Spectrophotometric Determination of Traces of Boron in Uranium

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Various methods for determining traces of boron in uranium and its compounds were investigated because of the effect of neutron absorption. Table I summarizes most of the previous literature on the photometric determination of boron in uranium. Spectrographic

TABLE I. SUMMARY OF LITERATURE ON THE PHOTOMETRIC DETERMINATION OF BORON IN URANIUM

Samples	Reagent	Separation	Range	Reference
U_3O_8	Carmine	—*	0.05—50 μg. B	1
U_3O_8	Carmine	—	1 p.p.m. B detd. (1 g. sample)	2
$UO_2(NO_3)_2$	Carmine	Distillation	0.1—0.5 p.p.m. (4 g. sample)	3
Al-U	Carminic acid	—	10—70μg. (0.5—2 g. sample)	4
U_3O_8	1, 1′-Dianthrimide	Ion exchange	0.2—2 p.p.m.	5
UF_6	Curcumin	Distillation		6
U_3O_8	Turmeric	Distn. from H_3PO_4 soln.	0.1—1.5 μg.	7
U, U compds.	Curcumin	Distillation	0.5—5 μg.	8
U	Curcumin	Solvent extn.	$>$0.1 p.p.m.	9
U-Zr, U-Zircaloy	Curcumin	EtOH extn.	0.015% detd.	10
U, UO_2Cl_2	Crucumin	—	3—50 p.p.m. (0.1 g. sample)	11
U	Curcumin	Distn. from HCl soln.	0.01—0.3 p.p.m (10 g. sample)	12
Al-U	Curcumin	Distn. from HCl soln.	$>$30 p.p.m.	13
U	Curcumin	Ion exchange		14

* — denotes that separation is not required.

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1) R. Cypres and P. Leherte, *Bull. soc. chim. Belges*, **63**, 101 (1954).

2) R. F. Cellini and L. G. Sánchez, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **8**, 364 (1956).

3) T. Nowicka-Jankowska and H. Szyszko, *Chemia Analityczna*, **1**, 285 (1956).

4) K. W. Puphal, J. A. Merril, G. L. Booman and J. E. Rein, *Anal. Chem.*, **30**, 1612 (1958).

5) A. R. Eberle, M. W. Lerner and H. Kramer, **NBL-143**, 5 (1958).

6) E. Staple, E. D. Marshall, F. Nelson and W. Simon, **AECD-4212** (1946. Decl. 1955).

7) C. J. Rodden, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, **8**, 197 (1956).

8) J. F. Possidoni de Albinati and R. H. Rodrguez Pasqués, ibid., **8**, 339 (1956).

9) J. Coursier, J. Huré and R. Platzer, ibid., **8**, 487 (1956).

10) J. Rynasiewicz and V. Consalvo, **KAPL-M-JR-8** (1956).

11) L. Silverman and K. Trego, *Anal. Chim. Acta*, **15**, 439 (1956).

12) Chemical Services Dept., **IGO-AM/S-124** (1958).

13) I. H. Crocker, **CRDC-811** (1958).

14) T. Takeuchi, T. Yoshimori and S. Shibayama, the 12th Annual Meeting of the Chem. Soc. of Japan, April, 1959.

methods are not included in the table. Curcumin methods are generally more sensitive than carmine methods. However, the curcumin methods which have been reported up to the present consist of varied procedures according to different authors. Moreover, the reasons for using each procedure are not always evident. Consequently, in order to obtain optimum conditions, the available methods have been critically studied.

As shown in Table I, a phosphoric acid or a hydrochloric acid medium appears to be widely used for the separation of boron as methyl borate from uranium. In the case of the phosphoric acid medium, that methanol vapor must be passed through a hot sample solution[7] is considered to be disadvantageous, since connection of two distilling flasks is necessary; Otherwise phosphoric acid solutions of uranium form gels. When the hydrochloric acid medium is employed, the removal of excess of water is not easily effected[15].

