Determination of Uranium in Thorium by X-Ray Fluorescent Spectroscopy. The Organometallic Precipitation Method

By Kichinosuke HIROKAWA and Hidehiro GOTÔ

(Received September 28, 1961)

For the determination of a small amount of uranium in thorium, Cheng[1] has suggested the PAN *o*-dichlorobenzene extraction method. This method[2], however, requires complicated procedures. Therefore, X-ray spectroscopy after organic precipitation separation was applied in this analysis. When the amount of uranium in thorium is determined by X-ray fluorescent spectroscopy, the effect of matrix element, thorium, is so great that it is necessary to isolate uranium from thorium. In order to separate them, the solvent extraction

---

1) K. L. Cheng, *Anal. Chem.*, **30**, 1028 (1958).

2) R. F. Clayton, *Analyst*, **83**, 13 (1948); A. R. Eberle, *Anal. Chem.*, **29**, 1134 (1957); H. Matsuyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 958 (1958).

method[1,2], accompanied by the precipitation method[3], is investigated here. In this study alizarin blue[4] is used as the precipitant for uranium, and an X-ray fluorescent spectroscopic determination for uranium is proposed.

Experimental and Results

Reagents.—An alizarin solution was prepared by the methed described in a previous report[4]. For the uranium standard solution, 1 g. of uranium nitrate, analytical grade, was dissolved in a 1 N sulfuric acid solution. The uranium content of this solution was determined as 8.5 mg. 1 ml. by the zinc amalgam reduction potassium permanganate titration method. The solution was then diluted to the proper concentration before being used.

For the thorium standard solution, 1.5 g. of thorium nitrate, analytical grade, was dissolved in water; the concentration of thorium in it was determined by weighing the oxide after precipitation with oxalic acid (0.0107 g. 1 ml.). The acetic acid-sodium acetate buffer solution was prepared by mixing 0.2N acetic acid and 0.2N sodium acetate. The glycine buffer solution was prepared by mixing 0.1M glycine solution and 0.1M hydrochloric acid. The hydrochloric, nitric and other acids used were of an analytical grade. A 0.2M EDTA solution, a 0.1% PAN methanol solution, a 1% potassium cyanate solution, and an *o*-dichlorobenzene and buffer solution of pH 10 were also used.

Apparatus. — A G. E. XRD-5 X-ray spectrometer with AEG-50S tungsten tube was used, as described in the previous paper[4].

Conditions for the Formation of Metal Alizarin Blue Precipitate.—Uranium reacts with alizarin blue and forms a red-violet precipitate at once in neutral solutions, while thorium first develops a blue color with alizarin blue and then gradually forms a blue precipitate. In this case, the presence of EDTA prevents the formation of thorium precipitate. On the basis of these facts, the following conditions for precipitation were set up.

One hundred and seventy micrograms of uranium were taken from the uranium standard solution, the pH value of which was controlled with hydrochloric acid, a glycine-hydrochloric acid buffer solution or an acetic acid-sodium acetate solution; then the total volume of the solution was made up to about 50 ml. with water. Ten milliliters of alizarin blue solution was added. After the solution had stood for a few miuntes, the precipitate formed was filtered and repeatedly washed with water. The precipitate was put into the original beaker together with the filter paper. The precipitate and the filter paper were decomposed with 5 ml. of sulfuric acid and 10 ml. or more if necessary, of nitric acid by heating. Then it was diluted to 50 ml. with water, and one-tenth of it was taken for the extraction. The uranium content in this solution was determined by the PAN-*o*-dichlorobenzene extraction method. These results are shown in Fig. 1. From these results, the uranium was precipitated completely with alizarin blue in the pH range of 2～10. The effects of the presence of EDTA at pH values from 2 to 6 were not visible, as is shown in Fig. 1.

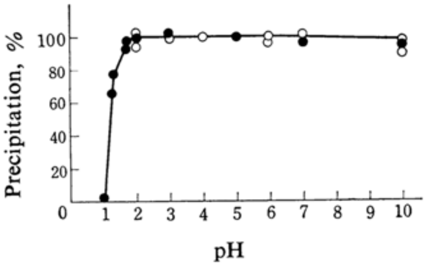

Fig. 1. Precipitation of U at various pH.
-○- 4 ml. of 0.2M EDTA soln. present.
-●- EDTA soln. not present.

Preparation of the Calibration Curve and Separation of Thorium.—In previous investigations, it was established that uranium forms a precipitate with alizarin blue in the presence of EDTA at pH values above 2. Therefore, the calibration curve for uranium was prepared as follows:

Various amounts of uranium, from 15 to 350 μg., were taken, and 4 ml. of a 0.2M EDTA solution and 20 ml. of an acetic acid-sodium acetate buffer solution (4; 6) were added; the pH value of this solution was controlled between 4 and 5, and its total volume was diluted with water to about 50 ml. After the addition of 10 ml. of the alizarin blue solution, the precipitate formed was filtered with the apparatus described in the previous report[4] and washed a few times with water. The precipitate on filter paper was fixed with cellophane tape directly and put in the sample holder with a round irradiation area 1.5 cm. in diameter and with aluminum plate backing. The fluorescent X-ray intensity from it was measured under the conditions of Table I. In Fig. 2, the calibration curves for uranium up to 100 μg. (a) and up to 350 μg. (b) are given. A spectrograph of the sample is shown in Fig. 3. The X-ray intensity of thorium caused by the absence of EDTA or by the unsatisfactory separation of thorium gives its peak at the notch part. According to the previous procedure, thorium below 0.05 g. was completely masked by EDTA and so was not affected. However, when the pH value of the solution was above 10 before the addition of EDTA, the peak of thorium appeared. As this thorium peak seemed to be due to thorium hydroxide, the addition of EDTA should be carried out before the control of the pH value.

