*Spectrophotometric Determination of Traces of Boron in Thorium**

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Although a few reports[1,2] have been published of the chemical determination of boron in thorium metal, no paper seems to be available pertaining to its determination in thorium oxide. This is probably due to the fact that it is very difficult to dissolve the oxide. Nitric acid or hydrochloric acid in the presence of a small amount of fluoride dissolves the oxide. However, this method of solution will not be directly applicable to the photometric determination of boron because of the interference of fluoride.

The authors have found that strong phosphoric acid[3] dissolves both thorium oxide and metal relatively easily. On the basis of this finding, a method has been developed for the determination of as little as a few tenths of a part per million of boron in thorium oxide or metal. After the dissolution of the sample, boron is separated as methyl borate, and finally determined by the curcumin method[4].

Experimental

Apparatus. — The quartz distilling apparatus and the spectrophotometer were the same as those described before[4].

Reagents.—*Strong Phosphoric Acid.*—Prepare from 85% orthophosphoric acid according to the direction of Kiba[3]. The orthophosphoric acid should preferably contain less than 0.05 ppm of B. When such an acid is not obtainable, purify it as follows. Transfer 150 ml. of 85% phosphoric acid, 30 ml. of water (redistilled), and 500 ml. of redistilled methanol to a one-liter quartz distilling flask. Connect the condenser, and heat the flask in a water bath, and continue distillation until no more liquid comes out. Add 150 ml. of water and distil again. Transfer the residue to a 500 ml. quartz beaker, and heat at 150~200°C for several hours. Cool, add 150 ml. of water, and repeat heating as above. Add 100 ml. of water and heat at 200~250°C until boiling ceases. Finally add 100 ml. of water and heat at 200~280°C until boiling ceases. Cool, and prepare the strong phosphoric acid in a suitable apparatus by heating the purified acid to 300°C.

Other solutions used were the same as those described previously[4].

Procedure.—Transfer 1.00 g. of thorium oxide or thorium metal sample to the distilling flask and add 5.0 ml. of the strong phosphoric acid using a syringe. Heat the flask on a sand bath at 200~250°C and shake the contents occasionally to hasten the solution of the sample. Stop heating when a clear sample solution has been obtained.

To the cold solution add 3 ml. of water (redistilled) and mix. Connect the flask with the condenser through the adapter, and immerse the flask in a one-liter beaker containing water (this serves as a water bath). Place a 100 ml. platinum dish containing 7.0 ml. of 0.1 N calcium hydroxide suspension and 10 ml. of water under the condenser. Add 20 ml. of methanol (redistilled) and mix the solution with a polyethylene rod and wash the rod with 10 ml. of methanol. Connect the tap funnel, and raise the temperature of the bath slowly to boiling point. Continue heating until no more liquid comes out. (This distillation will take 15~20 min.)

Remove the burner and replace the hot water by cold water. Add 20 ml. of methanol through the tap funnel and distil again. (This second distillation will take 10~15 min.) Lower the dish and wash down the stem of the condenser with water. Mix the distillate and washings and confirm the fact that the solution is alkaline. Evaporate the solution gently to dryness on a water bath.

To the residue add 2 ml. of water and 4.0 ml. of curcumin-oxalic acid solution (0.40 g. of curcumin and 50 g. of oxalic acid in one liter of ethanol). Then continue according to the directions previously described[4]. When the amount of boron is found by referring to the standard curve that has been prepared by omitting the separation step, a correction of +15 per cent is advisable.

Note. — Instead of the distilling flask, a quartz dish may be used for the dissolution of the sample. In this case, the process of solution is accelerated by stirring with a quartz rod. The clear sample solution should be transferred to the distilling flask while the solution is hot.

Results and Discussion

As pointed out by Rodden[5], thorium oxides that have been highly ignited are very difficult to dissolve. In the present work, thorium oxides that had been prepared by heating

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1) J. P. Burelbach and R. J. March, ANL-5240 (1953).

2) A. R. Eberle and M. W. Lerner, *Anal. Chem.*, 32, 146 (1960).

3) T. Kiba, *Chemistry and Chem. Ind.* (*Kagaku to Kogyo*), 11, 730 (1958).

4) H. Onishi, N. Ishiwatari and H. Nagai, This Bulletin, 33, 830 (1960).

5) C. J. Rodden, *Proceedings Internatl. Conf. Peaceful Uses Atomic Energy*, 8, 197 (1956).

thorium nitrate to 500 and 700°C were dissolved in strong phosphoric acid within 1 and 2 hr., respectively (quartz dish). When the distilling flask is used, a longer time is required.

The effects of phosphoric acid and thorium on the determination of boron are shown in Table I. Seven milliliters of 0.1 N calcium hydroxide suspension and the foreign substance, with or without 1 μg. of boron, were evaporated to dryness and then subjected to color development. The addition of 0.18 meq. of phosphoric acid resulted in about a 40 per cent decrease in absorbance. However, as shown below, no significant quantity of phosphoric acid comes out during methanol distillation.

