The Solvent Extraction and Spectrophotometric Determination of Uranium using Benzoyltrifluoroacetone as the Chelating Reagent

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It has been generally known that β-diketones are useful chelating reagents in analytical chemistry, chelate chemistry and radiochemistry. Fluorinated β-diketones such as TTA are especially useful in the solvent extraction of metals, because a fluoromethyl group increases the acidity of the enol form.[1]

As do many other metals, uranium reacts with β-diketones to form extractable chelates, which are widely utilized for the separation of the metal. The present authors have studied the chelates of uranium with acetylacetone (AA),[2] dibenzoylmethane (DBM)[3] and trifluoroacetylacetone (TFA),[4] and have developed methods for the extraction separation and the photometric determination of uranium using these β-diketones.

An extraction using benzoyltrifluoroacetone (BTFA), a fluorinated β-diketone, might have some advantages: Quantitative extraction can be expected at a lower pH range from the lower pK_D value of the reagent;[5] high extractability can be anticipated from its low solubility in water, and the extraction may be facilitated by the shielding effect of the phenyl group against hydration to the central metal.

From this view-point, the authors have investigated the solvent extraction of uranium as a BTFA chelate and will propose a procedure for the separation and the spectrophotometric determination of the element.

Experimental

Apparatus. — Spectrophotometric measurements were made with a Shimadzu automatic recording spectrophotometer, model UV-50, and a Hitachi photoelectric spectrophotometer, model EPU-2A, using 1 cm. transmission cells. Radioactivity countings were performed with a Kobe Kogyo NaI(Tl) (4.45 cm. × 5.08 cm.) well-type scintillation counter, model PS-300, connected to a transistorized scaler, model SA-230, and a Metro automatic decatron scaler, model D-5, using a Philips halogen-quenched G-M tube 1905. A Hitachi-Horiba glass electrode pH meter, model P, was used for the pH measurements.

The Standard Solution of Uranium, 100 μg./ml. — A stock solution was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ with water; the concentration was determined gravimetrically as U_3O_8. The stock solution was diluted to make the standard solution.

The Benzoyltrifluoroacetone Solution, 1 M. — 4.3232 g. of BTFA was dissolved and diluted to 20.0 ml. with acetone.

The EDTA-Ca Solution. 0.2 M.

Acetic acid. 1 M.

Boric acid. 1 M.

The Lutetium-177, Zirconium-Niobium-95 and Fission Products Solution. — The radioisotopes were obtained from ORNL. Lutetium and zirconium-niobium were converted to sulfate by fuming them with sulfuric acid. These sulfates and fission products solution were diluted to give a 1∼5 μc./ml. solution.

Organic Solvents. — Chloroform was purified by washing it with a diluted sodium hydroxide solution, water, diluted hydrochloric acid, and three portions of water, followed by distillation. Butyl acetate was washed with water and distilled. Reagent-grade benzene was used without further purification. All the other reagents used were reagent-grade materials.

Results and Discussion

Absorption Spectra. — The absorption spectra of the uranium BTFA chelate were obtained by the following procedure. To the solution containing 100 μg. of uranium, the pH of which adjusted to 5∼6, 0.1 ml. of a 1 M BTFA acetone solution was added. The solution was then diluted to 10 ml. and shaken with 10.0 ml. of benzene, chloroform or butyl acetate. The organic layer was separated, and the absorption was measured against the reagent blank.

Figure 1 shows the absorption curve of the uranium chelate in butyl acetate. The absorption curve exhibits a maximum at 380 mμ; that is almost the same as in the case of benzene or chloroform. For practical purposes, however, it seems suitable to make the measurements at a longer wavelength such as 385

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[1] G. H. Morisson and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons, New York (1957), p. 159.

[2] M. Tabushi, *Bull. Inst Chem. Res., Kyoto Univ.*, **37**, 237 (1959).

[3] T. Shigematsu and M. Tabushi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 265 (1960); T. Shigematsu, M. Tabushi and T. Tarumoto, *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 388 (1962).

