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The Spectrophotometric Determination of Thorium(IV) with 4-(2-Thiazolylazo)-resorcinol[*1]

Takayoshi SAKAI[*2] and Kôichi TONOSAKI

Chemical Department, Faculty of Science, Hirosaki University, Bunkyô-chô, Hirosaki

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The reagent 4-(2-thiazolylazo)-resorcinol (TAR) is an azo-dyestuff with a thiazol ring; it has a structure and properties similar to those of 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)-resorcinol (PAR), both of which have been extensively employed as metallochromic indicators and as reagents for the spectrophotometric determination of various metals. TAR has also been used for the spectrophotometric determination of nickel,1) niobium,2) copper and bismuth,3) uranium(VI),4) and palladium.5) Nickelss and his co-workers6) have recently reported the formation constant of TAR complexes with many metals, but not of any metals including thorium(IV).

It is found that thorium(IV) reacts with TRA in a hexamethylenetetramine buffer solution to form a stable complex. The present paper will describe the fundamental conditions for the spectrophotometric determination of thorium(IV).

Experimental

Reagents and Apparatus. *TAR Solution.* A 1×10^{-3}M TAR solution was prepared by dissolving 0.0553 g of the Dotite TAR reagent in 250 m*l* of 50% v/v methanol.

Buffer Solution. About a 10% w/v hexamethylenetetramine-potassium nitrate-nitric acid system solution was used for the pH adjustment; potassium nitrate was added in order to maintain a constant ionic strength. All the investigations were carried out at a constant ionic strength of 0.6.

The solutions of thorium(IV) and diverse ions, and the apparatus, were the same as those used in a previous work.7)

All the measurements were made at 25±0.5°C.

Procedure. To a sample solution containing up to 95 μg of thorium in a 25-m*l* volumetric flask, 2.5 m*l* of a 1×10^{-3}M TAR solution and 15 m*l* of a 10% w/v hexamethylenetetramine buffer solution with a pH of 7.4 were added; then the solution was diluted to the mark with water. The absorbance of the solution was then measured in a 1-cm cell at 615 mμ, using the reagent blank as a reference.

Results and Discussion

Absorption Curves. The carmine red Th(IV)-TAR complex formed in the pH range from 4.5 to 5.0 has the peak of its absorption curve at 525 mμ. However, a precipitate is sometimes formed. The red-violet complex with the peak at 585 mμ was formed in the pH range from 6.8 to 8.5 without any precipitate. Some of the results are shown in Fig. 1. The latter complex was recommended for the determination at 615 mμ, where the absorption of TAR was negligible.

The Effect of pH. A constant absorbance is obtained over the pH range from 6.8 to 8.5, as

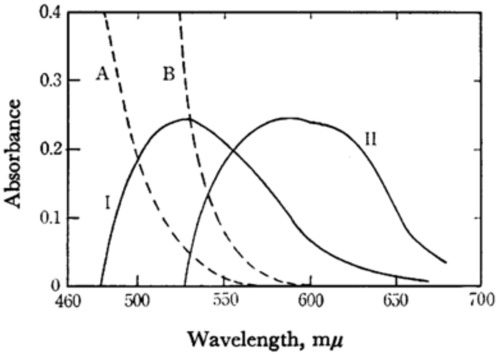

Fig. 1. Absorption curves of TAR and its thorium-(IV) complexes.
Th(IV): 46.4 μg, TAR: 4.0×10^{-5}M
TAR *vs.* water; A: pH 4.6, B: pH 7.4
Th(IV)-TAR complex *vs.* TAR; I: pH 5.0, II: pH 8.5

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[*2] Present address: Hachinohe Technical College, Tamonoki, Hachinohe, Aomori.

