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OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO**

**THE PREPARATION OF HIGH-PURITY PLUTONIUM
DIOXIDE AND PLUTONIUM(III) CHLORIDE SOLUTION**

LOS ALAMOS NATIONAL LABORATORY



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THE PREPARATION OF HIGH-PURITY PLUTONIUM
DIOXIDE AND PLUTONIUM(III) CHLORIDE SOLUTION

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ABSTRACT

A method is described for the preparation of high-purity plutonium dioxide. The purification process consists of a partial removal of impurities by electrolysis into a mercury cathode and a subsequent further purification by precipitation of the plutonium as the peroxide. The peroxide precipitate is ignited to the dioxide at 900° C. in a platinum-lined furnace under noncontaminating conditions. The product contained about 2 parts per million of manganese as the only detectable metal impurity exceeding the 1 part-per-million level. This high quality is readily reproduced batchwise.

The preparation of a high-purity plutonium(III) chloride solution is readily achieved by dissolving the above-mentioned peroxide in quartz-distilled hydrochloric acid.

ACKNOWLEDGEMENT

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CONTENTS

	Page
Abstract	3
Acknowledgement	3
Introduction	7
Apparatus and Reagents	10
Experimental Results and Discussion	17
Recommended Procedure	23
Quality of Product	24
Conclusions	25
References	27

ILLUSTRATIONS

Figure 1. Electrolysis Apparatus	12
Figure 2. Precipitation Apparatus	13
Figure 3. Filtration Apparatus	14
Figure 4. Drying Chamber	15
Figure 5. Ignition Furnace	16

TABLES

I. Removal of Certain Elements by Mercury Cathode Electrolysis	18
II. Purity of Plutonium Dioxide and Plutonium(III) Chloride Solution Prepared by Mercury Cathode Electrolysis and Peroxide Precipitation	22

INTRODUCTION

Plutonium metal and plutonium solutions are spectrochemically analyzed for impurities by cupferron extraction⁽¹⁰⁾ and carrier-distillation^(9,13) methods in this Laboratory. The first method involves the separation of plutonium from impurity elements by extracting it as the cupferrate into an organic phase. Many elements do not form an extractable chelate under the conditions of the procedure and thus remain in the aqueous phase which is subsequently used in the analysis. The carrier-distillation method involves conversion of the sample to the refractory oxide, PuO_2 , addition of a carrier, such as gallium sesquioxide, and subsequent excitation in a cratered graphite electrode with a direct current arc. The efficiency of the first method depends, in part, on the completeness of extraction of the plutonium and the non-extraction of the impurities into the organic phase. The success of the carrier-distillation method primarily depends upon the efficiency with which the carrier (and matrix) allows impurity elements to be volatilized into the arc without permitting the complex spectrum of the plutonium to be excited. Each method has played an important role in the spectrochemical analysis of plutonium metal as well as its solutions, and each has advantages that are often determined by the type of sample involved.

However, it has been pointed out in the excellent works of Scribner and Mullin,⁽¹¹⁾ Nachtrieb,⁽⁸⁾ and Ayers and Fassel⁽¹⁾ that, in general, the carrier-distillation method can best be applied when the matrix of the standards matches, as closely as possible, the physical properties of the sample material at the time of excitation by the direct current arc. One reason for this lies in the fact that the rate of volatilization of a given element varies with the nature of the refractory matrices, a fact well substantiated by Ayers and Fassel⁽¹⁾ and stated by Scribner and Mullin.⁽¹¹⁾ Recently,* Kofoed⁽⁵⁾ has shown that measured values for some elements, particularly chromium, copper, and nickel, in plutonium samples are lower when compared to U_3O_8 standards than to PuO_2 standards. This can be interpreted to mean that these elements are volatilized at a faster rate from the U_3O_8 .

