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The Spectrophotometric Determination of Thorium(IV) with Bromopyrogallol Red[*1,*2]

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Bromopyrogallol red reacts with thorium(IV) to form a stable complex with an absorption maximum at 645 mμ against a reagent blank. The maximum absorbance is obtained in the pH range of 5.6 to 5.9 when the solution is heated in a boiling water bath for 20 min. The color system obeys Beer's law in the range 6 to 106 μg of thorium in 25 m*l*. The molar absorptivity of the complex is calculated to be 5.0×10^4 at 645 mμ. The sensitivity of the reaction is 0.004 μg thorium per cm^2. The complex has the composition 1 to 2 in metal to ligand. The effect of diverse ions on the determination is also examined.

Bromopyrogallol red (5,5′-dibromopyrogallol sulfophthalein), which was first prepared by Vodak *et al.*1) as a chromogenic dye-stuff, reacts with many metal cations to form colored complexes and has widely been used as a metallochromic indicator in complexometric titrations. The present paper describes a new spectrophotometric method for the determination of thorium(IV), using bromopyrogallol red as a color reagent.

Various dye-stuffs, including thorin,2) neo-thorin,2) quinalizarin,3) naphthazarin,4) quercetin,5) eriochrome black T,6) solochromate fast red,7) arsenazo III,8) xylenol orange9) and methylthymol blue,9) have been used as color reagents in the spectrophotometric determination of thorium. No work has been reported, however, on the reaction between thorium(IV) and bromopyrogallol red.

It was found that in the presence of excess reagent, thorium(IV) reacts sensitively with bromopyrogallol red under heating to form a stable complex with a metal to ligand ratio of 1 to 2. This work was done to determine optimum conditions for the spectrophotometric determination of thorium(IV).

Experimental

Reagents. *Standard Thorium(IV) Solution.* About 1×10^{-2} M thorium(IV) solution was prepared by dissolving guaranteed reagent thorium(IV) nitrate tetrahydrate in about 0.1 N nitric acid. The solution was

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[*1] This work was presented at the Tohoku Branch Meeting of the Chemical Society of Japan, Hirosaki, October, 1967.

[*2] After this manuscript had been completed, the authors received a report by Vasilenko *et al.*12) The report was on the spectrophotometric study of the interaction of thorium(IV) with BPR. They applied a sodium acetate-hydrochloric acid medium as the buffer solution. The range of mesurement for thorium was 2 to 60 μg per 25 m*l* with a 1 to 2 complex at pH 5.0 and 630 mμ. The sensitivity of the reaction and the effect of diverse ions was not given.

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1) Z. Vodak and O. Leminger, *Collection Czech. Chem. Commun.*, **21**, 1522 (1956).

2) Nippon Kagakukai "Kagaku Binran (Chemical Handbook)" (in Japanese), Maruzen, Tokyo (1958), p. 1090.

3) P. Purushottam, *Z. Anal. Chem.*, **145**, 245 (1955).

4) T. Moellar and M. Tecotzky, *Anal. Chem.*, **27**, 1056 (1955).

5) O. Menis, D. L. Manning and G. Goldstein, *ibid.*, **29**, 1426 (1957).

6) P. E. Lott, K. L. Cheng and B. C. H. Kwan, *ibid.*, **32**, 1702 (1960).

7) J. Korkisch and G. E. Janauer, *ibid.*, **33**, 1930 (1961).

8) H. Onishi, *Japan Analyst*, **12**, 1153 (1963).

9) M. Otomo, *ibid.*, **14**, 229 (1965).

standardized by EDTA titration using xylenol orange[10] as an indicator. It was diluted with water to desired concentrations.

Bromopyrogallol Red (abbreviated BPR; MW, 558.16 as free acid) *Solution.* A 1×10^{-3} M BPR solution was prepared by dissolving the right amount of Dotite BPR reagent, which has been preserved in a desiccator overnight, in 50%v/v ethanol.

Stock solutions of diverse ions were prepared from their reagent grade chemicals in appropriate concentrations. A 0.25 M acetate buffer solution was also used for pH adjustment.

Apparatus. A Hitachi-Perkin Elmer spectrophotometer, model 139, was used with 1 cm glass cells. A Hitachi-Horiba glass-electrode pH meter, Model M-4, was used for pH measurement.

All measurements were carried out at 25±0.5°C.

Standard Procedure. To a sample solution containing up to 100 μg of thorium in a 50 m*l* Erlemeyer flask, 1.0 m*l* of a 1×10^{-3}M BPR solution and 10 m*l* of 0.25 M acetate buffer solution with a pH of 5.7 were added, and the solution diluted with water to about 20 m*l*. It was heated in a boiling water bath for 20 min. The solution was cooled with running water to room temperature, transferred to a 25 m*l* volumetric flask, and diluted to the mark with water. After the solution had been kept for 20 min at 25°C, the absorbance of the solution was measured at 645 mμ using the reagent blank as a reference.