In the determination of boron in uranyl sulfate, the authors found that a sulfuric acid medium was very suitable for the separation of boron as methyl borate, and that the above-mentioned disadvantage and difficulty could be avoided. Further investigation has shown that satisfactory results of analyses of U_3O_8 and uranium metal (after conversion into U_3O_8) can be obtained by using the same medium for the dissolution of the sample and distillation of methyl borate. These results are reported in the present paper.

Experimental

Apparatus.—The distilling apparatus (quartz) is shown in Fig. 1. The volume of the flask is about 300 ml. Absorbance measurements were made with a Hitachi Model EPU-2A spectrophotometer, using 1-cm. cells.

Reagents. — In purification and preparation of reagents, as well as in analysis, redistilled water was used. For purification by distillation described below, a quartz distilling apparatus was used. All the solutions (except hydrogen peroxide) were kept in polyethylene bottles.

Water, redistilled.—Small amounts of mannitol (dissolved in distilled water) are added to the flask for redistillation.

Sulfuric acid, 1 : 3.—In a quartz beaker 5 ml. of 48% hydrofluoric acid is added to 100 ml. of concentrated sulfuric acid and heated to strong fumes. After cooling water is added.

Hydrogen peroxide, 30%.—Purification was effected by modification of Luke's procedure[16]. A 2.5 g. portion of Amberlite IR-120 (H^+ form) and 7.5 g. of Amberlite IRA-400 (OH^- form) are transferred to a 100 ml. polyethylene beaker. While cooling, 60 ml. of cold 30% hydrogen peroxide is added and stirred for 10 min. The product is filtered through a paper (washed with water and dried) to a brown glass bottle and kept in a refrigerator.

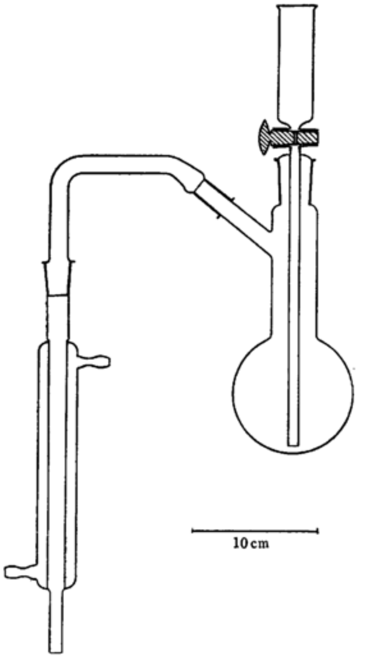

Fig. 1. Distilling apparatus.

Methanol, redistilled from sodium hydroxide.

Calcium hydroxide suspension, 0.1 N. — Distilled calcium is washed with water and the oxide scraped. One gram of calcium is dropped into a 500 ml. quartz flask and enough water is added cautiously. After cooling the contents are transferred to a bottle and diluted to 500 ml. with water.

Curcumin-oxalic acid solution[17,18].—A 0.40 g. portion of finely ground curcumin and 50 g. of oxalic acid are dissolved separately in ethanol. Both solutions are mixed and diluted with ethanol to 1 l.

Ethanol, redistilled from sodium hydroxide.

Standard boron solution.—A 0.5716 g. portion of boric acid is dissolved in 100 ml. of water (1.00 mg. B/ml.). From this stock solution 1 and 0.2 p.p.m. B solutions are prepared.

Procedure. — *Uranium metal.* — Ignite cautiously 1.00 g. of the sample in a platinum crucible at a low temperature. Then heat the crucible in an electric oven at about 800°C for one hour. Cool, and transfer the oxide formed to the distilling flask. Then continue as described below.

U_3O_8.—Transfer 1.00 g. of sample to the distilling flask and assemble the distilling apparatus. Place a 100 ml. platinum dish containing 10 ml. of water under the condenser. To the flask add 5 ml. of 1 : 3 sulfuric acid and 1 ml. of 30% hydrogen peroxide. Heat gently with a small flame until the sample is in solution. Replace the burner by an infrared lamp (300～500 W.) and distil excess of

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[15] H. Onishi, N. Ishiwatari and H. Nagai, the 12th Annual Meeting of the Chem. Soc. of Japan, Kyoto, April, 1959.

[16] C. L. Luke, *Anal. Chem.*, 27, 1150 (1955).

