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## ABSTRACTS

Determination of Silicon in Beryllium Metal and Oxide

Modifications have been made in the Carlson and Banks procedure for the determination of silicon in beryllium metal and oxide. The refractory oxide is dissolved directly in hydrofluoric acid. The identical procedure is used for metal after ignition to the oxide.

Fluorometric Determination of Aluminum in Beryllium by Standard Addition

Concentrations of beryllium over certain limits have a quenching effect on the fluorescence of the aluminum-Pontochrome Blue Black R complex. The analysis of trace amounts of aluminum can be carried out despite this quenching effect by the method of standard addition.

The Study of Plutonium Sulfate Tetrahydrate For Use As a Primary Analytical Standard

Samples of plutonium sulfate tetrahydrate prepared 9 to 12 months ago have been under investigation to determine the suitability of this compound as a primary analytical standard of plutonium. The compound has been determined experimentally to contain four molecules of water of crystallization. Plutonium sulfate tetrahydrate was found to lose a major portion of its water of crystallization when heated at 115°C. Indications, but no conclusive evidence, of the existence of another intermediate hydrate of plutonium(IV) sulfate, have been found. Microscopic examination of one-year old crystals of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  shows no evidence of the effect of any alpha radiolysis on the water of crystallization. Continued exposure to a fluctuating atmosphere has caused no apparent changes in crystal structure or weight. Heating  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  to 325°C has produced a dehydrated salt of weight equivalent to the formula,  $\text{Pu}(\text{SO}_4)_2$ . This material, although slightly hygroscopic, can be readily dried at 120°C and appears to be satisfactory for further investigation of its suitability as an alternate primary standard of plutonium.

The Determination of Sulfate in Plutonium Sulfate Tetrahydrate

A method is presented for the rapid determination of milligram quantities of sulfate in pure plutonium sulfates. Plutonium is adsorbed on Dowex-50 cation resin and an acidimetric titration is made of the displaced hydrogen ion which is equivalent to the sulfate content of the sample. A technique used for the prevention of plutonium hydrolysis in neutral solution is described. The method may be applied to the determination of sulfate in any pure plutonium sulfate.

### Uranium in Graphite Waste

A method is described for sampling and analyzing uranium in graphite waste. Sampling data indicate that representative sampling is obtained if the material is pulverized to less than 30-mesh size before reducing to 20 to 50-gram portions for analysis. A  $\text{HNO}_3$  (1+3) digestion is sufficient for extracting the total uranium in the waste material.

### Determination of Uranium in Various Types of Fuel Element Solutions

Details for the preparation of synthetic scrap solutions of (1) uranium-aluminum, (2) uranium-stainless steel, and (3) uranium-Zircaloy-2 are presented. Methods of analysis are described and precision data given for the determination of uranium in these solutions.

### Isotopic Abundance Measurements of Uranium with the Mass Spectrometer

Further evaluation of the isotopic abundance of uranium by mass spectrometric determination has been made, and comparisons are shown for National Bureau of Standards and New Brunswick Laboratory values of standard sample NBS-U-200.

## DETERMINATION OF SILICON IN BERYLLIUM METAL AND OXIDE

A. R. Eberle and M. W. Lerner

In the Carlson and Banks procedure for the determination of silicon in beryllium metal and oxide,<sup>1</sup> the oxide is dissolved in HCl. The resulting solution is treated with a small quantity of HF to convert the silicon to a form reactive for molybdisilicic acid formation. For beryllium metal, the sample is dissolved in NaOH solution to prevent loss of silanes and again the solution is treated with HF, after acidification with H<sub>2</sub>SO<sub>4</sub>, to insure the reactivity of the silicon.

The Carlson and Banks procedure is impractical for routine analysis because highly-fired beryllium oxide either does not dissolve, or dissolves extremely slowly, in HCl. In this study, however, it has been found that by dissolving these oxide samples directly in HF and complexing the fluoride with boric acid, the color development can be carried out in the usual manner.

Another modification is concerned with the analysis of metal powders or chips. Instead of the alkaline dissolution, ignition to the oxide at 1100°C with subsequent dissolution of the oxide in HF is used. No loss of silicon occurs and the blank is considerably reduced. The blank is further reduced by redistilling the HF from a nickel and Monel still. An all-Monel or all-nickel still would be equally satisfactory.

Apparatus and Reagents

Hydrofluoric Acid. Add 50 ml. of water to 150 ml. of 48% HF and redistill from a nickel and Monel still. Collect the first 150 ml. and store in polyethylene. Prepare dilute HF (1+19) from this acid and store in polyethylene.

Molybdate Reagent. Dissolve 25 g. of reagent-grade ammonium molybdate in 200 ml. of water. Add 50 ml. of H<sub>2</sub>SO<sub>4</sub> (2+3). Store in polyethylene.

Reducing Reagent. Dissolve 27 g. of reagent-grade sodium bisulfite, 2.0 g. of NaOH and 0.50 g. of 1-amino-2-naphthol-4-sulfonic acid in water and dilute to 250 ml. Store in polyethylene.

Ammonium Hydroxide. Cool in an ice-bath a quantity of water in a polyethylene bottle and saturate with ammonia gas.

Standard Silicon Solutions. Dissolve 7.56 g. of sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O) and 2 pellets of NaOH in water and dilute the solution to 500 ml. to give a solution containing 2.00 mg./ml. Dilute 5 ml. of this solution to 1000 ml. to give a solution containing 10γ/ml.



## Procedure

Standard Curve. Add to 150-ml. Bakelite beakers 20 ml. of dilute HF, 2.0 g. of boric acid, 4 ml. of molybdate reagent and from 0 to 50 $\gamma$  of silicon. Bring the volume to about 50 ml. and dissolve the boric acid by stirring. Using a meter, adjust the pH to 1.2 to 1.3 with ammonium hydroxide. Allow to stand 15 minutes and then add 30 ml. of HCl (1+1) followed by 2.0 ml. of the reducing reagent.

Transfer the solution to a 100-ml. graduate, dilute to volume and return the solution to the beaker. After 15 minutes, measure the absorbance of each standard in 2-cm. cells at 815 m $\mu$  against water as a reference.

Oxide Samples. To 200-mg. samples of oxide in a 125-ml. platinum dish add 20 ml. of the dilute HF. Warm on a steam bath and stir, adding water occasionally to retain the original volume, until the sample dissolves completely. Dissolve 2.0 g. of boric acid in the warm solution, bring the volume up to about 50 ml., and add 4 ml. of molybdate reagent. Transfer the solution to a Bakelite beaker and continue as described above with the exception that, since the pH will be 1.2 to 1.3 at this point, no pH adjustment is necessary. Measure the absorbance against water and calculate the silicon content by reference to the standard curve.

Metal Samples. Add a 100-mg. sample of powder or thin chips to a 125-ml. platinum dish. Spread the sample evenly and ignite in a muffle furnace at 1100°C for 30 minutes for powders, slightly longer for chips. (If the chips are fairly coarse, crush the particles with a platinum rod occasionally during the ignition period.) Continue as described above for oxide.

## Experimental and Results

Recovery Tests on Oxide. Spectrochemical standards were prepared from a high purity beryllium oxide containing from 0 to 200 p.p.m. of added silicon and many other metallic impurities. Recovery tests with the proposed procedure are shown in Table I. The silicon is recovered completely.

TABLE 1  
RECOVERY OF SILICON ADDED TO BERYLLIUM OXIDE

<u>Silicon, p.p.m.</u>		
<u>Added</u>	<u>Found</u>	<u>Amount Recovered</u>
0	12*	---
10	23	11
30	40	28
100	118	106
200	212	200

\* Average of 4 determinations

Silicon Loss on Heating Hydrofluoric Acid Solution of Oxide. The results in Table 1 show no significant loss of silicon as the tetrafluoride or fluosilicic acid when the oxides are dissolved as given in the proposed procedure. To determine the effect of continued heating of the HF solution of the sample, several samples of oxide were analyzed by: (1) the proposed procedure; (2) by evaporating the initial solution down to 2 to 3 ml.; (3) by evaporating the initial solution down to a moist gummy residue. The results, given in Table 2, indicate that a slight loss may occur if the solution is evaporated to 2 to 3 ml. A significant loss occurs if the sample is evaporated to a gummy residue. It is evident, therefore, that if sufficient water is always present during dissolution of the oxide with HF, no loss of silicon will occur even though the solution is hot and some HF and water is lost by evaporation.

TABLE 2

EFFECT OF HEATING HYDROFLUORIC ACID SOLUTION OF SAMPLE ON SILICON RECOVERY

<u>Sample No.</u>	<u>Silicon Found, p.p.m.</u>		
	<u>Proposed Procedure</u>	<u>Evaporation to 2-3 ml.</u>	<u>Evaporation to Moist Residue</u>
1	218, 223, 222, 221	197	168
2	120, 118, 115, 115	117	100
3	43, 45, 43	45	41
NBL-E-8467	10, 13, 10, 13	12	10

**Analysis of Metal.** Four beryllium metal samples were analyzed by: (1) direct dissolution in HF; (2) dissolution in NaOH solution; (3) ignition to the oxide and dissolution in HF as in the proposed procedure. The results are given in Table 3. Direct dissolution in HF, as expected, causes loss of silicon as silanes. Fair agreement is found between the results of the alkaline dissolution and those obtained by the proposed procedure. The somewhat lower results found with the alkaline dissolution technique may possibly be attributed to the adverse effect of large quantities of sodium ion on the sensitivity of the heteropoly blue procedure.<sup>1</sup>

TABLE 3  
ANALYSIS OF BERYLLIUM METAL BY DIFFERENT PROCEDURES

Sample No.	Silicon Found, p.p.m.		
	Method No. 1 <sup>A</sup>	Method No. 2 <sup>B,C</sup>	Proposed Procedure
1	265	550-590	560, 596, 540
2	391	600-710	710, 740
3	857	1164-1350	1588, 1460
4	713	1390-1550	1883, 1950

- A) Direct dissolution in HF.
- B) Dissolution in NaOH solution.
- C) Range of several values.

REFERENCE

1. Carlson, A. B. and Banks, C. V., Anal. Chem., 24, 472<sup>3</sup>(1952).

## FLUOROMETRIC DETERMINATION OF ALUMINUM IN BERYLLIUM BY STANDARD ADDITION

A. R. Eberle and M. W. Lerner

In a previous report on the determination of aluminum in beryllium,<sup>1</sup> it was noted that concentrations of beryllium over certain limits had a quenching effect on the fluorescence of the aluminum-Pontachrome Blue Black R complex. This quenching effect made the accurate analysis of materials containing less than 100 p.p.m. open to question. Accordingly, another procedure was needed for samples of this type.

In the procedure proposed here, this quenching effect is circumvented by adding aluminum to aliquots of the sample solution in the standard addition technique. The fluorescence of the added aluminum is then compared with that of the sample aliquot without the added aluminum.

Reagents

Pontachrome Blue Black R (Superchrome Blue B Conc. 140%, National Aniline Division, Allied Chemical and Dye Corp., New York 6, N. Y.), 0.1% in ethyl alcohol.

Procedure

Dissolve a 2-g. sample of metal in 40 ml. of  $H_2SO_4$  (1+1). Heat gently on a hot plate until the solution is clear. Cool, transfer to a 200-ml. volumetric flask, and dilute to volume. Transfer about 100 ml. of the solution to a 250-ml. separatory funnel. Add 250 mg. of cupferron and, after mixing, extract the iron and other elements with two 50-ml. portions of chloroform. Discard the chloroform phase. Use the extracted aqueous phase for the determination given below.

Add 10-ml. aliquots of the extracted solution to five 100-ml. beakers. For samples containing less than 50 p.p.m. aluminum, add 1.00, 2.00, and 5.00 ml., respectively, of a standard aluminum solution containing 1  $\gamma$ /ml. to three of the beakers. To a sixth beaker add 10 ml. of 10% (v/v) sulfuric acid as a reference solution. Add to each beaker 25 ml. of 28% ammonium acetate and 10 ml. of water to bring the pH to 4.8-4.9. Heat the solutions to boiling, cool to room temperature, and adjust the volumes to 50 ml.

Adjust the ultra-violet source intensity and sensitivity of the fluorometer to give nearly a full-scale reading with the sample aliquot containing the added 5  $\gamma$  of aluminum, and zero with the reference solution. Measure the fluorescence of the other two aliquots containing added aluminum and the two aliquots containing no added aluminum. Subtract the average of the latter two values from the values obtained

with the "spiked" aliquots to obtain a standard curve for 1.0, 2.0, and 5.0% of aluminum. Calculate the quantity of aluminum in the 10-ml. aliquot by comparing the average reading of the sample aliquots (with no added aluminum) with the standard curve.

For samples containing from 50 to 100 p.p.m. of aluminum, add quantities of aluminum up to 10% to the aliquots. Use a more dilute solution of the sample for the aliquots if the sample contains more than 100 p.p.m. aluminum.

### Experimental

The proposed procedure was tested by analyzing a standard sample, NBS-2686. This sample was analyzed previously<sup>1,2</sup> by the direct procedure, in which the fluorescence suitable aliquots of the sample solution is compared to that of standards containing no beryllium. By diluting the sample to the point at which no significant quenching occurred, a value of 58 p.p.m. was found.

The sample was dissolved and the resulting solution was extracted as described above. Various aliquots of the extracted solution up to 10 ml. were then analyzed by the direct procedure. Additional 10-ml. aliquots were then analyzed by the proposed procedure. The results are shown in Table 1.

TABLE 1

#### COMPARISON OF THE DIRECT AND STANDARD ADDITION PROCEDURES

<u>Method</u>	<u>Concentration of Be in Final Solution, mg./ml.</u>	<u>Aluminum Found, p.p.m.</u>
Direct	0.4	59
Direct	1.0	45, 45
Direct	2.0	32, 32, 32
Standard Addition	2.0	60, 62

The data confirm the quenching effect of concentrations of beryllium as beryllium oxide greater than 0.4 mg./ml. or 0.1 %/ml. or greater of aluminum. The data also show that the standard addition technique can compensate for the quenching effect.

The testing of the proposed procedure on samples containing less than 50 p.p.m. of aluminum is difficult because of the lack of suitable standards in the 0-50 p.p.m. range. Several samples of oxide have been analyzed and found to contain values less than 10 p.p.m. of aluminum but no other comparative values are available at present.

The procedure has also been used on "spiked" samples containing up to 2000 p.p.m. of aluminum. From 96 to 103% of the expected values for aluminum were obtained. The advantage of the standard addition technique here is that separate standard solutions need not be prepared.

#### REFERENCES

1. Eberle, A. R. and Highfill, J. P., NBL-147 (November 1958), pp. 13-15.
2. Eberle, A. R. and Petretic, G. J., NYO-2014 (January 1951).

THE STUDY OF PLUTONIUM SULFATE TETRAHYDRATE  
FOR USE AS A PRIMARY ANALYTICAL STANDARD

G. E. Pietri

Previous experiments showed that plutonium sulfate tetrahydrate could be prepared by evaporating a dilute  $H_2SO_4$  solution of plutonium in the +4 oxidation state. A preliminary evaluation of the composition and stability of  $Pu(SO_4)_2 \cdot 4H_2O$  indicated its suitability for further study. Testing has continued on samples of material prepared up to 12 months ago. The compound has been studied under both fluctuating laboratory conditions and controlled humidity changes. In addition, the thermal stability of  $Pu(SO_4)_2 \cdot 4H_2O$  at higher temperatures has been investigated. The water of crystallization has been determined by analysis. Furthermore, the material has been studied in relation to the possible intermediate hydrates, the formation of anhydrous plutonium sulfate, and the effect of alpha radiolysis on the water of crystallization. Present information indicates that, after one year of testing,  $Pu(SO_4)_2 \cdot 4H_2O$  is sufficiently stable for use as an analytical standard; and that, "anhydrous" plutonium sulfate, as prepared in this laboratory from the tetrahydrate, may prove to be an acceptable alternate standard.

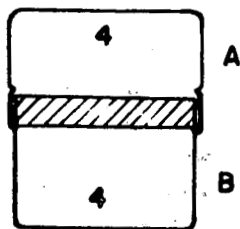
Apparatus and Reagents

Weighing Bottles, conventional Parr-type, 4-ml. capacity, inverted so that the wide cap acts as a base for greater stability in handling, Figure 1.

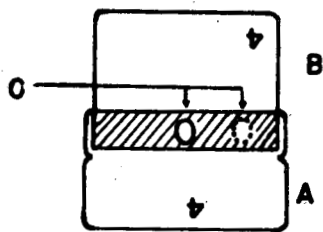
Weighing Bottles, with vent hole, made by drilling a  $1/8$ "-diameter hole in both the cap and body of conventional Parr-type, 4-ml. capacity vessels, at the ground glass interface, Figure 1. The bottles are inverted so that the wide cap acts as a base for greater stability in handling.

Heating Apparatus, consisting of a micro drying oven dome with thermometer ( $-10$  to  $400^\circ C$ ), No. 11-467-12, Fisher Scientific Company, mounted on a thermostatically-controlled hot plate, Fisher No. 11-494. For hydrate and dehydration studies, a thin Nichrome wire is used to support the weighing bottles in the apparatus, as shown in Figures 2 and 3. For determining transition points by the thermocouple method, a Nichrome wire is used to retain a weighing bottle in place so as to allow a Chromel-Alumel thermocouple to be imbedded in the sample and attached to a Brown Recorder (0-10 mv. range), Model No. 153X17V-X-30, Minneapolis Honeywell Company, Figure 4.

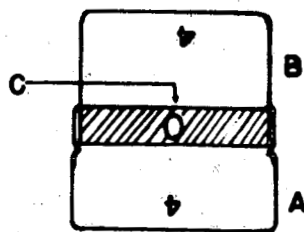
Balance, semi-micro, Model No. B-6, Mettler Instrument Company.