Results and Discussion

Absorption Curves. The absorption curves of the solutions containing thorium(IV) and BPR at various pH values are shown in Fig. 1. These curves were obtained by measuring the absorbance of the colored solutions against the reagent blank which contained the same amount of BPR.

Below pH 4.6, the solution had an absorption maximum at about 620 mμ. The curves obtained at pH 4.8 (Curve V) had shoulders at about 630 mμ. Between pH 5.5 and 6.3, however, the solutions gave absorption curves with an absorption maximum at about 645 mμ. Therefore, it may be said that in the presence of excess BPR, two complexes are formed between thorium(IV) and the reagent; the complex with an absorption maximum at about 645 mμ was used for the determination of thorium.

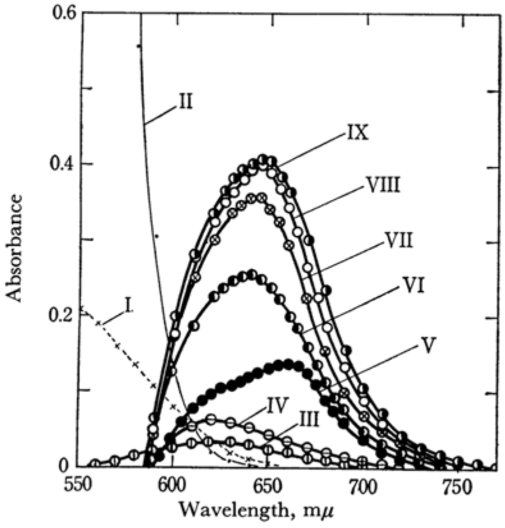

Fig. 1. Absorption cruves of BPR and its thorium complex in the presence of excessive reagent
BPR: 4.01×10^{-5} M, Th(IV): 47.1 μg in 25 m*l* (8.11×10^{-6} M), μ: 0.1. BPR *vs.* water — pH: I, 14.0; II, 6.22. Thorium-BPR complex *vs.* BPR — pH: III, 2.30, 4.10, IV, 4.60; V, 4.78; VI, 5.05; VII, 5.53; VIII, 5.60—5.95; IX, 6.05—6.30.

The Effect of pH. The absorbance of the solution as a function of pH was measured at 645 mμ. From the curve shown in Fig. 2 (Curve I), it is found that the maximum absorbance is obtained in the pH range 5.6 to 6.2. Between pH 5.6 and 5.9, the absorbance of the solution remained almost unchanged for several hours, while above pH 6.0, the complex showed a tendency to precipitate when the solution was allowed to stand for more than about 2 hr. The color development was, therefore, made at pH 5.7.

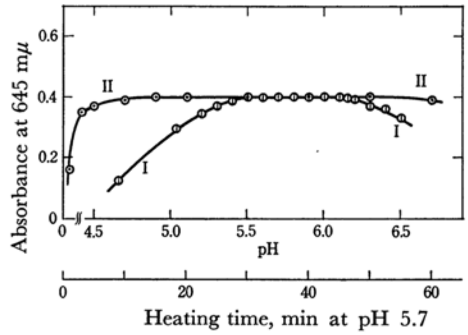

Fig. 2. Effects of pH and heating time.
I: pH, II: Heating time, Th(IV): 47.1 μg. BPR: 4.01×10^{-5} M, μ: 0.1, Reference: Reagent blank

The Effect of Heating Time. The color reaction of BPR with thorium(IV) is very slow at room temperature; several hours were required for complete color development. The effect of heating time on color formation was examined in a boiling water bath at a constant pH of 5.7. As shown in Fig. 2 (Curve II), maximum color development was obtained when the solution was heated for 15 to 40 min.

The Effect of the Amount of Reagent. The effect of the reagent concentration on color development was examined. It is seen in Fig. 3 that constant absorbance is obtained with 0.6 to 1.6 m*l* of a 1×10^{-3} M BPR solution. Therefore, 1.0 m*l* was chosen as the working volume of the reagent.

Color Stability. The absorbance of the solution prepared at pH 5.7 was measured as a function of time following the preparation of the solution.

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[10] K. Ueno, "Kireto Tekitei (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 313.