[17] W. T. Dible, E. Truog and K. C. Berger, *Anal. Chem.*, 26, 418 (1954).

[18] I. Muraki and K. Hiiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 845, 850 (1957).

water. Heat several times the side arm of the flask to remove water droplets. Stop heating when fumes begin to appear. Cool.

Immerse the flask in a 1 l. beaker containing water (this serves as a water bath). Add 5.0 ml. of 0.1 N calcium hydroxide suspension to the platinum dish and raise the dish so that the tip of the condenser is in the solution. (The dish is protected from the heat of the burner by an appropriate shield.) From the tap funnel add 30 ml. of methanol. Raise the temperature of the bath slowly to approximately 95°C, giving a slow but steady distillation of methyl borate and methanol*. Continue heating until no more liquid comes over. Remove the burner and replace the hot water by cold water. Add 2.0 ml. of 0.1 N calcium hydroxide suspension to the solution in the dish. Add 20 ml. of methanol through the tap funnel and distil again. Lower the dish and wash down the stem of the condenser. Mix the distillate and washings with a quartz stirring rod (confirm that the solution is alkaline), and evaporate gently to dryness on a water bath.

To the residue add 2 ml. of water and 4.0 ml. of curcumin-oxalic acid solution and mix with a quartz stirring rod. Wash the rod with a small amount of water. Evaporate the solution on a water bath at 55±3°C, and allow to remain for 30 min. after the contents are dry. Cool the dish to room temperature (in a desiccator). Extract the colored products with 9 : 1 ethanol by stirring with a quartz rod. Transfer the colored solution to a 25 ml. volumetric flask and make up to volume with 9 : 1 ethanol. Mix, transfer the contents to a centrifuge tube, cover the tube with parchment paper, fasten the paper with a rubber band, and centrifuge at about 3000 r.p.m. for 10 min. Transfer the clear solution to a 1 cm. cell, and measure the absorbance at 550 mμ, using 9 : 1 ethanol as the reference.

Establish the standard curve by taking, for example, 0, 0.2, 0.5, and 1 μg. of boron, adding 7 ml. of 0.1 N calcium hydroxide suspension, and proceeding as described above. Run a blank, preferably in duplicate, throughout the entire procedure. As the recoveries of boron are low, a correction of +15% is advisable. When the standard curve is established by including the separation, this correction is naturally unnecessary.

Results and Discussion

Spectrophotometric Determination of Boron. —In general, it may be summarized that the variable factors in the curcumin methods are use of alkalis (sodium hydroxide[8,12,13,19] and calcium hydroxide[7,18]), addition of hydrochloric acid, amounts of curcumin and oxalic acid, and extractants (ethanol[7,18], methanol[8], acetone[8,11]) of the colored products. Spicer and Strickland[19] used a glycerol-sodium hydroxide reagent, of composition of 1% sodium hydroxride, 0.1% sodium chloride, and 3% glycerol, to collect methyl borate. In this case hydrochloric acid must be added before adding curcumin. Muraki and Hiiro[18] used calcium hydroxide, and did not add hydrochloric acid, while other workers (e. g., Ref. 7) added the acid.

The preparation of curcumin-oxalic acid solution, described by Muraki and Hiiro[18], appears most satisfactory, because the preparation is simple, and the solution is stable. When the solution has been allowed to stand for 2 days after preparation, the absorbance becomes practically constant (Fig. 2). The workers mentioned[18] allowed the solution to stand for 7∼10 days before use. The solution can be kept for one month at room temperature in the dark.