Conventional Bottle,  
Normal Position,  
Capped



Vented Bottle  
Inverted Position,  
Closed



Vented Bottle  
Inverted Position,  
Open

A, 'Top'  
B, 'Bottom'  
C, 1/8-in. vent-hole

FIGURE 1. WEIGHING BOTTLES



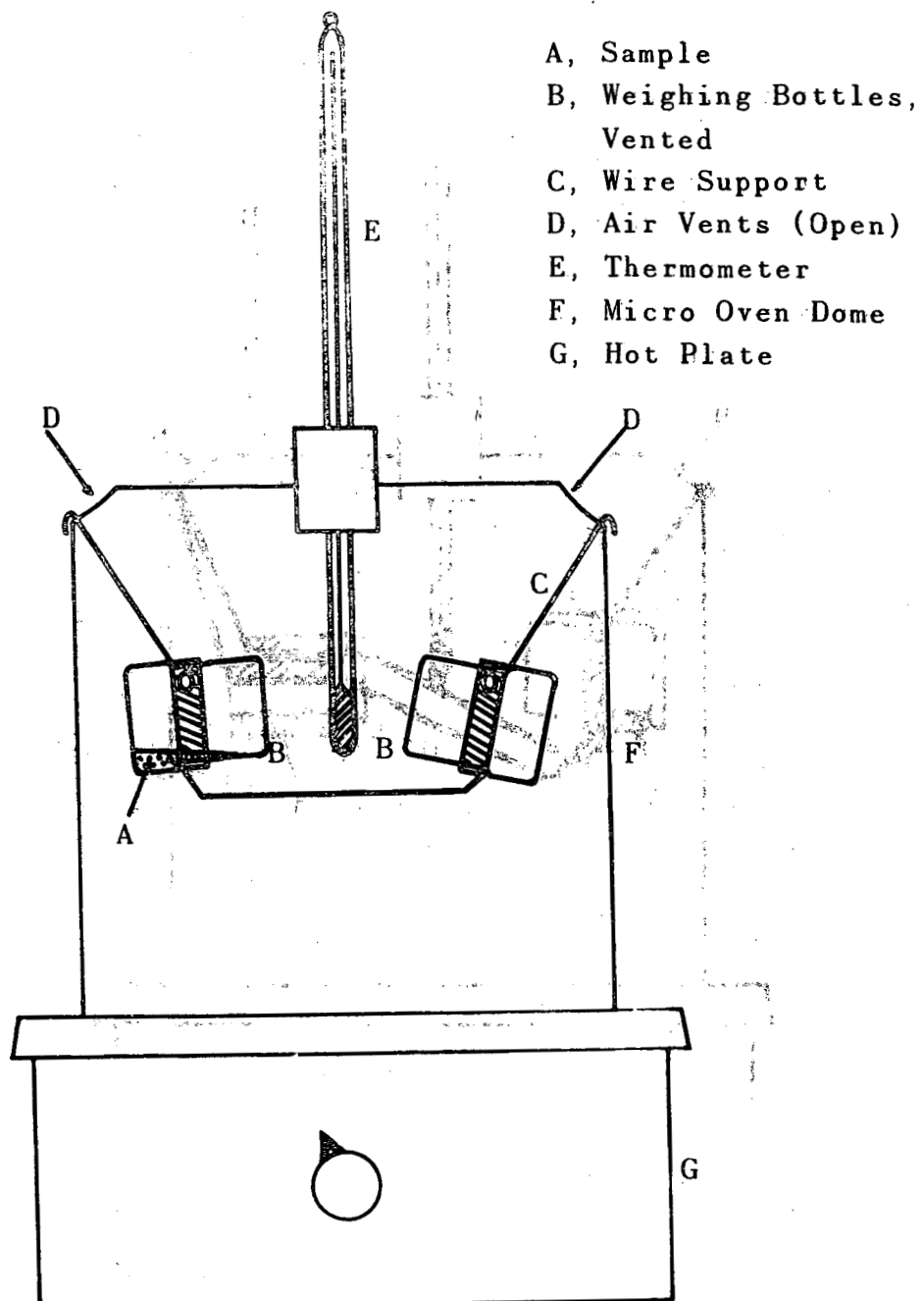


FIGURE 2. HEATING APPARATUS: DEHYDRATION STUDIES

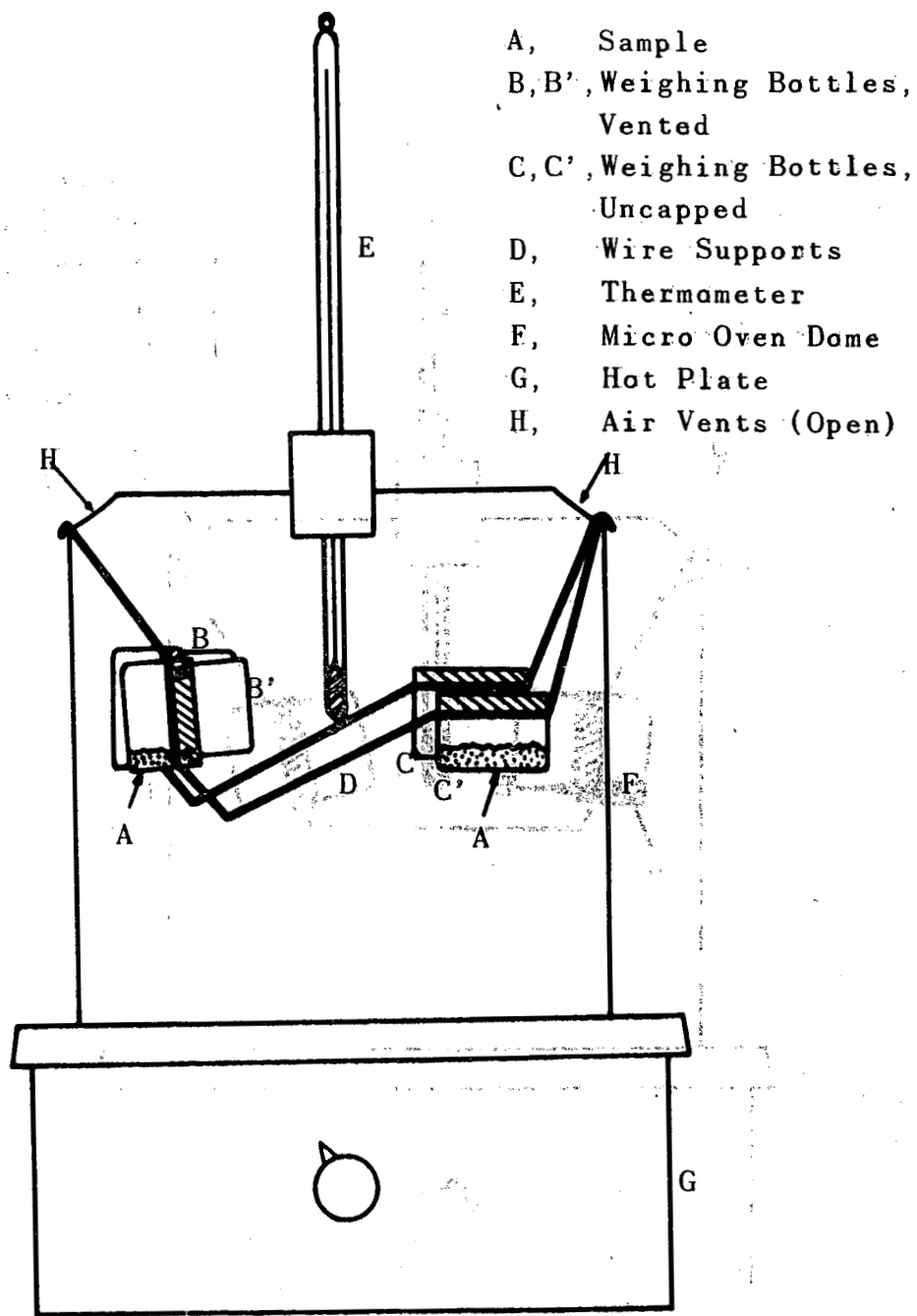


FIGURE 3. HEATING APPARATUS: HYDRATE INVESTIGATION

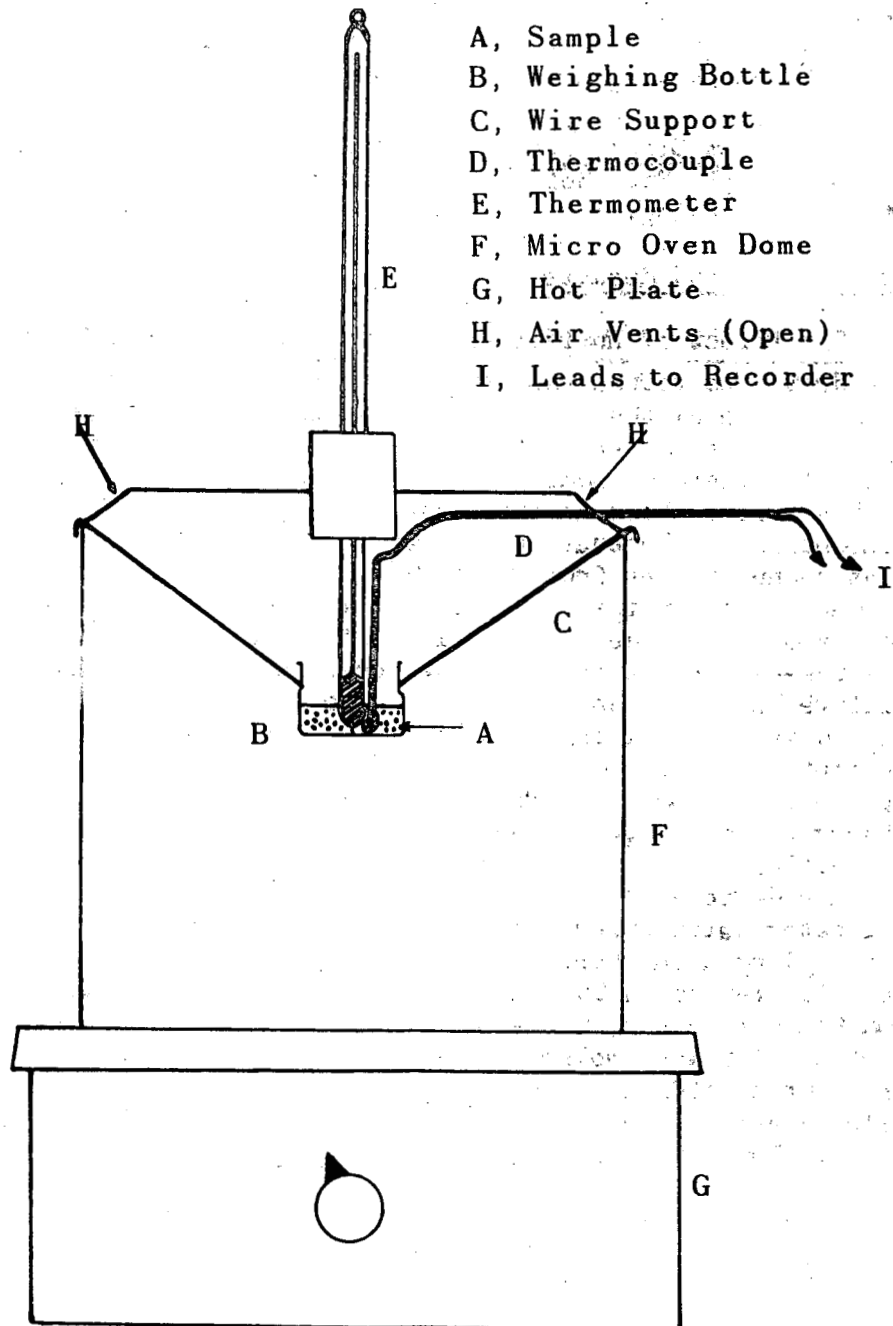


FIGURE 4. HEATING APPARATUS: TRANSITION POINT INVESTIGATION

Microscope, Model No. GK-201, Bausch and Lomb Optical Company, with maximum magnification factor of 75.

Plutonium Sulfate Tetrahydrate,  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , prepared in this laboratory by evaporation of a  $\text{H}_2\text{SO}_4$  solution of plutonium (IV) made from high purity plutonium metal (99.96%) obtained from Handord Atomic Products Operation and Los Alamos Scientific Laboratory.

Potassium Dichromate, National Bureau of Standards primary standard  $\text{K}_2\text{Cr}_2\text{O}_7$ , sample No. 136A, is used directly from its container without preliminary drying.

### Experimental and Results

The Effect of Humidity on  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The adsorbed moisture<sup>2</sup> on hydrated compounds cannot be adequately removed by heating without decomposition of the compound in most cases.<sup>3</sup> For use as a standard material it is important that a hydrate be relatively non-hygroscopic in an atmosphere of some reasonable relative humidity. Previous studies<sup>1</sup> have shown no appreciable weight change of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in a uncontrolled fluctuating laboratory atmosphere nor in known constant relative humidities from 17 to 75%. A series of supplementary tests was made to determine the effect of varying the relative humidity on the compound. Three separate lots of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  of about 2 g. each were taken from the material used previously for testing under static relative humidity conditions. Each lot of material was placed in weighed vented weighing bottles of the design shown in Figure 1 with the vent holes closed, and reweighed. For comparison purposes, an empty weighing bottle tare as well as a bottle containing 2 g. of primary standard  $\text{K}_2\text{Cr}_2\text{O}_7$  were similarly prepared. The vent holes in the bottles were exposed and the samples with tares were placed in the same desiccator. A set of four desiccators was used, each desiccator maintaining a different relative humidity in the range of 17 to 75% by using various concentrations of  $\text{H}_2\text{SO}_4$  as the humidistat, Table 1. Periodically for nearly 4 months, the bottles were removed from the desiccator, the vent holes were closed, and the bottles weighed. The vent holes in the bottles were reopened and the bottles placed in another desiccator for further testing. Results of these tests, Figure 5, indicate that there is no appreciable effect of relative humidity change on  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in the range of 17 to 75%.

TABLE 1

#### SULFURIC ACID HUMIDISTATS

<u>Relative Humidity, %</u>	<u>Sulfuric Acid, Weight %</u>
17	60
36	50
57	40
75	30

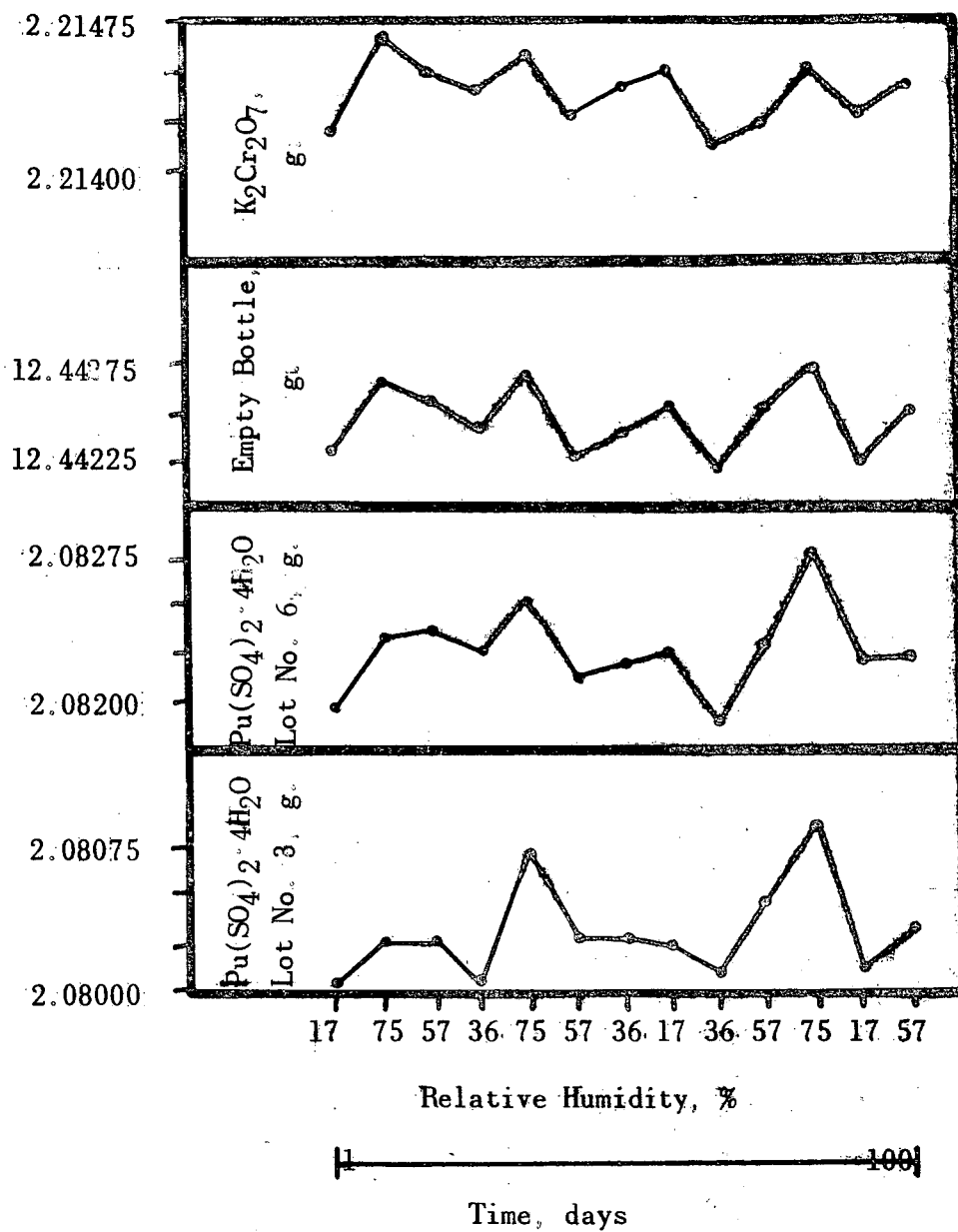


FIGURE 5. VARIATION OF  $Pu(SO_4)_2 \cdot 4H_2O$  WEIGHT WITH RELATIVE HUMIDITY CHANGES

The Stability of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Considerable doubt has been expressed about the stability of a hydrated compound of an alpha-emitter because of the possibility of radiation-induced decomposition of the water of crystallization.<sup>4</sup> Contrary to this theory, the initial investigation of the stability of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  had shown that the plutonium content of the compound had not changed after 5 to 7 months of observation. In additional tests, crystals from five different lots of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  were mounted on the underside of the glass window in the roof of a gloved box, Figure 6. The crystals were held in place by a strip of plastic tape which allowed access to the gloved box atmosphere. A microscope with a 75-power magnification factor was mounted on the top of the glass window and focused on the crystals. Periodic examinations of the crystals were made.

