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Per J. Brown, FSS-16 Date: 11-8-95  
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Per ALDR(TID-1400-82) Sept-Oct 1974

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AN IMPROVED SPECTROPHOTOMETRIC METHOD FOR THE  
DETERMINATION OF BORON IN PLUTONIUM METAL

by

Jack W. Frazer  
Charles F. Metz

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Per NPA - 6-18-79

By Janyado Deb 11-15-95

SPECIAL RE-REVIEW  
FINAL DETERMINATION  
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TECHNOLOGY--PLUTONIUM

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TECHNOLOGY-PLUTONIUM

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ABSTRACT

A modification of a previously developed procedure<sup>(2)</sup> is described wherein plutonium is separated by precipitation as the oxalate and the boron determined in the supernatant, using a modification of Naftel's<sup>(4)</sup> curcumin procedure. The trace amounts of plutonium remaining in the supernatant do not interfere with the subsequent color reaction. No evidence of "carrying" of boron by the plutonium oxalate was found. The range of detection and estimation of boron is from 0.025 to 0.3 micrograms.

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## INTRODUCTION

The problems involved in the analysis of various materials of interest to this laboratory for trace amounts of boron are discussed by Metz<sup>(1)</sup>,<sup>(2)</sup> in Reports LA-303 and LA-340. Among these, requirements of determining submicrogram amounts of boron in materials soluble only in hydrochloric acid, materials containing borides soluble only in nitric acid, and materials containing large amounts of fluoride received special consideration and modifications of Naftel's procedure<sup>(4)</sup> were developed that permitted the determination of as little as 0.05 microgram of boron in such materials. Specifically, procedures were described for the quantitative distillation of methyl borate from a hydrochloric acid solution, from a nitric acid solution and from solutions containing high concentrations of fluoride ion. Complete descriptions of the equipment are given in the above reports and will not be repeated here. Also described are contamination difficulties and the precautions necessary for their prevention in the determination of such micro-amounts of boron involved in this work.

Although the above procedures were considered satisfactory from the standpoint of sensitivity, accuracy and precision, the distillation of such small quantities of boron as methyl borate from plutonium solutions was accompanied by danger from superheating and carry-over of plutonium from too rapid distillation. The quartz stills were expensive and somewhat fragile. The procedure was also rather time con-

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suming. However, as it developed later, one of the most insurmountable difficulties was the procurement of quartz-ware free from boron. When it became necessary to replace the stills due to breakage, it was practically impossible to obtain quartz-ware, from which new stills were fabricated, that was boron-free. In most cases, after months of effort to remove boron from the fabricated stills, they remained unusable because of the high blank. This was finally traced to the conditions under which the flasks, tubing, and joints were manufactured.

The present work was undertaken in an attempt to find a shorter procedure and to eliminate the use of quartz stills and the contamination problems they introduced. At the time of the original work, it was thought that the distillation of boron as methyl borate was necessary because of interference of plutonium with the curcumin color reaction. However, as shown by this work, small amounts of plutonium do not interfere. Thus the necessity for the distillation was eliminated.

#### APPARATUS AND REAGENTS

##### Apparatus

1. Spectrophotometer, Beckman Quartz, Model DU, using Beckman Corex cuvettes having a 1.00 cm light path.
2. Centrifuge, International Clinical, with maximum speeds of from 2000 to 3400 rpm.
3. Twelve Pyrex caps approximately 1 in. deep, to be used as covers

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for the quartz centrifuge tubes during sample dissolving.

Two racks as shown in Fig. 1, made of 1/4-in. plexiglass and the clips of phosphor bronze.

4. Oven, Fisher Junior Drying 10 x 12 x 12 in., 110 volts a.c., 660 watts. A glass air-delivery tube was inserted through one of three original vents in the top of the oven and extended downward along the wall of the oven to 3-1/2 in. from the floor, from where it was run to the center of the oven and down to a point near the floor. Compressed air from the laboratory line was filtered through cotton, passed through a pressure gage, and on through the air-delivery tube in the oven. The air was deflected by striking a 5-in. quartz watch glass placed on the floor of the oven directly under the air-delivery tube outlet. The shelf provided with the oven was removed and in its place was installed a circular shelf 9 in. in diameter. This shelf was made from 1/4-in. mesh copper screening soldered to a half-inch brass ring 9 in. in diameter. Supporting the revolving copper shelf was a brass rod 1/2-in. in diameter and 4-1/2-in. long extending through the center vent, and connected to a small 3-rpm motor. In one of the three original vents was placed a 60° C thermometer having 0.2° C graduations. It was necessary to drill and grommet four more vents in the top of the oven to allow the compressed air to escape. See Fig. 2.
5. 3 Bottles, Quartz, inverted stopper, 250 cc.

