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Solvent Extraction of Uranium with Chloroform as Acetylacetonate

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Conditions for the extraction of uranium with chloroform as its acetylacetonate were investigated. Extraction recovery of uranium acetylacetonate was increased with increasing concentration of acetylacetone in aqueous solution, and the pH value profitable to extraction was 6~7.

The presence of sodium chloride increased the extraction yield of uranium acetylacetonate, and the favourable extraction pH range was broadened to 5~7.2. An addition of ethylenediaminetetraacetic acid solution resulted in the decrease of extraction, but its effect was prevented by the addition of sodium chloride. In the presence of ethylenediaminetetraacetic acid, the extraction pH range was 7~7.5.

By the use of ethylenediaminetetraacetic acid as a masking agent, uranium was separated from the activity of mixed fission product and from thorium by extracting with chloroform as acetylacetonate, and its recovery was about 95 per cent.

INTRODUCTION

Uranium is extracted with organic solvents, as its chelates or ion association complexes with cupferrone, dibenzoylmethane, 8-hydroxyquinoline or with nitrate ion. Krishen and Freiser¹⁾ reported on a method for the extraction of uranium, in which acetylacetone was used as both a chelating reagent and an extracting solvent. In the method, uranium could be extracted as acetylacetonate from an aqueous solution whose pH was 4~6. It is, however, not practical, because a great deal of acetylacetone was needed.

In the author's work the solvent extraction of uranium acetylacetonate was carried out with chloroform. The detailed conditions of the method were described in the present paper.

APPARATUS AND MATERIALS

Apparatus

Spectrophotometric measurements were made with Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, using 1.0 cm silica transmission cells. Horiba's Glass electrode pH meter, Model M-3 was used for the pH measurements, and β -countings were made with Metro's EIT Scaler, Model 6E, with G-M tube (Kobe Kogyo's endwindow type 132, 1.68 mg./cm²).

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Materials

Standard solution of uranium, 100 μg U/ml; a stock solution was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water, and its concentration was determined by the gravimetric method as U_3O_8 . The stock solution was diluted to make a standard solution containing 100 μg . of uranium per its one milliliter.

5% Acetylacetonate solution; 25 g. of acetylacetonate were dissolved and diluted to 500 ml. with water.

10% EDTA solution; 25 g. of disodium salt of ethylenediaminetetraacetic acid were dissolved in water and made up to 250 ml.

50% Potassium thiocyanate solution; 250 g. of KSCN were dissolved and diluted to 500 ml. with water.

Stannous chloride solution; 20 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 20 ml. of conc. hydrochloric acid by warming. Four milliliters of this solution were diluted fresh daily to 50 ml. with water.

Chloroform; CHCl_3 was successively washed with dil. NaOH solution, water, dil. HCl solution and three times with water, and then distilled.

EXPERIMENTAL

I. Analytical Method for the Determination of Uranium

In order to obtain the chemical recovery, uranium was determined colorimetrically by the thiocyanate method described as follows.

Procedure. Organic layers, separated after extraction, were air-dried and treated with perchloric acid for the decomposition of organic matters²⁾. Perchloric acid was evaporated nearly to dryness, and the residue was dissolved with 0.5 ml. of 5*N*-sulphuric acid and a few milliliter of water. The solution was transferred into a 20 ml. volumetric flask, added with 2.0 ml. of stannous

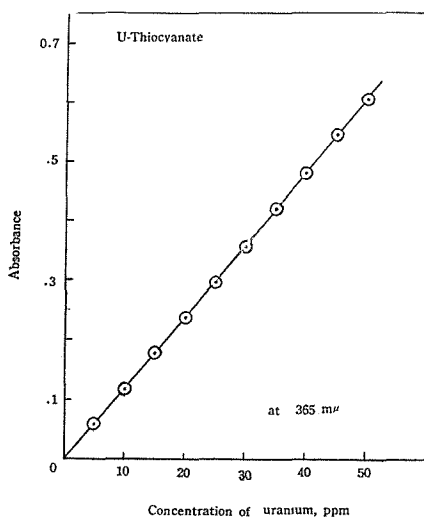


Fig. 1. Analytical curve for the determination of uranium.

chloride solution, freshly prepared, and 5 ml. of 50% potassium thiocyanate solution, and then diluted to the mark with water. Absorbance was measured at $365\text{ m}\mu$ against the reagent blank. Uranium was determined from the analytical curve shown in Fig. 1.