No visible change in the general lots of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  under microscopic examination was noted over a period of 13 months except that in some instances agglomerates of crystals have separated into individual unfractured crystals. In addition, exposure to the fluctuating glovedbox atmosphere during this period, again, has caused no apparent change in the material.

The Thermogravimetry of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Previous tests have shown that when  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  is heated, no significant loss in weight is found up to 60°C. A continuation of this study was made at higher temperatures using three portions of the compound taken from the same lot of stock material in order to: (1) investigate other possible hydrates; and, (2) test the stability of the heated material in air.

In order to trace the course of the dehydration of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  upon heating, a thermogram was run. Two vented weighing bottles, Figure 1, were heated at 110°C for 4 hours, cooled, and weighed. One portion (350 mg.) of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was placed in one of the vented weighing bottles and weighed with the vent hole closed. The second vented weighing bottle used as a tare was also weighed. The vent hole in both bottles was opened, and the bottles were suspended in air in the apparatus shown in Figure 2. Starting at 25°C the material was heated at 5 to 10° intervals for known periods of time. After each heating period, the weighing bottles were removed from the heating apparatus, the vent hole was closed, and the bottles allowed to cool for about 1 hour in air. At the end of the cooling period, the bottles were weighed, prepared for the next heating period, and remounted in the heating apparatus. All samples were heated to apparent constant weight for each heating period up to 100°C. To date,  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  has been heated to 325°C and the data are presented in the graphs, Figures 7, 8, and 9. Further heating of the material at even higher temperatures is anticipated in order to complete the thermogram. As noted in a previous investigation, the first small but

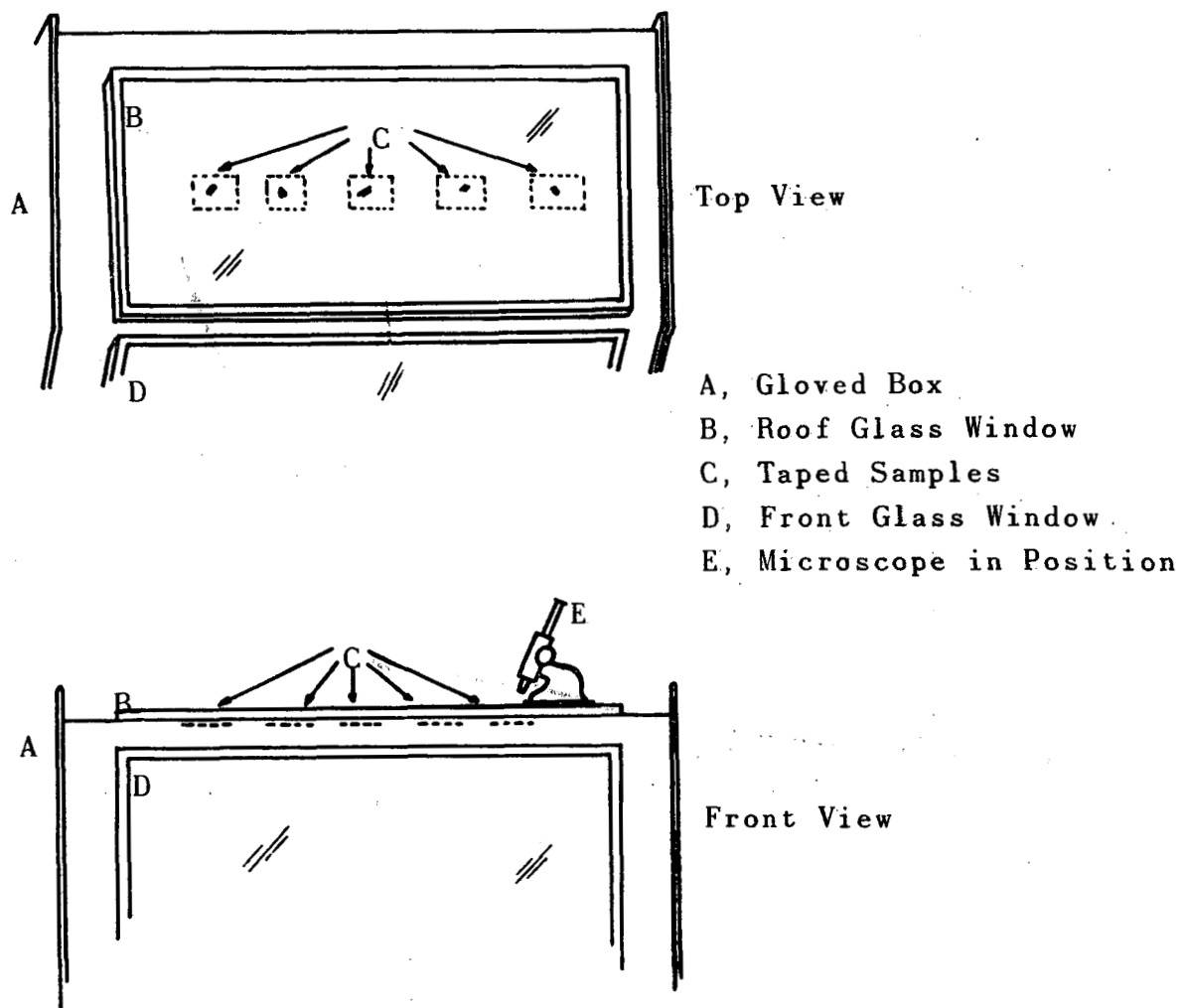


FIGURE 6. MICROSCOPIC EXAMINATION OF  
 $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  CRYSTALS IN GLOVED BOX

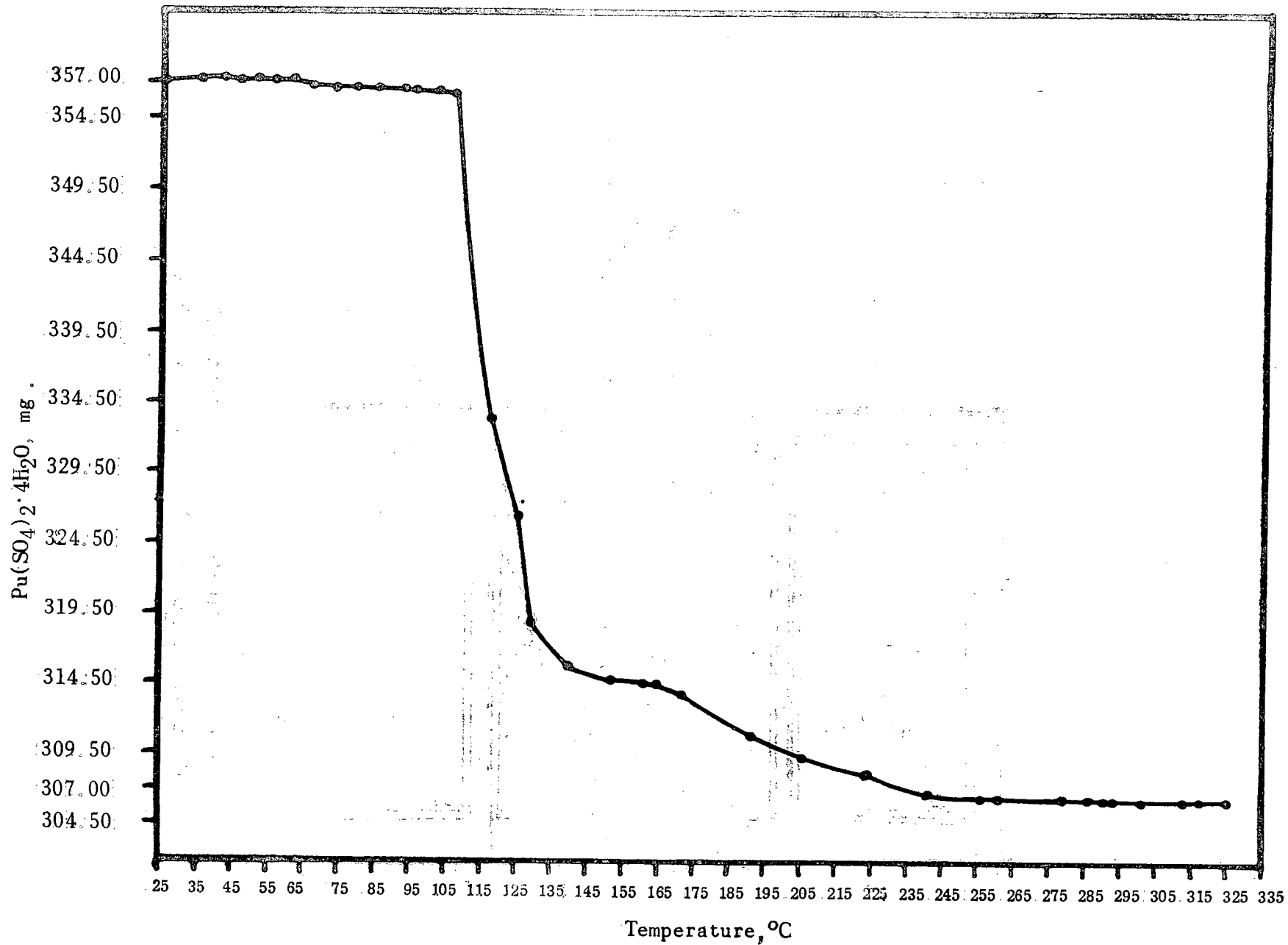


FIGURE 7. WEIGHT CHANGE OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  WITH TEMPERATURE (24 to 324°C RANGE)



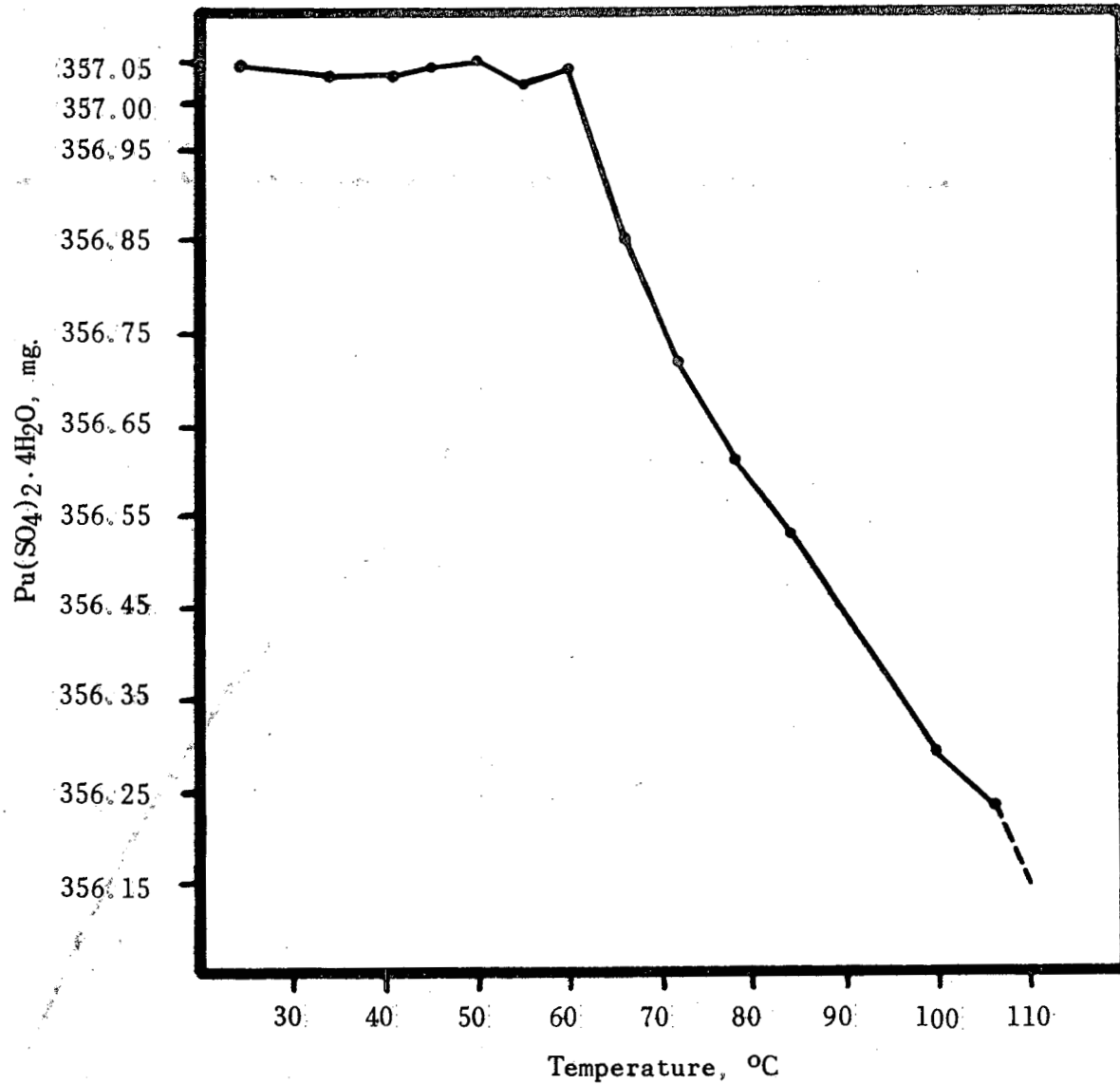


FIGURE 8. WEIGHT CHANGE OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$   
WITH TEMPERATURE (24 to 106°C RANGE)

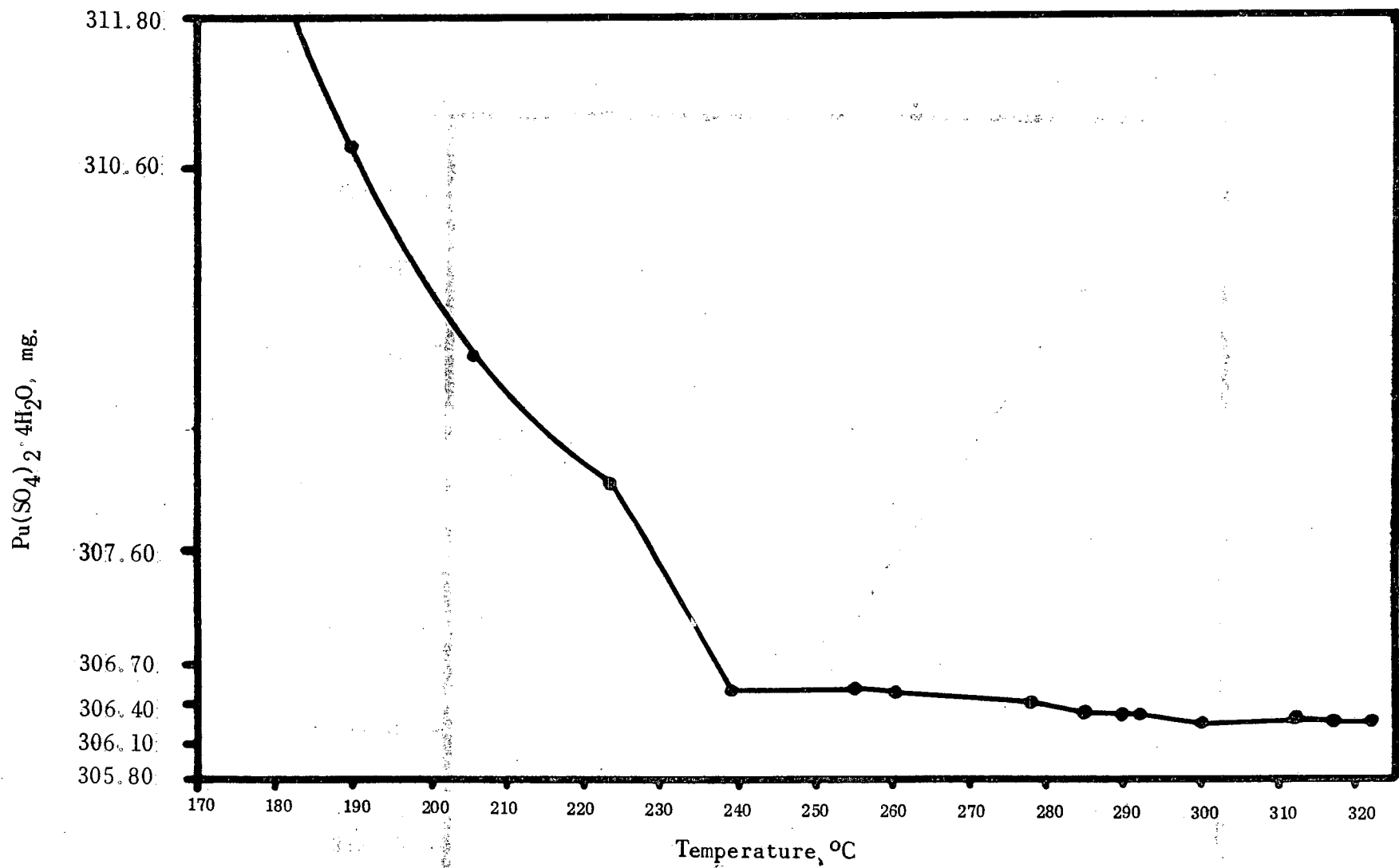


FIGURE 9. WEIGHT CHANGE OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  WITH TEMPERATURE (180 to 325°C RANGE)

significant loss in weight (0.05%) occurred at about 65°C. Present tests show an increased loss (0.2%) at 100°C and a major weight loss at 116°C. The material continued to lose weight up to about 150°C at the prescribed heating rate of 5 to 10°C per 24 hours. From 150 to 165°C, the rate of weight loss slowed slightly to give a short plateau in the curve which may indicate the existence of another hydrate of plutonium sulfate. At 240°C, the compound appeared to have approached constant weight. From 280 to 325°C the sample weight varied less than 1 part in 1000, as shown in Table 2. The average weight loss in this range was found to be 14.23% as compared to a theoretical value of 14.32% for the complete loss of water upon formation of the anhydrous salt from plutonium sulfate tetrahydrate. These results indicate that the hydrated plutonium(IV) sulfate prepared in this laboratory contains four molecules of water crystallization. Previous work had only estimated this value empirically by subtracting the sum of the experimentally determined plutonium and sulfate content from 100 percent. Table 3 compares these values.