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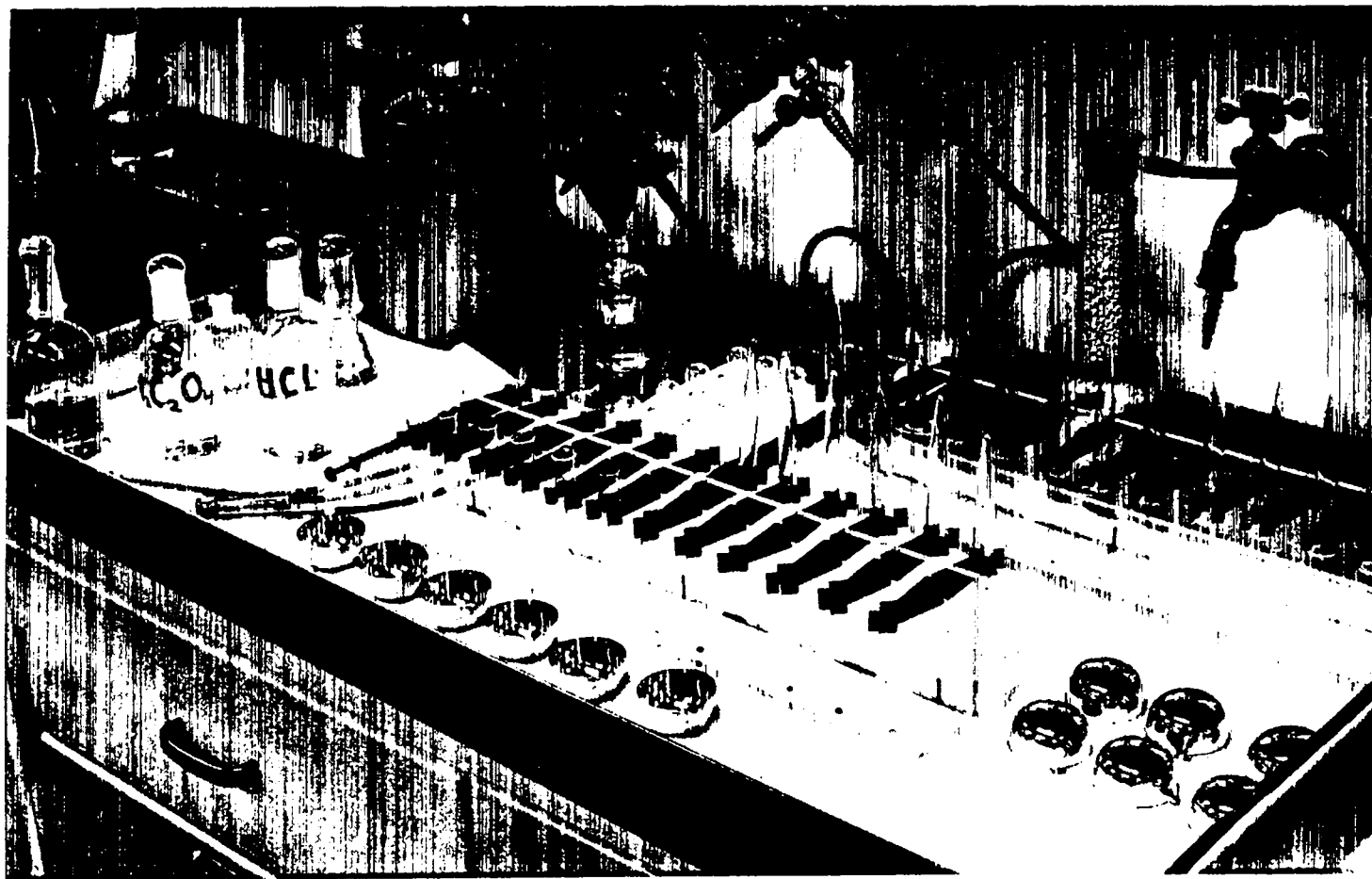


