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The Coprecipitation and the Spectrophotometric Determination of Uranium as Dibenzoylmethane Chelate

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The coprecipitation and direct-photometric method was applied to the uranium β-diketonate system; uranyl ion was coprecipitated as dibenzoylmethanate with *o*-phenylphenol and determined spectrophotometrically after the precipitate was dissolved in butyl acetate. The effect of ligand concentration on the per cent coprecipitation-pH curve was studied and the curve was not affected by the ligand concentration in the range from 2×10^{-2} to 4×10^{-4} M. Over the 200 mg of *o*-phenylphenol, an almost quantitative coprecipitation was obtained, though the absorbance slightly decreased with the increase in the coprecipitant amount (about 2% per 1g *o*-phenylphenol). As many diverse ions interfered with the determination of uranium, the solution of calcium-EDTA chelate was used as a masking agent. When a small amount of alkylamine was added, the recovery of uranium became more complete. The effect of alkylamine was probably caused by the adduct formation of uranium chelate with alkylamine.

It has been considered that the coprecipitation of metal chelates with organic compounds is a very attractive problem in the sense of the theoretical treatment[1] and especially of the practical technique. The authors have been much interested in this subject and already reported the coprecipitation of ferric oxinate with some organic compounds and proposed a method for the photometric determination of ferric iron in very dilute solution.[2] The general procedure consists of three steps: Metal ions are allowed to react with a chelating reagent; the metal chelate formed is collected with an adequate organic coprecipitant; and the precipitate separated is then dissolved in a suitable organic solvent, followed by the absorbancy measurements. By this procedure, the metal ion present in much low concentration can be easily concentrated and determined, and the method is suitable, if the chelate-forming reaction is selective to the metal ion to be analysed, or if the absorbance of the metal chelate is not affected by the presence of diverse ions.

In the present research, the coprecipitation and the direct-photometric determination of uranium was investigated by using β-diketone and *o*-phenylphenol (OPP) as a chelating reagent and organic coprecipitant, respectively. Beta-diketones have been widely utilized for the solvent extraction of metal ions,[3] and is recognized to be a very useful reagent for the separation and the photometric determination of uranium, because uranium can

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[1] W. P. Tappmeyer and E. E. Pickett, *Anal. Chem.*, **39**, 1709 (1962).

[2] T. Shigematsu, M. Matsui, M. Munakata and T. Sumida, This Bulletin, **41**, 609 (1968). b) M. Matsui, M. Munakata and T. Shigematsu, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 273 (1967).

[3] See, for example, a) J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, London (1964). b) G. H. Morisson and H. Freiser, "Solvent Extraction in Analytical Chemistry, "John Wiley & Sons, New York (1957).

be selectively extracted by masking diverse ions with EDTA-calcium.[4,5] However, most of β-diketones show comparatively high absorption near the absorption maximum of the uranium chelates, and therefore the concentration of the reagent must be kept excactly constant, or the low concentration is desirable. In the coprecipitation method, the almost quantitative recovery was attained even in the low concentration (4×10^{-4} M) of the reagent and when the larger volume of sample solution was handled, the addition of a Lewis base such as *n*-butylamine *etc.* prevented the decrease of the recovery, and accordingly, the determination of uranium was not essentially influenced by the reagent blank. As previously described, OPP is one of the most suitable coprecipitants for such a methal chelate as oxinates.[2]

Experimental

Apparatus. Spectrophotometric measurements were made with a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer using 1.00 cm transmission cells. A Hitachi-Horiba glass electrode pH meter, model M3 was used for the pH measurements.

Materials. β-Diketones were obtained from the Dozindo Co., Ltd., Research Laboratories. A stock solution of uranium was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in water; the concentration was determined gravimetrically as U_3O_8. *o*-Phenylphenol (OPP) was purified by the distillation under the pressure of 8—10 mmHg in the nitrogen atmosphere. Butyl acetate was purified by washing with water, followed by distillation. All the other reagents used were the reagent-grade materials and used without further purification.

Procedure. For investigating the effect of various factors, the following procedure was designed: An aliquot of the uranium stock solution, 5 m*l* of 0.2 M EDTA-calcium solution and 1 m*l* of 1 M acetic acid solution are taken in a 100 m*l* Erlenmeyer flask. The solution is diluted to 50 m*l*, and the pH of the solution is adjusted to a desired value with a dilute sodium hydroxide or hydrochloric acid solution. One-half milliliter of a β-diketone-acetone solution ($0.4—8\times 10^{-3}$ M) and a suitable amount of *o*-phenylphenol which is previously smashed into fine pieces are added. After shaken with a mechanical shaker, the mixture is filtrated through a glass filter No. 3 and the precipitate is then dissolved in butyl acetate. The organic solution is made clear by filtering through a filter paper, transferred to a 10 m*l* measuring flask and the absorbance is obtained.