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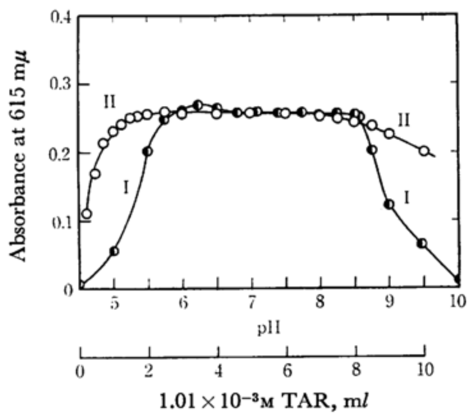

Fig. 2. Effects of pH and the amount of reagent.
Th(IV): 46.4 μg, Reference: reagent blank
I: pH, TAR: 1.01×10^{-4}M
II: Addition of TAR at pH 7.4

is shown in Fig. 2(I). The color development was, therefore, made at pH 7.4.

The Effect of the Amount of Reagent. It may be seen in Fig. 2(II) that a maximum and constant absorbance is obtained with 2 to 6 m*l* of a 1×10^{-3}M TAR solution. A 2.5-m*l* portion of the reagent was used in further experiments.

Color Stability. The absorbance of the solution containing the complex remained almost constant for at least 2 hr.

Calibration Curve. The color system follows Beer's law in the range from 2.4 to 95.2 μg of thorium in 25 m*l*. The molar absorptivity is 3.15×10^4. According to Sandell's notation,[8] the sensitivity of the reaction is 0.008 μg of thorium per cm² at 615 mμ. The reproducibility of the method was also examined. The standard deviation was calculated to be 0.003 (1.2%) in absorbance (mean of 10 determinations of 46.4 μg thorium).

The Effect of Diverse Ions. These results are listed in Table 1. Many elements interfere seriously.

Table 1. Effect of diverse ions on determination at pH 7.4
Thorium taken: 46.4 μg (0.20 μmol)

Ion	Tolerance limit* μmol
Sulfate	290
Chloride	250
Acetate	50
Be	20
Ag	2.5
Tl(I)	1.0
Ce(III)	0.7
Al, Cd	0.20
Zn, Sr, Ni, Mn	0.15
V(VI)	0.10
Nd, Pb	0.05
Hg, Pd, V(IV), tartrate, citrate	0.02
Bi, Co, La, Ti(IV), Y	0.01
Cr, Cu, Ga, In, Yb, Zr(IV), fluoride, phosphate, oxalate, NTA	0.005
Fe(III), EDTA	<0.005

* Value which gives less than 3% relative error

A Comparison with Other Methods. Several methods have been summarized in a previous work;[7] the method proposed here is comparable with the quercetin method[9] in sensitivity and also in selectivity.

Composition of the Complex. The continuous-variation method and the mole-ratio method were used to determine the composition of the thorium-TAR complex. The results of the mole-ratio method are shown in Fig. 3. It seems that a 1 : 3[*3] complex is mainly formed under the conditions investigated, although some lower complexes may also be formed when the ligand-to-metal ratio is less than three. According to the method of Harvey and Manning,[10] the apparent formation constant of the 1 : 3 complex was 7.4×10^{16} at pH 7.4.

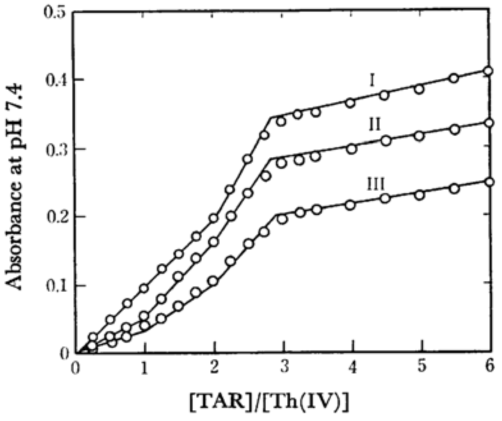

Fig. 3. Mole ratio method.
[Th(IV)]: 6.0×10^{-6}M, I: 585 mμ, II: 615 mμ, III: 635 mμ

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[8] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1950), p. 49.

[9] O. Menis, D. L. Manning and G. Goldstein, *Anal. Chem.*, **29**, 1426 (1957).

[*3] Studies of the mechanism of the reaction are in progress.

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