In this procedure, the colour of uranium thiocyanate complex is stable at least for an hour. Acetylacetone interferes the development of the colour, but it can be easily decomposed by fuming with perchloric acid.

II. Extraction of Uranium

1. **Effect of concentration of acetylacetone.** The different amount of acetylacetone was added to the solution containing $500\ \mu\text{g}$ of uranium. The pH value was adjusted to 7.0 with NaOH solution, and the solution was diluted to 50 ml. The extraction was made with 10 ml. followed by two successive 5 ml. portions either of chloroform or of chloroform containing 1% acetylacetone.

A quantity of uranium, extracted into the organic layer, was determined by the above mentioned procedure. Fig. 2 indicated the effect of the concentration of acetylacetone on the extraction of uranium.

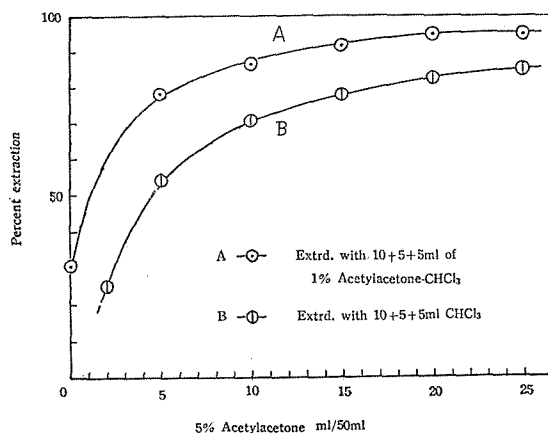


Fig. 2. Effect of concentration of acetylacetone.

As shown in Fig. 2, 1% acetylacetone-chloroform solution is better than pure chloroform, as an extracting solvent. It is because uranium acetylacetonate (solid) is found to be hardly soluble in chloroform, in the absence of excess acetylacetone*, and because the excess reagent must be extracted almost completely with a first 10 ml. of solvent.

2. **Effect of pH value.** The effect of pH value was examined in the following three conditions.

A: Sample solutions, containing $500\ \mu\text{g}$. of uranium and 2 ml. of 5% acetylacetone solution per 50 ml., were shaken with 10+5+5 ml. of chloroform.

B: Solutions, containing $500\ \mu\text{g}$ of uranium and 20 ml. of 5% acetylacetone solution, were extracted with 10+5+5 ml. of 1% acetylacetone-chloroform solu-

* Further work will deal with the characteristics of uranium acetylacetonate.

tion.

C: The conditions were the same with B, except adding 5 g of sodium chloride.

The experimental results were presented in Fig. 3.

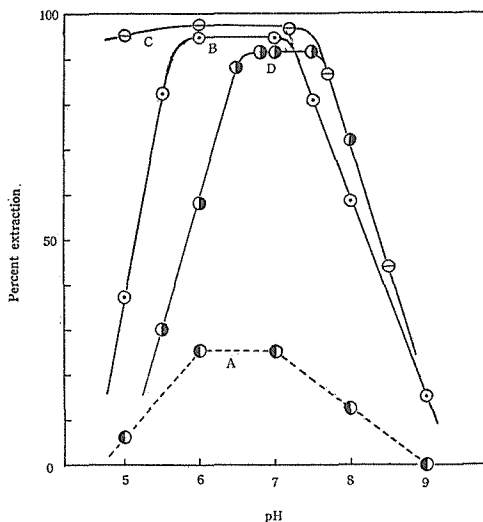


Fig. 3. Effect of pH value. (Extraction curves for uranium)

A: 2 ml. of 5% acetylacetonate was used, extracted with chloroform.

B: 20 ml. of the reagent was used, extracted with 1% acetylacetonate-chloroform.