TABLE I. EFFECT OF PHOSPHORIC ACID AND THORIUM ON THE DETERMINATION OF BORON*

Addition	Absorbance		
	Blank	1.0 μg. B	Difference
——	0.060	0.370	0.310
0.30 ml. 0.18 N H_3PO_4	0.060	0.340	0.280
0.50 ml. 0.18 N H_3PO_4	0.061	0.314	0.253
1.0 ml. 0.18 N H_3PO_4	0.050	0.246	0.196
0.56 mg. Th (as $ThCl_4$)	0.056	0.357	0.301
1.1 mg. Th (as $ThCl_4$)	0.055	0.325	0.270

* In the presence of 0.7 meq. of $Ca(OH)_2$.

TABLE II. EFFECT OF WATER ON THE DISTILLATION OF BORON

In each case 5.0 ml. of strong phosphoric acid was used.

Water added, ml.	Recovery of 1 μg. B, %*
1.0	79
2.0	78
3.0	89
4.0	81
5.0	92
6.0	72

* Average of duplicate experiments.

Table II shows the effect of water on the distillation of boron. When water was not added to 5.0 ml. of strong phosphoric acid, methanol distillation was not successful. This was probably due to the formation of methyl phosphate. In the table recoveries were calculated by referring to the standard curve obtained without distillation of boron. In the subsequent work, 3.0 ml. of water was adopted.

TABLE III. DISTILLATION OF BORON FROM PHOSPHORIC ACID SOLUTION

5.0 ml. of strong phosphoric acid solution was heated at 200~250°C for 2 hr. After cooling 3 ml. of water was added and MeOH distillation followed.

B taken, μg.	B found, μg.	Average recovery, %
0.20	0.17, 0.17	85
0.50	0.46, 0.45, 0.47, 0.39	88
1.00	0.88, 0.81, 0.90 0.79, 0.90, 0.88	86

TABLE IV. DETERMINATION OF BORON IN THORIUM OXIDE

B added, ppm	B found, ppm*
0.20	0.22, 0.18
0.50	0.46, 0.45
1.00	0.86, 0.92

* Includes the original B content of thorium oxide (<0.05 ppm B).

TABLE V. DETERMINATION OF BORON IN STANDARD THORIUM OXIDES AND THORIUM METAL

Sample	Boron, ppm	
	NBL	Proposed method
NBL-26-6, ThO_2	2	1.8, 1.9
NBL-26-5, ThO_2	3	2.9, 2.7
NBL-26-3, ThO_2*	4.4	4.7, 4.4
NBL analyzed sample No. 19 Th**	about 1	0.58, 0.46, 0.46, 0.43

* Other certified values, based on metal (in ppm): 100 each Al, Fe, Mo, P, Si, V, Zn, 35 Be, 10 each Bi, Co, Cu, Mg, Mn, Ni, Pb, Sn, 1 each Ag and Cd.

** Other certified values (in ppm): about 20 Al, about 150 Be, <10 Ca, <5 Cu, 140 Fe, <10 Mg, about 2 Mn, about 10 Ni, about 4 Pb, about 20 Si, about 2 U, 60 N, 230 C.

Table III summarizes the results of methanol distillation of boron in the absence of thorium. The distillation was made according to the proposed procedure. The reagent blank against the blank of direct color development was about 0.2 μg. of boron. The average recovery of 0.2 to 1 μg. of boron is calculated to be 86%. The standard deviation for 1 μg. of boron is 5.6%. The recovery of 86% is comparable to that of the methanol distillation from a sulfuric acid medium[4].

Known amounts of boron were added to thorium oxide (1 g., Société de Produits Chimique des Terres Rares, France) and the boron was determined by the proposed procedure except that +15% were not applied (Table IV). A recovery of about 86% is indicated after correcting for the original boron content of the sample.

The standard samples of thorium oxide and thorium metal, issued by the New Brunswick Laboratory (NBL), were analyzed by the proposed method, and the results are shown in Table V. It is seen that the NBL values for thorium oxide samples agree quite well with the values obtained by applying the proposed method. Because the NBL value for the thorium metal is very approximate, it is not possible to check the accuracy of the proposed method directly. Duplicate analyses of the thorium metal that was converted into oxide by heating to 600°C for several hours gave 0.67 and 0.59 ppm B (average 0.63 ppm). Since this average agrees within an experimental error with the average of 0.48 ppm (Table V), it is not likely that insoluble boron remains after dissolution of thorium metal in strong phosphoric acid. Furthermore, the average value of 0.48 ppm B agrees reasonably well with the value of 0.35 ppm which was obtained by the spectrochemical determination employing the carrier distillation technique[6]. Consequently, it is considered that the proposed method is successfully applicable to thorium metal. As curcumin can not be used in the method described by Eberle and Lerner[2], the proposed method seems to be more practicable.

Summary

Procedure is described for the spectrophotometric determination of a few tenths of a part per million of boron in thorium oxide or metal. The sample was brought into solution with strong phosphoric acid. After diluting the solution with water, boron was separated by distillation as methyl borate, and finally determined by the curcumin method. The error is not likely to exceed ±0.1 ppm for 0.2～1 ppm of boron.

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[6] T. Nakazima and H. Fukushima, *Japan Analyst* (*Bunseki Kagaku*), 9, 830 (1960).