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AEC RESEARCH AND DEVELOPMENT REPORT

THE SPECTROPHOTOMETRIC DETERMINATION OF BORON IN PLUTONIUM USING AN OXALATE SEPARATION

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THE SPECTROPHOTOMETRIC DETERMINATION OF BORON
IN PLUTONIUM USING AN OXALATE SEPARATION

ABSTRACT

An improved method for the determination of boron in plutonium is reported. Precipitation of plutonium (III) acid oxalate prior to color development with curcumin results in increased precision, greater speed, and lower costs. Results are presented of a statistical study involving all variables.

INTRODUCTION

Of the several methods reported in the literature for the determination of boron^(1, 2, 3), the spectrophotometric method of Naftel is the best known and most widely used. The procedure, as adapted for routine plutonium analysis at Hanford and Los Alamos, involved separation of the boron as methyl borate by distillation from hydrochloric acid solution in quartz apparatus, and measurement of color intensity produced with curcumin reagent. Disadvantages of this method include poor control of conditions, loss of boron in the evaporation of excess alcohol⁽⁴⁾, time consumption, and cost of equipment.

Intensity of the color developed with curcumin, in the absence of interfering elements, is sufficient to permit detection of submicrogram amounts of boron; work reported here, accordingly, was directed mainly toward a change in the separation step and improved color development conditions. Results of a similar investigation at Los Alamos⁽⁵⁾ show that a rapid and complete separation can be accomplished by precipitation of plutonium as the insoluble oxalate. Boron remains in the supernatant quantitatively.

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EXPERIMENTAL

Fifty milligram samples of plutonium metal were dissolved in 3 ml Lusteroid cones with 2.2 N HCl*. By analogy with the iron-boron system⁽⁶⁾ boron is present in plutonium as the boride, and readily converted to boric acid. The plutonium was precipitated upon the addition of a saturated solution of oxalic acid (22.2% $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 65% ethyl alcohol). Oxalate ion is an excellent precipitant, both because of the very low solubility of $\text{Pu}(\text{HC}_2\text{O}_4)_3$ (ca. 10^{-15} m/l), and because of the beneficial effect of the oxalic acid on color development. Optimum volume of the precipitant is 700 μl for 50 mg of plutonium; the bluish-gray precipitate packs well and has a definite composition corresponding to the above formula. Leaching of the precipitate yielded no boron, and the supernatant was found to contain very little plutonium, indicating that only one separation is necessary. Addition of 1000 μl or more of precipitant, on the other hand, resulted in a light green to gray precipitate, of poor packing characteristics and variable composition.

The supernatant was transferred to a 25 ml shallow platinum dish by means of a quartz pipet, and 250 μl of an alcoholic solution containing 1 g/l curcumin was added. Either quartz or boron-free glass should be used throughout. Results of studies of varying amounts of curcumin showed that color development is unchanged in the range of 0.1 to 0.5 mg. With the 0.25 mg employed, Beer's Law is followed for boron concentrations up to 0.7 μg .

The mixture was evaporated to dryness at 55°C in a special oven which provides a constant temperature and air flow, and identical conditions for each dish by means of a rotating shelf. (See Figure 1 and discussion on apparatus). The residue was taken up in 3 ml of ethyl alcohol and the optical density read at 540 m μ . Blank corrections were determined

* Note - All alcohol and water must be quartz distilled.

by adding the reagents directly to the platinum dishes and repeating the procedure. The spectrophotometer factor would correctly be determined by adding boron to pure plutonium solutions. Owing to the difficulty of obtaining boron-free plutonium, an alternative procedure was chosen. A factor was determined by adding the boron and reagents directly to platinum dishes, then the per cent boron recovery was determined by adding boron to ordinary plutonium samples. The original factor was then corrected for per cent recovery.