C: same to B, except adding 5 g. of NaCl.

D: same to C, except adding 1 ml. of 10% EDTA.

Ninety five percent of uranium were recovered when the extraction was made at a pH value between 5.8 and 7.2, in relatively high concentration of the reagent. By adding sodium chloride, not only the percent extraction increased, but pH range, giving a good recovery, broadened. On the other hand, uranium could be extracted only 25% in the condition recommended to the extraction of beryllium²⁾.

3. Effect of ethylenediaminetetraacetic acid. For the separation of uranium from many other metals, the use of EDTA as a masking agent was tested.

In the presence of EDTA, the extraction of uranium was considerably inhibited. However, the extraction recovery of uranium could be increased by the addition of sodium chloride as well as in the case of beryllium²⁾.

Influences of EDTA and of NaCl were given in Fig. 4, and the effect of pH on uranium recovery was shown by the curve D in Fig. 3. In this case uranium acetylacetonate was extracted in the presence of 1 ml. of 10% EDTA solution and 5 g. of NaCl per 50 ml. of sample solution.

Maximum extraction yield, 92%, was obtained at pH 7~7.5, using 1 ml. of 10% EDTA and 5 g. of sodium chloride.

4. Procedure for the separation of uranium. From the experimental results, the procedure for the separation of uranium was designed as follows.

To the sample solution, add 1 ml. of 10% EDTA solution and 5~10 g of

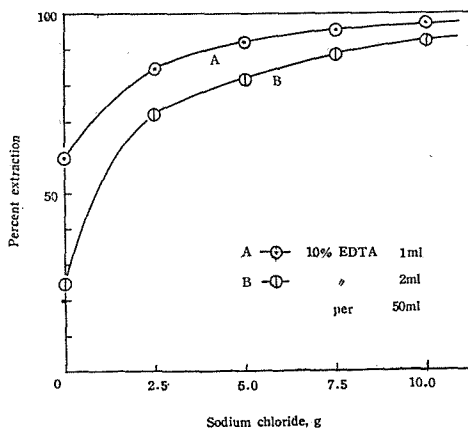


Fig. 4. Effect of EDTA and NaCl.

sodium chloride, and dilute to about 30 ml. Adjust the pH to 7, add 20 ml. of 5% acetylacetonate solution and adjust the pH to 7.0 again. Transfer the solution into a 100 ml. separating funnel and dilute to approximate 50 ml. Uranium acetylacetonate was then extracted with 10+5+5 ml. of 1% acetylacetonate-chloroform solution. By means of this procedure, 90~95% of uranium can be separated into organic layer.

III. Separation of Uranium from Mixed Fission Product and from Thorium

In order to test the reliability of the proposed procedure, the separations of uranium from mixed fission product and from thorium were carried out.

From fission product. Uranium was extracted from sample solutions which contained 500 μg . of uranium and mixed fission product (radioactivity : *ca.* 50,000 cpm., measured by G-M counter).

The recovery of uranium was about 90% and the radioactivity found in the solvent layer (dried) was only 5.8 ± 2.0 cpm. (mean value of three experiments). So the decontamination factor is of magnitude in the order of 10^4 .

From thorium. The solutions, containing 200 μg . or 1 mg. of thorium, were treated according to the above mentioned separation procedure. Thorium extracted was determined colorimetrically by Neo-thorone method³⁾. The amount of thorium in the solvent layers were less than 0.5 μg . and 2.0 μg ., respectively, so the extraction yield of thorium was about 0.2%. This results indicate that the procedure is successfully applied to the separation of uranium from thorium.

SUMMARY

The separation of uranium by liquid-liquid extraction as acetylacetonate was investigated.

Uranium acetylacetonate was extracted over 95% with chloroform, containing 1% of acetylacetonate, from an aqueous solution having pH value 5.8~7.2 and containing 2% acetylacetonate.

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By the use of EDTA as a masking agent, uranium could be separated from mixed fission product and from thorium; the chemical yield of uranium was 90~95%, the decontamination factor was about 10^4 , and only 0.2% of thorium was extracted.

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