The lack of sufficient quantities of pure plutonium dioxide to prepare the necessary standards has resulted in the practice of using uranium as a stand-in when analyzing plutonium by the carrier-distillation method. As usually practiced, the spectra of the impurity elements excited from the plutonium dioxide samples are compared with the spectra of the same elements as excited from standard samples having an uranium oxide (U_3O_8) matrix. Since the physical properties of uranium oxide only roughly approximate those of plutonium dioxide (PuO_2 is 35 percent denser), the

*This reference added in proof.

recovery of impurity elements, present at the same concentration, from the two matrices may differ considerably. That this practice is open to serious question is indicated by Kofoed.⁽⁵⁾

The work described here was undertaken to make available sufficient quantity of plutonium dioxide suitable for use as a matrix for standards. It emphasizes the chemical processing as well as the equipment found necessary for preparation of the dioxide of satisfactory purity.

The preparation of high-purity plutonium chloride solutions is also described in this report. Although not a necessary part of the above problem, its preparation is included because it was a comparatively simple process once a sufficiently pure peroxide was obtained. High-purity chloride is vital to precision analysis by the cupferron method.

A literature survey indicated that a satisfactory product might be obtained by removing some of the impurity elements by electrolysis into a mercury cathode and others by either solvent extraction or precipitation from acid solution. For example, it was known that (1) elements below manganese in the electromotive force series may be removed from acid solution by such an electrolysis,^(6,7,12) (2) separation from certain light elements had been made by extracting plutonium cupferrate into an organic solvent,⁽¹⁰⁾ (3) continuous diethyl ether extraction with sodium nitrate as a salting-out agent removed 99.5 percent of the plutonium from a nitric acid solution,⁽¹⁴⁾ and (4) purification of plutonium had been achieved by the precipitation with

oxalate ion⁽¹⁴⁾ and also with hydrogen peroxide.⁽⁴⁾ These precipitation reactions were particularly efficient in separating plutonium from the light elements.

The method described in this report was found to yield a satisfactory product and was selected for that purpose as well as for convenience of operation. Involved are a partial removal of impurities by electrolyzing them into a mercury cathode and a subsequent further purification by precipitating the plutonium as the peroxide.

APPARATUS AND REAGENTS

Apparatus

1. Dry-box, stainless steel, 90 inches wide, with safety glass windows.
2. Glassware
 - a. Electrolysis cell,⁽²⁾ quartz (Figure 1).
 - b. Micropipettes, quartz, two sizes, 50- and 200- μ l. (Figure 2).
 - c. Pipettes, transfer, quartz, 1-ml. (Figures 1, 2).
 - d. Syringes, glass, with tygon tubing fittings, for pipettes (Figures 1, 2).
 - e. Cylinder, graduated, quartz, 30-ml. (Figures 2, 3).
 - f. Flasks, volumetric, quartz, two sizes, 50- and 100-ml. (Figures 1, 2).
 - g. Beakers, fluorothene, 250-ml. (Figure 2). Paraffined borosilicate beakers are an excellent substitute.
 - h. Flask, suction filter, paraffined borosilicate glass, 500-ml., attached to a vacuum trap (Figure 3).
 - i. Beakers, quartz, 100-ml. (Figure 2).

- j. Watch glasses, quartz or paraffined borosilicate glass, for electrolysis cell and precipitation beaker.
3. Platinum Ware
- a. Crucibles, Gooch, 20-ml. (Figure 3).
 - b. Crucibles, standard shape, 7-ml. (Figure 5).
 - c. Spatula (Figure 3).
4. Miscellaneous
- a. Direct current source, output of 5 amperes at 20 volts.
 - b. Magnetic mixer (Figure 2).
 - c. Magnetic stirring bar.
 - d. Filter paper, Whatman No. 40, cut to fit 20-ml. Gooch crucibles (Figure 3).
 - e. Drying chamber, borosilicate glass, connected to a glass water aspirator (Figure 4).
 - f. Heater, nichrome elements and stainless steel reflector (Figure 4).
 - g. Furnace, special design, with platinum liner and stainless steel case (Figure 5).
 - h. Controller for furnace.

Reagents

- 1. Water, distilled from and stored in quartz.
- 2. Hydrochloric acid, 6.24 N, distilled from and stored in quartz (constant-boiling fraction is collected).
- 3. Sulfuric acid, concentrated, distilled from vacuum quartz-still and stored in quartz.
- 4. Hydrogen peroxide, 30 percent, tin-free, Buffalo Electric Company.
- 5. Mercury, redistilled.
- 6. Nitric acid, concentrated, C.P. grade.