[4] T. Shigemtsu, M. Tabushi and M. Matsui, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[5] L. G. van Uitert, W. C. Fernelius and E. Douglas, *J. Phys. Chem.*, **75**, 457 (1953).

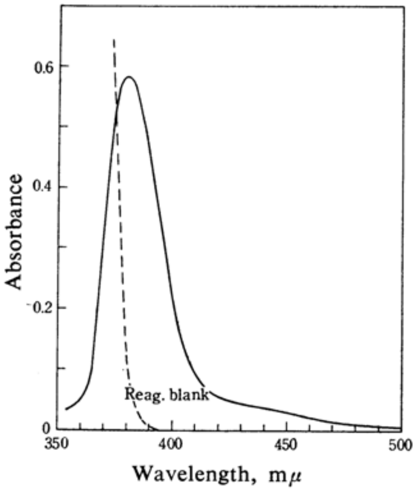


Fig. 1. Absorption spectrum of uranium BTFA chelate.
Solvent: butyl acetate U: 10.0 p.p.m
BTFA: 1×10^{-2} M

mμ, because of the quite high absorption of the reagent blank found around and below 380 mμ. Measurements were therefore performed at 385 mμ and 400 mμ in the following experiments.

The Effect of pH. — The effect of the pH value on absorbance and, consequently, on the extraction of uranium was studied by extracting 100 μg. of uranium with 10.0 ml. of an organic solvent from 10 ml. of an aqueous solution, which had a variable pH value and which contained 0.1 ml. of 1 M BTFA and sodium chloride or acetic acid at and below pH 7, or boric acid above pH 7 in the final concentration of 0.1 M. The influence of EDTA was also studied by using a solution containing 0.02 M EDTA-Ca and 0.1 M acetic acid.

The absorption of the reagent blank extracted from an acidic or neutral solution is independent of the pH value, but it is affected by the pH when the extraction is made from an alkaline solution. In the latter case absorbances of the reagent blank in benzene or chloroform media decreased, while that in a butyl acetate medium increased, with an increase in the pH value. Accordingly, the effect of pH in an alkaline solution was examined by measuring absorbances at 400 mμ but not at 385 mμ.

The results are shown in Figs. 2, 3 and 4.

These figures reveal that butyl acetate is convenient as an extracting solvent for the uranium BTFA chelate, because the absorbance is kept constant over a wider pH range and the acetate buffer hardly affects the extraction, as may be seen in Fig. 4. The phenomenon that butyl acetate is superior in the extraction of the uranium β-diketone chelate has previously been recognized in the acetylacetone and dibenzoylmethane systems.

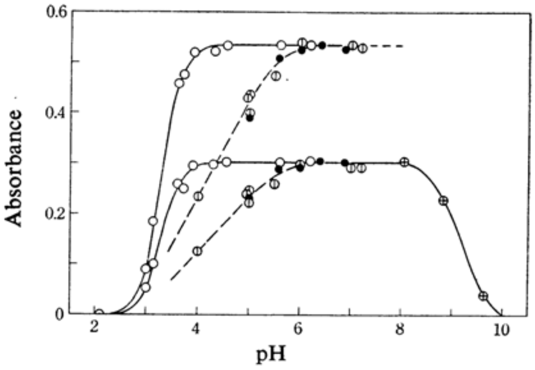


Fig. 2. Effect of pH.
Solvent: benzene U: 10.0 p. p. m.
BTFA: 1×10^{-2} M
Aqueous solution:
-○- 0.1 M NaCl, -⦶- 0.1 M acetate,
-⊕- 0.1 M borate, -●- 0.02 M EDTA-Ca
and 0.1 M acetate

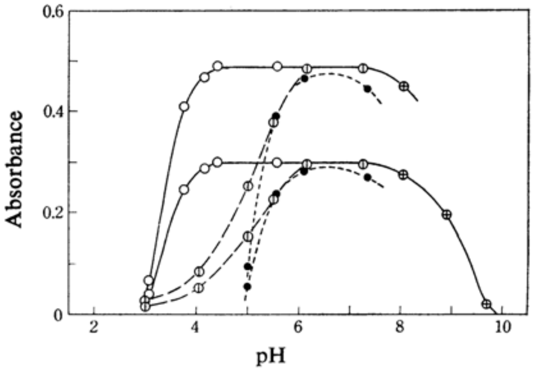


Fig. 3. Effect of pH.
Solvent: chloroform
Others are same to in Fig. 2.