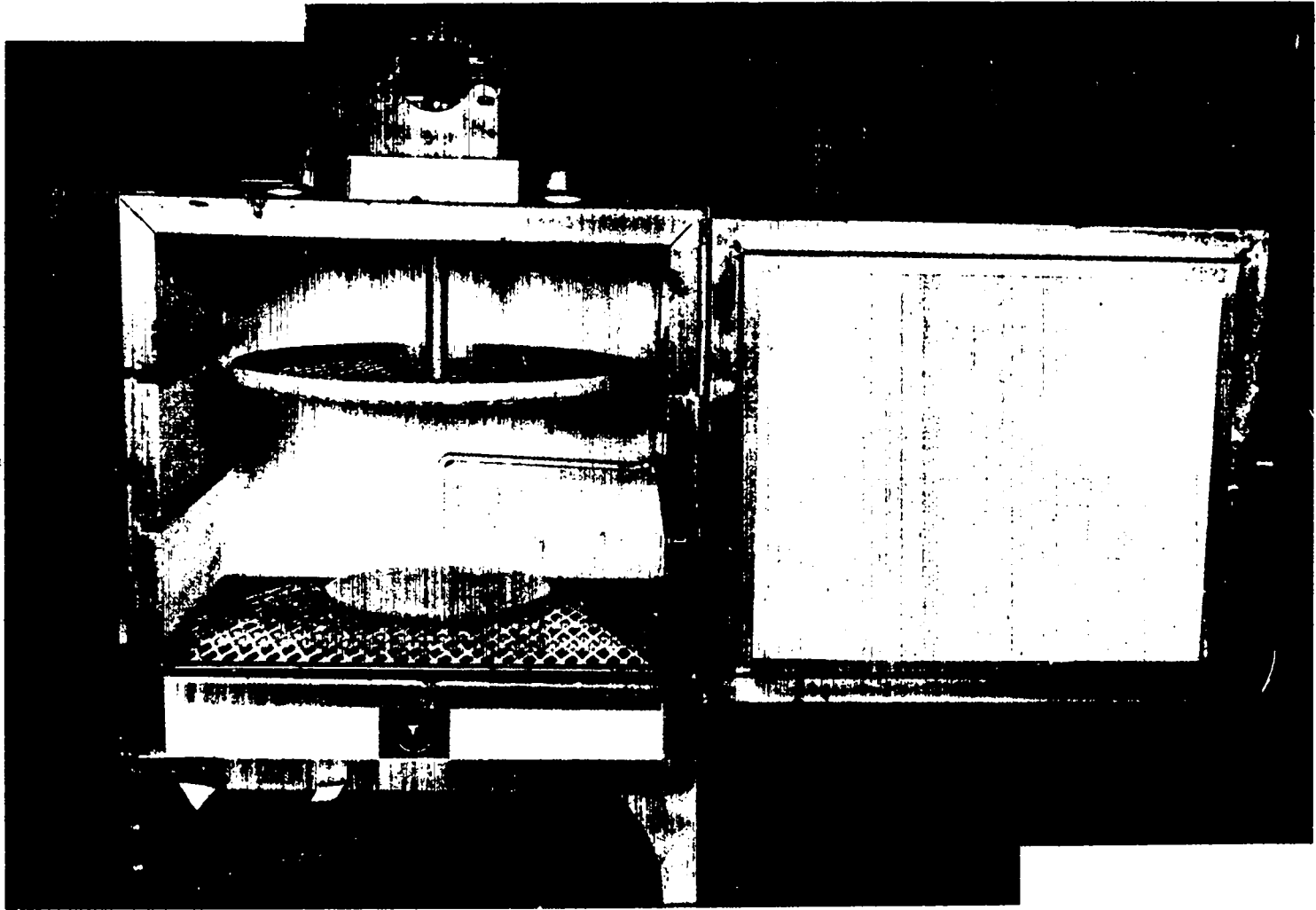
Fig. 1

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Fig. 2

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6. 1 Bottle, Quartz, inverted stopper, 500 cc.
7. 1 Bottle, Quartz, inverted stopper, 1000 cc.
8. 1 Bottle, dropping with pipet, 60 ml.
9. 1 Bottle, dropping with pipet, 125 ml.
10. 12 Dishes, platinum, 55 mm diameter.
11. 1 Flask, volumetric, Quartz, 100 ml.
12. 1 Flask, Erlenmeyer, Quartz w cap 50 cc.
13. 1 Pipet, capillary, 100 microliters, with syringe control.
14. 1 Pipet, capillary, 200 microliters, with syringe control.
15. 2 Pipets, Quartz capillary, 250 microliters, with syringe control.
16. 1 Pipet, Quartz capillary, 500 microliters, with syringe control.
17. 1 Pipet, Quartz capillary, 1.05 ml, with syringe control.
18. 1 Pipet, Kimbel 5 ml, 0.1 ml graduations.
19. 7 Spatulas, platinum, 5 in. long.
20. 4 Syringes, tuberculin, 1 cc.
21. 2 Syringes, hypodermic, 2 cc.
22. 12 Tubes, Centrifuge Quartz, 5 ml.
23. 12 Tubes, Centrifuge Pyrex, 5 ml capacity with 3 ml calibrations.

#### Reagents

Water, distilled from a quartz still and stored in fused-quartz bottles.

Calcium hydroxide, 0.1 N suspension, prepared by adding 0.200 gm of boron-free calcium metal to 100 ml of quartz-distilled water in a quartz volumetric flask. Solutions were kept stoppered and discarded after three days.

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Hydrochloric acid, 6 N, Baker's C. P., usually found to be sufficiently free from boron. The concentrated acid was diluted 1:1 with quartz-distilled water and stored in a quartz bottle.

Curcumin, 0.1 percent in 95 percent ethyl alcohol. Eastman's best grade of curcumin was used. The alcoholic solution was stored in a quartz bottle and should not be kept over ten days.

Ethyl alcohol, 95 percent was re-distilled from sodium hydroxide in a quartz still and stored in Corning 728 glass and quartz.

