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The Spectrophotometric Determination of Zirconium(IV) with Bromopyrogallol Red*1

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Zirconium(IV) reacts with an excess of bromopyrogallol red to form a violet complex. The constant absorbance of a solution containing the complex is obtained in the pH range from 5.0 to 5.4 at 670 mμ. About 25 min is required to complete the chelate formation in a boiling water bath. The complex thus formed is stable for at least 3 hr. The color system obeys Beer's law in the range from 4 to 35 μg zirconium in 25 m*l*. The sensitivity of the reaction is 0.002 μg per cm^2 for an absorbance of 0.001. In composition the complex has a metal-to-ligand ratio of 1:2. The molar absorptivity and the apparent formation constant of the complex are calculated to be 7.01×10^4 at 670 mμ and 1.11×10^9 at pH 5.2 respectively. The effect of diverse ions on the determination is examined.

Bromopyrogallol red (BPR or H_4L) has been used as a reagent for the spectrophotometric determination of many metallic cations, including silver(I),1) uranium(IV),2) yttrium(III) and cerium(III),3) titanium(IV)4) bismuth(III),5) indium(III),6) niobium(V),7) scandium(III),8) and thorium(IV).9) It is found that BPR reacts with zirconium(IV) under heating to form a violet complex. The present paper describes the fundamental conditions for applying the reaction to the spectrophotometric determination of zirconium.

Experimental

Reagents and Apparatus. *Standard Zirconium Solution.* About a 1×10^{-2} M zirconium(IV) solution

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1) R. H. Dagnall and T. S. West, *Talanta,* **8**, 711 (1961).

2) V. F. Lukjaov and E. P. Duderova, *Zh. Analit. Khim.,* **16**, 60 (1960).

3) J. Herrington and K. C. Steed, *Anal. Chim. Acta*, **22**, 180 (1960).

4) V. Suk, I. Nemcova and M. Malat, *Collect. Czech. Chem. Commun.*, **30**, 2538 (1965).

5) V. Suk and M. Smetanava, *ibid.*, **30**, 2535 (1965).

6) Sn. T. Talipan, Kr. S. Abdultaeva and G. P. Gorkovaya, *Uzbeksk. Khim.*, **6**, 16 (1962): *Chem. Abstr.*, **58**, 12122 (1963).

7) R. Belcher, T. V. Ramakrishna and T. S. West, *Talanta,* **12**, 681 (1965).

8) T. Shimizu, *ibid.*, **14**, 473 (1967).

9) K. Tonosaki and T. Sakai, This Bulletin, **42**, 456 (1969).

was prepared by dissolving a guaranteed zirconyl nitrate dihydrate in 0.2 N perchloric acid. The solution was standardized by EDTA titration, using xylenol orange[10] as the indicator.

The solutions of BPR, diverse ions, and the buffer, and the apparatus were the same as those used in a previous work.[9]

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

Standard Procedure. To a sample solution containing up to 32 μg of zirconium in a 50 m*l* Erlenmeyer flask, 1.2 m*l* of a 1×10^{-3} M BPR solution and 10 m*l* of a 0.25 M acetate buffer solution with a pH value of 5.2 were added. The mixture was then heated in a boiling water bath for 25 min. The solution was cooled with running water to room temperature. transferred into a 25 m*l* volumetric flask, and then diluted to the mark with water. After 10 min, the absorbance of the solution was measured at 670 mμ using a reagent blank as the reference.

Results and Discussion

Absorption Curves. Figure 1 shows that the maximum absorption of the zirconium - BPR complex is found at 670 mμ.

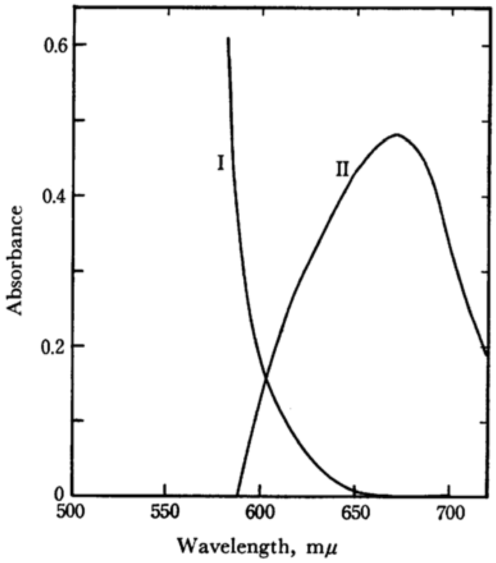

Fig. 1. Absorption curves of BPR and its zirconium complex.

