The Spectrophotometric Determination of Uranium with Xylenol Orange[1]

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The uranyl ion forms a weak, red chelate with xylenol orange in a slightly acid solution buffered with sodium acetate and acetic acid. The uranium(IV) ion, however, reacts sensitively with this reagent to form a stable, intensely reddish-violet complex, while uranium(VI) is reduced to uranium(IV) by ascorbic acid in an acetate buffer solution in the presence of xylenol orange.

Buděšínský[2] has recently proposed a method for determining uranium with xylenol orange, using uranium(IV) sulfate as a starting material. He has also indicated that the optimum pH value range for color development is 1.2 to 1.6 and that a complex of 1 to 1 is formed between xylenol orange and uranium.

The present results, however, differ appreciably from those reported by Buděšínský; the complex has its maximum absorption at 568 mμ, the maximum absorption develops over the pH value range 3.5 to 3.7, and the results of the mole ratio method and the continuous variation method show a complex consisting of two molecules of xylenol orange to one uranium(IV) ion.

Experimental

Reagents.—An approximate 10^{-4} M uranyl nitrate solution was prepared by the dilution of a 10^{-2} M uranyl nitrate solution previously standardized against EDTA by using xylenol orange as an indicator[3].

A pH value 3.6 buffer solution was prepared in the usual manner with sodium acetate and acetic acid.

All the other reagents and apparatus used were the same as those reported previously[4].

Procedure.—Into a 25 ml. Erlenmeyer flask an aliquot of the solution containing up to 120 μg. of uranium was pipetted, after which 10 ml. of the acetate buffer solution and 1 ml. of 5% ascorbic acid were added. The volume was made to about 20 ml. with distilled water, and the flask was covered with a watch-glass. After being boiled gently for about 20 min., the solution was cooled with water to room temperature and transferred to a 25 ml. volumetric flask, and the volume was made up to the mark with distilled water. Within the following 30 min., the absorbance of the solution was then measured at 568 mμ, with reference to a blank solution.

Results and Discussion

Absorption Spectra.—The absorption spectra of xylenol orange and its uranium(IV) chelate are presented in Fig. 1. Inspection of the

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[1] Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[2] B. Buděšínský, *Collection Czechoslov. Chem. Commun.*, 27, 226 (1962).

[3] K. Ueno, "Kireto Tekitei (Chelatometric Titration)" (In Japanese), Nankodo, Tokyo (1960), p. 320.

[4] M. Otomo, This Bulletin, 36, 137 (1963).

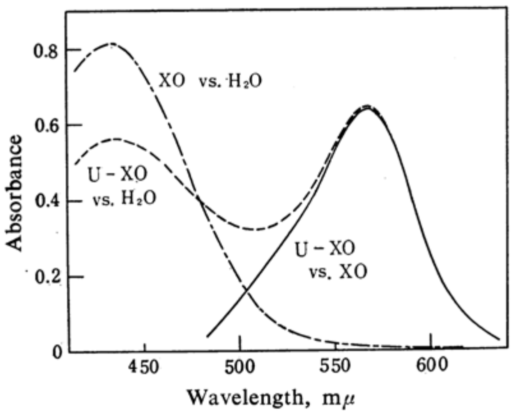

Fig. 1. Absorption spectra of xylenol orange and its uranium complex.
U: 71 μg. XO: 6×10^{-5} M

curves shows that the maximum absorption of red uranium-xylenol orange chelate lies at 568 mμ, at which point the reagent does not absorb appreciably. The spectrum is very similar to that shown by thorium-xylenol orange chelate⁽⁵⁾. The maximum color development was observed over the pH value range from 3.5 to 3.7, the values of which are considerably higher than those reported by Buděšínský.

Effect of Heating Time.—As in the case of the complexometric titration of uranium with EDTA⁽³⁾, the chelating reaction of xylenol orange with uranium is made to take place only by boiling a uranium(VI) solution in the presence of ascorbic acid and xylenol orange. The maximum absorbance is attained after about 20 minutes' boiling (Fig. 2). About 1 ml. of 5% ascorbic acid is a sufficient amount to reduce the uranyl ions quantitatively.