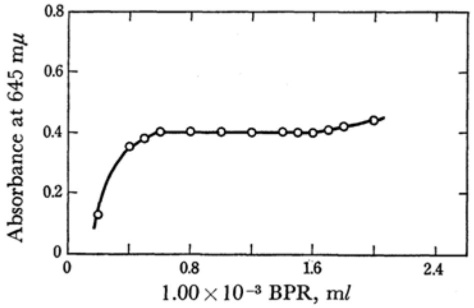

Fig. 3. Effect of addition of BPR.
Th(IV): 47.1 μg, pH: 5.70, μ: 0.1, Reference: Reagent blank

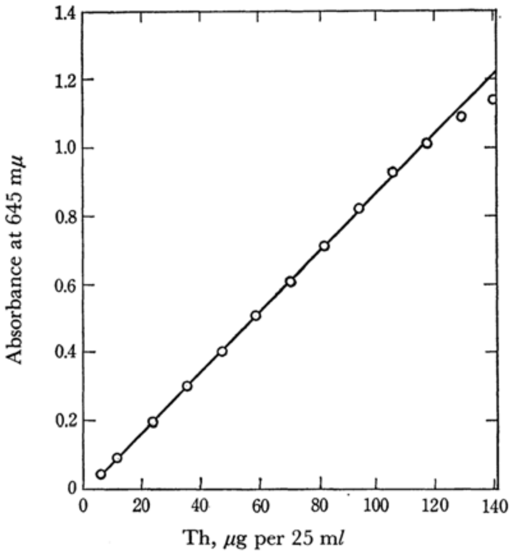

Fig. 4. Calibration curve.
BPR: 4.10×10^{-5} M, pH: 5.70, μ: 0.1, Reference: Reagent blank

TABLE 1. COMPARISON WITH OTHER REAGENTS

Reagent	Molar absorptivity $\times 10^4$	Sensitivity μg/cm^2
Bromopyrogallol Red	5.08(645 mμ)	0.004
Thorin[2)		0.03(545 mμ)
Neo-thorin[2)		0.02(600 mμ)
Quinalizarin[3)		0.02(590 mμ)
Naphthazarin[4)	2.24(620 mμ)	0.01
Quercetin[5)	3.30(422 mμ)	0.007
Eriochrome Black T[6)	3.50(700 mμ)	0.004
Solochromate Fast Red[7)	1.39(490 mμ)	0.017
Arsenazo III[8)	13.00(665 mμ)	
Xylenol Orange[9)	7.70(568 mμ)	0.003
Methylthymol Blue[9)	3.94(568 mμ)	0.006

There was no change in absorbance over a period of 24 hr.

Calibration Curve. From the foregoing results, a calibration curve for the determination of thorium was prepared in the manner described above. Figure 4 shows that Beer's law is obeyed over the range 6 to 106 μg (0.2 to 4.2 ppm) of thorium at 645 mμ and pH 5.7. According to Sandell's notation,11) the sensitivity of the reaction is 0.004μg of thorium per cm^2. The molar absorptivity is calculated to be 5.08×10^4. The latter two values were compared with those of other methods as listed in Table 1. This indicates that the proposed method is less sensitive than the arsenazo III method.8) However, it compares with the xylenol orange method9) in sensitivity. The reproducibility of the method was examined using a solution containing 47.6 μg of thorium. From data obtained from twelve determinations, the standard deviation was calculated to be 0.0036 (0.88%) in absorbance.

The Effect of Diverse Ions. The effect of diverse ions on the determination of thorium was examined. The results are summarized in Tables 2 and 3, from which it is seen that cobalt(II), nickel(II), zinc(II), strontium(II), sulfate and chloride ions do not interfere, but many other ions, especially aluminum(III), lanthanum(III), zirconium(IV), yttrium(III), cadmium(II), fluoride,

TABLE 2. EFFECT OF CATIONS ON DETERMINATION AT pH 5.7

Thorium taken: 46.0 μg (0.20 μmol)
Cations added: each 0.20 μmol

Cation	μg Th found	Relative error (%)
Ag(I)	49.2	+ 6.9
Al(III)	0.0	−100.0
Be(II)	42.9	− 6.8
Bi(III)	62.8	+ 36.6
Cd(II)	21.3	− 53.7
Ce(III)	31.9	− 30.7
Co(II)	45.6	− 0.9
Cr(III)	41.6	− 9.6
Cu(II)	60.1	+ 30.7
Fe(III)	36.4	− 20.9
Ga(III)	32.5	− 29.4
Hg(II)	44.1	− 4.1
In(III)	24.5	− 46.8
La(III)	98.6	+114.4
Nd(III)	61.0	+ 32.6
Ni(II)	46.0	± 0.0
Pb(II)	43.6	− 5.2
Sr(II)	44.6	− 3.0
Ti(IV)	24.2	− 47.4
U(VI)	47.8	+ 3.9
V(IV)	41.6	− 9.6
Y(III)	74.1	+ 60.9
Yb(III)	43.7	− 5.0
Zn(II)	45.5	− 1.1
Zr(IV)	91.6	+ 99.1