Oxalic acid, 15 percent. 30 gm of C. P. crystals were dissolved in 200 ml of quartz-distilled water. Stored in a quartz bottle.

Oxalic acid, 11 percent, for analyzing plutonium samples. 21.4 gm of C. P. crystals were dissolved in 200 ml of quartz-distilled water. Stored in a quartz bottle.

Standard boric acid solution. Stock solution prepared by dissolving 35.7 milligrams of  $H_3BO_4$  crystals and diluting to 250 ml with quartz-distilled water. 10 ml of this stock solution diluted to 250 ml contained 1 microgram of boron per milliliter. Both solutions were stored in quartz flasks.

#### EXPERIMENTAL

Since a sufficiently sensitive colorimetric procedure <sup>(3)</sup> already existed, the questions to be answered here were whether plutonium would interfere with the color reaction and, if so, how it might be removed other than by distillation.

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Preliminary work involved dissolving a sample of high-purity plutonium metal in 6 N hydrochloric acid and pipeting 0.5 ml portions of this solution, each containing approximately 50 milligrams of plutonium, into separate 50-ml platinum dishes containing 0.5 ml of 0.1 N calcium hydroxide suspension. To each dish was added a known amount of boron from a standard solution, 0.5 ml 15 percent oxalic acid and 0.5 ml of 0.1 percent curcumin reagent, the dishes placed in the drying oven and evaporated to dryness under the conditions described under RECOMMENDED PROCEDURE. The color was extracted with ethyl alcohol, the extracting solution filtered, made up to volume, and the optical density read on the Beckman Spectrophotometer at 540 millimicrons. The sensitivity was low, but the characteristic color was observed.

A similar series of experiments was performed in which the plutonium was precipitated as the oxalate, the precipitate centrifuged off, the supernatant transferred to platinum dishes, hydrochloric acid and curcumin added, and evaporation and color development carried out as described under RECOMMENDED PROCEDURE.