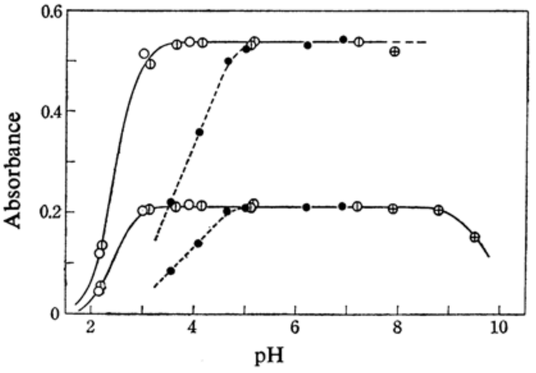
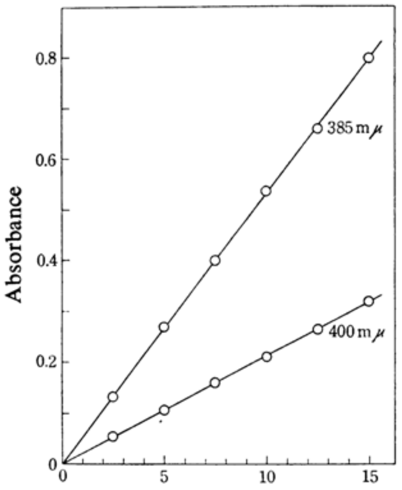


Fig. 4. Effect of pH.
Solvent: butyl acetate. Others are same to in Fig. 2.

Analytical Procedure and Calibration Curve. —From the above experimental results, a procedure for the spectrophotometric determination of uranium was designed as follows.

To a sample solution containing 5∼150 μg. of uranium, add 1 ml. of a 1 M acetic acid and 0.2 M EDTA-Ca solution. Dilute the solution to about 10 ml., adjust the pH to 5.5∼6.0, and add 0.1 ml. of a 1 M BTFA acetone solution. After it has been left standing for 10∼15 min., extract the uranium chelate with 10.0 ml. of butyl acetate and then measure the absorbance at 385 mμ or 400 mμ against the reagent blank.



Concn. of U, p. p. m.

Fig. 5. Calibration curve.
Solvent: butyl acetate BTFA: 1×10^{-2} M
pH: 5.5∼6.0

The analytical curves for uranium are shown in Fig. 5. Beer's law is followed up to 15 p.p.m., and the molar extinction coefficients are 14400 at 385 mμ and 5000 at 400 mμ.

Diverse Ions. — To investigate the influence of several metal ions, the measurements were made on a solution containing a proper amount of foreign cations with 100 μg. of uranium. The results are presented in Table I.

Silver, chromium(III), iron(III), tin(IV), titanium and large amounts of aluminum interfere because of the formation of hydroxide; a few milligrams of copper precipitate when the chelating reagent is added and a milligram or more of tungsten and vanadium(V) gives a negative error.

TABLE I. INFLUENCE OF DIVERSE IONS
(U present: 100 μg.)