Results and Discussion

Because the adding method of the organic coprecipitant in an organic coprecipitation technique is an important factor, its effect on the coprecipitation behavior of uranium was studied by using the uranium-dibenzoylmethane (DBM)-OPP system. The following procedures were examined[4]: (A) OPP, which was freshly precipitated from alkaline solution with an acid, was added to a sample solution. (B) OPP dissolved in an alkaline solution was added to a buffered sample solution. (C) OPP, which was smashed in a mortar, was added to a sample solution. (D) OPP dissolved in acetone was added to a sample solution. As shown in Fig. 1, (A) and (B) were excellent, (C) was fairly effective, but (D) was not so effective. In the subsequent experiment, the procedure (C) was employed, because in the procedure (A) or (B), the pH value of the sample solution must be adjusted again after the addition of OPP. Effect of the concentration of the chelating agent was studied over the range 2×10^{-2} to 4×10^{-4} M, and the per cent coprecipitation-pH curve of uranium is shown in Fig. 2. The curve of uranyl dibenzoylmethanate is not affected by the reagent concentration in the range studied: This indicates that the system is not in a equilibrium state in the concentration over the solubility of DBM. The curve of uranyl thenoyltrifluoroacetone (TTA) complex, on the other hand, shifted to the lower pH value as the TTA concentration was increased. The same tendency was observed in the case of benzoyltrifluoroacetone or benzoylacetone. This difference in the behavior may be caused by the solubility of

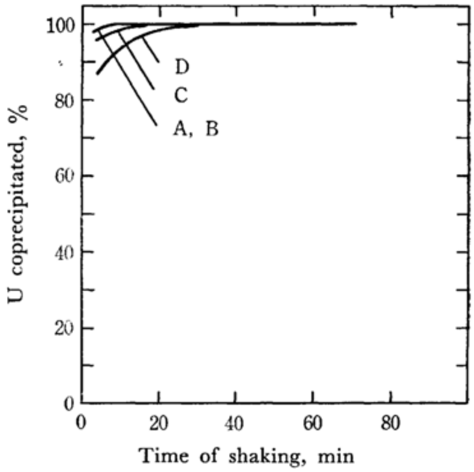

Fig. 1. Effect of adding methods of the coprecipitant on coprecipitation.

UO_2^{2+}: 8×10^{-6} M, DBM: 4×10^{-4} M, OPP: 500 mg, aqueous phase: 50 m*l*, organic phase: 10 m*l* of butyl acetate.

A: fresh precipitation from alkaline solution with an acid.

B: precipitation in a buffered sample solution from alkaline solution.

C: smashed in a mortar.

D: dissolution in acetone.

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[4] T. Shigematsu, M. Tabushi and M. Matsui, This Bulletin, **37**, 1333 (1964).

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

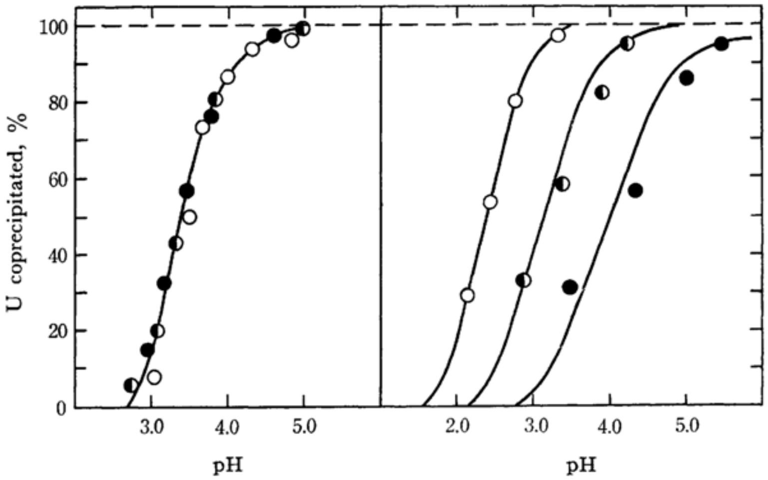

Fig. 2. Effect of β-diketone concentration on the coprecipitation of uranyl chelate.
Left: DBM ○ 2×10^{-2} M, ◐ 4×10^{-3} M, ● 4×10^{-4} M.
Right: TTA ○ 2×10^{-2} M, ◐ 4×10^{-3} M, ● 4×10^{-4} M.
Shaking for 30 min, others are the same as in Fig. 1.