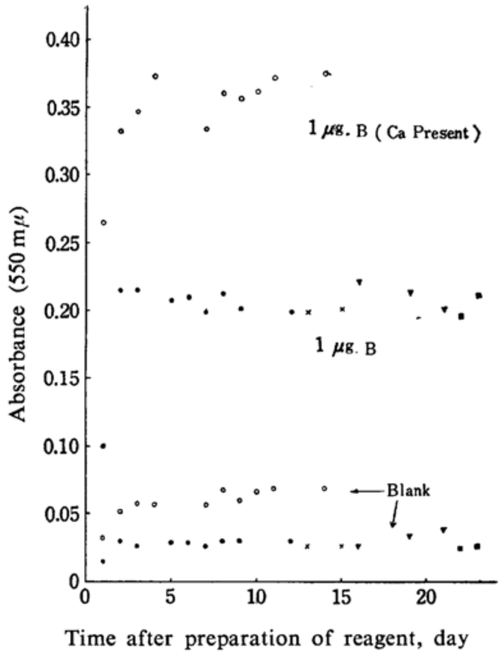

Fig. 2. Aging of curcumin-oxalic acid reagent
○ With Wako-Eastman curcumin and other points with Koso curcumin (cf. Table VII). ●: 97%(v./v.) EtOH, ○ and × : 87% (v./v.) EtOH, ▼ : MeOH, ■ : acetone.

Table II shows the effects of alkalis and extractants on the determination of boron. In each case 4 ml.[18] of curcumin-oxalic acid solution was used. It is seen that the presence of calcium hydroxide increases the absorbance of colored solution*, while that of sodium chloride decreases the absorbance. Addition of hydrochloric acid to calcium hydroxide is not

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* This distillation requires about 15 min., and the second distillation about 10 min.

[19] G. S. Spicer and J. D. H. Strickland, *Anal. Chim. Acta*, **18**, 523 (1958).

* Data obtained by Muraki and Hiiro[18] also indicate this phenomenon.

TABLE II. EFFECTS OF ALKALIS AND EXTRACTANTS ON THE DETERMINATION OF BORON

	97% (v./v.) EtOH	87% (v./v.) EtOH	MeOH	Acetone
Blank				
Mean absorbance	0.029	0.028	0.034	0.026
No. of expts.	16	4	6	4
Std. deviation, %	9.0	8.6	9.4	8.7
1 μg. B				
Mean absorbance	0.208	0.200	0.214	0.204
No. of expts.	16	4	6	4
Std. deviation, %	3.7	1.8	5.6	4.7
5 ml. of 0.1 N Ca $(OH)_2$ was added				
Blank				
Mean absorbance	0.038	0.039	0.053	0.039
No. of expts.	6	4	4	4
Std. deviation, %	10	4.4	4.0	3.6
1 μg. B				
Mean absorbance	0.249	0.245	0.265	0.269
No. of expts.	6	4	4	4
Std. deviation, %	1.3	1.0	2.3	4.4
2 ml. of glycerol-NaOH reagent was added. 2 ml. of 1 N HCl was added after removal of glycerol				
Blank				
Mean absorbance	0.028	0.026	0.029	0.024
No. of expts.	4	4	4	4
Std. deviation, %	18	6.9	11	10
1 μg. B				
Mean absorbance	0.148	0.152	0.151	0.139
No. of expts.	4	4	4	4
Std. deviation, %	4.3	3.1	3.3	4.1

TABLE III. COMPARISON OF SEVERAL CURCUMIN PRODUCTS

	Vol. of 0.1 N $Ca(OH)_2$ soln., ml.	Absorbance*		
		Blank	1 μg. B	Difference
Koso Chemical Co., Ltd.	5	0.038	0.249	0.211
Tokyo Kasei Kogyo Co., Ltd.	5	0.072	0.380	0.308
Tokyo Kasei Kogyo Co., Ltd.	7	0.075	0.371	0.296
Kanto Chemical Co., Inc.	7	0.069	0.367	0.298
Wako Pure Chemical Industries, Ltd.-Eastman Kodak Co.	7	0.062	0.357	0.295

* Average of 6—12 determinations.