To determine if the amount of plutonium oxalate precipitated from solution might influence the results, a similar series of experiments was repeated in which the amount of plutonium was increased to 60 milligrams.

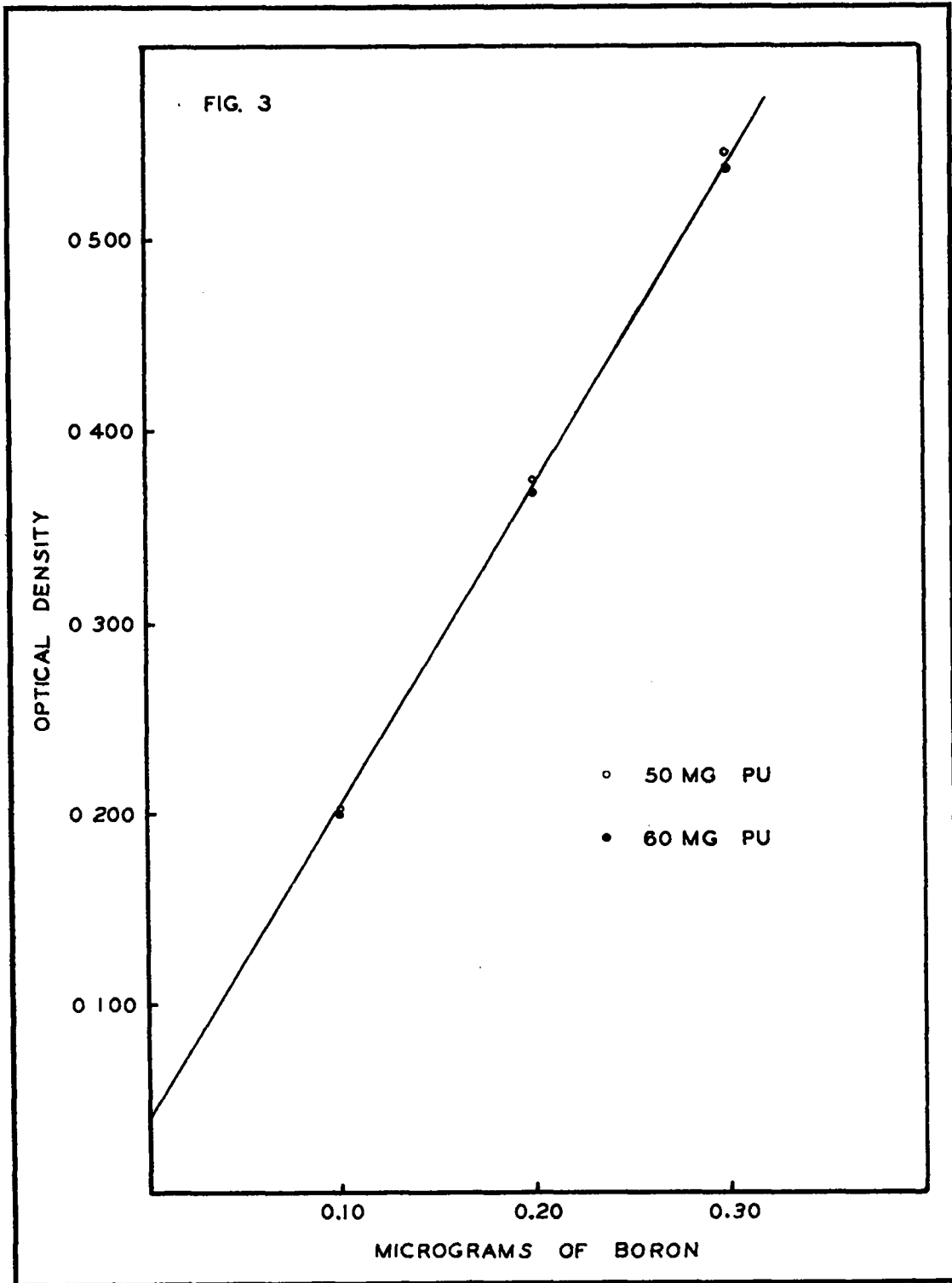
The standard curves as determined from these two sets of data are shown in Fig. 3. A slight difference in the specific extinction

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coefficients was noticeable (1.817 and 1.790). The cause of this was not further investigated. From an operational standpoint, it perhaps is not too significant, due to the desirability of keeping the sample size between 50 and 60 milligrams.