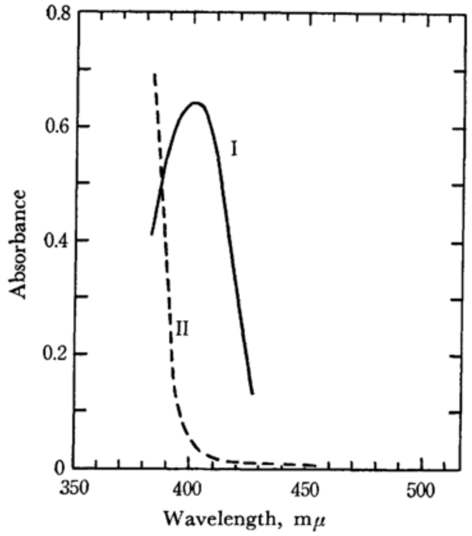

Fig. 3. Absorption spectra of uranyl DBM chelate.
I: UO_2^{2+} 4×10^{-5} M, DBM 2×10^{-2} M, pH 6.0, shaking for 30 min.
II: reagent blank.

β-diketone in water. The curve shifts to lower pH with the increase in the reagent concentration, until it probably arrives at the solubility of the reagent. The phenomenon that uranium acetylacetonate can not be coprecipitated well, may be due to the larger solubility of acetylacetone in comparison with that of other β-diketones. Because the photometric determination of uranium is influenced by the reagent blank (Fig. 3), it is desirable that the amount of the reagent contained in the precipitate is as small as possible. Since β-diketone is coprecipitated together with uranyl β-diketone chelate even when the reagent concentration does not exceed its solubility, the β-diketone which possessed the larger solubility did not always show lower reagent blank than the one which possessed the smaller solubility did. In the proceeding experiments, DBM was used as a chelating reagent, from the consideration described just above and other reasons, that is, uranium could be effectively and almost quantitatively coprecipitated in the relatively low concentration of the reagent, and the extinction coefficient of the uranyl chelate was larger than that of other uranyl β-diketone chelates.

A polar solvent was used for dissolving the precipitate, because the absorbance of uranyl-DBM chelate decreased in the nonpolar solvent (*e. g.*,

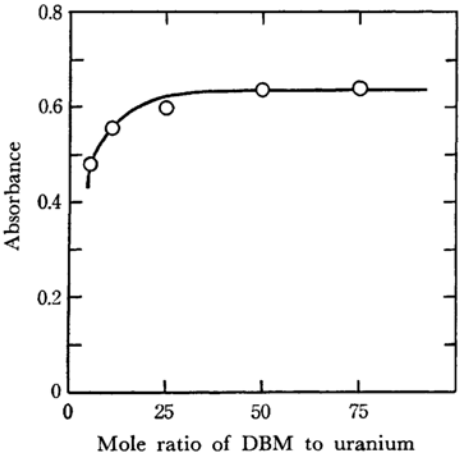

Fig. 4. Effect of reagent concentration.
UO_2^{2+} 4×10^{-5} M, pH 6.0, shaking for 30 min, others are the same as in Fig. 1.

benzene) with the lapse of time.5) Normal-butyl acetate was an excellent solvent, because of its good separating property from water and of the larger extinction coefficient in comparison with other polar solvents (*e. g.*, *n*-hexyl alcohol, cyclohexanone).

The effect of the mole ratio of DMB to uranium is shown in Fig. 4: The constant absorbance can be obtained when the mole ratio is larger than fifty, while below fifty the absorbance decreases with the decrease of DBM concentration, and this is owing to the incomplete coprecipitation of uranium and to the decomposition of the chelate in the solvent: The decomposition may be caused by OPP.