TABLE IV. EFFECT OF FOREIGN SUBSTANCES ON THE DETERMINATION OF BORON

Addition	Absorbance		
	Blank	1 μg. B	Difference
—	0.072	0.380	0.308
1 ml. 0.1 N HCl	0.053	0.373	0.320
2 ml. 1 N HCl	0.031	0.285	0.254
1 ml. 0.2 N H_2SO_4	0.073	0.397	0.324
2.0 ml. 0.2 N H_2SO_4	0.046	0.292	0.246
2.5 ml. 0.2 N H_2SO_4	0.083	0.303	0.220
1 ml. 0.2 N HCOOH	0.224	0.502	0.278
20 ml. H_2O, 50 ml. MeOH	0.082	0.374	0.292
1 mg. U (as UO_2SO_4)	0.080	0.394	0.314

TABLE V. DISTILLATION OF BORON AS METHYL BORATE

Acid solution	B taken, μg.	B found,* μg.	Av. recovery, %
5 ml. 1 : 3 H_2SO_4	1.00	0.82, 0.79, 0.84, 0.86, 0.89, 0.82	84
5 ml. 1 : 3 H_2SO_4, 1 ml. 30% H_2O_2	0.50	0.41, 0.45	86
5 ml. 1 : 3 H_2SO_4, 1 ml. 30% H_2O_2	1.00	0.91, 0.83	87
5 ml. 1 : 3 H_2SO_4, 1 ml. 30% H_2O_2, 1 ml. 0.1 N HCl	0.20	0.20, 0.16	90
5 ml. 1 : 3 H_2SO_4, 1 ml. 30% H_2O_2, 1 ml. 0.1 N HCl	0.50	0.38, 0.44	82
5 ml. 1 : 3 H_2SO_4, 1 ml. 30% H_2O_2 1 ml. 0.1 N HCl	1.00	0.89, 0.81, 0.86, 0.89, 0.89, 0.80	86

* Based on the standard absorbance obtained by omitting methanol distillation (direct color development).

recommended (cf. Table IV). When the glycerol-sodium hydroxide reagent is used, addition of 2 ml. of 1 N hydrochloric acid gives the maximum absorbance. From the data in Table II, it may be concluded that, on the basis of sensitivity and simplicity in manipulation, calcium hydroxide is superior to glycerol-sodium hydroxide (and sodium hydroxide) and that 87% ethanol (=9 : 1) gives most reproducible results. The method of Silverman and Trego(11) is not sensitive enough to be used for the present purpose.

The absorbances of the colored solutions (ethanol and acetone) remain practically constant for 2 hours after the beginning of extraction of colored products. After that there is a gradual decrease in absorbance. The absorbance of a methanolic solution tends to decrease more rapidly than that of other solutions.

For the purpose of studying the influence of curcumin of different origins, several products were examined (Table III).

The effects of some foreign substances on the determination of boron were investigated (Table IV). Five ml. of 0.1 N calcium hydroxide suspension and the foreign substance, with or without 1 μg. of boron, was evaporated to dryness and then subjected to color development. The addition of 2 milliequivalent of hydrochloric acid to 0.5 milliequivalent of calcium hydroxide resulted in about a 20% decrease in absorbance (1 μg. B). If the same quantity of the acid is added to 0.7 milliequivalent of calcium hydroxide, the absorbance is low by as much as 40%. The effect of formic acid was investigated because of the possible formation formic acid during methanol distillation(20). During evaporation of the methanolic solution about 5% of boron is lost. A loss of 4% was reported by Spicer and Strickland(19) during evaporation of methanolic solution in the presence of glycerol-sodium hydroxide reagent.

Separation of Boron from Uranium. — Table V summarizes the results of methanol distillation from sulfuric acid solution. Excess of water was removed by heating and methanol distillation was carried out as described in the procedure. Larsen(21) states that the addition of chloride in catalytic amounts to a mixture of sulfuric acid and hydrogen peroxide increases the rate of solution of uranium very markedly. This is the reason that 0.1 milliequivalent of hydrochloric acid was added in some cases. The effect of this solution method will be discussed later.

