	10	50
Cd(II)	0.5	49
Ce(IV)	0.7	50
Co(II)	0.01	50
	0.1	81
Cr(III)	0.1	50
	0.5	53
Cu(II)	1.0	54
Hg(II)	0.5	50
In(III)	0.1	52
Mg(II)	10	50
Mn(II)	0.5	50
Mo(VI)	0.5	84
Ni(II)	0.1	53
Pb(II)	1.0	50
Sb(III)	0.1	51
Sn(IV)	0.5	48
Sr(II)	10	50
Ti(IV)	0.2	84
V(II)	0.5	94
Zn(II)	0.5	49

* 50 μg of ferric ion was taken.

The Effect of Diverse Ions. The effect of diverse ions was examined with a solution containing 50 μg of iron and diverse ions. The pH value of the solution was adjusted to 4.50. Of the 21 cations tested, titanium(IV), vanadium(V) and molybdenum(VI) gave a positive error, while common di- and tervalent cations had little effect on absorbance, as shown in Table 1.

Applications. The effect of the volume of the solution, and the amount of coprecipitant on the absorbance of the organic phase was examined in order to determine iron in natural water, and in reagent grade sodium chloride. As shown in Table 2, a nearly quantitative recovery was obtained when the coprecipitant increased as the volume of the sample solution increased.

TABLE 2. THE EFFECT OF THE VOLUME OF THE SOLUTION AND THE AMOUNT OF COPRECIPITANT

Volume m*l*	Carrying reagent g	Percent copptn.
100	0.25	99
200	1.0	101
500	1.5	100
1000	3.0	102

Filtered sea and fresh water were acidified to pH 1 with concentrated hydrochloric acid (Sea water was collected in the open sea off Shirahama, Wakayama Pref., and fresh water from Lake Biwa.). Aliquots of these waters were put into Erlenmeyer flasks and 3 g of *o*-phenylphenol was added. These samples were treated according to the procedure used in this study. The results of the determination of iron in aliquots and commercial reagent sodium chloride (guaranteed reagent, and chemical pure grade) are shown in Table 3. These values were determined by the method of standard addition. The method provides several important advantages over the usual method of determination of trace elements in extremely dilute solutions described previously.

TABLE 3. THE ASSAY OF IRON IN NATURAL WATERS AND SODIUM CHLORIDE

Sea water (Shirahama)	7.0×10^{-6} g/*l*
	6.8×10^{-6}
	7.7×10^{-6}
Fresh water (Biwako)	12.0×10^{-6}
	12.4×10^{-6}
Reagent grade NaCl,	
Guaranteed reagent	7.0×10^{-6} %
Chemical pure reagent	2.0×10^{-6}