TABLE I. OPERATING CONDITIONS FOR THE DETERMINATION OF U

Excitation source	50 kV. 10 mAp.
Spectral line (Å) $\text{LiF}_{2\theta}$°	$\text{U}L\alpha_1$ (0.911 Å) 26.14°
Fixed counting	10000 counts
Irradiation area	1.5 cm. in diameter

---

[3] Seberka et al, *Chem. Listy*, **47**, 512 (1953).

[4] K. Hirokawa, *J. Japan Inst. Metal* (*Nippon Kinzoku Gakkaishi*), **23**, 688 (1959); K. Hirokawa and H. Gotô, This Bulletin, **35**, 961 (1962).

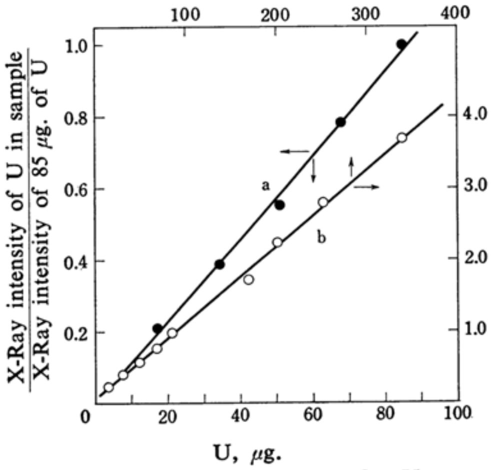

Fig. 2. Calibration curve for U.

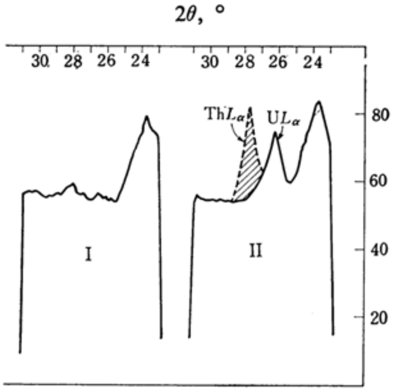

Fig. 3. X-Ray spectrogram of U separated from Th.
I, Blank; II. 68 μg. of U

Determination of Uranium in Thorium. — As in previous studies, a small amount of uranium in thorium was analyzed as follows:

Procedure. — From 0.1 to 0.5 g. of the sample was dissolved with a small amount of nitric acid as well as possible. This solution was diluted to 100 ml. with water, and one-tenth or one-fifth of this solution was put into a beaker. Four milliliters of EDTA solution and 20 ml. of an acetic acid-sodium acetate buffer solution were added to this solution. The pH of this solution was controlled at 4～5, and the total volume of this solution was increased to about 50 ml. The milliliters of an alizarin blue solution was added and the specimen for X-ray was prepared by the method described in the section dealing with the preparation of the calibration curve. The prepared specimen was irradiated with X-ray under the same conditions as listed in Table I, and the uranium content was determined from the intensity ratio of the uranium in the sample against that of the standard sample (85.0 μg. of U in this experiment). The amount of uranium in thorium was determined with this method; the results obtained are shown in Table II. These results agreed well with those obtained by the PAN *o*-dichlorobenzene extraction method.

TABLE II. DETERMINATION OF U IN Th

Sample	Chem. anal., %	X-Ray anal., %
A	0.32	0.30
B	0.44	0.48
C	0.45	0.43
D	0.22	0.23
E	0.17	0.18

Discussion

Various other precipitants for uranium can be considered besides alizarin blue. This alizarin blue solution, however, has the advantage of forming the precipitate over a wide pH range. When this alizarin blue solution is used, copper, iron and silver form precipitates under the same conditions, although these precipitations were masked by the addition of EDTA⁴⁾. When the thorium metal was dendritic and porous, the non-destructive method could not be applied. Therefore, analysis using oxide powder was tried. An X-ray spectrographs of a thorium sample containing 2 and 4% of uranium oxide form were obtained, as is shown in Fig. 4. From this spectrograms, it was considered that uranium content below 1% was difficult to determine without separation because of the high background of X-ray due to thorium near the uranium peak.

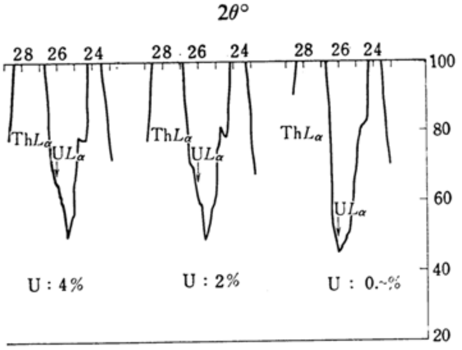

Fig. 4. X-Ray spectrograms of U in Th as oxide without separation.

Summary

A method for the determination of a small amount of uranium in thorium using the separation method with precipitation, combined with X-ray fluorescent spectroscopy, was investigated. About 100 μg. of uranium in thorium could be determined simply and rapidly by using alizarin blue as the precipitant for uranium and EDTA as the masking reagent for thorium.

The Research Institute for
Iron, Steel and Other Metals
Tohoku University
Katahira-cho, Sendai