SPECIAL APPARATUS

1. Constant Temperature Oven (See Figure 1)

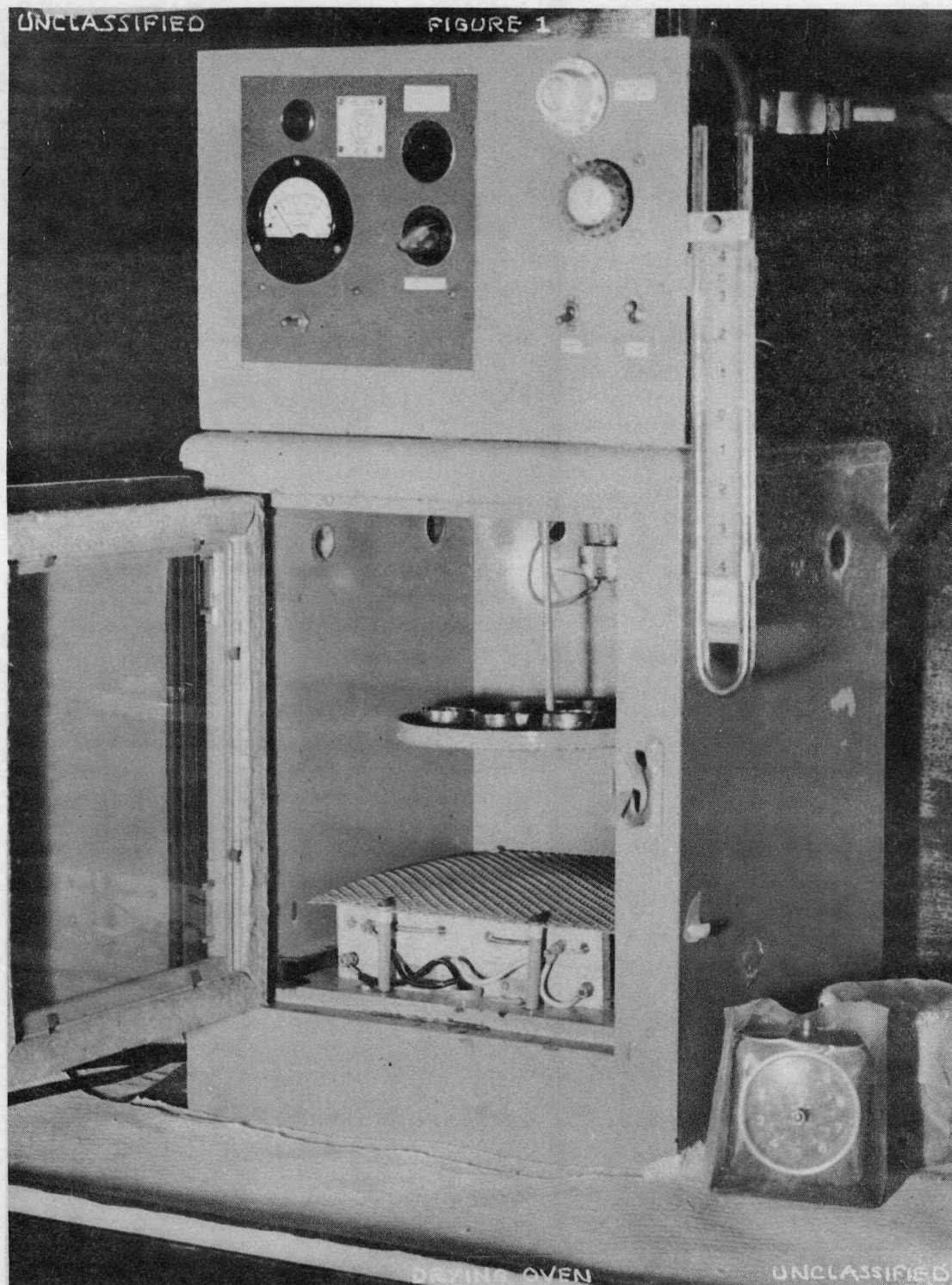
The oven employed in this study is a modified 12"xl2"xl2" Precision Scientific Oven. The heating element and relay are replaced by a 600 watt Calrod element wired to a 5 amp Variac. A smaller element, 100 watt coil, is mounted above the Calrod unit and wired to a Thermocap Relay. This combination will maintain the temperature at $55^{\circ} \pm .2^{\circ}\text{C}$ if a 25 gauge capacitance wire is used and a thermometer with $5.7^{\circ}\text{C}/\text{inch}$. Air at 5# mercury pressure is passed through four jets at the bottom of the oven, over the heating elements, and out through four $3/4$ " holes near the top. A 9" diameter rotating shelf made of $1/4$ " mesh copper screen is connected to a 2 rpm motor. The interior of the oven is coated with an acid resistant paint. For further details of an oven of this type, see report LA-1344.

2. Centrifuge (See Figure 2)

An International Clinical Centrifuge is adapted to hold 16 3 ml centrifuge cones. The brass centrifuging head, Model 215, is fitted with Lucite inserts, each of which is drilled with four $1\ 3/4$ " x $7/16$ " holes.

3. Two magnetic stirring units. One is modified for perimeter stirring of 16 samples simultaneously. (See Figure 3) The original magnet is replaced by a diagonally magnetized Alnico - 5 magnet, measuring 2 " x $1\ 1/2$ " x $1\ 1/2$ ". A Lucite sample holder is made to replace the original aluminum cover.