TABLE 2

WEIGHT VARIATION OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  WITH TEMPERATURE

<u>Temperature, °C</u>	<u><math>\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}</math>, g.</u>
278	0.30639
285	0.30631
290	0.30630
292	0.30628
300	0.30620
312	0.30627
317	0.30623
324	0.30621

TABLE 3

WATER OF CRYSTALLIZATION IN  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ 

<u>Method</u>	<u><math>\text{H}_2\text{O}</math> Molecules</u>	<u><math>\text{H}_2\text{O}</math> Percent</u>
Theoretical	4.00	14.32
Empirical	3.96	14.20
Experimental	3.97	14.23

Other investigators<sup>5,6</sup> have prepared an "anhydrous" plutonium sulfate by other means and have found the material to be very hygroscopic. Accordingly, a qualitative study of the stability in air of the anhydrous plutonium sulfate as prepared in this laboratory was started. The

"dehydrated"  $\text{Pu}(\text{SO}_4)_2$  obtained by heating the tetrahydrate to various temperatures between 290 and 325°C was exposed to uncontrolled laboratory atmosphere of relative humidities of about 60 and 70% for various periods of time. The weight of the compound before and after exposure was recorded. The results presented in Table 4 show that a small but significant amount of moisture was absorbed after 24 hours at 60% relative humidity by  $\text{Pu}(\text{SO}_4)_2$  formed at about 290°C. Plutonium sulfate formed at about 325°C was more resistant to moisture absorption at 60% relative humidity. At about 70% relative humidity this material absorbed moisture within 24 hours. In all cases, the original weight of the material before exposure to the atmosphere was obtained by heating either at the temperature of formation of the compound or at 120°C, Table 5. Moreover, there was no difficulty encountered in weighing the material to constant weight in an atmosphere of 70% relative humidity using normal techniques, Table 6.

TABLE 4

STABILITY OF "ANHYDROUS  $\text{Pu}(\text{SO}_4)_2$ " IN AIR

<u>Relative Humidity, %</u>	<u>Temperature of Formation, °C</u>	<u>Testing Period, hours</u>	<u>Weight Gain, <math>\text{Pu}(\text{SO}_4)_2</math>, %</u>
60	290	24	0.05
60	290	96	0.61
60	325	4	<0.01
60	325	28	0.06
60	325	44	0.05
60	325	68	0.03
60	325	92	0.06
70	325	72	0.25
70	325	96	0.52

TABLE 5

EFFECT OF REHEATING MOIST "ANHYDROUS  $\text{Pu}(\text{SO}_4)_2$ " AFTER EXPOSURE TO AIR\*

<u>Temperature of Formation, °C</u>	<u>Initial Weight of Sample, g. **</u>	<u>Reheating temperature, °C</u>	<u>Final Weight of Sample, g.</u>
290	0.30628	290	0.30630
290	0.30628	120	0.30627
325	0.30621	325	0.30619
325	0.30621	120	0.30614
325	0.30621	120	0.30617

\* at relative humidities of 60 and 70%

\*\* at temperature of formation

TABLE 6

STABILITY OF "ANHYDROUS  $\text{Pu}(\text{SO}_4)_2$ " WEIGHINGS IN AIR \*

<u>Time, minutes</u>	<u>Weight, g.</u>
0	0.30621
15	0.30620
30	0.30618
45	0.30625
60	0.30622
75	0.30626
90	0.30617

\* at relative humidity of 70%

Since the thermogravimetric examination showed that a considerable loss in water of crystallization occurred at about  $115^\circ\text{C}$  and a short period of relatively stable weight occurred at  $150^\circ\text{C}$ , the second and third portions of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  were heated at approximately  $115^\circ\text{C}$  in order to obtain information about other possible hydrates. Two vented weighing bottles and two conventional weighing bottles of the type shown in Figure 1, were heated at  $110^\circ\text{C}$  for 4 hours, cooled, and weighed. One portion (600 mg.) of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was placed in a vented weighing bottle and weighed with the vent hole closed. An empty vented weighing bottle for use as a tare was also weighed. For comparison purposes, the other portion, 600 mg. of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was placed in the lower half of a conventional weighing bottle, capped, and weighed. A similar empty vessel was weighed for taring purposes. The four weighing bottles, vented ones with the vent holes exposed, and the conventional ones with the caps removed in order to allow greater access to the atmosphere, were suspended in air in the heating apparatus shown in Figure 3. The temperature of the heating apparatus was maintained at  $120^\circ \pm 2^\circ\text{C}$  by manipulating the rheostat of the thermostatically-controlled hot plate until the thermometer reached the desired temperature. Periodically, the weighing bottles were removed from the heating apparatus, either capped or their vent holes closed, and allowed to cool in air for 1 hour. At the end of the cooling period, the weighing bottles were weighed, prepared for further heating as before, and returned to the heating apparatus. Examination of the results available at this time, Figures 10 and 11, indicates that by the method used at this laboratory: (1) the complete removal of the water of crystallization of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  at  $118$  to  $122^\circ\text{C}$  is a very slow process; (2) there is no significant difference in the rate of weight loss in a sample with large exposed surfaces (uncapped weighing bottle) or in material having less access to air (vented weighing bottle); (3) there is no conclusive evidence of intermediate hydrates of plutonium(IV) sulfate containing between 1 and 4 molecules of water. An apparent inflection in the graph does occur,

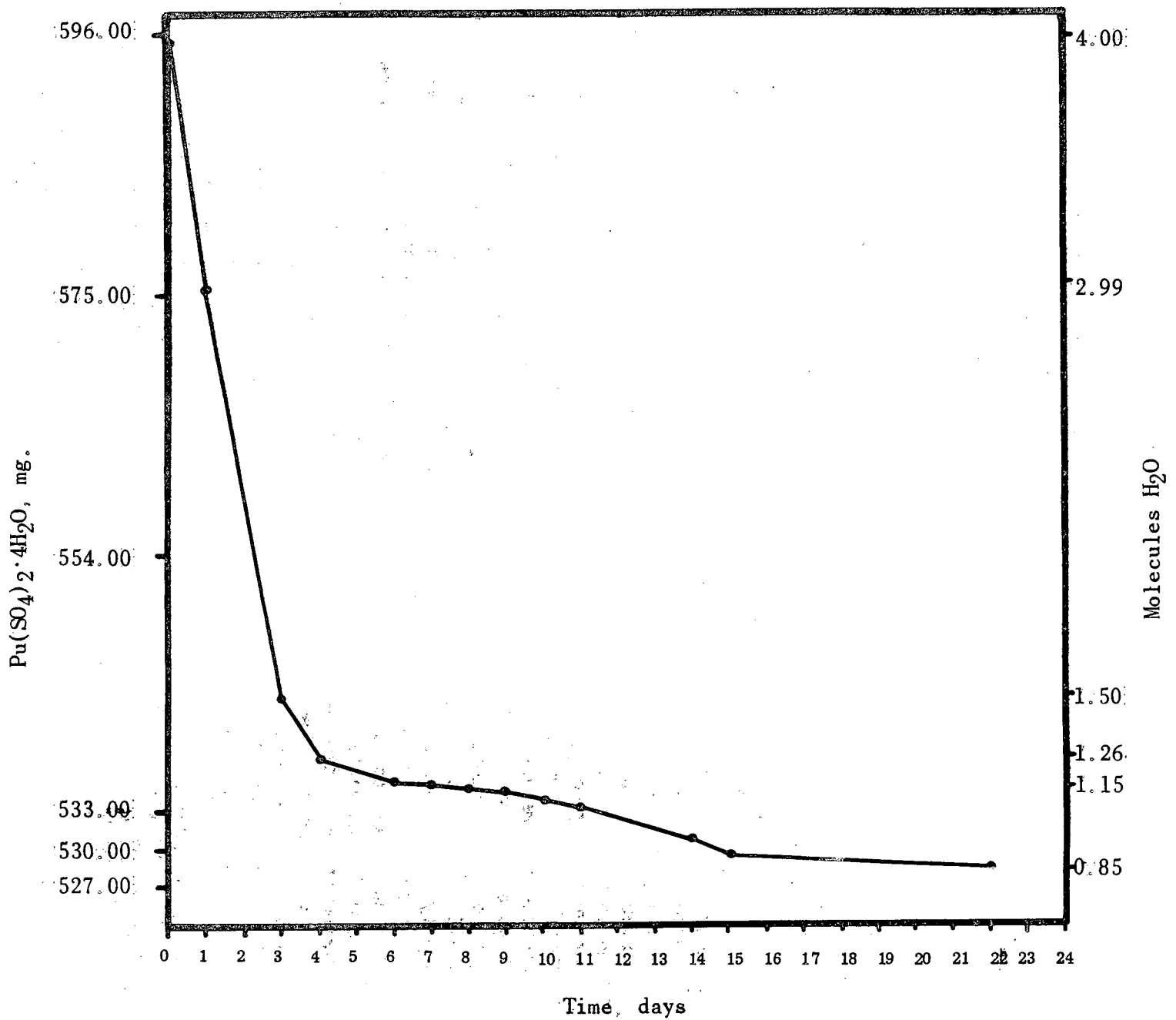


FIGURE 10. LOSS OF WEIGHT OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  at  $120 \pm 2^\circ\text{C}$  IN VENTED WEIGHING BOTTLE

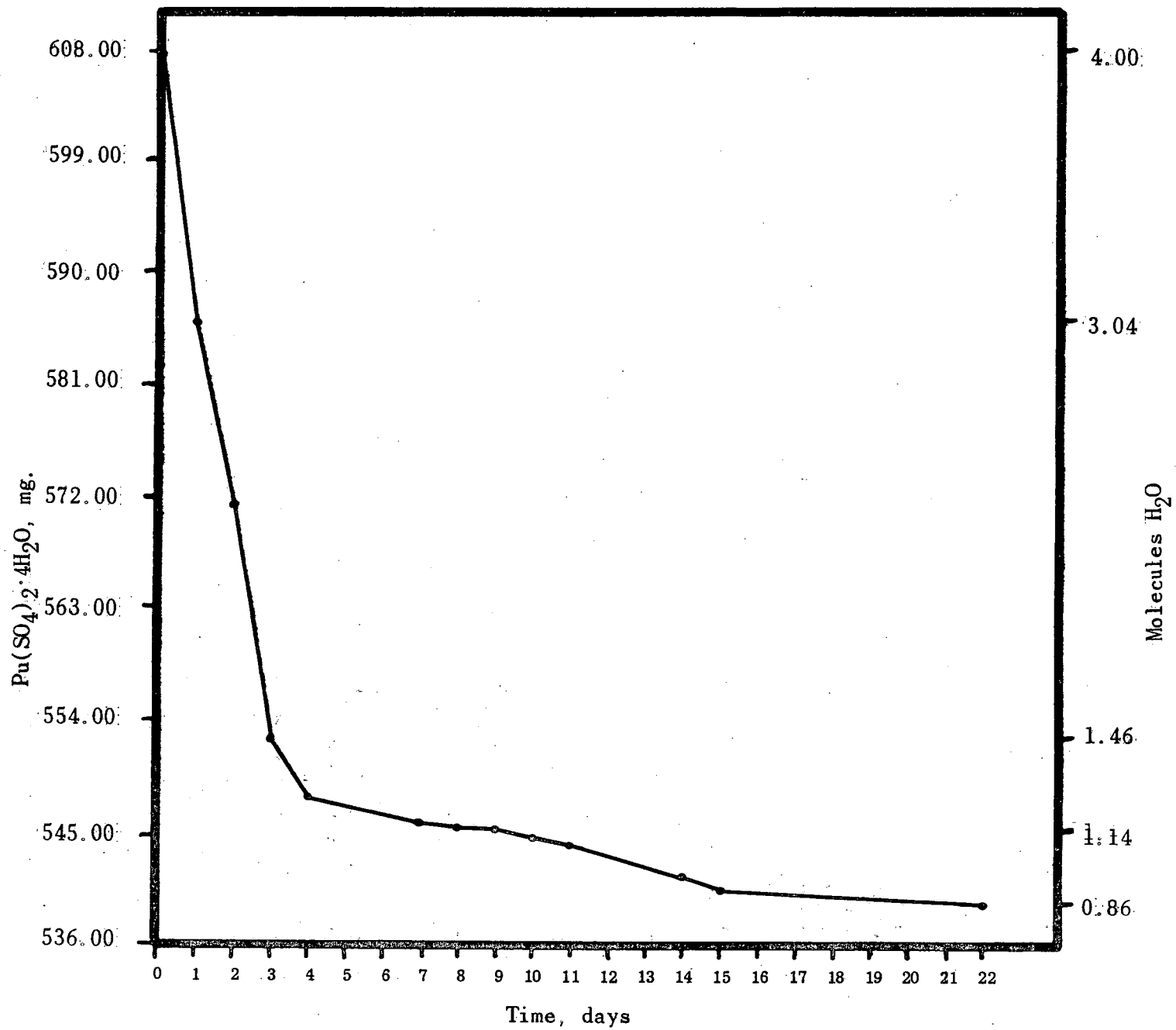


FIGURE 11. LOSS OF WEIGHT OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  AT  $120 \pm 2^\circ\text{C}$  IN UNCAPPED WEIGHING BOTTLE

however, at a point where the weight of the compound is equivalent to plutonium sulfate with 1.15 molecules of water. Further investigation of possible hydrates at this point and with less than one molecule of water is being made.

Preliminary tests on the thermal stability of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  using the thermocouple method showed an "apparent phase transition temperature" at about  $60^\circ\text{C}$ . The heating curve for the compound became non-linear after about  $110^\circ\text{C}$  and no further work at or above this temperature was attempted. With the discovery of a large loss of weight when the hydrate was heated at  $115^\circ\text{C}$ , a reinvestigation of the phase transition at this temperature was started. Using the apparatus shown in Figure 3 and the procedure previously used, two portions (375 mg.) of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  from one lot of material prepared nine months previously, were heated from  $25^\circ$  to  $140^\circ\text{C}$ . The temperature rise of the oven was regulated to about  $5^\circ\text{C}$  per minute in order to produce a linear response on the recorder at about  $110^\circ\text{C}$  when an empty weighing bottle was heated, and to detect more easily any inflection in the curve when the sample was heated. A plot of the heating curve of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in Figure 12, again shows a slight divergence from linearity at about  $110^\circ\text{C}$ . Further work is contemplated to determine the nature of these two points.

### Discussion

The overall accuracy expected in the determination of the effect of changes in controlled relative humidity on  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , Figure 5, was not attained because of a number of unavoidable occurrences which arose during the testing period. Weight changes of the weighing bottles used showed that the outer glass surfaces inconsistently gained or lost varying amounts of water up to about 0.6 mg. from one weighing to another. This situation was remedied to some extent by wiping the bottles after removal from the desiccator and allowing them to equilibrate for 10 minutes in air. This technique, however, did not correct any adsorption-desorption process on the inner surfaces of the vessels. The moisture problem was a constant source of discrepancy in the tests as it prevented both the samples and the tares from returning to their true weight when placed in the same relative humidity again. It is now apparent that the previous humidity tests in static and fluctuating atmospheres made in this laboratory were also affected to some extent with this condition which has been experienced by other investigators.<sup>7</sup>

Initial studies indicate that the anhydrous  $\text{Pu}(\text{SO}_4)_2$  prepared from  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  crystals, by heating to constant weight at about  $290$  to  $325^\circ\text{C}$ , Figure 7, may be useful as an alternate analytical standard for plutonium and warrants further investigation. Experimental work suggests that the mode and temperature of preparation, Table 4, may govern the hygroscopic properties of anhydrous plutonium sulfate.