Ion present mg.	U found (μg.)		Remark
	385 mμ	400 mμ	
Ag^+ 10			oxide ppt.
Al^{3+} 10			hydroxide ppt.
2	99.4	100.0	
Bi^{3+} 10	101.3	100.9	
Cd^{2+} 10	100.7	100.5	
Co^{2+} 10	108.1	106.6	
Cu^{2+} 10			ppt. by adding BTFA
2	102.3	104.3	
Cr^{3+} 1			hydroxide ppt.
Cr^{6+} 1	98.0	99.1	
Mn^{2+} 2	103.0	104.3	
Fe^{3+} 1			hydroxide ppt.
0.2	107.0	121.3	
Ni^{2+} 10	101.1	101.4	
Mo^{6+} 10	99.6	101.4	
Pb^{2+} 10	100.0	100.5	
Sn^{4+} 1			hydroxide ppt.
Ti^{4+} 1			hydroxide ppt.
Th^{4+} 1	100.9	99.5	
W^{6+} 2	59.2	60.7	
V^{5+} 5	26.8	26.5	
1	99.6	100.9	
Zn^{2+} 10	100.0	100.0	

The Extraction Recovery of Uranium. — Extractability was estimated by determining uranium remaining in the aqueous layer by means of the DBM method.

Uranium was extracted as the BTFA chelate by the above procedure, and the aqueous layer was washed with 10 ml. of butyl acetate. The pH value of the solution was adjusted to 6.5, and 0.5 ml. of a 5% DBM acetone solution was added. The uranium DBM chelate was extracted with 10.0 ml. of butyl acetate, and the absorbance was measured at 410 mμ or 420 mμ against the reagent blank.

The extraction recovery of the uranium BTFA chelate was found to be more than 99.9 per cent.

The Separation from Lutetium-177, Zirconium-Niobium-95 and Fission Products.—Extractions were carried out on a solution containing

TABLE II. DECONTAMINATION FACTORS OF LUTETIUM-177, ZIRCONIUM-NIOBIUM-95 AND FISSION PRODUCTS

Nuclide	Decontamination factor	
	(1)*	(2)*
Lutetium-177	1.2×10^3	2.5×10^3
Zirconium-niobium-95	4.0×10^3	6.3×10^3
Fission products (gross γ)	1.7×10^2	2.4×10^2
Fission products (gross β)	1.1×10^2	1.6×10^2

*(1) Radioactivities were measured on organic and aqueous solution obtained by the described procedure.
(2) Measurements were made after organic layers were washed with 10 ml. of aqueous solution, which had the composition similar to the extraction condition.

TABLE III. COMPARISON OF FOUR β-DIKETONE METHODS

β-Diketone	pK_D*	Concn.** (M)	pH***	Molar extinction coef. and wavelength
Trifluoroacetylacetone	8.7	2×10^{-2}	4~7.5	4690 at 358 mμ
Benzoyltrifluoroacetone	9.2	1×10^{-2}	3.5~8.5	14000 at 385 mμ
Acetylacetone	12.7	5×10^{-2}	6~7.5	2640 at 365 mμ
Dibenzoylmethane	13.7_5	1×10^{-2}	5~9	20300 at 400 mμ

* The pK_D values were obtained in 74.5 vol. per cent dioxane (Ref. 5).

** Concentration in organic layer after distribution.

*** In the absence of EDTA-Ca.

100 μg. of uranium and 1~5 μc. of lutetium-177, zirconium-niobium-95 or mixed fission products. One milliliter of the counting samples pipetted out from the solvent and from each of the aqueous layers, and γ- and β-activities were measured with a well-type NaI(Tl) scintillation counter and a G-M counter respectively.

The decontamination factors summarized in Table II indicate that the extraction procedure recommended for the determination of uranium can be successfully applied to the separation of uranium from rare earth elements, zirconium and mixed fission products.

In Table III, the method proposed in this paper is compared with the methods using AA, TFA, and DBM as the reagents.

The order of the minimum pH value for the complete extraction do not agree with that of the pK_D value; AA and DBM, and TFA and BTFA, are reversed. This may be due to the difference in solubility in water and to the shielding effect of the phenyl group.

As is shown in Table III, the uranium BTFA chelate can be extracted at the lowest pH value and from the widest pH range among the chelates of these four β-diketones. Therefore, the BTFA method is most suitable for the extraction of uranium, although it is less sensitive than the DBM method with regard to the spectrophotometric method.

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