Spectrophotometric Determination of Uranium with Neo-thorone

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In an earlier communication[1] a photometric method for the determination of uranium with Neo-thorone (*o*-arsonophenylazo-chromotropic acid) was briefly described. The purpose of this paper is to treat the same subject in detail. Several colorimetric methods recently reported for the determination of uranium were based on the complex formation with such a reagent as dibenzoylmethane[2], 2-acetoacetylmethane[3], diethyldithiocarbamate[4], potassium ferrocyanide[5], potassium thiocyanate[6], or on the formation of peroxide with hydrogen peroxide[7].

Hydrogen peroxide is the common reagent used for the colorimetric determination of uranium, but it is not very sensitive. Kuznetsov[8] has reported a qualitative test; a very sensitive color reaction of uranium with *o*-arsonophenylazo-chromotropic acid. Neo-thorone in a solution of pH 1 or 2 has been used as a chromogenic reagent to determine thorium[9] and fluoride[10].

Experimental

Apparatus.—A Hitachi Model EPV-2 Spectrophotometer with 1 cm. cells was used for all absorbance measurements.

Reagents.—Neo-thorone (0.1%): dissolve 0.1 g. of reagent grade chemical (Hayashi Chemical Works, Osaka) in water and dilute to 100 ml.

Standard uranium nitrate solution: Dissolve 1.20 g. of reagent grade uranyl nitrate in water and dilute to 1 liter to prepare a stock solution. It was standardized gravimetrically by the oxine method. An aliquot of this solution was diluted to give a solution containing 5 μg. of uranium per ml.

Sodium ethylenediaminetetra-acetate (2%): Dissolve 20 g. of disodiumdihydrogen ethylenediaminetetra-acetate dihydrate in water and dilute to 1 liter.

Sodium acetate-acetic acid buffer: Dissolve 12 g. of sodium acetate in water and dilute to 1 liter. A 0.1 N acetic acid solution was used to make a buffer solution.

Other reagents were analytical grade chemicals.

General Procedure.—The following procedure was used to determine uranium in aqueous solution. The sample solution was adjusted to contain from 2 to 10 μg. of uranium per ml. One ml. aliquot was pipetted into 25 ml. glass stoppered volumetric flask. One ml. of 0.1% solution of Neo-thorone and 5 ml. of buffer solution of pH 6.0 were added, and then the solution was made up to 25 ml. with water. The solution was allowed to stand for five minutes, and then the absorbance was measured at 600 mμ, against a reference solution. The amount of uranium was determined by comparison with a previously prepared absorbance-uranium concentration curve.

Results and Discussion

Spectral Properties. — The absorption spectrum of an aqueous solution of Neo-thorone was obtained with water as the reference. The absorption peak of Neo-thorone in a buffered solution of pH 1.0~6.0 was found at 510 mμ. (Fig. 1). The absorption spectra of the aqueous solution of uranium—Neo-thorone complex at pH 2.0, 3.0 and 6.0 are shown in Fig. 2. Correction was applied for the reagent blank.

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[2] J. H. Yoe, F. Will III, and R. A. Black, *Anal. Chem.*, **25**, 1200 (1953).

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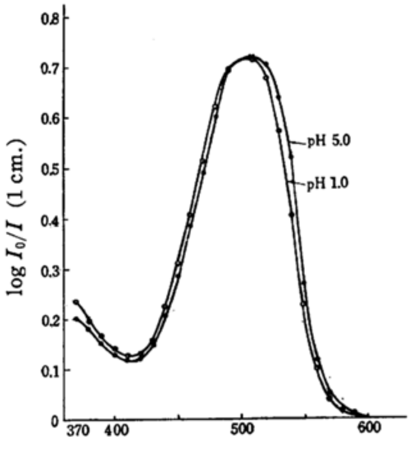

Fig. 1. Absorption spectra of Neo-thorone.

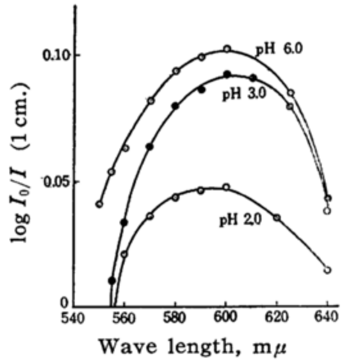

Fig. 2. Absorption spectra of uranium—Neo-thorone complex.