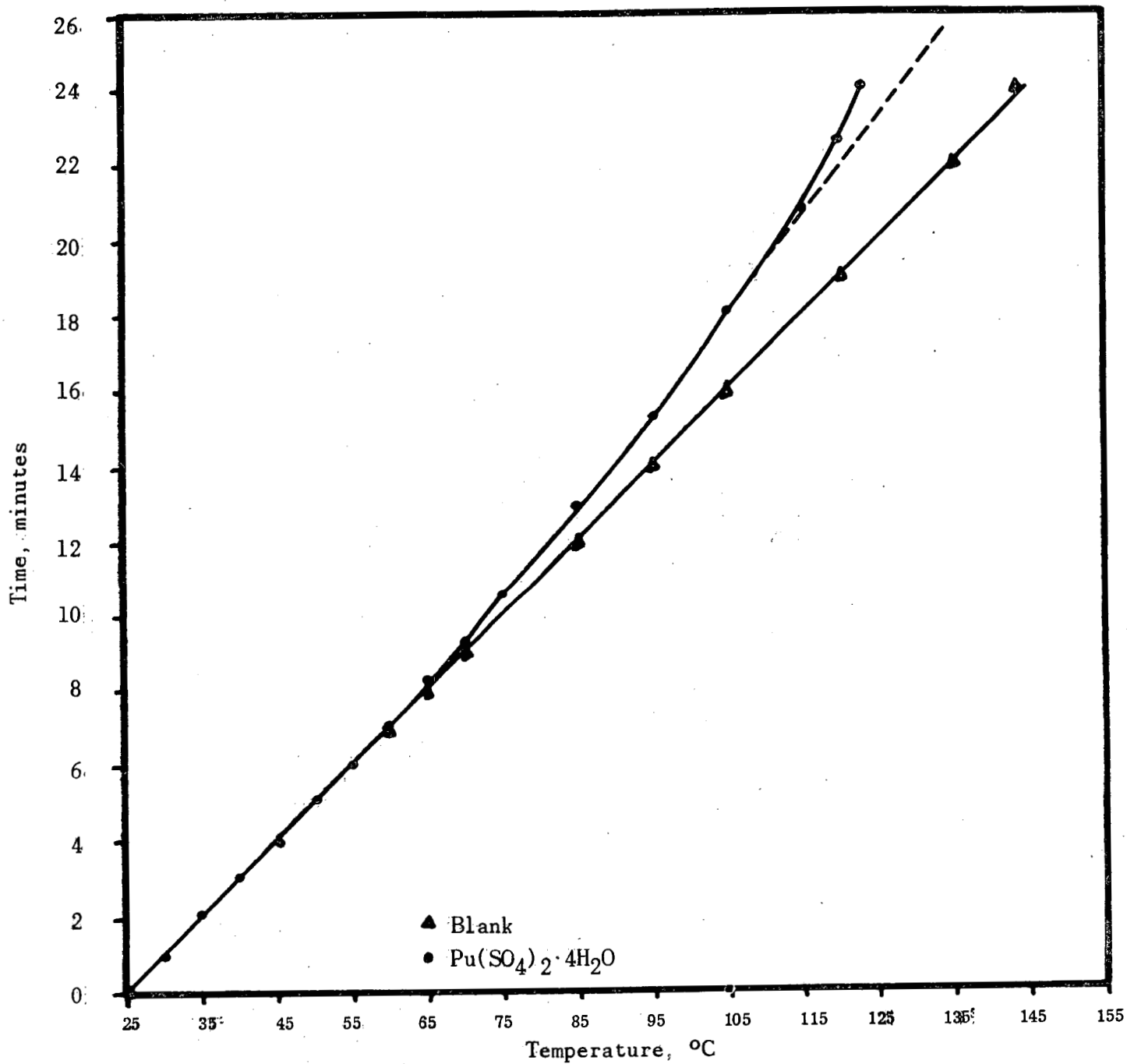


FIGURE 12. HEATING CURVE OF  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (THERMOCOUPLE METHOD)

The study of other hydrate forms of plutonium sulfate hydrates, Figures 9, 10, and 11, containing less than four molecules of water of crystallization was based on the different dissociation pressure of each hydrate formed. At constant temperature, each simple hydrate has a dissociation pressure below which it is stable.<sup>8</sup> Upon heating the tetrahydrate at constant temperature, a loss in weight should occur until the dissociation pressure of the hydrate once again equals the ambient water vapor pressure. At this point, constant weight, indicative of the formation of a lower hydrate, is attained; the weight remains constant as long as the temperature and the ambient vapor pressure does not vary. (Since the dissociation pressure is temperature dependent, the next lower hydrate should be similarly formed by raising the temperature slightly.) During this test the ambient water vapor pressure was known to vary and constant weight for any lengthy period of time was not to be expected. Nevertheless, significant inflections on the heating curve corresponding to changes in hydrate form should be apparent. Since it was not possible to record the weighings of the hydrate continuously during the heating process, it is not unlikely that these significant inflections were obscured or even completely by-passed. The results of this investigation should be interpreted only on a qualitative basis.

The curve, Figure 12, obtained for  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in testing its thermal stability by the thermocouple method showed little resemblance to thermograms similarly obtained with other hydrated compounds in the original calibration runs. Pending further investigation, it appears that the use of the term "phase transition temperature" for both of the inflections obtained for  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  at  $60^\circ$  and  $110^\circ\text{C}$  may be a misnomer since an inflection on the heating curve may not only be caused by a change in hydrate form but by any physical circumstance, such as evolution of gas, which would cause absorption of energy in the system.<sup>9</sup> For the advocates of alpha radiolysis, a convenient explanation for the small loss of weight at the first divergence in the heating curve ( $60^\circ\text{C}$ ), on heating the material from room temperature to  $100^\circ\text{C}$ , may be considered as the release of internal gaseous decomposition products from the hydrate's crystal structure. The loss in weight and the inflection at  $60^\circ\text{C}$  cannot be attributed to the removal of water of hygroscopicity alone since the magnitude of this weight loss is out of proportion to the results obtained from the humidity testing of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  by a factor of 3.

The investigation of the effect of alpha radiolysis on  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  poses a problem. The radiation decomposition of water in a simple solid-liquid system is known to produce predominantly elemental hydrogen hydrogen peroxide and free hydroxyl radicals.<sup>10</sup> By analogy, it has been presumed that this reaction also takes place in the water of crystallization of the tetrahydrated plutonium sulfate. Since neither macroscopic-microscopic examination nor determination of plutonium content, nor total

weight change over a period of a year have given any indication of instability of the compound, it may be postulated that alpha radiolysis: (1) does not occur in any significant, presently-detectable degree in  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ; (2) if occurring, even after a considerable period of time, produces a state of equilibrium indistinguishable from the initial state;<sup>11</sup> or, (3) may cause the formation of decomposition products which are contained within the structure of the hydrate by adsorption, or by dissolution in the water of crystallization.

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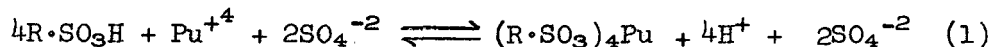
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## THE DETERMINATION OF SULFATE IN PLUTONIUM SULFATE TETRAHYDRATE

C. E. Pietri and J. A. Baglio

In evaluating various compounds for use as possible primary analytical standards of plutonium, it became necessary to determine the exact composition of pure  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . A method based on an oxidimetric titration was developed for the determination of plutonium.<sup>1</sup> The determination of sulfate with similar accuracy in the presence of plutonium, however, presented a problem since it was known that the classic  $\text{BaSO}_4$  precipitation is plagued by coprecipitation contamination.<sup>2, 3</sup> Previous determinations of sulfate in plutonium sulfate solutions by  $\text{BaSO}_4$  precipitation have given results biased by 0.3 to 2 percent.<sup>4, 5</sup> In order to improve the accuracy of the sulfate determination, a number of methods,<sup>6, 7</sup> including ion exchange techniques<sup>8</sup> have been used to remove some of these contaminating ions prior to the gravimetric determination. Since the ion exchange separation may be applied to pure substances containing only sulfate ions as the anionic species, it would be well suited to high purity  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  because the sulfate ion in this compound after separation may be determined volumetrically, rather than gravimetrically, by a more rapid, simple titration of the liberated acid.<sup>9, 10, 11</sup>

Based on previous work with uranium<sup>12</sup> and the knowledge that plutonium, in any of its oxidation states, is adsorbed on Dowex-50 resin from dilute solution,<sup>13, 14</sup> a sulfate determination after ion exchange separation was investigated. The method developed at this laboratory consists of adsorbing the plutonium on Dowex-50 cation resin followed by an acidimetric titration of the displaced hydrogen ion which is equivalent to the sulfate content of the sample. The ion exchange reaction, simplified, is:



In neutral and low acid solutions, ion exchange is complicated by the complex hydrolysis of plutonium sulfate. Apparently, the basic plutonium salts resulting from the hydrolysis prevent the complete formation of all the sulfate-equivalent free acid. A technique for the prevention of this plutonium hydrolysis in neutral solution (a prerequisite for this method) was utilized for the adsorption of plutonium on a cation exchange resin.

Reagents and Apparatus

Plutonium Sulfate Tetrahydrate,  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , prepared by evaporation of  $\text{H}_2\text{SO}_4$  solution of plutonium(IV)<sup>15</sup> made from high purity

plutonium metal (99.96%) obtained from Hanford Atomic Products Operation and Los Alamos Scientific Laboratory.

Ferrous Sulfate Heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , reagent grade.

Sodium Hydroxide Solution, 0.04000N, prepared by dissolving 1.60 g. of reagent grade NaOH in 500 ml. of distilled water (carbonate-free) and diluting to 1000 ml. in a volumetric flask. The normality of this solution is determined by titrating against a known weight of potassium acid phthalate, National Bureau of Standards primary standard No. 84e.

Distilled Water, carbonate-free, prepared by boiling distilled water in a quartz beaker for one hour.

Phenolphthalein Indicator Solution, prepared by dissolving 1 g. of the salt in 100 ml. of ethyl alcohol.

Ion Exchange Resin. About 50 g. of Dowex-50 (X-8, 50-100 mesh, hydrogen-form, analytical grade) is washed free of "fines" with distilled water. The resin, loaded in an ion exchange column similar to that shown in Figure 1, is washed with 2N HCl until the effluent is of the same acidity as the wash solution. It is further rinsed with carbonate-free distilled water until 25 ml. of the effluent gives a constant value of less than 0.2 ml. when titrated with standardized 0.04000N NaOH. The resin is stored in 100 ml. of carbonate-free distilled water. In order to prevent plutonium hydrolysis, a portion of the resin is placed on a sheet of absorbent filter paper and allowed to drain, but not air-dry, for about 30 seconds before mixing with the sample.

Ion Exchange Column. A buret, or ion exchange column, shown in Figure 1, is loaded with 10 cm. of wet cation resin.

Buret, 50-ml. capacity, 0.1-ml. subdivisions.

Hot Plate, with thermostatic heat control.

### Procedure

Weigh by difference to  $\pm 0.02$  mg. a sample of any pure plutonium sulfate containing from 20 to 50 mg. of sulfate and place in a 30-ml. flask. Add approximately 3 g. of slightly moist Dowex-50 cation resin to the flask. Add enough distilled water to make a thick slurry and shake the resin-sample mixture well. Place the flask on a thermostatically-controlled hot plate set at  $60^\circ\text{C}$ . (The temperature is regulated beforehand by manipulating the rheostat until the desired temperature is reached on a thermometer immersed in a beaker of water previously placed on the hot plate.) Agitate the resin-sample slurry frequently by swirling the flask in a circular motion. Continue heating and agitating until no visible traces of the sample are apparent. Heat the

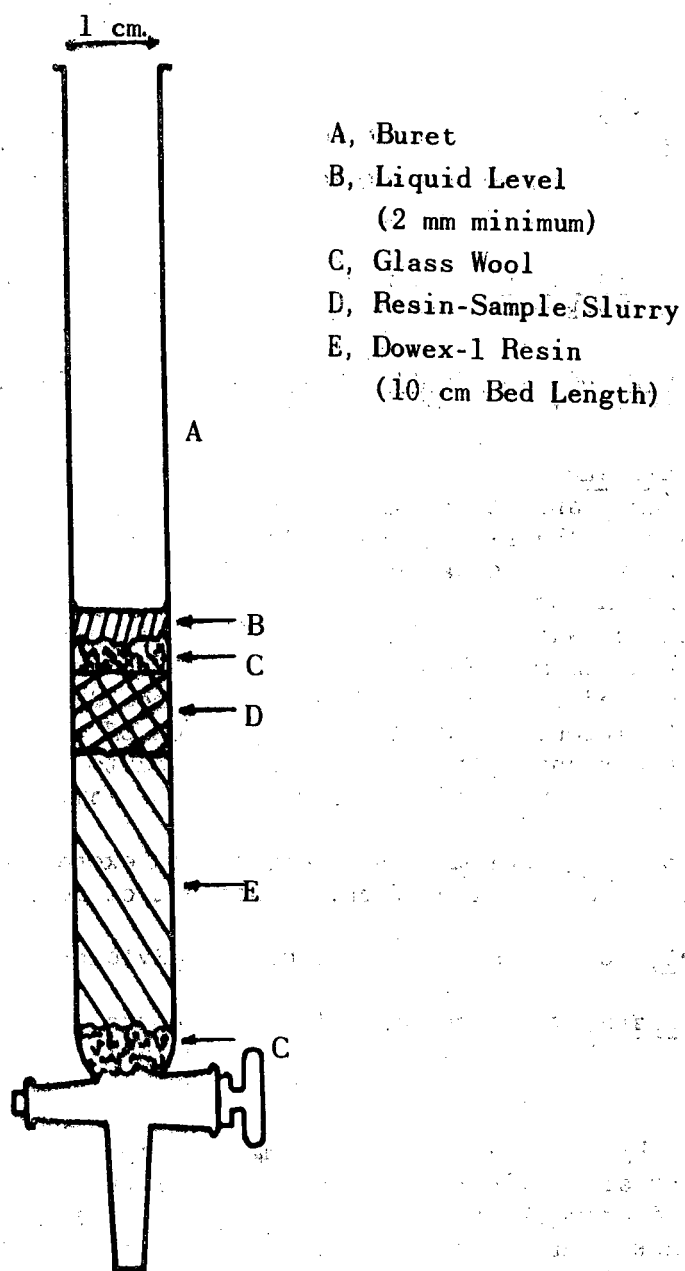


FIGURE 1. ION EXCHANGE COLUMN

slurry for an additional 10 minutes. Remove the flask from the hot plate and carefully pour the resin slurry into a previously prepared ion exchange column containing Dowex-50 resin. Allow the resin slurry to settle and insert a glass wool plug on top of the resin bed. Place a 100 ml. beaker under the tip of the column to collect the effluent. Adjust the flow rate of the solution to about 3 ml. per minute. When the liquid level in the column reaches about 2 mm. from the top of the resin bed, stop the flow of liquid. Rinse the original flask, which held the sample-resin slurry, with 5 ml. of distilled water. Add the washings to the column and collect the effluent as before. Repeat the washing step four additional times making sure that the sides of the column are washed.

Insert a Teflon-covered stirring bar in the beaker containing the acid effluent and place the beaker on a magnetic stirrer set to agitate the solution. Add 2 drops of phenolphthalein indicator to the solution. Titrate the solution with standardized 0.04000N NaOH until the appearance of a faint pink color. Record the volume of NaOH used. Prepare a blank solution by passing carbonate-free distilled water through the ion exchange column and collect 26 ml. of the effluent. Titrate this blank with standardized NaOH, as before, and record the volume. Correct the sample titer by subtracting the blank. Calculate the sulfate content of the sample as follows:

$$\%SO_4 = \frac{48.03 \times A(B-C)}{D}$$

Where: A = concentration of standard NaOH, N

B = volume of NaOH used to titrate sample, ml.

C = volume of NaOH used to titrate blank, ml.

D = weight of sample, g.

### Experimental

Initial Experiments. Preliminary studies were made using ferrous sulfate heptahydrate as a substitute for plutonium sulfate tetrahydrate. Using the outlined procedure and omitting the initial treatment of the sample with resin to prevent hydrolysis, the sulfate content of the samples was determined and found to be within 0.04% of the theoretical value. No difference in results was found when hydrolyzed and unhydrolyzed samples were used.

On the basis of the data obtained for the ferrous sulfate samples, additional studies with plutonium were considered justified.

Plutonium Separation and Hydrolysis Studies. An attempt was made to separate plutonium from samples of  $Pu(SO_4)_2 \cdot 4H_2O$  in neutral solutions regardless of the rapid hydrolysis which would occur when the

material was dissolved in water. Previous studies with hydrolyzed iron showed the method successful with this element. Four 80 to 102-mg. samples of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  were placed in beakers and 5 ml. of distilled water was added. As expected, the samples did not dissolve appreciably; instead, the solutions rapidly turned brown and a brown precipitate began to form. The slurries were passed through the ion exchange column, washed, and titrated with standardized NaOH according to the outlined procedure. (The initial treatment of the sample with resin to prevent hydrolysis was omitted.) Some of the solid remained at the top of the column by the filtering action of the resin, a small amount of material was adsorbed on the column as indicated by a thin, dark band, and the remainder of the material passed through the resin bed with the effluent. The data, Table 1, shows low, erratic results apparently caused by formation of plutonium hydrolysis products.

TABLE 1

THE DETERMINATION OF SULFATE IN HYDROLYZED  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ 

(Ion Exchange Separation-Acidimetric Titration)

<u>Sample Weight, mg.</u>	<u>SO<sub>4</sub> Found, %</u>
102.21	30.88
79.96	29.72
92.09	32.19
94.21	35.02

Since plutonium in aqueous solutions begins to hydrolyse at acidities less than 0.1N,<sup>16</sup> samples of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  were acidified to prevent this hydrolysis. Four 98-mg. samples of plutonium sulfate tetrahydrate were dissolved in known amounts of standardized 0.1N  $\text{HNO}_3$ , as is usually recommended, and were added to the resin column. The column was washed with a known volume of the acid. The acid remaining in the column was removed by washing with distilled water. The acid effluent from the column was collected and titrated with standardized NaOH according to the outlined procedure. A correction for the initial amount of acid added to dissolve the sample and wash the column was made on the total titer.<sup>17</sup> The data in Table 2 show poor results. Apparently a small error in the amount of acid added to the sample to prevent hydrolysis is magnified when the acid "spike" is subtracted from the relatively small total titer. Further investigation of this modification in the titration method was discontinued.