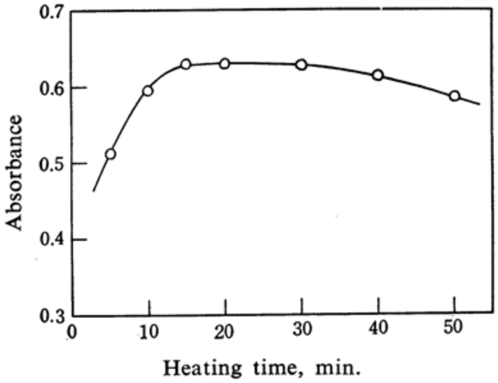

Fig. 2. Effect of heating time.
U: 71 μg. XO: 6×10^{-5} M

Effect of Excess Reagent.—For 20 to 100 μg. of uranium, 1 to 1.5 ml. of a 1×10^{-3} M xylenol orange solution is required. Much as in the previous cases of the color development of xylenol orange complexes of zirconium⁽⁶⁾ and iron⁽⁷⁾, large amounts of xylenol orange tend to decrease the absorbance.

Stability of Color. — Figure 3 shows the stability of the color produced with uranium and xylenol orange. The absorbance began to be recorded as soon as the solution was transferred to the volumetric flask. The intensity of the color decreases slowly with time. However, during the first 10 to 30 min. the absorbance remains practically constant.

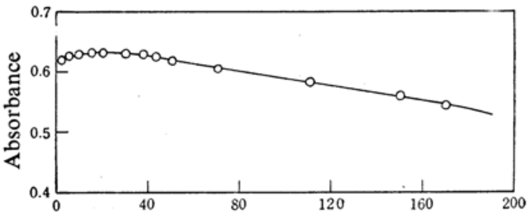

Fig. 3. Stability of color.
U: 71 μg. XO: 6×10^{-5} M

Beer's Law. — Beer's law is obeyed in the range from 20 to 100 μg. (0.8 to 4 p. p. m.) of uranium at 568 mμ. Under the conditions of the spectrophotometric determination, the molar extinction coefficient was found to be 51000.

Effect of Anions. — Chloride, nitrate, sulfate and borate do not interfere. Large amounts of phosphate, fluoride, tartrate and citrate reduce the absorbance considerably. Oxalate, NTA and EDTA interfere with the color reaction because they form more stable complexes with uranium than xylenol orange does.

Effect of Cations.—Of the 26 cations tested, aluminum(III), bismuth(III), chromium(III), copper(II), iron(III), palladium(II), thorium(IV), titanium(IV), vanadium(IV) and zirconium(IV) interfere with the uranium determination. Among the above cations, copper, iron and palladium give large negative errors.

Complex Formation.—Xylenol orange forms 1 to 1 complexes with some bi-, ter- and quadri-valent metals, including zinc(II)⁽⁸⁾, iron(III)⁽⁷⁾, bismuth(III)⁽⁹⁾, rare earths⁽¹⁰⁾, vanadium(IV)⁽⁴⁾ and zirconium(IV)⁽⁶⁾. Buděšínský reported that uranium(IV) and thorium(IV) also form 1 to 1 complexes with this reagent in a slightly acid medium.

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5) M. Otomo, unpublished. (Presented at the Tōhoku Branch Meeting of the Chemical Society of Japan, Yonezawa, October, 1961.)

6) K. L. Cheng, *Talanta*, **2**, 266 (1959).

7) K. L. Cheng, ibid., **3**, 147 (1959).

8) K. Studlar and I. Janousek, ibid., **8**, 203 (1961).

9) H. Onishi and N. Ishiwatari, This Bulletin, **33**, 1581 (1960).

10) K. Tonosaki and M. Otomo, ibid., **35**, 1683 (1962).