BPR: 4.80×10^{-5} M, Zr(IV): 18.2 μg in 25 m*l* (7.97×10^{-6} M), μ: 0.1, I: BPR *vs.* water, II: zirconium-BPR complex *vs.* BPR, pH: 5.23.

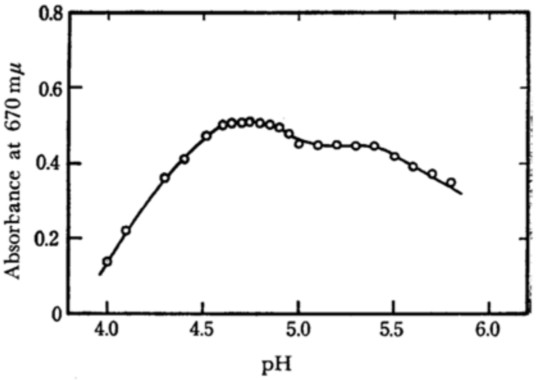

Fig. 2. Effect of pH.
Zr(IV): 18.2 μg, BPR: 4.00×10^{-5} M, μ: 0.1,
Reference: Reagent blank

The Effect of pH. As is shown in Fig. 2, the maximum absorbance is obtained in the pH range from 4.7 to 4.8. The complex formed below pH 4.9 showed a tendency to precipitate on standing, probably because of its uncharged form.[*4] A constant absorbance is obtained over the pH range from 5.0 to 5.4. All the absorbance readings were taken within this range, since the absorbance of the solution containing the complex remains almost constant for at least 3 hr after heating.

The Effect of Heating Time. It requires several hours at room temperature to complete the reaction between zirconium and BPR. The reaction was, however, accelerated by heating. The maximum absorbance was obtained when a solution containing zirconium and BPR was heated in a boiling water bath for from 20 to 35 min.

The Effect of the Amount of Reagent. The maximum, and almost constant, absorbance was obtained when from 1 to 3 m*l* of a 1×10^{-3} M BPR solution was added to a solution containing 18.2 μg of zirconium. The order of the addition of the reagents was not critical.

Calibration Curve. Beer's law is found to hold in the range from 4 to 35 μg of zirconium in 25 m*l*. The sensitivity of the reaction was calculated according to Sandell's notation[11] and found to be 0.002 μg of zirconium per cm^2. The reproducibility of the method was examined using a solution containing 18.2 μg of zirconium. From the data obtained by eleven determinations, the standard deviation was calculated to be 0.003 (2.8%) in absorbance.

The Effect of Diverse Ions. The results are listed in Table 1.

A Comparison with Other Methods. Table 2 indicates that the proposed method is comparable with the morin method[16] in sensitivity.

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[10] K. Ueno "Kireto Tekitei (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 325.

[*4] It was found experimentally that zirconium forms a 1 : 1 complex with BRR at lower pH values. Since, as will be mentined below, BPR may exist mainly as the anionic species, H_3L^-, in the pH range from 1 to 4, the formula of the 1 : 1 complex may be represented as an uncharged form, $ZrO(H_2L)$.

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

TABLE 1. EFFECT OF DIVERSE IONS AT pH 5.2

Zirconium taken: 18.2 μg (0.20 μmol)

Tolerance limit* μmol	Ions
large excess	chloride
0.2	sulfate, Co, Pb
0.1—0.05	Ag, Cd, In, fluoride, oxalate
0.04—0.01	Be, Bi, Ce(III), Cu, Ga, Hg, La, Mn, Ni, Pd, Sm, Th(IV), Ti(IV), Tl(I), Tl(III), U(VI), V(IV), W(VI), Y, Yb, Zn, phosphate, tartrate, citrate
0	Cr, Fe(III), Nd, EDTA

* Value which gives less than 3% relative error

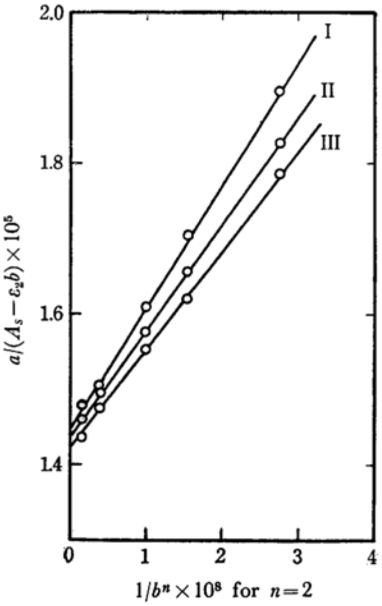

Fig. 3. Plots of $a/(A_s-\varepsilon_2 b)$ vs. $1/b^n$ at pH 5.5. Zr: 3.87×10^{-6} M, BPR: 7.74×10^{-5}—2.32×10^{-4} M, μ: 0.5, I: 680 mμ, II: 665 mμ, III: 670 mμ