TABLE 2

THE DETERMINATION OF SULFATE IN ACIDIFIED  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$   
 (Ion Exchange Separation-Acidimetric Titration)

<u>Sample Weight, mg.</u>	<u>SO<sub>4</sub> Found, %</u>
98.89	38.47
98.44	38.69
95.07	38.00
97.39	37.77
	Average
	38.23 ± 0.40

Returning to the separation of plutonium in neutral solutions, the dissolution of plutonium hydrolysis products by ion exchange techniques was attempted since similar treatments had dissolved such "insoluble" substances as  $\text{BaSO}_4$ .<sup>18</sup> A 10-mg. sample of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was placed in a 50-ml. flask and hydrolyzed by adding 10 ml. of distilled water. About 2 g. of Dowex-50 resin were added, and the beaker was heated with shaking. After about 30 minutes, some of the hydrolyzed plutonium sulfate remained. An additional hour of heating and shaking failed to completely adsorb the material. Apparently the material could be dissolved but only at a very slow rate, Table 3.

TABLE 3

THE DISSOLUTION OF HYDROLYZED  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  BY ION EXCHANGE TECHNIQUE

<u>Time, Minutes</u>	<u>Dissolution</u>
30	Slight
90	Slight, improved
150	Increased
210	Extensive
270	Nearly complete

Prevention of Plutonium Hydrolysis. A second experiment was made using ion exchange techniques. This time, an attempt was made to forestall the hydrolysis of plutonium. A means of adsorbing plutonium on the resin from neutral solution was used. A 10-mg. sample of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was placed in a beaker and approximately 1 g. of slightly moist Dowex-50 resin was added. A small amount of distilled water was added so as to form a thick slurry and the resin-sample mixture was stirred well. The mixture was warmed at about  $60^\circ\text{C}$  and stirred. After about 10 minutes nearly all of the solid  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  had disappeared. About 5 ml. of distilled water was added and the heating continued. After 5 minutes the solution was clear indicating that adsorption on the resin had taken place successfully without any perceptible hydrolysis occurring.

Determination of the Blank Correction. A slight error of 0.05 ml. in the determination of the titer value for the distilled water blank in the titration method results in a relative error of 0.15% in the sulfate content of the sample. An error as large as 0.4% relative can occur if the blank correction is not applied. In preliminary experiments with distilled and deionized water the blank correction was very high and contributed a significant error to the sulfate determination. When distilled water was boiled to remove dissolved  $\text{CO}_2$ , the blank was reduced appreciably, Table 4.

TABLE 4

## REDUCTION OF THE BLANK CORRECTION

<u>Water Treatment</u>	<u>Blank, ml.*</u>
Distilled	0.35
Distilled, Deionized	0.32
Distilled, Boiled	0.13 - 0.15
Distilled, Boiled, Deionized	0.14 - 0.15

\* 0.03387N NaOH

Results

Following the prescribed method, the sulfate composition of the initial lot of plutonium sulfate tetrahydrate, prepared for standards work from high purity plutonium metal, was found to be 38.19% as compared to the theoretical value of 38.17%. Additional samples of other lots of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  were analyzed for sulfate as shown in Table 5.

TABLE 5

THE DETERMINATION OF SULFATE IN  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$   
(Ion Exchange Separation-Acidimetric Titration)

<u>Sample Weight, mg.</u>	<u>SO<sub>4</sub> Found, %*</u>
118.18	38.22
95.55	38.05
104.12	38.00
109.89	38.19
Average	38.12 ± 0.09

\* Theoretical value = 38.17%

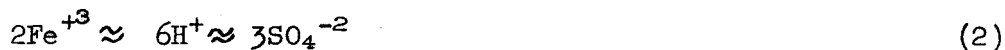
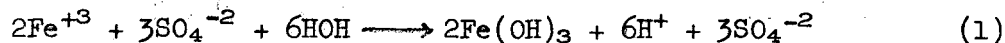
### Discussion

The accuracy of this method appears to be limited by the acidimetric titration which needs further refinement. Inspection of the experimental data shows that a variation of 0.1 ml. in the titration produces a 0.3% change in the sulfate content. By using a more dilute solution of less than 0.02N sodium hydroxide instead of the present 0.04N base, the change is reduced more than half its original value. In addition, a more accurate determination of the endpoint may be obtained by a potentiometric titration. An alternate method would consist of a titration with weight burets coupled with a potentiometric endpoint determination.

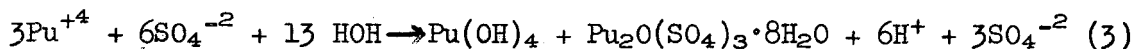
The technique used to prevent hydrolysis of  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in neutral solution is based on differences in dissolution, hydrolysis, and ion exchange equilibrium rates of the material. Probably, the initial slight dissolution of solid  $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in water is sufficiently more rapid than the hydrolysis of the plutonium ions formed. Accordingly, these plutonium ions, when in close proximity to a cation resin, are rapidly adsorbed, and hydrogen ions are released into the solution. The hydrogen ions produced tend to reverse the hydrolysis reaction, and with less competition for plutonium ions from hydrolysis, more exchange on the resin takes place. Heating the resin-sample slurry accelerates the ion exchange adsorption of plutonium and thereby increases the hydrogen-ion concentration of the solution. A similar technique based on differences in solubility is used to separate

"insoluble"  $\text{BaSO}_4$  from "insoluble"  $\text{SrSO}_4$ .<sup>18</sup>

In the case of ferrous salts (air-oxidized to ferric on standing), hydrolysis does not interfere with the method, as is indicated by preliminary experimental data, since an equivalent amount of hydrogen ions is produced in the reaction:



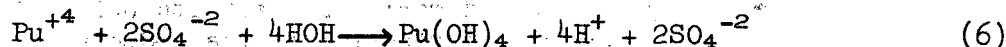
Plutonium sulfates, however, probably hydrolyze to a mixture of hydroxides and basic sulfate;<sup>19</sup> the complex hydrolysis, in this instance, cannot produce an equivalent amount of free hydrogen ions as occurs with ferric ions. For descriptive purposes a possible reaction is postulated as:



Equivalency would require:



If the plutonium hydrolysis was of a simple nature as occurs with iron, Equation (1), an equivalent amount of free acid might be formed as follows:



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## URANIUM IN GRAPHITE WASTE

T. J. Siddons, J. S. Paller, and J. P. Highfill

In the casting operations at the Savannah River plant, E. I. duPont de Nemours and Company, Aiken, South Carolina, several types of graphite articles become contaminated with enriched uranium. When they are no longer useful, they are collected, sampled, and either discarded or sent to another installation for the recovery of the uranium. In the past the recovered amount frequently failed to agree with the amount accountability records indicated was present. The reason for this discrepancy was thought to be non-representative sampling. In April 1959 a test program was set up between the Savannah River Plant (SRP) and New Brunswick Laboratory (NBL) for the purpose of studying this problem and eliminating the cause for the non-agreement.

Details of the Test ProgramI. Materials

SRP selected twenty-two (22) waste graphite items for the test program. The items consisted of five (5) crucibles, three (3) stirring rods, three (3) thermocouple rods, three (3) molds, three (3) cores, three (3) pouring cups, and two (2) skimming paddles. They separated the items into the above-mentioned categories, then sampled and analyzed each article for uranium by colorimetric procedures. The SRP sampling directions were as follows:

(a) Crucibles and Molds

The crucible or mold was broken into chunks. Two pieces per crucible, or one piece per mold was selected from a section at about the middle of the article. One drilling was made from each piece, and the material was used for analysis. In the case of crucibles, a composite was made of two drillings.

(b) Rods and Cups

Material from one drilling through the middle of the item was used for the analytical sample.

(c) Cores

Material from a drilling 1/2-inch into the core at the midway

point was used for analysis.

(d) Paddles

Material from a drilling through the blade at a point 2 inches from the bottom was used for the analytical sample.

II. Purpose

The test program then called for shipment of the unused portions of the various items to NBL for the following purposes:

- (a) Recommend improvements in SROO sampling.
- (b) Sample according to these improvements.
- (c) Ash and dissolve each article completely. Analyze for uranium in order to provide correct overall analysis for comparison with SRP results.
- (d) Return a portion of the solution, or a small representative sample of the pulverized, non-acid treated waste graphite to SROO for cross-checking purposes.

III. NBL Sampling Procedure

NBL proposed and carried out the following sampling and analytical scheme.

- (a) Each item was individually crushed in a jaw-type crusher.
- (b) The particle size of the crushed material was further reduced to -30 mesh by means of a Braun type pulverizer.
- (c) The pulverized graphite was blended overnight, either in a V-type blender or by rolling in a barrel equipped with baffles, depending on the weight of the item.
- (d) After blending, the material was reduced to a 40 to 100 gram sample by means of Jones riffle samplers. This portion was split in order to obtain two 20 to 50 gram samples, one of which was used for determining the uranium content at NBL, and is designated as the "Small Sample" in Table 1. The other portion was forwarded to SROO for cross checking. The balance of the pulverized graphite constitutes what is termed the "Large Sample" in Table 1.

#### IV. NBL Preparation of Waste Graphite for Uranium Analysis

In order to prove the feasibility of sample splitting, both the small and large samples from each item were carried through the next steps.

(a) The pulverized samples were digested at steam bath temperature for 60 hours in  $\text{HNO}_3$  (1+3). The insoluble residues, comprising the bulk of the samples, were filtered on No. 42 Whatman paper by means of suction, and washed with hot water until free of acid.

(b) The filtrate plus washings were made to volume and retained for determining the  $\text{HNO}_3$  soluble uranium.

(c) The residues were transferred to nickel trays and ashed at 850 C.

(d) The ash from each sample was decomposed by digesting with aqua regia at steam bath temperature and filtering the acid insoluble through No. 42 Whatman filter paper. The paper and residue was then ignited, the residue treated with  $\text{HF-H}_2\text{SO}_4$ , and finally fused with potassium pyrosulfate. The fusion cake was added to the aqua regia soluble portion, made to volume, and retained for determination of  $\text{HNO}_3$  insoluble uranium.

#### V. NBL Analytical Method for Uranium in Waste Graphite

Aliquots from both the  $\text{HNO}_3$  soluble, and  $\text{HNO}_3$  insoluble portions, were diluted to suitable volumes for fluorometric determinations of uranium.

In the case of the ash solutions, the uranium content was expected to be very low. Two 25-ml. aliquots from each solution were transferred to 50-ml. volumetric flasks. To one flask a "spike" of 5 micrograms of uranium was added. Both flasks were then diluted to volume.

Two estimated concentrations were used in the case of the  $\text{HNO}_3$  soluble uranium solutions. One concentration was made 100 times greater than the other. From preliminary fluorometric readings calculations were made for the proper size aliquots and dilutions to give concentrations of approximately 100 micrograms of uranium per 100 ml. The solutions were then used for the routine fluorometric uranium measurements.

(a) Twenty-ml. aliquots of the above solutions were used for analysis. The sulfate and chloride ions were eliminated by two or more reprecipitations of the  $\text{R}_2\text{O}_3$  group with ammonium hydroxide.



(b) A nitrate solution was made of the final  $R_2O_3$  group precipitate and the solution was saturated with magnesium nitrate hexahydrate.

(c) The uranium was extracted with ethyl acetate.

(d) A 1-ml. aliquot of the ethyl acetate layer was transferred to a gold dish, dried, and fused with the sodium fluoride and sodium-potassium carbonate flux.

(e) The relative intensity of fluorescence was determined, compared with known standards, and the relationship translated to quantitative uranium results.

### Results

Table 1 shows both SRP and NBL analytical data obtained from the test program. Due to the abnormally high amount of alloy found in Crucible 3, the uranium results for this item were not considered in the overall evaluation of the program.

### Summary

(a) There is a bias between the two sampling methods (SRP vs NBL). A statistical evaluation of the data shows the SRP sampling is in error for accountability purposes for weights of objects above a certain minimum. An error of one gram or more of uranium exists if the weights of the various items are greater than the following: molds - 200 grams; cups - 300 grams; cores - 2500 grams; crucibles - 300 grams; paddles - 75 grams; thermocouple rods - 100 grams, and stirring rods - 500 grams.

(b) There is a good agreement between SRP and NBL on the uranium content based on NBL sampling. In most instances this is comparing SRP colorimetric work against NBL fluorometric results.

(c) NBL's differences in the total uranium content between the small and large samples are not significant for accountability purposes. The results justify the scheme of sub-splitting the crushed graphite down to a reasonable sample weight, providing there is less than the following starting weights of material: molds - 120,000 grams; cups - 30,000 grams; cores - 50,000 grams; crucibles - 10,000 grams; paddles - 8,000 grams; thermocouple rods - 20,000 grams; and stirring rods - 25,000 grams.

(d) With the exception of the crucible items, the amount of uranium retained in the  $\text{HNO}_3$  insoluble is insignificant and no further analysis is required. This results in an appreciable saving of time, since it eliminates ashing of the graphite and decomposition of the ash residue.

Statistically, the above statement holds true for accountability work, providing the weights of the various items are less than the following: molds - 300,000 grams; cups - 600,000 grams; cores - 700,000 grams; crucibles - 3,000 grams; paddles - 100,000 grams; thermocouple rods - 100,000 grams; and stirring rods - 60,000 grams.

NOTE: The weights given in (a), (c), and (d) were derived from the 95% confidence limits of the average percentage differences grouped by types.

TABLE 1  
URANIUM IN GRAPHITE WASTE

Item	Weight (g)	A	B	A-B	C	B-C	D	C-D
		SRP Sampling SRP Results (Colorimetric) (%)	NBL Sampling SRP Results Small Sample (Colorimetric) (%)	SRP Sampling vs NBL Sampling SRP Results (%)	NBL Sampling NBL Results Small Sample (%)	NBL Sampling SRP Results vs NBL Results Small Sample (%)	NBL Sampling NBL Results Large Sample (%)	NBL Sampling NBL Results (small) vs NBL Results (large) (%)
Mold 1	21,842	.143	.001	+.142	HNO <sub>3</sub> Sol. U .0006		HNO <sub>3</sub> Sol. U .00045	
					HNO <sub>3</sub> Insol. U .00002		HNO <sub>3</sub> Insol. U .00003	
					Total U .00062	+ .0004	Total U .00048	+ .0001
Mold 2	22,110	.035	.0018	+.033	HNO <sub>3</sub> Sol. U .0015		HNO <sub>3</sub> Sol. U .0013	
					HNO <sub>3</sub> Insol. U .00003		HNO <sub>3</sub> Insol. U .00005	
					Total U .00153	+ .0003	Total U .00135	+ .0002
Mold 3	20,245	.040	No Results	-----	HNO <sub>3</sub> Sol. U .0006		HNO <sub>3</sub> Sol. U .0006	
					HNO <sub>3</sub> Insol. U .00002		HNO <sub>3</sub> Insol. U .0001	
					Total U .00062	-----	Total U .0007	-.0001
Cup 1	2,141	.000	.0008	-.001	HNO <sub>3</sub> Sol. U .0015		HNO <sub>3</sub> Sol. U .0008	
					HNO <sub>3</sub> Insol. U .00001		HNO <sub>3</sub> Insol. U .00001	
					Total U .00151	-.0007	Total U .00081	+ .0007
Cup 2	1,813	.024	.0035	+.020	HNO <sub>3</sub> Sol. U .0030		HNO <sub>3</sub> Sol. U .0030	
					HNO <sub>3</sub> Insol. U .00002		HNO <sub>3</sub> Insol. U .00002	
					Total U .00302	+ .0005	Total U .00302	None

TABLE 1 (Continued)

Item	Weight (g)	A	B	A-B	C	B-C	D	C-D
		SRP Sampling SRP Results (Colorimetric) (%)	NBL Sampling SRP Results Small Sample (Colorimetric) (%)	SRP Sampling vs NBL Sampling SRP Results (%)	NBL Sampling NBL Results Small Sample (%)	NBL Sampling SRP Results vs NBL Results Small Sample (%)	NBL Sampling NBL Results Large Sample (%)	NBL Sampling NBL Results (small) vs NBL Results (large) (%)
Cup 3	2,103	.099	.0040	+.095	HNO <sub>3</sub> Sol. U .0039	+.0001	HNO <sub>3</sub> Sol. U .0030	+.0009
					HNO <sub>3</sub> Insol. U .00004		HNO <sub>3</sub> Insol. U .00005	
					Total U .00394		Total U .00305	
Core 1	6,715	.012	.0005	+.012	HNO <sub>3</sub> Sol. U .0006	-.0001	HNO <sub>3</sub> Sol. U .0005	None
					HNO <sub>3</sub> Insol. U .00001		HNO <sub>3</sub> Insol. U .00005	
					Total U .00061		Total U .00055	
Core 2	7,113	<.0001	.0011	-.001	HNO <sub>3</sub> Sol. U .0024	-.0013	HNO <sub>3</sub> Sol. U .0018	+.0006
					HNO <sub>3</sub> Insol. U .00004		HNO <sub>3</sub> Insol. U .00003	
					Total U .00244		Total U .00183	
Core 3	6,895	.009	.001	+.008	HNO <sub>3</sub> Sol. U .0013	-.0003	HNO <sub>3</sub> Sol. U .0011	+.0002
					HNO <sub>3</sub> Insol. U .00002		HNO <sub>3</sub> Insol. U .00003	
					Total U .00132		Total U .00113	
Crucible 5	12,485	.108	.019	+.089	HNO <sub>3</sub> Sol. U .020	-.001	HNO <sub>3</sub> Sol. U .018	None
					HNO <sub>3</sub> Insol. U .00003		HNO <sub>3</sub> Insol. U .002	
					Total U .02003		Total U .020	

TABLE 1 (CONTINUED)