On the basis of the standard absorbance obtained by omitting the methanol distillation (i. e., direct color development), the average recovery of 1 μg. of boron from sulfuric acid solution is 84% (standard deviation 4.2%). Addition of hydrogen peroxide to sulfuric acid does not affect the recovery of boron (average 87%). The weighted average of recovery from the sulfuric acid-hydrogen peroxide-hydrochloric acid mixture is 85% (standard deviation 4.9% for 1 μg. B). The loss may be due to incomplete distillation of methyl borate, volatilization of boron during the evaporation of distillate, and slight difference in the composion between the sample solution and the standard solution. Most of the previous papers (cited in Table I) lack the information

TABLE VI. DETERMINATION OF BORON IN URANYL SULFATE

1.0 g. of U (as UO_2SO_4) in 5 ml. of 1 : 3 H_2SO_4 was taken in each determination

B added, μg.	B found, μg.	B recovered, μg.
0	0.10, 0.10	
0.20	0.26, 0.35	0.16, 0.25
0.50	0.48, 0.54	0.38, 0.44
1.00	0.99, 0.94	0.89, 0.84

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20) M. Codell and G. Norwitz, *Anal. Chem.*, **25**, 1446 (1953).

21) R. P. Larsen, *Anal. Chem.*, **31**, 545 (1959).

TABLE VII. DETERMINATION OF BORON IN U_3O_8 AND URANIUM METAL

Sample	B present, p. p. m.	B found, p. p. m.***		
		1	2	3
U_3O_8*	0.5	0.59, 0.57	0.62, 0.60	0.59, 0.57
U metal**	0.23		0.22, 0.22, 0.23	

* New Brunswik Laboratory, NBL-65-3. Certified values of other constituents (in p. p. m.): 0.2 Cd, 12 Cr, 12 Cu, 28 Fe, 6 Mn, 1.0 Mo, 22 Ni, 50 P, 25 Si, 0.6 Ag, 20 V.

** New Brunswick Laboratory analyzed sample No. 16. Other certified values (in p. p. m.): 10 Al, 410 C, 2 Cu, 45 Fe, 1 Pb, 2 Mg, 6 Mn, 45 Ni, 40 N, <1 K, 50 Si, <0.1 Ag, 2 Na, 0.3 Th.

*** Three methods of standardization were studied:

1. Based on the standard curve involving MeOH distillation.
2. Seven ml. of 0.1 N $Ca(OH)_2$ solution evaporated to dryness. Color development followed. +15% correction.
3. Twenty ml. of water and 50 ml. of MeOH evaporated to dryness in the presence of $Ca(OH)_2$. Color development followed. +10% correction.

on the recoveries of boron, and the calibration curves were constructed by including the distillation step. A calculation from the data reported by Muraki and Hiiro[18] gives an apparent recovery of 80% for 0.2~2.0 μg. of boron. Also, a recovery of 75% is calculated from Luke's results[22] that were obtained by the distillation of 0.2~0.6 μg. of boron from chloride solutions.

Known amounts of boron were added to uranyl sulfate (1 g. U) solution and the boron was separated by distillation after removing excess of water (Table VI). A recovery (weighted average) of 87% is obtained with 0.2~1 μg. boron. When a correction factor of +15% (100/87=1.15) is applied, the error is not likely to exceed ±0.1 p. p. m. for this concentration range.

The results of analyses of standard samples of U_3O_8 and uranium metal, obtained in applying the proposed method, are shown in Table VII. The reagent blank (against the blank of direct color development) was about 0.1 μg. of boron. The U_3O_8 sample dissolved in the mixture of sulfuric acid and hydrogen peroxide readily. Three methods of standardization give essentially the same results.

The mixture of sulfuric acid-hydrogen peroxide-hydrochloric acid, described by Larsen[21], does not dissolve uranium readily unless the sample is very fine or thin. Anodic dissolution of uranium appears promising*. Since the solution of U_3O_8 in sulfuric acid and hydrogen peroxide is easily effected, uranium metal was converted in to the oxide by ignition. From the table it is seen that boron is not lost by the heat-treatment. Because the state of this element in uranium is not well known, and other standard metal samples were not available, further experiments were not made.

Summary

Procedure is described for the spectrophotometric determination of 0.1~1 p. p. m. of boron in uranium (metal, U_3O_8, and uranyl sulfate). Uranium metal was first converted to U_3O_8, and the oxide was dissolved in sulfuric acid and hydrogen peroxide. Boron was separated by distillation as methyl borate from sulfuric acid solution, and finally determined by the curcumin method.

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* Larsen[21], and preliminary work of the present authors.

22) C. L. Luke and S. S. Flaschen, *Anal. Chem.*, 30, 1406 (1958).