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COLORIMETRIC DETERMINATION OF BORON IN PLUTONIUM METAL

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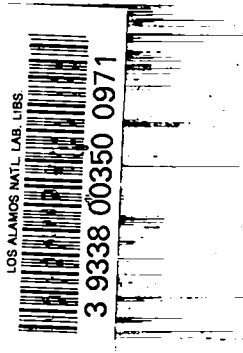
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ABSTRACT

The metal sample is dissolved in a slight excess of 6N HCl. The boron is distilled as methyl borate in a specially designed quartz still. Evaporation of the excess methanol is made on a steam bath in an atmosphere of nitrogen. The boron is estimated colorimetrically using Naftel's curcumin procedure modified to fit the quantities of boron involved. The range of detection and estimation is from 0.05 micrograms to 0.5 micrograms of boron.



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COLORIMETRIC DETERMINATION OF BORON IN PLUTONIUM METAL

INTRODUCTION

This report is a supplement to the longer and more general Report LA-303, which treats the determination of boron in various materials. In fact, some of the work discussed in the general report, such as the analysis of uranium, was carried out with the idea of applying a similar method to plutonium metal. Actually it was possible to use identical methods of analysis for these two metals. Since the same apparatus, procedure and technique were used here, detailed descriptions will not be given except in the cases of actual changes in the procedure. For detailed descriptions of apparatus, procedures for distillation, evaporation and color development, and also for general precautions to be observed, the reader is referred to the general boron report mentioned above.

REAGENTS AND APPARATUS

Following are listed the reagents, their purification and conditions of storage:

Distilled water. Distillation from a double Barnstead still was found to produce water sufficiently low in boron. It was stored in a quartz bottle. If, however, distilled water from such a source is not sufficiently low in boron it should be made slightly alkaline with sodium hydroxide and redistilled through a quartz still equipped with an efficient spray trap.

Calcium hydroxide, 0.1N suspension. This was prepared by adding 0.50 g boron-free calcium metal* to 200 ml distilled water and making up to 250 ml

* Calcium metal essentially free from boron was obtained from the Electro Metallurgical Company, Niagara Falls. The metal was electrolyzed out of a molten bath (free from borates), and was distilled in vacuo in an iron retort.

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in a quartz volumetric flask. A very-fine-grained suspension of $\text{Ca}(\text{OH})_2$ resulted when calcium metal ground to -20 to +80 mesh was slowly added to the water. The suspension was kept stoppered, shaken well before using, and discarded after three days.

Methanol, absolute. Du Pont's methanol was redistilled from sodium hydroxide in a quartz still equipped with an efficient spray trap; it was stored in Corning 728 glass or quartz bottles.

Hydrochloric acid, 6N. Baker's concentrated c.p. acid was found sufficiently free from boron. When removed from the original bottle it was stored in quartz bottles. The concentrated acid was diluted with distilled water and stored in quartz bottles.

Ethyl alcohol, 95 percent. This was redistilled from sodium hydroxide in a quartz still and stored in Corning 728 glass or quartz.

Curcumin, 0.1 percent in 95 percent ethyl alcohol. 0.25 g Eastman's best grade of curcumin was dissolved in 250 ml 95 percent ethyl alcohol and the solution kept in a Corning 728 glass flask.

Oxalic acid, 15 percent solution of c.p. crystals in distilled water. A stock solution was made by dissolving 35.7 mg of c.p. H_3BO_3 crystals and diluting to 250 ml with quartz-distilled water. 10 ml of stock solution diluted to 250 ml contained 1 microgram of boron per ml. Both solutions were stored in quartz flasks.

A complete description of the fused-quartz stills and all other additional apparatus is given in Report LA-303. The only change to be noted is in the Coleman Universal Model 11 Spectrophotometer. For this analysis, the spectrophotometer was equipped with a side-cuvette carrier and Beckman Corex

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cuvettes having a 1.00-cm light path. [REDACTED]

ANALYTICAL PROCEDURE

1. Preparation of the Standard Curve.

It was anticipated that the analysis of plutonium metal for boron would involve quite small quantities of boron because, (1) the amount of metal available for samples would be small and, (2) the desired boron content of the metal would be low. For these reasons it seemed advisable to increase the sensitivity for small quantities of boron. This was done by reducing the volume of the final solution to 3 ml before estimating the optical density. This necessitated using smaller cuvettes than described in Report LA-303. This modification in procedure gave a new standard curve with specific extinction value 2.1. The procedure for preparing such a standard curve was as follows:

2.5 ml of freshly prepared 0.1N Ca(OH)_2 suspension was added to each of four platinum dishes of 40-ml capacity. To successive quadruplicate sets of dishes containing this base were added 0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 micrograms of boron as boric acid, (standard boric acid solution). The contents of each dish was evaporated to dryness in an atmosphere of nitrogen on a steam bath and allowed to cool. Immediately to the contents of each dish was added, (1) 0.25 ml 6N HCl and the dish swirled gently to dissolve all residue, (2) 0.50 ml 0.1 percent curcumin in 95 percent alcohol, (3) 0.50 ml 15 percent oxalic acid and the dish swirled again for final mixing. The dishes were placed in the drying oven described in Report LA-303 and heated for 30 minutes beyond drying at a temperature of $55^\circ \pm 3^\circ\text{C}$. The dishes were then removed and allowed to cool. [REDACTED]

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The color was quantitatively extracted from each residue with 95 percent ethyl alcohol and the solution filtered through a medium-porosity sintered-glass filter into a 3-ml volumetric flask. Final dilution to 3 ml was made with additional alcohol. Each solution was transferred to a Beckman Corex cuvette having a light path of 1.00 cm. The cuvettes were placed in the side carrier and the optical density read on the Coleman Model 11 Spectrophotometer at a wave length of 540 $m\mu$. The reference solution was 95 percent ethyl alcohol. The average of the optical density values for the four or more determinations for each concentration of boron was plotted against micrograms of added boron present. Table I shows the readings obtained and Fig. 1 the resulting standard curve.

Table I

Concentration - Optical Density Data

| Optical Densities | Micrograms of Boron Present | | | | | | |
|----------------------|-----------------------------|-------|-------|-------|-------|-------|-------|
| | 0 | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 |
| | 0.055 | 0.193 | 0.256 | 0.363 | 0.450 | 0.571 | 0.700 |
| | 0.063 | 0.156 | 0.296 | 0.405 | 0.445 | 0.601 | 0.715 |
| | 0.053 | 0.169 | 0.262 | 0.400 | 0.482 | 0.570 | 0.714 |
| | 0.070 | 0.180 | 0.269 | 0.370 | 0.440 | 0.567 | 0.673 |
| | 0.082 | 0.165 | 0.264 | | 0.448 | | 0.692 |
| | 0.052 | 0.154 | 0.289 | | 0.466 | | 0.680 |
| | | 0.190 | 0.260 | | 0.473 | | |
| Average | 0.063 | 0.172 | 0.271 | 0.385 | 0.458 | 0.577 | 0.696 |