Composition of the Complex. The method described by Benesi and Hildebrand[20] is used to determine the composition of the complex. Since BPR may exist mainly as the anionic form, H_2L^{2-}, in the pH range from 5 to 8,[*5] and zirconium(IV), as ZrO^{2+}, the formation of the complex with a metal-to-ligand ratio of 1:*n* can be represented as;

$$ZrO^{2+} + nH_2L^{2-} \rightleftarrows ZrO(HL)_n{}^{(3n-2)-} + nH^+ \quad (1)$$

$$K' = [\{ZrO(HL)_n\}^{(3n-2)-}]/[ZrO^{2+}][H_2L^{2-}]^n \quad (2)$$

where K' is the apparent formation constant at a given pH value. The following relation may finally be derived as a result of the transformation of Eq. (2):

$$a/(A_s-\varepsilon_2 b) = 1/\varepsilon_3 + 1/K'\varepsilon_3 b^n \quad (3)$$

where A_s is the absorbance of the solution containing the complex and ligand added in excess to a definite

TABLE 2. COMPARISON WITH OTHER METHODS

Reagent	Molar absorptivity $\times 10^4$	Sensitivity μg/cm²
Bromopyrogallol Red	7.01 (670 mμ)	0.002
Pyrocatechol Violet[12]	4 (655 mμ)	
Gallein[13]	0.77 (530 mμ)	0.02
N-Methyl anabasine-α-azoresorsinol[14]	1.05 (530 mμ)	
Arsenazo III[15]	12.5±0.3 (670 mμ)	
Morin[16]	7.30 (420 mμ)	
8-Hydroxyquinoline[17]	1.47 (386 mμ)	
Chromazurol S[18]	4.1±0.04 (560 mμ)	
Molybdate[19]	0.475 (725 mμ)	

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[12] J. P. Young and J. C. White *Talanta,* **1**, 263 (1958).

[13] L. Kekedy and G. Balogh, *Studia Univ. Babes-Bolyai, Ser. Chem.,* **8**, 204 (1963); *Chem. Abstr.,* **61**, 12631 (1964).

[14] Sh. T. Talipov, R. Kh. Dzhiynbaeva and M. Abdurakhmanov, *Nauchn Tr. Tashkentsk. Gos. Univ. No.* **264**, 146 (1964); *Chem. Abstr.,* **65**, 14427 (1966).

[15] N. V. Mel'chakova, M. N. Stanislavskaya and V. M. Peshkova, *Zh. Analit. Khim.,* **19**, 701 (1964); *Chem. Abstr.,* **61**, 7699 (1964).

[16] T. Ito and Y. Hoshino, *Bunseki Kagaku (Japan Analyst),* **13**, 257 (1964).

[17] R. T. Van Santen, J. H. Schlewitz and C. H. Toy, *Anal. Chim. Acta,* **33**, 593 (1965).

[18] I. S. Mustafin and V. S. Shchukina, *Zh. Analit. Khim.,* **21**, 309 (1966); *Chem. Abstr.,* **65**, 3000 (1966).

[19] J. C. Guyon and C. C. Clowers, *Anal. Chim. Acta,* **37**, 401 (1967).

[20] M. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.,* **71**, 2703 (1949).

[*5] The stepwise acid dissociation constants of BPR have been determined by Suk[21] as $K_1=(6.92\pm 0.27)\times 10^{-1}$, $K_2=(4.07\pm 0.09)\times 10^{-5}$, $K_3=(7.41\pm 0.10)\times 10^{-10}$, and $K_4=(5.37\pm 0.32)\times 10^{-12}$.

[21] V. Suk, *Collect. Czech. Chem. Commun.,* **31**, 3127 (1966).

amount of zirconium, where *a* and *b* are the total concentrations of zirconium and the ligand respectively, and where ε_2 and ε_3 are the molar absorptivities of the ligand and the complex respectively. Only a choice of *n* equal to two made the data interpretable, showing that a 1 : 2 complex is formed between zirconium and BPR. Some of the results are shown in Fig. 3. From the intercept of the straight line, ε_3 was calculated to be 7.01×10^4 at 670 mμ, and K', as a mean value of the values obtained at five wavelengths between 660 and 680 mμ, was found to be 1.11×10^9 at pH 5.2.

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