The effect of the amount of coprecipitant, OPP, is indicated in Fig. 5. The absorbance rapidly diminishes when OPP amount is less than 200 mg. The reason for this low absorbance is attributed to both the loss by the filtration of the precipitate and the decrease in the coprecipitation recovery, because OPP becomes a liquid state in such a small amount. Above 200 mg, the absorbance slightly decreases with the increase in OPP amount (about 2% per 1 g OPP). This unexpected phenomenon is probably resulted from the adduct formation of the chelate with OPP, but not from the coprecipitation yield. Figure 6 indicates the evidence of the adduct formation: The per cent coprecipitation-pH curve shifts somewhat to lower pH as the OPP amount increases, just like in the case of the adduct formation in the solvent extraction of metal chelates.6)

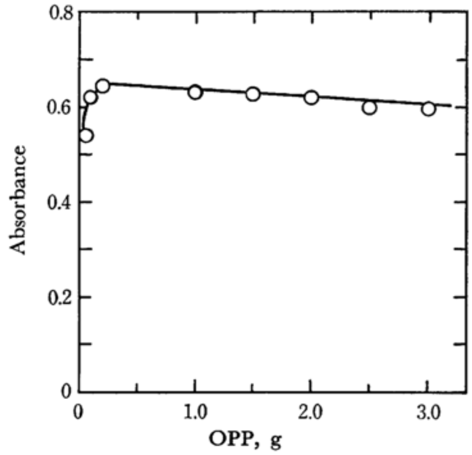

Fig. 5. Effect of coprecipitant, OPP.
UO_2^{2+} 4×10^{-5} M.

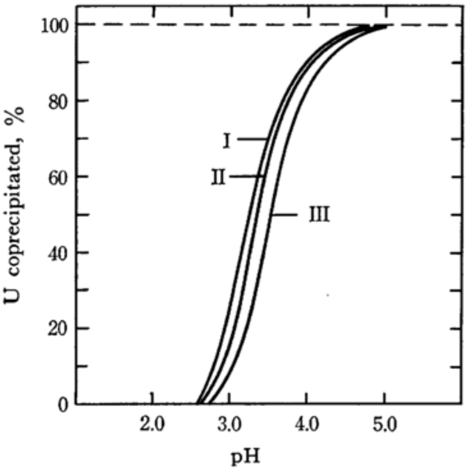

Fig. 6. Effect of OPP amount on per cent coprecipitation *vs.* pH curve.

OPP: I 30 g, II 1 g, III 300 mg

Determination of uranium may be interfered by many diverse ions, and therefore, an available masking agent must be used. When 5 m*l* of 0.2 M EDTA solution and calcium chloride equivalent to EDTA (0.02 M Ca-EDTA in the final concentration) were added as a masking agent, the per cent coprecipitation-pH curve of uranyl bis-dibenzoylmethane chelate shifts about one pH unit to alkali side, but the extraction coefficient is the same with that obtained in the absence of EDTA in the pH region above 6.04) (Fig. 7).

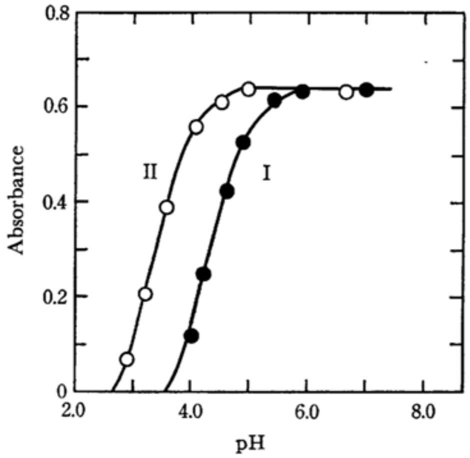

Fig. 7. Effect of masking agent, calcium-EDTA chelate.

I. 0.02 M of Ca-EDTA, II. no masking agent.

From the above experimental results, the conditions for the coprecipitation and the direct-photometric determination of uranium was controlled as follows. The concentration of DBM, acetic acid and EDTA-calcium are 8×10^{-4} M, 0.02 M and 0.02 M, respectively; pH, 6.0; and the volume, about 50 m*l*. One gram of OPP is added and the precipitate was dissolved and diluted to 10 m*l* with butyl acetate.

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6) a) H. M. N. H. Irving and D. N. Edington, *J. Inorg. Nucl. Chem.*, **27**, 1359 (1965). b) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, This Bulletin, **39**, 165 (1966).