The optical density-concentration curves of Fig. 3 were plotted from the experimental values shown in Table I.

Table I

Optical Density-Concentration Relationships for the Boron-Curcumin Color Reaction

<u>Wt. Pu Precipitated From Solution</u>	<u>Number of Determinations</u>	<u>Micrograms of Boron Added</u>	<u>Mean Optical Density</u>	<u>Percent Standard Deviation</u>
50	18	0.0	0.040	(Blank)
50	18	0.1	0.202	2.78
50	18	0.2	0.375	2.50
50	17	0.3	0.545	2.97
60	12	0.0	0.040	(Blank)
60	12	0.1	0.200	3.34
60	10	0.2	0.368	1.49
60	12	0.3	0.537	3.54

Statistical treatment of the above data indicated that over the range covered and under the conditions of the experiments, 95 percent of the determinations of known amounts of boron were within  $\pm 6$  percent of the known value.

Further checks on the reliability of the method by repeated analyses of portions of samples taken from a larger piece of metal were not made. This was not considered practical because of lack of information

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on the homogeneity of plutonium metal regarding its boron content.

During the course of the investigation it was discovered that somewhat more reproducible results were obtained if the precipitation of the plutonium oxalate was always made from the same volume of solution. Since the boron was always added as a stock solution containing 1 microgram per milliliter, it was necessary to add 0.3, 0.2, and 0.1 milliliter of water, respectively, to those solutions to which 0.0, 0.1, and 0.2 microgram of boron were added. This was incorporated into the analytical procedure by adding 1.05 ml of a 10.7 percent oxalic solution in place of 0.75 ml of a 15 percent solution.

Much has been written<sup>(4),(5)</sup> concerning the relationship between evaporation rate and intensity of color produced by a specific amount of boron. The idea occurred that if any such relationship exists, a constant and uniform rate of evaporation would yield more reproducible results. After first observing that the rate of evaporation of various dishes placed simultaneously in the oven was not uniform and, further, that the slower the rate the less sensitive was the color reaction, a motor-driven, rotating shelf was constructed and installed. This is described under Apparatus and shown in Fig. 2. As a result, the rate of evaporation of the contents of several dishes placed in the oven simultaneously was observed to be quite uniform and a corresponding improvement in the reproducibility of the experimental values was noted.

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Much has also been written concerning the optimum amounts and ratio of hydrochloric to oxalic acid during the evaporation and color-development step. No further investigation of this factor was made in this work but the amounts shown in steps 1 and 3 of RECOMMENDED PROCEDURE have previously been used<sup>(2)</sup> and found to be satisfactory. It is quite likely that other quantities and ratios would work equally well.

The procedure as recommended was found to apply equally well to the determination of boron in high-purity plutonium metal containing up to 1 percent gallium.

#### RECOMMENDED PROCEDURE

##### Caution

Any work involving the handling of plutonium-containing materials should be done under approved conditions and in laboratories designed for the adequate protection of the worker. Rules recommended by the Health Group for the safe handling of such materials should be rigidly followed.

This procedure applies to the determination of trace amounts of boron in high-purity plutonium metal and high-purity plutonium metal containing up to 1 percent of gallium.

1. Using a quartz capillary pipet with syringe control, add 250 microliters of 6 N HCl to each quartz centrifuge tube.\* Cover tubes with the Pyrex caps described under Apparatus.
2. Add a sample of metal weighing between 45 and 65 milligrams to each

\* The amounts of hydrochloric and oxalic acids stated here are sufficient to dissolve the sample and precipitate plutonium(III) oxalate and to provide the necessary excess of these acids, and in the proper ratio, that are required in the color-development step.

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centrifuge tube and immediately replace Pyrex cap. Dissolving is very vigorous, resulting in a fine spray.