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

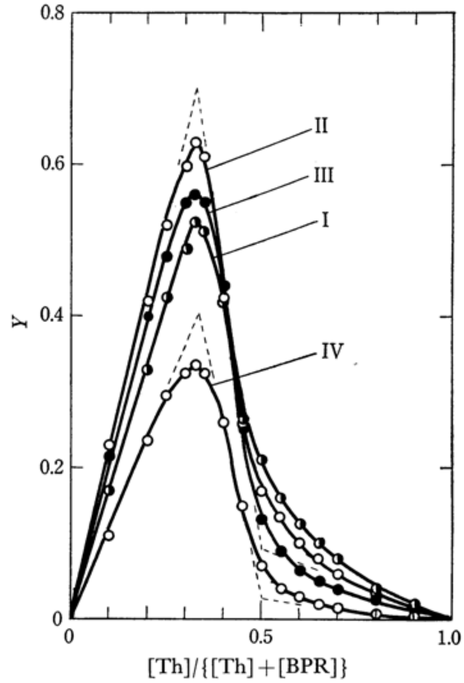

Fig. 5. Continuous variation method. [Th]+[BPR]=4.0×10^{-5} M, pH: 5.7, μ: 0.1, I: 620 mμ, II: 640 mμ, III: 660 mμ, IV: 680 mμ, Reference: Water

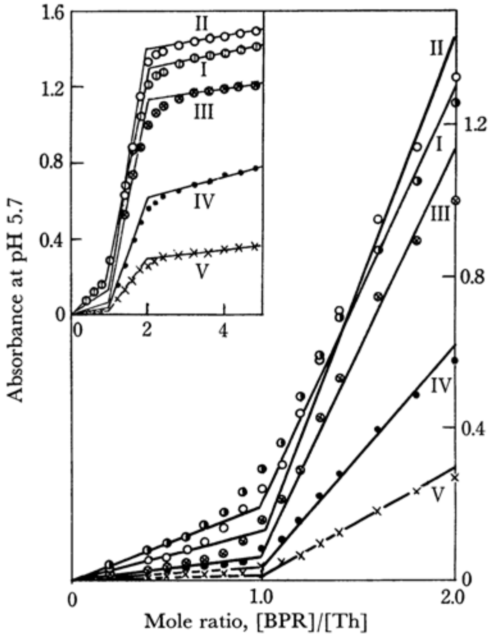

Fig. 6. Mole ratio method. Th(IV): 2.0×10^{-5} M, μ: 0.1, I: 620 mμ, II: 640 mμ, III: 660 mμ, IV: 680 mμ, V: 700 mμ

oxalate, tartrate, citrate, phosphate, NTA and EDTA do interfere with the determination of thorium.

TABLE 3. EFFECT OF ANIONS AND COMPLEXING AGENTS ON DETERMINATION OF THORIUM AT pH 5.7

Thorium taken: 46.0 μg (0.20 μmol)

Anion or complexing agent added	Molar excess over thorium	Th found μg	Relative error %
F^-	1	40.5	−12.0
	2	25.5	−46.8
	10	4.4	−90.5
Cl^-	250	46.4	+ 0.9
	500	47.7	+ 3.4
	1000	47.8	+ 3.9
$H_2PO_4^-$	0.1	45.7	− 0.7
	0.5	35.0	−23.9
	1	10.4	−77.5
SO_4^{2-}	500	46.0	± 0.0
	1000	45.0	− 1.1
$C_2O_4^{2-}$	1	40.5	−12.0
	2	34.6	−30.0
	10	31.9	−33.1
Tartrate $C_4H_4O_6^{2-}$	0.5	50.8	+10.4
	1	49.6	+ 7.8
	10	47.4	+ 3.0
	20	42.2	− 8.3
Citrate $C_6H_5O_7^{3-}$	0.1	46.8	+ 1.7
	0.5	37.5	−18.5
	1	20.5	−55.5
NTA	0.1	40.5	−12.0
	0.5	47.3	+ 2.8
EDTA	0.01	44.8	− 2.6
	0.1	43.1	− 6.3

Composition of the Complex. Attempts were made to characterize the thorium(IV)-BPR complex by two usual methods, the continuous variation method and the mole ratio method. These experiments were performed at a constant pH value of 5.7. Absorbance measurements were made at four wavelengths between 620 and 680 mμ. As shown in Fig. 5, the results obtained with the method of continuous variations indicate that thorium(IV) forms chiefly a 1 to 2 complex with BPR at pH 5.7. The results obtained with the mole ratio method (Fig. 6) show that a 1 to 1 complex is also formed under the same conditions. It may be concluded, therefore, that depending on the amount of reagent, two complexes of different compositions, 1 to 1 and 1 to 2, are formed between thorium(IV) and BPR. It was found, moreover, that another 1 to 1 complex with an absorption maximum at 550 mμ was formed in the pH range 1.3 to 4.2.

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12) V. D. Vasilenko, M. V. Shanya and V. I. Bolbas, *Zh. Analit. Khim.*, **22**, 1818 (1967).