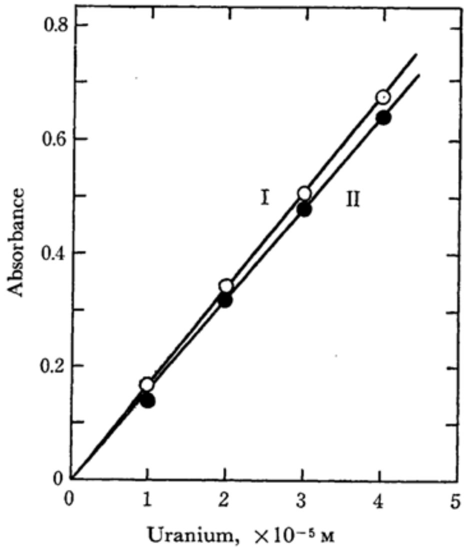

Fig. 8. Calibration curve of uranium.
I. extraction method, II. coprecipitation method

In Fig. 8, calibration curves for uranium are presented. One is obtained by this coprecipitation method and the other is obtained by extracting uranium with 10 m*l* of butyl acetate containing 1 g of OPP, from about 10 m*l* of aqueous solution including 4×10^{-3} M DBM, 0.02 M acetic acid and 0.02 M EDTA-calcium. Beer's law is obeyed up to 10 ppm, and the molar extinction coefficients at 400 mμ are 16100 (this method) and 16800 (liquid-liquid extraction), respectively. This difference may be due to the fact that the coprecipitation recovery of uranium is not precisely quantitative, but about 96 per cent. When a small amount (0.1 m*l*) of *n*-butylamine or *n*-hexylamine was added to the coprecipitation system, the recovery became complete, and two analytical curves quite well agreed. The effect of amines will be described later in this paper.

TABLE 1. INFLUENCE OF DIVERSE IONS
U present: 94 μg; DBM: 8×10^{-3} M; pH: 6.50

Ion	Present (mg)	U found (μg)	Ion	Present (mg)	U found (μg)
Mg^{2+}	2	93.0	Mo^{6+}	5	94.0
V^{5+}	1	94.3	Cd^{2+}	5	96.3
Cr^{6+}	1	96.0	Ba^{2+}	5	93.5
Mn^{2+}	1	94.7	Pb^{2+}	10	92.3
Fe^{3+}	1	93.0	Th^{4+}	1	95.2
Co^{2+}	1	94.5	Al^{3+}	2	*
Ni^{2+}	5	92.4	Ti^{4+}	1	*
Cu^{2+}	1	95.2	Ag^{+}	1	*
Zn^{2+}	5	93.4	Sn^{4+}	1	*
Sr^{2+}	5	94.5	Bi^{3+}	5	*

* Hydroxide or oxide of coexisting ion was precipitated.

To investigate the influence of several metal ions, the measurements were made on a solution containing a proper amount of foreign cations with 94 μg of uranium. The results are summarized in Table 1. Aluminum, titanium, silver, tin(IV) and bismuth(III) interfer because of the formation of hydroxide.

TABLE 2. RECOVERY OF URANYL ION FROM 500 m*l* OF SAMPLE SOLUTION
U: 8×10^{-7} M, DBM: 8×10^{-5} M, pH: 6.5, OPP: 2.0 g

Organic solvent	Volume (m*l*)	U pptd. (%)
Acetone	0.5	42.3
	1.0	49.1
	5.0	72.3
	10.0	97.1
	12.0	*
n-Butylamine	1.0	99.8
	2.0	99.7
n-Hexylamine	1.0	99.6
	2.0	100.0
Pyridine	0.5	*
Tri-butyl phosphate	0.5	*

* Precipitate became liquid.

Recovery of uranium decreased with the increase in volume of sample solution. Although the element may be quantitatively recovered by rising the DBM amount, then the influence of the reagent blank appears. In order to remove the difficutly, a Lewis base was added to the sample solution. The results are presented in Table 2. Uranium was almost completely recovered from 500 m*l* of sample solution by adding *n*-butylamine or *n*-hexylamine. Pyridine or tri-*n*-butyl phosphate could not be employed, because the precipitate became a liquid state. This effect of Lewis bases on coprecipitation of uranium is probably caused by the adduct formation, and is the same phenomenom as the "synergistic effect" in the solvent extraction of metal chelates.[7-10] By increasing the DBM amount, uranium can be essentially quantitatively collected from larger volume: For example, the use of 4×10^{-5} M DBM and 5 m*l* of *n*-butylamine gave satisfactory yield on 2 *l* of sample.

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7) A. E. Comyns, B. M. Gatehause and E. Wait *J. Chem. Soc.*, **1958**, 4655.

8) L. Sacconi, G. Carroti and Paoletti, *ibid.*, **1958** 4257.

9) W. W. Wendlandt, J. L. Bear and G. R. Horton, *J. Phys. Chem.*, **64**, 1289 (1960).

10) H. M. N. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **15**, 158 (1960).