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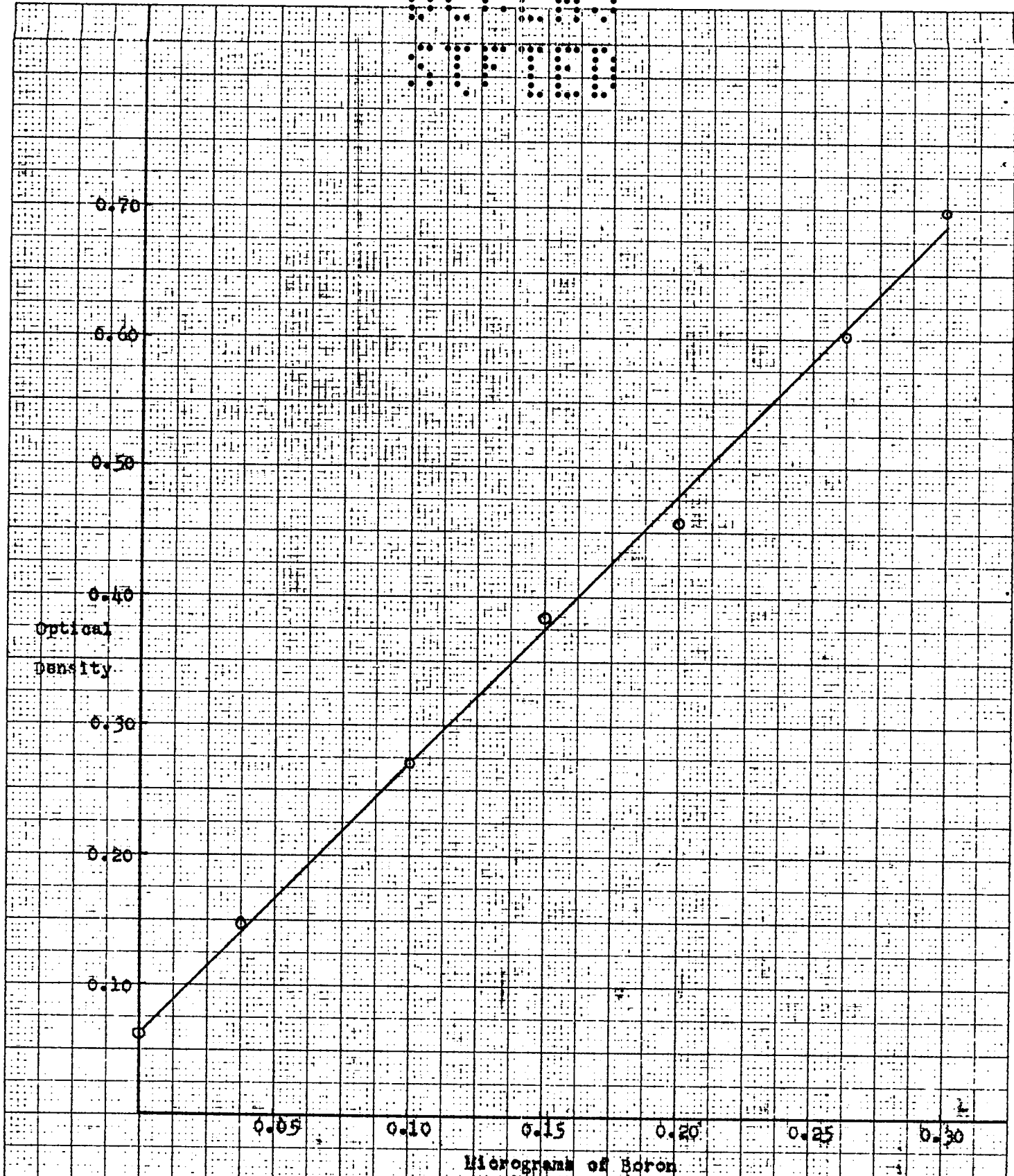


Fig. 1. STANDARD CURVE

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2. Purity of Reagents.

Since it was desirable to employ as pure reagents as possible, it was necessary to determine a "total reagent blank" each time a new lot of any one reagent was prepared or used. It was also necessary to know what portion of the total optical density was contributed by the reagents in order to calculate the boron present in a sample. Serious contamination of one or more reagents, causing a high optical density for the "total reagent blank", necessitated checking individual reagents for purity. This happened infrequently once suitable sources of reagents were obtained. Description of procedures for checking individual reagents are given in Report LA-303.

The total reagent blank was determined as follows: The apparatus was the same as described in Report LA-303. 0.25 ml 6N HCl was pipetted into each of the four quartz distilling flasks. 8 to 10 ml purified methanol was added to each and the flasks immediately connected to the condensers. 45 ml purified methanol was distilled through each flask and collected in 2.5 ml .1N $\text{Ca}(\text{OH})_2$ which had been pipetted into a 50-ml quartz beaker. The receiving beaker was placed in the carbon dioxide-free atmosphere as described in Report LA-303.

Immediately after completion of distillation each beaker, containing the distillate, was placed on the steam bath and evaporated to dryness in an atmosphere free from carbon dioxide (nitrogen gas was used).

The color development and estimation of the optical density were carried out exactly as described on page 6 of this report.

3. Analysis of the sample.

The metal was cut into pieces of approximately 50 mg weight after which the oxide coating was removed in the following manner: The cut pieces

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of metal were placed in a tungsten basket which served as the cathode in an electrolytic cell containing a solution of 50 percent syrupy phosphoric acid and 50 percent ethylene glycol as electrolyte. Platinum wire served as the anode. A current was passed for several seconds which reduced the oxide. The pieces of metal were rinsed in concentrated nitric acid, then in water and finally in acetone and allowed to dry.

The metal pieces were weighed and added to 0.25 ml 6N HCl in the distilling flasks. Energetic dissolving action of the acid liberated some heat although only a very small portion of the distilling flask became warm to the touch. Experiments indicated insufficient heat was generated to cause loss of boron through volatilization. Five minutes or less was usually sufficient time for the sample to dissolve.