FIGURE 1



DRYING OVEN

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FIGURE 2



CENTRIFUGE

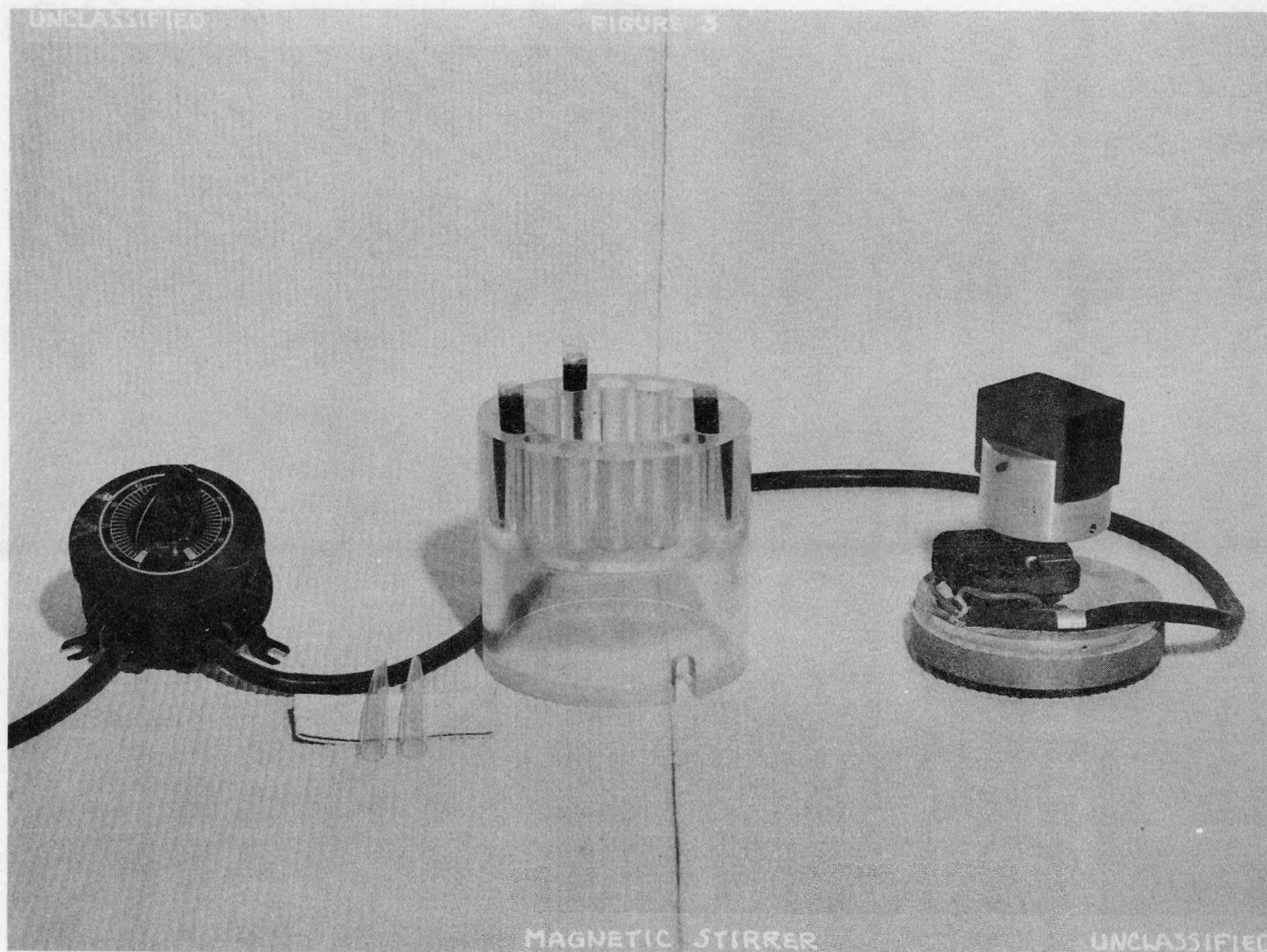
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FIGURE 3

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MAGNETIC STIRRER

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4. Beckman Spectrophotometer, Model DU, and 1 cm Corex cuvettes.

RESULTS AND CONCLUSIONS

Statistical studies were made of all the variables, including concentration of each component in the drying mixture, drying time and temperature. Of the latter two, drying time was found to effect the intensity of the color, faster drying (through increased air flow) causing more color development. The oven temperature should be held to $55^{\circ} \pm 3^{\circ}\text{C}$ for good precision. The use of calcium hydroxide in the analysis, as reported in LA-1344, was studied and found to be unnecessary. Omission of this reagent eliminated a centrifuging step toward the end of the analysis. Alcoholic content of the solutions was varied over a wide range and gave the best reproducibility at concentrations between 40 and 55%. When over 76% was used, esterification of the oxalic acid resulted.