Item	Weight (g)	A	B	A-B	C	B-C	D	C-D
		SRP Sampling SRP Results (Colorimetric) (%)	NBL Sampling SRP Results Small Sample (Colorimetric) (%)	SRP Sampling vs NBL Sampling SRP Results (%)	NBL Sampling NBL Results Small Sample (%)	NBL Sampling SRP Results vs NBL Results Small Sample (%)	NBL Sampling NBL Results Large Sample (%)	NBL Sampling NBL Results (small) vs NBL Results (large) (%)
Crucible 1 12,931		.132	.13	+.002	HNO <sub>3</sub> Sol. U .12		HNO <sub>3</sub> Sol. U .11	
					HNO <sub>3</sub> Insol. U .0007		HNO <sub>3</sub> Insol. U .010	
					Total U .1207	+.01	Total U .120	+.0007
Crucible 2 10,664		.201	.20	+.001	HNO <sub>3</sub> Sol. U .13		HNO <sub>3</sub> Sol. U .17	
					HNO <sub>3</sub> Insol. U .001		HNO <sub>3</sub> Insol. U .009	
					Total U .131	+.07	Total U .179	-.048
Crucible 3 11,153		.303	1.50	did not use	HNO <sub>3</sub> Sol. U 2.14		HNO <sub>3</sub> Sol. U 1.92	
					HNO <sub>3</sub> Insol. U .008		HNO <sub>3</sub> Insol. U 0.25	
					Total U 2.148	did not use	Total U 2.17	did not use
Crucible 4 12,890		.216	.15	+.066	HNO <sub>3</sub> Sol. U .18		HNO <sub>3</sub> Sol. U .19	
					HNO <sub>3</sub> Insol. U .0004		HNO <sub>3</sub> Insol. U .013	
					Total U .18	-.03	Total U .203	-.023
Paddle 1 625		.11	.0035	+.107	HNO <sub>3</sub> Sol. U .0047		HNO <sub>3</sub> Sol. U .0029	
					HNO <sub>3</sub> Insol. U .00003		HNO <sub>3</sub> Insol. U .00003	
					Total U .00473	-.001	Total U .00293	+.002

TABLE 1 (Continued)

Item	Weight (g)	A SRP Sampling SRP Results (Colorimetric) (%)	B NBL Sampling SRP Results Small Sample (Colorimetric) (%)	A-B SRP Sampling vs NBL Sampling SRP Results (%)	C NBL Sampling NBL Results Small Sample (%)	B-C NBL Sampling SRP Results vs NBL Results Small Sample (%)	D NBL Sampling NBL Results Large Sample (%)	C-D NBL Sampling NBL Results (small) vs NBL Results (large) (%)
Paddle 2	324	.030	.014	+0.016	HNO <sub>3</sub> Sol. U .016 HNO <sub>3</sub> Insol. U .0001 Total U - .0161	-0.002	HNO <sub>3</sub> Sol. U .015 HNO <sub>3</sub> Insol. U .0013 Total U .0163	-.0002
TC Rod 1	175	.351	.0083	+0.343	HNO <sub>3</sub> Sol. U .0083 HNO <sub>3</sub> Insol. U .00004 Total U .00834	None	HNO <sub>3</sub> Sol. U .0096 HNO <sub>3</sub> Insol. U .00008 Total U .00968	-.001
TC Rod 2	165	.188	.0092	+0.179	HNO <sub>3</sub> Sol. U .0083 HNO <sub>3</sub> Insol. U .00004 Total U .00834	+0.009	HNO <sub>3</sub> Sol. U .0080 HNO <sub>3</sub> Insol. U .0003 Total U .0083	None
TC Rod 3	120	.112	.0031	+0.109	HNO <sub>3</sub> Sol. U .0020 HNO <sub>3</sub> Insol. U .0001 Total U .0021	+0.001	HNO <sub>3</sub> Sol. U .0020 HNO <sub>3</sub> Insol. U .00008 Total U .00208	None
Stir Rod 1	333	.050	.0035	+0.047	HNO <sub>3</sub> Sol. U .0039 HNO <sub>3</sub> Insol. U .0001 Total U .0040	-0.0005	HNO <sub>3</sub> Sol. U .0041 HNO <sub>3</sub> Insol. U .00007 Total U .00417	-.0002

TABLE 1 (Continued)

Item	Weight (g)	A	B	A-B	C	B-C	D	C-D
		SRP Sampling SRP Results (colorimetric) (%)	NBL Sampling SRP Results Small Sample (Colorimetric) (%)	SRP Sampling vs NBL Sampling SRP Results (%)	NBL Sampling NBL Results Small Sample (%)	NBL Sampling SRP Results vs NBL Results Small Sample (%)	NBL Sampling NBL Results Large Sample (%)	NBL Sampling NBL Results (small) vs NBL Results (large) (%)
Stir Rod 2	312	.051	.0040	+.047	HNO <sub>3</sub> Sol. U .0020	+.002	HNO <sub>3</sub> Sol. U .0020	-.0005
					HNO <sub>3</sub> Insol. U .00006		HNO <sub>3</sub> Insol. U .0006	
					Total U .00206		Total U .0026	
Stir Rod 3	411	.080	.0036	+.076	HNO <sub>3</sub> Sol. U .0035	None	HNO <sub>3</sub> Sol. U .0025	+.0010
					HNO <sub>3</sub> Insol. U .00006		HNO <sub>3</sub> Insol. U .00005	
					Total U .00356		Total U .00255	

Note: &lt; = less than

## DETERMINATION OF URANIUM IN VARIOUS TYPES OF FUEL ELEMENT SOLUTIONS

W. A. Peavy and J. P. Highfill

A uranium scrap recovery program from fuel pin elements was begun during the last half of 1959 by the U. S. Atomic Energy Commission, under the Technical Services Section, New York Operations Office. In order to assist this group in evaluating commercial laboratories for the analytical phase of this work, the New Brunswick Laboratory was requested to prepare and analyze synthetic solutions of (1) uranium-aluminum, (2) uranium-stainless steel, and (3) uranium-Zircaloy-2. The solutions, along with methods of analysis, were made available to interested parties. The needed information for granting contracts was collected relative to the selecting of a commercial laboratory.

The methods of analysis, details of preparing synthetic solutions, and New Brunswick Laboratory's analysis of these solutions appear in the following order.

- A. Uranium in Uranium-Aluminum Alloy Solution.
- B. Uranium in Uranium-Stainless Steel Solution.
- C. Uranium in Uranium-Zircaloy-2 Solution.

Apparatus

(a) Jones Reductor (see Figure 1) - Transfer the zinc amalgam (prepared as described under Reagent g) to the reductor. Keep the amalgam covered at all times with  $H_2SO_4$  (5+95). Tamp it in place with a heavy glass rod. Pass 100 ml. of  $H_2SO_4$  (5+95) followed by 100 ml. of water through the reductor, collecting the washings in a 500-ml. flask. Titrate the solution with 0.02N potassium permanganate to a faint pink end point. Repeat the operation until a blank titration of 0.05 ml. of potassium permanganate is obtained. Check the reductor each time it is used for a series of samples.

(b) Buret - 100-ml. capacity with a 50-ml. reservoir bulb, Normax grade.

(c) Electrical Heaters, provided with a mechanical shaker.

(d) Infra-red Lamps (500 watts).

(e) Eberback Dyna-Cath, Magnetic Mercury Cathode.



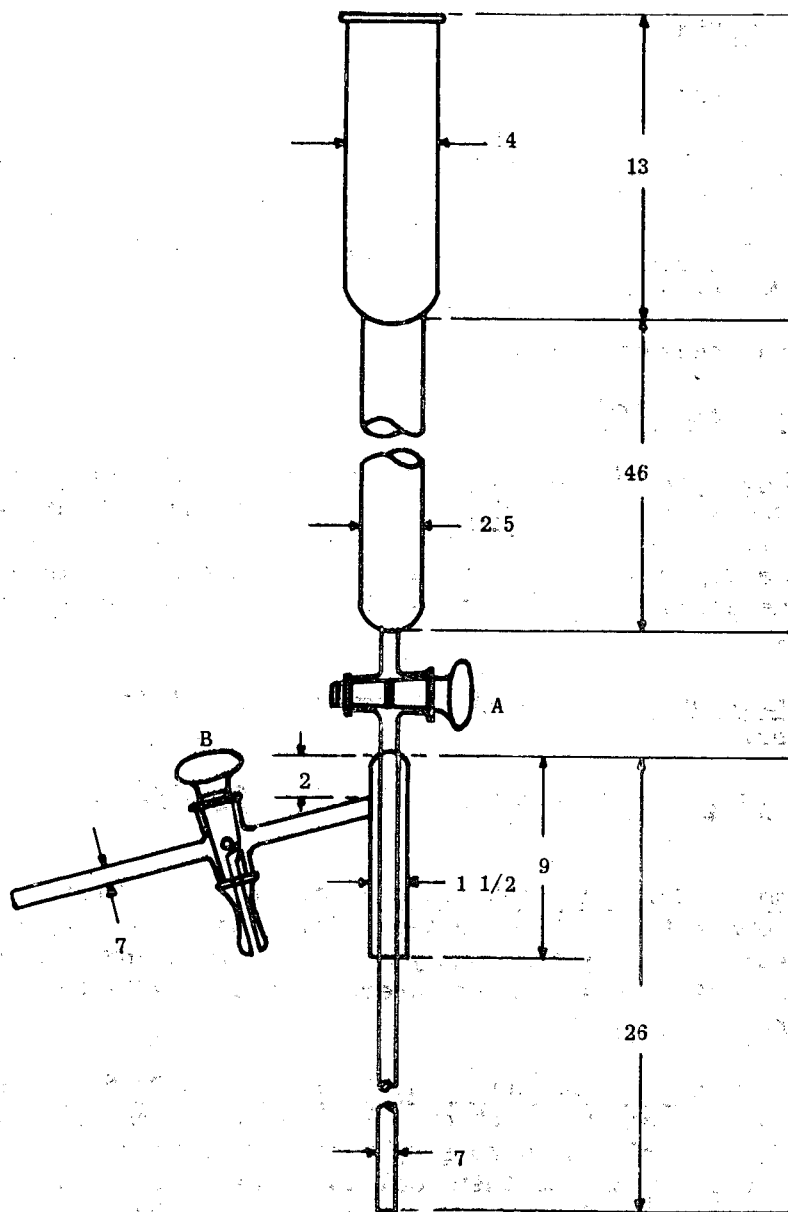


FIGURE 1. SKETCH OF JONES REDUCTOR.  
 STOPCOCK A, STRAIGHT 3-mm BORE. STOPCOCK B,  
 THREE-WAY. DIMENSIONS IN CENTIMETERS.

Reagents

- (a) Hydrogen Sulfide.
- (b) Cupferron, reagent grade.
- (c) Cupferron Solution, 6% - Dissolve 6 g. of cupferron in 100 ml. of water. Keep in a refrigerator to prevent decomposition.
- (d) Potassium Permanganate, 2% - Dissolve 2 g. of potassium permanganate in 100 ml. of water.
- (e) Chloroform, reagent grade.
- (f) Perchloric Acid, 70%.
- (g) Zinc Amalgam, 3% - Dissolve 26 g. of mercuric chloride in 750 ml. of hot water containing 5 ml.  $\text{HNO}_3$ . Cool to room temperature and transfer the solution to a strong flask. Add 700 g. of zinc metal (20 mesh) and shake vigorously for 2 minutes to completely amalgamate the zinc. Wash the amalgam several times with water, and several times with  $\text{H}_2\text{SO}_4$  (5+95).
- (h) Ferric Chloride Solution, 4% - Dissolve 4 g. of ferric chloride in 100 ml. of water.
- (i)  $\text{H}_3\text{PO}_4$  -  $\text{H}_2\text{SO}_4$  Mixture - Mix 350 ml. of  $\text{H}_3\text{PO}_4$  (85%) with 150 ml.  $\text{H}_2\text{SO}_4$ .
- (j) Diphenylamine Sulfonate Indicator - Add 0.32 g. of barium diphenylamine sulfonate to 90 ml. of water. Stir and add 0.5 g. of anhydrous sodium sulfate. Mix thoroughly and allow to stand overnight. Filter through a No. 42 Whatman filter paper. Dilute the filtrate to 100 ml. with water.
- (k) Potassium Dichromate Solution, approximately 0.027N. Standardization of potassium dichromate solution - Ignite approximately 4 g. of National Bureau of Standards standard sample of  $\text{U}_3\text{O}_8$  (NBS-950) in a furnace at  $900^\circ\text{C}$  for one hour and then cool in a desiccator. Weigh 1.5000 g. of the standard in duplicate and transfer to 500-ml. Erlenmeyer flasks. Wash down the sides of the flasks, add 20 ml. of  $\text{H}_2\text{SO}_4$  (1+1) and 10 ml. of  $\text{HNO}_3$ . Evaporate to strong  $\text{SO}_3$  fumes and fume for 3 minutes. Cool, rinse down the sides of the flasks with water and repeat the fuming step three times. Add 90 ml. of water and heat to boiling. Cool to room temperature, transfer the solutions to 200-ml. volumetric flasks and make to volume at  $25^\circ\text{C}$ . Take a 50-ml. aliquot and a 25-ml. aliquot from each flask at  $25^\circ\text{C}$  and proceed with the

reduction and titration as described in the procedure for "Uranium in Uranium-Aluminum Alloy Solution". Calculate the titration blank as follows:

$2x(\text{titration of the } 0.1875\text{-g. sample}) - (\text{titration of the } 0.3750\text{ g. sample}) = \text{titration blank, expressed in ml. of potassium dichromate solution.}$

Calculate the titer as follows:

$$\frac{A}{B-C} = D$$

where:

A = grams of  $U_3O_8$ . (Certificate value for NBS-950 is 99.94%  $U_3O_8$ ).

B = milliliters of potassium dichromate.

C = titration blank.

D = grams of  $U_3O_8$  per milliliter of potassium dichromate solution.

Use a factor of 0.8480 for converting  $U_3O_8$  to uranium per milliliter of potassium dichromate solution.

#### A. Uranium in Uranium-Aluminum Alloy Solution.

##### 1. Analytical Procedure

(a) Transfer an aliquot of the uranium-aluminum synthetic solution at  $25^\circ\text{C}$  to a tared weighing bottle, and obtain the weight of the sample. The aliquot should contain between 0.160 and 0.300 g. of uranium. Transfer the sample to a 600-ml. beaker, add 20 ml. of  $H_2SO_4$  (1+1), evaporate under an infra-red lamp until  $SO_3$  fumes appear, and continue fuming for 30 minutes. Cool, rinse down the side walls of the beaker and repeat the fuming step. Allow the solution to cool, and add 180 ml. of water. Warm on a hot plate until all salts are in solution.

(b) Transfer the solution to a 500-ml. suction flask. Place a rubber stopper loosely in the neck of the flask. Pass a stream of hydrogen sulfide (Reagent a) into the flask through the side arm for 30 minutes. Cork up the side arm and tighten the stopper in the neck of the flask. Allow the solution to stand overnight. Filter off the sulfides, using a No. 40 Whatman paper. Wash the precipitate thoroughly with  $H_2SO_4$  (2+98) that is saturated with hydrogen sulfide. The volume

of the filtrate should be about 225 ml. when washing is complete. Evaporate the filtrate to 90 ml. (In some cases, the sulfide step can be omitted due to the absence of the hydrogen sulfide group. In the scrap recovery work cadmium is often added as a safety precaution in quantities that make it advisable to remove as the sulfide).

(c) Add potassium permanganate solution, 2% (Reagent d), until the solution is pink. Cool in an ice bath until the temperature is below 5°C. Transfer the solution to a 250-ml. separatory funnel. Add 25 ml. of cupferron solution, 6% (Reagent c) and shake a few times. Allow to stand for 3-4 minutes. Add 25 ml. of cold chloroform (Reagent e) and shake vigorously. Allow to stand until the separation into layers is complete. Drain off most of the chloroform. Repeat the extractions with portions of chloroform until the extract is colorless and add 5 ml. of cupferron solution. If the precipitate is white and remains white after standing a short time and does not impart a brown color to the next portion of chloroform, the extraction is complete.

(d) Transfer the aqueous layer to the original beaker and add 15 ml. HNO<sub>3</sub>. Evaporate the solution to fumes of SO<sub>3</sub> under an infra-red lamp for 30 minutes. Cool, wash down the sides of the beaker with 10-15 ml. of water, and add 1 ml. of perchloric acid (Reagent f). Evaporate and fume 4 times to completely remove the cupferron decomposition products and HNO<sub>3</sub>. Cool and wash down the side walls between each fuming.

(e) Dilute the solution to 100 ml., heat to boiling, and add dropwise a 2% solution of potassium permanganate until the solution is pink. Cool to room temperature and pass the solution through a Jones reductor. (Apparatus a). The rate of flow through the reductor should be about 75 ml. per minute. Do not permit the level of the liquid to go below the surface of the amalgam at any time. Follow with three 30-ml. portions of H<sub>2</sub>SO<sub>4</sub> (5+95) and then with three 30-ml. portions of water, collecting the washings with the reduced solution. Transfer the solution to a 600-ml. beaker. Bubble air through the solution for 15 minutes, keeping the beaker covered with a split watch glass. Rinse off the cover and aerator.

(f) Add to the reduced solution 20 ml. of freshly prepared ferric chloride solution (Reagent h). Stir and add 15 ml. of the H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> acid mixture. Add 8 drops of diphenylamine-sulfonate indicator (Reagent j). Titrate with standard potassium dichromate solution (Reagent k) to a permanent purple end point. If the temperature of the titrating solution varies from 25°C, the volume should be corrected according to Table 1, "Temperature Correction Chart for Titrating Solutions."

(g) Calculate the grams uranium per gram of solution as follows:

$$\text{grams U/gram of solution} = \frac{(B-C) \times D}{A}$$

TABLE 1  
 TEMPERATURE CORRECTION CHART FOR TITRATING SOLUTIONS  
 TEMPERATURES IN °C., VOLUMES IN ml.