3. Using a quartz capillary pipet with syringe control, add 1.05 ml of 10 percent oxalic acid to each tube and stir well with the platinum spatulas.\*
4. Centrifuge the samples two minutes at full speed.
5. Add 0.5 ml of 0.1 N  $\text{Ca}(\text{OH})_2$  suspension to each of the platinum dishes.
6. Using a 0.5 ml quartz capillary pipet with syringe control, transfer the supernatant from the quartz centrifuge tubes to the platinum dishes. If care is taken, practically all the liquid can be removed from the precipitate.
7. Using a quartz capillary pipet with syringe control, add 0.5 ml of 0.1 percent curcumin solution to each of the platinum dishes. Rotate dishes so the liquid will be thoroughly mixed.
8. Place the platinum dishes on the rotating shelf in the oven for one hour and ten minutes at a temperature of  $55^\circ \pm 3^\circ \text{C}$ . Five pounds per square inch air pressure was used. The desired air flow through the oven will require different air pressures depending upon the size of the air-delivery tube, length of connecting hose, and the resistance of the pressure gage. Therefore, it is necessary to select a pressure such that the air flow through the oven will be sufficient to take the platinum dishes containing a normal sample to dryness in 30 to 40 minutes at a temperature of  
\* See note on preceding page.

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55° ± 3° C. This selected air flow should be used for the standard curve calibrations and for all samples thereafter.

9. Remove the dishes from the oven and with 95 percent ethyl alcohol extract the color into a 5 ml Pyrex centrifuge tube. Make volume up to 3 ml with 95 percent ethyl alcohol.
10. Centrifuge and carefully pour the supernatant into Corex cuvettes having a 1-centimeter light path.
11. Read the optical density on a Beckman Quartz Spectrophotometer at 540 mμ wavelength. The reference liquid used may conveniently be 95 percent ethyl alcohol.
12. A reagent blank was determined by the above procedure but with the elimination of steps 2 and 4 and by addition of the reagents mentioned in steps 1 and 3 directly to the platinum dishes prior to adding the 0.1 N Ca(OH)<sub>2</sub> suspension. A new reagent blank should be run whenever fresh reagents are prepared, and whenever there is suspicion that one of the reagents has become contaminated.

Calculation of Results

Weight of Plutonium Sample	50 mg
Optical Density of Reagent Blank	.024
Optical Density of Sample Analysis	.212
Optical Density of Standard Curve Blank	.040
Optical Density of Sample Analysis corrected to standard curve	(.040-.024) + .212 = .228

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The optical density of .228 on the standard curve for a 50-60 milligram sample is found to be equivalent to 0.11 microgram of boron.

#### Cleanliness Precautions

Proper cleaning of apparatus is a very important part of the analysis.

The methods for cleaning each piece of apparatus are:

- (1) Quartz centrifuge tubes are cleaned with concentrated HCl to remove the plutonium oxalate. They are then washed with ordinary distilled water and finally rinsed three times with quartz-distilled water and finally rinsed three times with quartz-distilled 95 percent ethyl alcohol. They are placed in an inverted position in the rack to dry.
- (2) Platinum dishes are filled with concentrated C. P. HCl and allowed to stand at least five minutes. Next they are washed thoroughly with ordinary distilled water and rinsed three times with quartz-distilled 95 percent ethyl alcohol.
- (3) Quartz pipets are rinsed with the liquid to be used.
- (4) The platinum spatulas are stored in a quartz Erlenmeyer flask filled with concentrated HCl. Before using they are rinsed with distilled water and quartz-distilled 95 percent ethyl alcohol and allowed to dry.

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## CONCLUSIONS

1. Small amounts of plutonium do not interfere with the curcumin-color reaction of boron.
2. An improved procedure for determining trace amounts of boron in high-purity plutonium metal and high-purity plutonium metal containing 1 percent gallium was developed in which most of the plutonium is separated by precipitation as the oxalate and the curcumin-color reaction permitted to take place in the supernatant liquid.
3. The rate of evaporation of the curcumin-containing supernatant was found to affect the color intensity caused by a specific amount of boron. A rotating shelf was developed and installed in the drying oven which resulted in uniform drying rates and improvements in the reproducibility of the color intensity.
4. The reproducibility of the procedure for duplicate analyses appeared to be about  $\pm 6$  percent at the 95 percent confidence level.

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