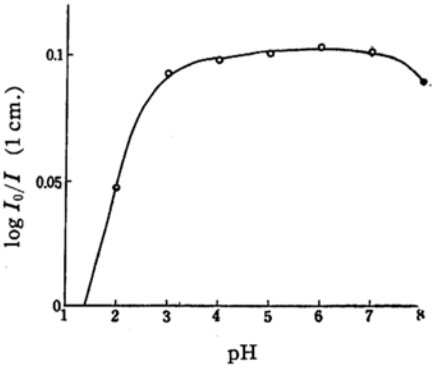

Fig. 3. Effect of pH on the color intensity.

Effect of pH. — Solutions of pH range 1.0∼8.0 were prepared as previously described. The complex provides maximum intensity over a pH range of 5.0 to 7.0 (Fig. 3), the absorbance being constant over this range. With increasing pH values above 7.0, the color intensity decreased. All absorbance measurements were performed at 600 mμ.

Effect of Reagent Concentration. — The optimum amount of Neo-thorone was sought by adding various amounts of 0.1% solution of Neo-thorone to a solution containing 20 μg. of uranium, and the result is shown in Fig. 4. Corrections were made for reagent blank. In all cases the pH values were maintained constant. When more than 0.5 ml. of 0.1% Neo-thorone solution per 25 ml. was added, the absorbance become practically constant. The reagent blank increased slightly with increasing Neo-thorone concentration. Therefore, 1 ml. of 0.1% Neo-thorone solution was taken each time in the present work.

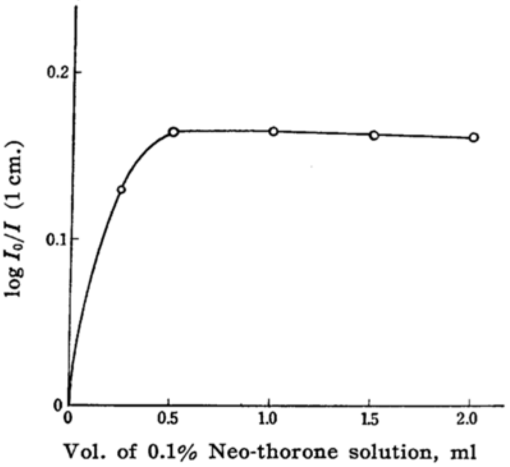

Fig. 4. Effect of Neo-thorone concentration. (20 μg. U taken, pH 6.0)

Temperature Effect. — Throughout the present investigation the experiments were carried out at room temperature which ranged from 10 to 25°C. In this range the temperature had no remarkable influence on the absorbance of uranium-Neo-thorone complex.

Stability of Color. — The color of the uranium—Neo-thorone complex in aqueous medium seemed to develop fully after a few minutes, and its intensity did not change for at least 4 hours, as shown in Table I.

TABLE I

STABILITY OF COLOR

Time after color developed. min.	Absorbancy (at 600 mμ) 20 μg.U/25 ml.	120 μg.U/25 ml.
5	0.081	0.429
15	0.080	0.429
60	0.081	0.429
120	0.082	0.428
240	0.081	0.429

Calibration Curve.—The calibration curve is shown in Fig. 5. It was found that the system conformed to Beer's law in the concentration range from 0 to 40 μg. of uranium per 25 ml.

Composition of Complex.—The composition of uranium—Neo-thorone complex was determined by the continuous variation method. The results obtained are shown in Fig. 6. From these results, the ratio of uranium to Neo-thorone would be 1 : 1*.