A statistical experiment was made of the two most critical variables, oxalic and hydrochloric acids. The results of this study are listed in Tables I and II. The spectrophotometer factors in units of optical density/ μg boron were determined for four combinations of HCl and oxalic acid, with four concentrations of boron. The units used are millequivalents HCl added and $\text{mg H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ added.

TABLE I

Analysis of Covariance

<u>Source</u>	<u>Sums of Squares</u>	<u>°F</u>	<u>Mean Square</u>
Between the four factors	.009898	3	.003299
Deviations of points from the four lines	.000641	16	.000040
Replications	.000154	24	.000007

TABLE II

<u>HCl (me)</u>	<u>Oxalic Acid (mg)</u>	<u>Factor OD/μg</u>	<u>Sums of Squares of Deviations</u>
.40	90	2.09	.000092
.40	20	1.72	.000073
.12	90	2.68	.000205
.12	20	2.14	.000271

The test showed that both variables had a highly significant effect on the factor, and that low HCl and high oxalic acid constitute optimum conditions. The standard deviation within any one set of conditions was ± 0.007 optical density as compared with ± 0.046 for all conditions.

A precision study was made using conditions as near the optimum as possible (sufficient HCl to dissolve the metal is required), with Fabrication Plant samples and routine analytical personnel. Duplicate analyses were made on each sample. The results of this study are as follows:

Blank mean 0.023 μ g B
Precision, 95% level, blanks ± 0.0072 μ g B
Sample mean 0.046 μ g B
Precision, 95% level, on average of duplicates . . ± 0.0053 μ g B

Variance Analysis

<u>Source</u>	<u>Sum of Squares</u>	<u>°F</u>	<u>Variance</u>
Between samples	1,202.92	38	31.65578
Within samples	39.95	39	1.02435
Total	1,242.87	77	

An "F" test made on these results showed the ratio of the variances for "between samples" versus "within samples" to be highly significant on the 99% confidence level.

PROCEDURE (0.01 - 0.30 μ g boron)

A. Determination of the spectrophotometer factor

1. Pipet a blank and 10, 20, and 30 μ l quantities of standard boric acid solution (5 μ g B/ml) into platinum dishes. Add 400 μ l of 2.2 N HCl and 350 μ l of 22.2% oxalic acid (65% alcoholic). Add 250 μ l of a curcumin solution (0.1% Eastman Curcumin in 95% alcohol) and 350 μ l of 65% ethyl alcohol in water. Swirl to mix.
2. Evaporate the solution to dryness in an oven maintained at $55^{\circ} \pm 3^{\circ}\text{C}$ and constant air flow, leaving 30 minutes beyond dryness. Dissolve the residue in 3 ml of 95% ethyl alcohol and transfer to 1 cm Corex cells and read in the spectrophotometer against ethyl alcohol at a wave length of 540 m μ .

B. Sample Analysis

1. Weigh 50 mg of metal and dissolve slowly with 400 μ l of 2.2 N HCl in a 3 ml Lusteroid centrifuge cone. Add 700 μ l of oxalic acid and stir in the magnetic stirrer. Centrifuge for two minutes at full speed and transfer the supernatant to a platinum dish. Add 250 μ l of curcumin solution.
2. Complete the analysis as above. Reagent blanks should be run concurrently with samples, and after each change of spectrophotometer factor, determine the average per cent recovery by adding 10 μ l of the boron standard to dissolved samples.

SUMMARY

The spectrophotometric determination of boron in plutonium metal using curcumin as the color developing agent has a sensitivity of 0.01 μ g

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and a precision of $\pm 0.005 \mu\text{g}$ (95% confidence level) for the average of duplicate determinations. Fifty milligrams of the metal is dissolved in hydrochloric acid and the bulk of the plutonium removed by precipitation of the oxalate in presence of ethyl alcohol. Curcumin is added and after evaporation to dryness at 55°C the residue is dissolved in ethyl alcohol. The boron content is determined from the absorption measured at $540 \text{ m}\mu$ using a Beckman Model DU Spectrophotometer. The method is empirical, the concentrations of hydrochloric acid, oxalic acid, and ethyl alcohol as well as the drying time and temperature must be controlled. Due to the high sensitivity of the method rigid control of boron contamination is essential. The principle difference in the method reported here and that in LA-1344 is that precipitation is made out of highly alcoholic solution, resulting in a different product. Other differences include omission of calcium hydroxide, modification of the determination of the spectrophotometer factor, and several differences in manipulation techniques.

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