In this work, the mole ratio of xylenol orange and uranium was studied by the continuous variation method and by the mole ratio method. As is shown in Figs. 4 and 5, both methods indicate clearly that, as with thorium5), a complex of 1 to 2 between uranium and this reagent is formed under the conditions so far studied.

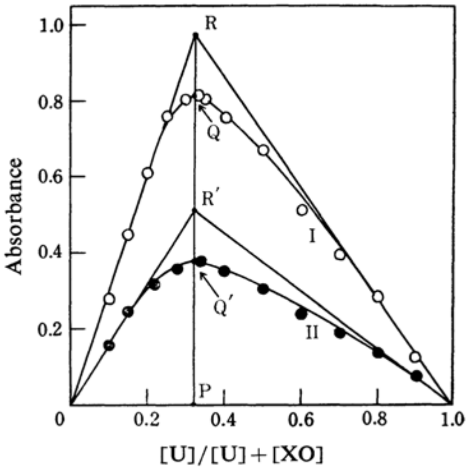

Fig. 4. Continuous variation method.
I: $[U]+[XO]=6\times10^{-5}$ M
II: $[U]+[XO]=3\times10^{-5}$ M

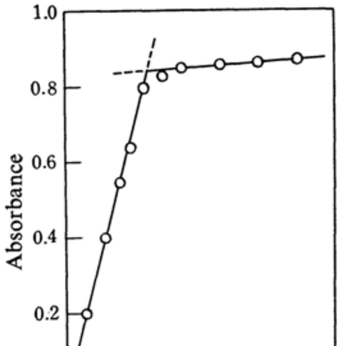

Fig. 5. Mole ratio method.
$[U]$: 8×10^{-6} M

In the course of spectrophotometric studies of the metal complexes of xylenol orange, it was recently found that such cations as gallium(III)11), thallium(III)11) and also iron(III)12) form 1 to 2 complexes with xylenol orange in a slightly acid or a neutral medium, while they give 1 to 1 complexes in a more acid solution. This is an interesting fact; details of the results will be shown eleswhere. In addition, Leonard and West13) have suggested that a 1 to 2 complex can be formed between thorium(IV) and alizarin complexan, since thorium adopts an eight co-ordinate configuration. Being capable of adopting a configuration similar to that of thorium, uranium(IV) seems to be considered to form a 1 to 2 complex with alizarin complexan and also with xylenol orange. It seems, therefore, that some differences between the results shown by Budensinsky and those obtained here may be attributed to the differences in the experimental conditions used.

The formation constant, K, was then calculated from the curves shown in Fig. 4, on the basis of the following relationships14):

$$K=C(1-\alpha)/(\alpha C)(2\alpha C)^2 \qquad (1)$$

$$\alpha=(E_m-E_s)/E_m \qquad (2)$$

where C is the total concentration of the complex in moles per liter, assuming no dissociation, α is the degree of dissociation, E_m (PR or PR′) is the maximum absorbance obtained from the horizontal portion of the curves, and E_s(PQ or PQ′) is the absorbance at the stoichiometric molar ratio of xylenol orange to uranium in the complex. This ratio was found to be 2.9×10^{11}.

Summary

A new spectrophotometric method for determining trace amounts of uranium has been developed. This method is based on the coloration of xylenol orange with uranium(IV) formed by the reduction of uranium(VI) in the presence of ascorbic acid. The effects of the pH value, reagent and boiling time have been thoroughly investigated, and experimental conditions which make possible the determination of 20 to 100 μg. of uranium have been devised. The mole ratio of the complex between uranium and this reagent has also been discussed.

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11) M. Otomo, unpubished. (Presented at the 15th Anaual Meeting of the Chemical Society of Japan, Kyoto, April, 1962).

12) M. Otomo, unpublished.

13) M. A. Leonard and T. S. West, *J. Chem. Soc.*, **1960**, 4477.

14) A. E. Harvey, Jr., and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).