After dissolving the sample, 8 to 10 ml purified methanol was added to each distilling flask which was immediately connected to the condenser. 45 ml purified methanol was distilled through the distillation flask, keeping the volume in the flask practically constant. The distillate was caught in 2.5 ml 0.1N $\text{Ca}(\text{OH})_2$ suspension in a 50-ml quartz beaker. The receiving beaker was kept in an atmosphere free from carbon dioxide. Immediately upon completion of distillation, evaporation was made on a steam bath in an atmosphere of nitrogen. After dryness was reached each beaker was cooled. Color development, extraction of color and estimation of optical density were carried out as described above, page 6.

EXPERIMENTAL RESULTS

During the early stages of the work, uranium metal was used as a "stand in" for plutonium. Table II, which is reproduced (in part) from Report LA-303

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Table II

Recovery of Boron From Uranyl Chloride tions

| Added Boron, Micrograms | 0.05 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|--|------|-----|-----|-----|-----|-----|
| | 70 | 91 | 90 | 97 | 94 | 87 |
| | 106 | 79 | 90 | 92 | 91 | 91 |
| Percent Recovery of Boron | 66 | 89 | 94 | 91 | 97 | 95 |
| | 90 | 79 | 87 | 87 | 88 | 86 |
| | 66 | | | | | |
| | 98 | | | | | |
| | 70 | | | | | |
| Number of Determinations | 7 | 4 | 4 | 4 | 4 | 4 |
| Arithmetical Mean, percent | 81 | 85 | 90 | 92 | 93 | 90 |
| Average Deviation from the Mean, percent | 15 | 5 | 2 | 3 | 3 | 3 |

The data indicate smaller and more erratic recoveries in case of 0.05 micrograms of added boron than for larger amounts.

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shows the recoveries obtained for added quantities of boron. The experimental work that led to the data in Table II was as follows: 10 g of uranium metal was added to 8 ml concentrated HCl. H_2O_2 (30 percent) was added until the oxide was dissolved, by conversion to uranyl chloride. An additional 9 ml of concentrated HCl was added to provide an excess of 10 ml of concentrated HCl. Distilled water was added to make a final volume of 100 ml. 1 ml, containing 100 mg uranium as UO_2Cl_2 and 0.1 ml concentrated HCl in excess, was pipetted into the distillation flask, the boron added in the form of boric acid, (standard boric acid solution), and distillation, evaporation, and color development carried out as described above, page 6.

Similar experiments were carried out on recovery of added boron from solutions of plutonium tri-chloride. The metal sample, weighing between 20 and 80 milligrams, and prepared as described on pages 8 and 9, was added to 0.20 ml 6N HCl in the distillation flask. After the sample had completely dissolved, boron was added in the form of boric acid (standard boric acid solution). Distillation of methanol, evaporation and color development were carried out as previously described. Table III shows the data obtained.

Table III contains all the data so far obtained on the recovery of added boron from plutonium solutions. No data have been discarded. There seemed to be no correlation between size of sample and percent recovery. As in the case for uranium (Table II), the recovery obtained for 0.05 micrograms of added boron seemed to be smaller and more erratic than for larger amounts. In the case of 0.05 micrograms of added boron, however, a rather severe test of the method was involved because the boron content of the plutonium metal was two or three times as large as the amount of boron added. The possibility remains, however, that for determining quantities of boron in the neighborhood

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Table III

Recovery of Boron From Plutonium Chloride Solutions

| Added Boron, Micrograms | 0.05 | 0.1 | 0.15 | 0.5 |
|---|------|-----|------|-----|
| Percent Recovery of Boron | 76 | 93 | 85 | 86 |
| | 56 | 104 | 83 | 95 |
| | 82 | 95 | 85 | 85 |
| | 108 | 107 | 100 | 66 |
| | 68 | | | |
| | 108 | | | |
| | 114 | | | |
| | 64 | | | |
| Number of Determinations | 8 | 4 | 4 | 4 |
| Arithmetical Mean, percent | 84 | 100 | 88 | 83 |
| Average Deviation from the Mean, percent | 19 | 6 | 6 | 8 |

of 0.05 micrograms, a reduction of the dimensions of the stills as well as the volume of methanol would increase the recovery factor.

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