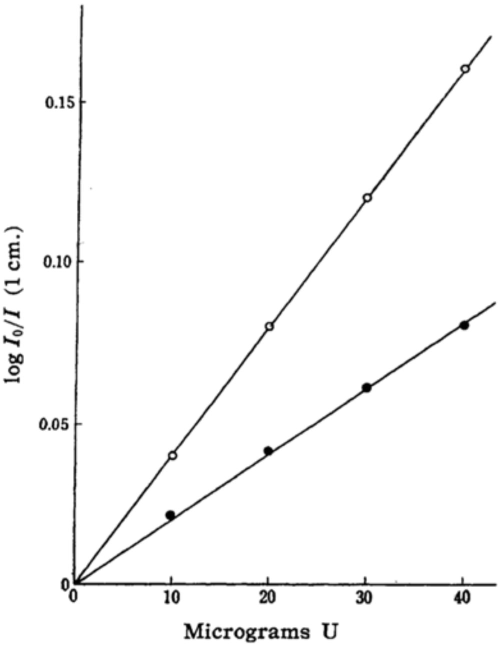

Fig. 5. Calibration curve, ○ pH 6.5, ● 1.0 ml. 1% sodium ethylenediaminetetra-acetate present.

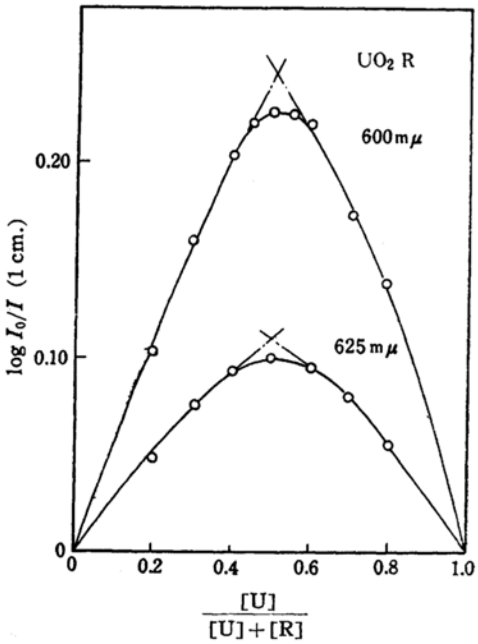

Fig. 6. Continuous variation method.

Effects of Foreign Ions.—A study was made on the effects of several anions and cations. Oxalate, fluoride, and phosphate interfered. A few grams of sodium, potassium, and ammonium which were present in the solution as acetate, sulfate, chloride, and nitrate did not interfere. Many of the cations, for example, aluminum, copper, iron(III), indium, titanium, zinc, thorium, cerium, and zirconium interfered because they formed respective complexes with Neo-thorone. But a proper amount of such metals as aluminum, iron(III), zinc, zirconium, thorium and lead can be masked by the use of sodium ethylenediaminetetra-acetate. For example absorbance measurements when using the ethylenediaminetetra-acetate as masking agents, were made for solutions containing aluminum, iron(III), zinc and thorium. The results are presented in Table II.

TABLE II
DETERMINATION OF URANIUM IN THE PRESENCE OF Al, Fe, Zn AND Th

U taken (μg.)	Metals added (mg.) Al	Fe	Zn	Tn	U found (μg.)	Error (μg.)
0.0	0.4				0.3	+0.3
10.0	0.4				10.2	+0.2
20.0	0.4				20.0	±0.0
0.0		1.0			0.1	+0.1
10.0		1.0			10.3	+0.3
20.0		1.0			20.2	+0.2
0.0			0.2		0.2	+0.2
10.0			0.2		10.1	+0.1
20.0			0.2		20.5	+0.5
0.0				0.2	0.1	+0.1
10.0				0.2	10.1	+0.1
20.0				0.2	20.0	±0.0
10.0	0·2	0.5	0.1		9.8	−0.2
20.0	0.2	0.5	0.1		20.4	+0.4

As shown Table II; aluminum, zinc, iron(III) and thorium do not interfere.

Summary

The spectrophotometric method for the determination of microquantities of uranium with Neo-thorone was established. By this method 5 to 40 μg. of uranium in

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* In preparing this paper, H. Matsuyama, T. Hara and K. Koyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 958 (1958). have reported independently a similar method for the determination of uranium by Neo-thorone. However they have stated that the complex was composed of 2 moles of uranium to 3 moles of Neo-thorone.

25 ml. solution can be determined easily and accurately. Interference by a small amount of aluminum, zinc, lead, thorium and iron could be avoided by using sodium ethylenediaminetetra-acetate. Therefore, complete separation of iron, thorium, and aluminum is not necessary.

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