	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°	31°	32°	33°	34°	35°	36°	37°	38°	39°	40°
10 ml	+0.02	+0.01	+0.01	+0.00	0.00	0.00	0.00	-0.01	-0.01	-0.01	-0.02	-0.02	-0.03	-0.03	-0.03	-0.04	-0.04	-0.05	-0.05	-0.05	-0.06
20	+0.03	+0.03	+0.02	+0.01	+0.01	0.00	-0.01	-0.01	-0.02	-0.03	-0.04	-0.04	-0.05	-0.06	-0.07	-0.08	-0.08	-0.09	-0.10	-0.11	-0.12
30	+0.05	+0.04	+0.03	+0.02	+0.01	0.00	-0.01	-0.02	-0.03	-0.04	-0.05	-0.07	-0.08	-0.09	-0.10	-0.11	-0.12	-0.14	-0.15	-0.16	-0.17
40	+0.07	+0.05	+0.04	+0.03	+0.01	0.00	-0.01	-0.03	-0.04	-0.06	-0.07	-0.09	-0.10	-0.12	-0.13	-0.15	-0.17	-0.18	-0.20	-0.22	-0.23
50	+0.08	+0.07	+0.05	+0.04	+0.02	0.00	-0.02	-0.03	-0.05	-0.07	-0.09	-0.11	-0.13	-0.15	-0.17	-0.19	-0.21	-0.23	-0.25	-0.27	-0.29
60	+0.10	+0.08	+0.06	+0.04	+0.02	0.00	-0.02	-0.04	-0.06	-0.09	-0.11	-0.13	-0.15	-0.18	-0.20	-0.23	-0.25	-0.27	-0.30	-0.32	-0.36
70	+0.12	+0.10	+0.07	+0.05	+0.03	0.00	-0.02	-0.05	-0.07	-0.10	-0.13	-0.15	-0.18	-0.21	-0.23	-0.26	-0.29	-0.32	-0.35	-0.38	-0.40
80	+0.14	+0.11	+0.08	+0.06	+0.03	0.00	-0.03	-0.05	-0.08	-0.11	-0.14	-0.17	-0.20	-0.24	-0.27	-0.30	-0.33	-0.37	-0.40	-0.43	-0.46
90	+0.15	+0.12	+0.09	+0.06	+0.03	0.00	-0.03	-0.06	-0.10	-0.13	-0.16	-0.20	-0.23	-0.26	-0.30	-0.34	-0.37	-0.41	-0.45	-0.49	-0.52
100	+0.17	+0.14	+0.10	+0.07	+0.04	±0.00	-0.03	-0.07	-0.11	-0.14	-0.18	-0.22	-0.26	-0.29	-0.33	-0.38	-0.42	-0.46	-0.50	-0.54	-0.56

where:

A = weight of sample solution.

B = milliliters of potassium dichromate solution.

C = titration blank, expressed in milliliters of potassium dichromate solution.

D = grams of uranium per milliliter of potassium dichromate solution.

If the uranium is enriched with the isotope  $U^{235}$ , the isotopic content will be needed for calculating the atomic weight of uranium and making the necessary corrections for the uranium found.

## 2. Preparation of Solution

(a) Fourteen liters of a synthetic solution containing 5.4 g. uranium per liter and 25 g. of aluminum per liter in 0.1N  $HNO_3$  were prepared. The solution was bottled in one-quart bottles, fitted with molded plastic screw caps and taped with Scotch pressure-sensitive tape.

(b) Weights of the following chemicals were put into solution in 0.1N  $HNO_3$  and made to 14 liters with the same strength acid. Dry air was bubbled through the solution overnight before bottling.

89.1475 g.  $U_3O_8$  (MS-ST)  $\approx$  75.6000 g. uranium

4868.3 g.  $Al(NO_3)_3 \cdot 9H_2O$   $\approx$  350.0 g. aluminum

(c) The weight of the 14-liter solution was 35.5625 pounds or 16,131.15 g.

$$\frac{75.6000 \text{ grams U}}{16,131.15 \text{ grams soln.}} = 0.004687 \text{ g. U/g. soln.}$$

## 3. Analytical Results

(a) Three one-quart bottles of the solution were selected at random (Bottles 6, 9, and 11) and analyzed in triplicate for uranium content. The results are reported in Table 2.

TABLE 2

## ANALYSIS OF SYNTHETIC SOLUTION A

(g. U/g. soln.)

<u>Bottle 6</u>	<u>Bottle 9</u>	<u>Bottle 11</u>
0.004688	0.004687	0.004689
0.004689	0.004688	0.004689
0.004688	0.004687	0.004689

0.004688±0.000002 (95% confidence level per single determination)

(g. U/liter)

5.403	5.403	5.405
5.405	5.403	5.405
5.405	5.403	5.405

5.404±0.003 (95% confidence level per single determination)

B. Uranium in Uranium-Stainless Steel Solution.1. Analytical Procedure

(a) Transfer an aliquot of the uranium-stainless steel synthetic solution at 25°C to a tared weighing bottle, and obtain the weight of the aliquot. The sample should contain between 0.160 and 0.300 g. of uranium. Transfer the sample to a 600-ml. beaker, add 15 ml. of perchloric acid (Reagent f), and evaporate to strong fumes of perchloric. Cool, dilute to 200 ml. with water.

(b) Transfer the solution to a Dyna-Cath mercury cell (Apparatus e). Electrolyze the solution for 30 to 45 minutes at 10 amperes. Drain off the solution, rinse out the cell with water, and collect the washings with the main solution.

(c) Add a few drops of HNO<sub>3</sub> to the solution and heat to boiling. Add NH<sub>4</sub>OH dropwise until precipitation is complete, and the solution has an odor of ammonia. (Prepare the NH<sub>4</sub>OH by saturating water with NH<sub>3</sub>). Filter the precipitate through a No. 40 Whatman filter paper and wash the precipitate 3 or 4 times with warm 2% ammonium chloride solution.

(d) Dissolve the preprecipitate with hot HCl (1+4), and wash the paper free of acid with hot water. Add 20 ml. of H<sub>2</sub>SO<sub>4</sub> (1+1) to the filtrate and evaporate to strong SO<sub>3</sub> fumes. Cool, dilute to 100 ml., and warm until all salts are in solution.

(e) Complete the determination as described under A, Section 1, steps (c) through (g).

## 2. Preparation of Solution

(a) Fourteen liters of a synthetic uranium-stainless steel solution were prepared and bottled in one-quart bottles. The composition of the solution corresponds to No. 304B stainless steel minus the silicon, with 10.8% uranium added. This approximates the composition for this type of scrap solution. The 2% silicon normally found was omitted from the synthetic solution due to the expected difficulty of keeping it in solution.

(b) The make-up of the solution for analysis is shown in Table 3.

TABLE 3

### COMPOSITION OF SYNTHETIC SOLUTION SIMILAR TO NO. 304B STAINLESS STEEL

Element	Composition of 304B S/S minus Si (%)	Composition of Scrap Soln. with 10.8% U added (%)	Composition of Scrap Soln. Based on 6.20 g. U/liter (g./l)
Mn	1.00	0.892	0.51
P	0.04	0.036	0.020
S	0.03	0.027	0.016
Ni	8.00	7.136	4.10
Cr	18.00	16.056	9.22
Fe	72.93	65.053	37.35
U		10.800	6.20
Total	100.00	100.000	

(c) Weights of the following chemicals were put into solution with  $\text{HNO}_3$  (5%) and made to 14 liters with the same strength  $\text{HNO}_3$ . Dry air was passed through the solution overnight before bottling.

Mn 0.51 g./liter x 14 = 7.14 g. Mn x 3.258 = 23.26 g.  $\text{Mn}(\text{NO}_3)_2$  or 46.5 ml. (50% Soln.).

P 0.020 g./liter x 14 = 0.28 g. P x 2.291 = 0.64 g.  $\text{P}_2\text{O}_5$ .

S 0.016 g./liter x 14 = 0.22 g. S x 3.059 = 0.67 g.  $\text{H}_2\text{SO}_4$  or 0.70 g.  $\text{H}_2\text{SO}_4$  (96.4%).

Ni 4.10 g./liter x 14 = 57.4 g. Ni x 4.955 = 284.4 g.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .



Cr 9.22 g./liter x 14 = 129.1 g. Cr x 7.694 = 993.3 g.  $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ .

Fe 37.35 g./liter x 14 = 522.9 g. Fe x 7.234 = 3,782.7 g.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

U 6.20 g./liter x 14 = 86.80 g. U x 1.1792 = 102.3546 g.  $\text{U}_3\text{O}_8$  (MS-ST).

(d) The weight of the 14-liter solution was 36.750 pounds or 16,669.89 g.

$$\frac{86.80 \text{ g. U}}{16,669.89 \text{ g. soln.}} = 0.005207 \text{ g. U/g. soln.}$$

### 3. Analytical Results

(a) Three one-quart bottles were selected at random (Bottles 2, 7, and 10) and analyzed in triplicate for uranium. The results are reported as shown in Table 4.

TABLE 4

#### ANALYSIS OF SYNTHETIC SOLUTION B

(g. U/g. soln.)

<u>Bottle 2</u>	<u>Bottle 7</u>	<u>Bottle 10</u>
0.005196	0.005193	0.005195
0.005197	0.005194	0.005193
0.005195	0.005196	0.005194

$0.005195 \pm 0.000003$  (95% confidence level per single determination)

(g. U/liter)

6.191	6.189	6.189
6.192	6.187	6.187
6.189	6.191	6.188

$6.189 \pm 0.003$  (95% confidence level per single determination)

### C. Uranium in Uranium-Zircaloy-2 Solution.

#### 1. Analytical Procedure

(a) Transfer an aliquot of the uranium-Zircaloy-2 synthetic solution at 25°C to a tared weighing bottle, and obtain the weight of the sample. The aliquot should contain 0.160 g. to 0.300 g. of uranium. Transfer the sample to a 600-ml. beaker, add 20 ml.  $\text{H}_2\text{SO}_4$  (1+1),

evaporate under an infra-red lamp until  $\text{SO}_3$  fumes appear, and continue fuming for 30 minutes. Cool, rinse down the side walls of the beaker, and repeat the fuming step. Allow the solution to cool, and add 180 ml. of water. Warm on a hot plate until all salts are in solution.

(b) Transfer the solution to a 500-ml. suction flask. Rinse out the beaker with water. Place a rubber stopper loosely in the neck of the flask. Pass a stream of hydrogen sulfide through the side arm. Cork up the side arm and tighten the stopper in the neck of the flask, and allow the solution to stand overnight. Filter off the sulfides through a No. 40 Whatman paper. Wash the precipitate with  $\text{H}_2\text{SO}_4$  (2+98) saturated with hydrogen sulfide. Evaporate the filtrate to 90 ml.

(c) Add potassium permanganate solution (Reagent d) until the solution is pink. Cool in an ice bath until the solution is below  $5^\circ\text{C}$ . Transfer the solution to a 250-ml. separatory funnel. Add 15 g. of cupferron (Reagent b) and shake several times to insure complete precipitation. Extract the precipitate with 25 ml. of cold chloroform (Reagent e). Allow to stand until the separation into layers is complete. Drain off most of the chloroform into a second separatory funnel for further treatment. Repeat the extraction with portions of chloroform until the extract is colorless, retaining all of the chloroform. Continue the step with cupferron solution (Reagent c) until there is no further precipitation. Drain the aqueous layer into the original 500-ml. flask and rinse the funnel several times with water. Wash the combined chloroform layers with 50 ml. of cold  $\text{H}_2\text{SO}_4$  (1+9). Add the acid washings to the main aqueous portion.

(d) Add 15 ml. of  $\text{HNO}_3$ , evaporate to fumes of  $\text{SO}_3$ , and fume for 3-4 minutes. Cool, wash down the sides of the flask, and add 1 ml. of perchloric acid (70%). Evaporate the solution to strong fumes 4 times to completely remove the cupferron decomposition products plus  $\text{HNO}_3$ . Rinse down the side walls with a little water between each fuming. Add 100 ml. of water and warm until all salts are in solution.

(e) Add  $\text{NH}_4\text{OH}$  to the hot solution until it is ammoniacal plus a few drops in excess. Filter the precipitate through a No. 40 Whatman paper, wash the precipitate 3 or 4 times with warm ammonium chloride solution (2%). Dissolve the precipitate with hot  $\text{HCl}$  (1+3), and wash the paper free of acid with hot water. Add 15 ml. of  $\text{H}_2\text{SO}_4$  (1+1) to filtrate and evaporate to  $\text{SO}_3$  fumes. Cool, dilute the solution to 100 ml., heat to boiling, and add potassium permanganate solution (Reagent d), dropwise, until the solution is pink.

(f) Complete the determination for uranium as described under A, Section 1, steps (e) through (g).

## 2. Preparation of Solution

(a) Fourteen liters of a synthetic uranium-Zircaloy-2 solution were prepared and bottled in one-quart polyethylene bottles. The composition of the solution corresponds to that of Zircaloy-2 with 5.20% uranium added, and approximates the make-up for this type of scrap for processing.

(b) The composition of the solution prepared for analysis is shown in Table 5.

TABLE 5

## COMPOSITION OF URANIUM-ZIRCALOY-2 SYNTHETIC SOLUTION

Element	Composition of	Composition of Zircaloy-2	Composition of Soln.
	Zircaloy-2	plus 5.20% U	(Based on 6.095 g. U/liter)
	(%)	(%)	(g./l)
Al	0.008	0.008	0.009
Cr	0.100	0.095	0.112
Cu	0.005	0.005	0.006
Fe	0.120	0.114	0.134
Mn	0.005	0.005	0.006
Mo	0.005	0.005	0.006
Ni	0.050	0.047	0.055
Sn	1.45	1.375	1.613
W	0.010	0.009	0.011
Ti	0.005	0.005	0.006
V	0.005	0.005	0.006
Zr	98.237	93.127	109.245
U		5.200	6.095

(c) Weights of the following chemicals were put into solution in 15%  $H_2SO_4$  plus 2% HF, and were thoroughly blended prior to bottling.

Al 0.009 g./liter x 14 = 0.126 g. Al x 12.3547 = 1.5567 g.  $Al_2(SO_4)_3 \cdot 18H_2O$ .

Cr 0.112 g./liter x 14 = 1.568 g. Cr x 4.6364 = 7.2699 g.  $Cr_2(SO_4)_3 \cdot 5H_2O$ .

Cu 0.006 g./liter x 14 = 0.084 g. Cu x 2.511 = 0.2109 g.  $CuSO_4$ .

Fe 0.134 g./liter x 14 = 1.876 g. Fe x 4.978 = 9.3387 g.  $FeSO_4 \cdot 7H_2O$ .

Mn 0.006 g./liter x 14 = 0.084 g. Mn x 3.0768 = 0.2585 g.  $Mn SO_4 \cdot H_2O$ .

Mo 0.006 g./liter x 14 = 0.084 g. Mo x 1.500 = 0.126 g.  $MoO_3$  or  $0.1575$  g.  $MoO_3$  (80%).

Ni 0.055 g./liter x 14 = 0.770 g. Ni x 4.9549 = 3.8153 g. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

Sn 1.613 g./liter x 14 = 22.582 g. Sn.

W 0.011 g./liter x 14 = 0.154 g. W x 1.794 = 0.2763 g. Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O.

Ti 0.006 g./liter x 14 = 0.084 g. Ti x 1.6681 = 0.1401 g. TiO<sub>2</sub>.

V 0.006 g./liter x 14 = 0.084 g. V x 2.2962 = 0.1929 g. NH<sub>4</sub>VO<sub>3</sub>.

Zr 109.245 g./liter x 14 = 1,529.43 g. Zr x 3.8961 = 5,958.81 g.  
Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O.

U 6.095 g./liter x 14 = 85.33 g. U x 1.1792 = 100.6211 g. U<sub>3</sub>O<sub>8</sub> (MS-ST).

(d) The weight of the 14-liter solution was 44.25 pounds or 20,071.80 g.

$$\frac{85.33 \text{ g. U}}{20,071.80} = 0.004251 \text{ g. U/g. soln.}$$

### 3. Analytical Results

(a) Bottles 4, 8, and 11 were selected at random and analyzed in triplicate for uranium. The results are reported in Table 6.

TABLE 6

#### ANALYSIS OF SYNTHETIC SOLUTION C

(g. U/g. soln.)

<u>Bottle 4</u>	<u>Bottle 8</u>	<u>Bottle 11</u>
0.004237	0.004239	0.004239
0.004238	0.004243	0.004239
0.004239	0.004243	0.004241

0.004240 ± 0.000004 (95% confidence level per single determination)

(g. U/liter)

6.068	6.072	6.072
6.070	6.077	6.072
6.072	6.077	6.074

6.073 ± 0.005 (95% Confidence level per single determination)

## ISOTOPIC ABUNDANCE MEASUREMENTS OF URANIUM WITH THE MASS SPECTROMETER

H. O. Finley and E. E. Leuang, Jr.

The present procedure for the analysis of uranium by mass spectrometry is being further evaluated by additional measurements in the determination of the isotopic content of the National Bureau of Standards NBS-U-200 uranium sample.<sup>1</sup> A solid source, triple-filament arrangement was used in these measurements.

The previous evaluation of the NBS-U-200 standard by this laboratory was based on two charges from which an average of three assays was reported. The values for these two charges, and the values for two more recent charges, are listed in Table 1, in weight percent.

A report of the Advisory Committee for Standard Reference Materials and Methods of Measurement contains the National Bureau of Standards best estimate of pooled values for the isotopic composition of a uranium oxide ( $U_3O_8$ ) material listed as NBS-U-200.<sup>2</sup> The Provisional Certificate for Standard Sample U-200 issued by the National Bureau of Standards also contains values for the isotopic composition. These are listed in Table 2. For comparative purposes, the values obtained by New Brunswick Laboratory were converted to atom percent and also listed. A statistical comparison of the data indicates that there is no significant difference between New Brunswick Laboratory's values and either set of National Bureau of Standards' values.

## REFERENCES

1. Finley, H. O. and Leuang, E. E., Jr., NBL-159 (May 1960), pp. 108-115.
2. Report No. 8, Advisory Committee for Standard Reference Materials and Methods of Measurement, National Bureau of Standards Meeting, May 17 and 18, 1960.