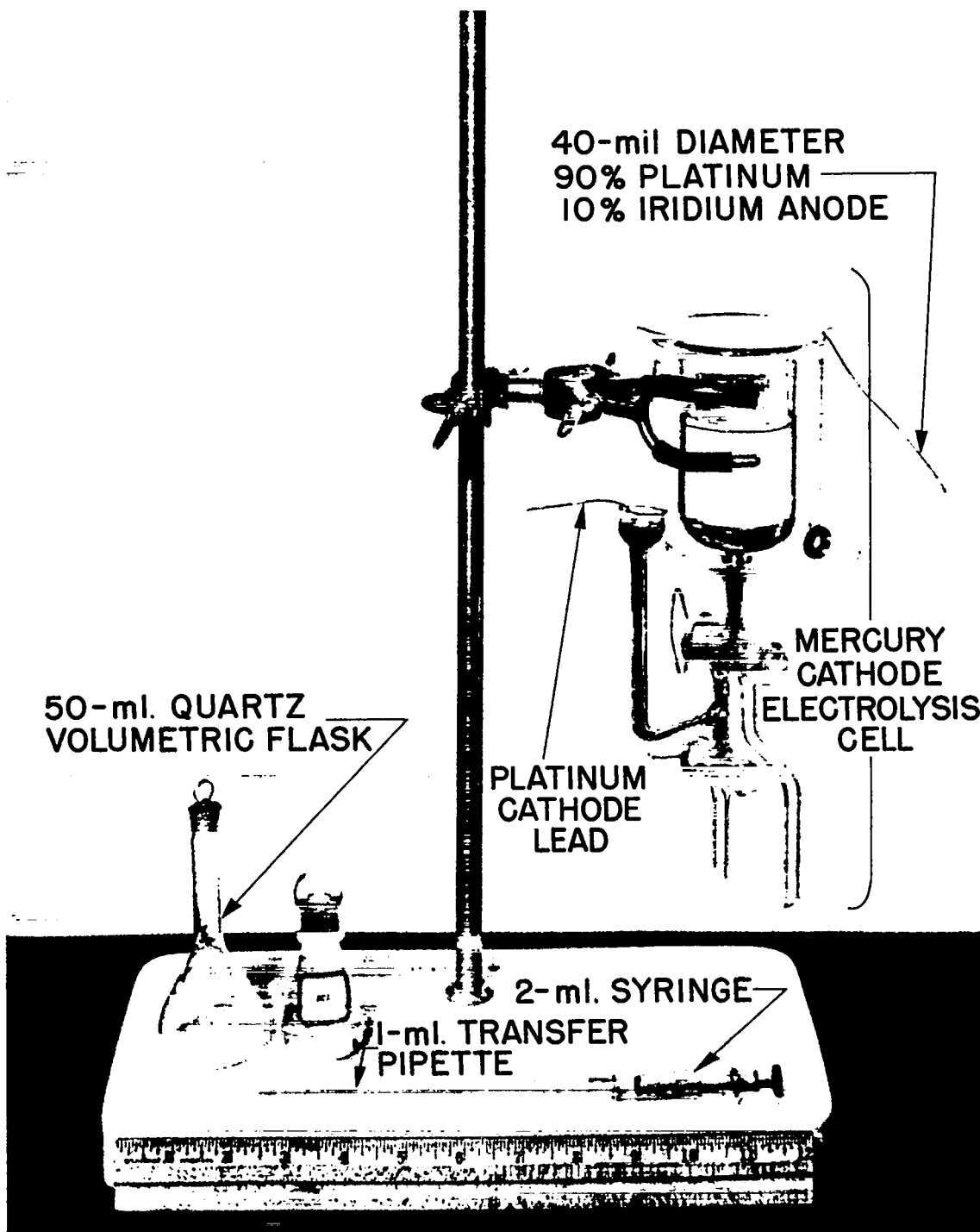


Figure 1. Electrolysis Apparatus

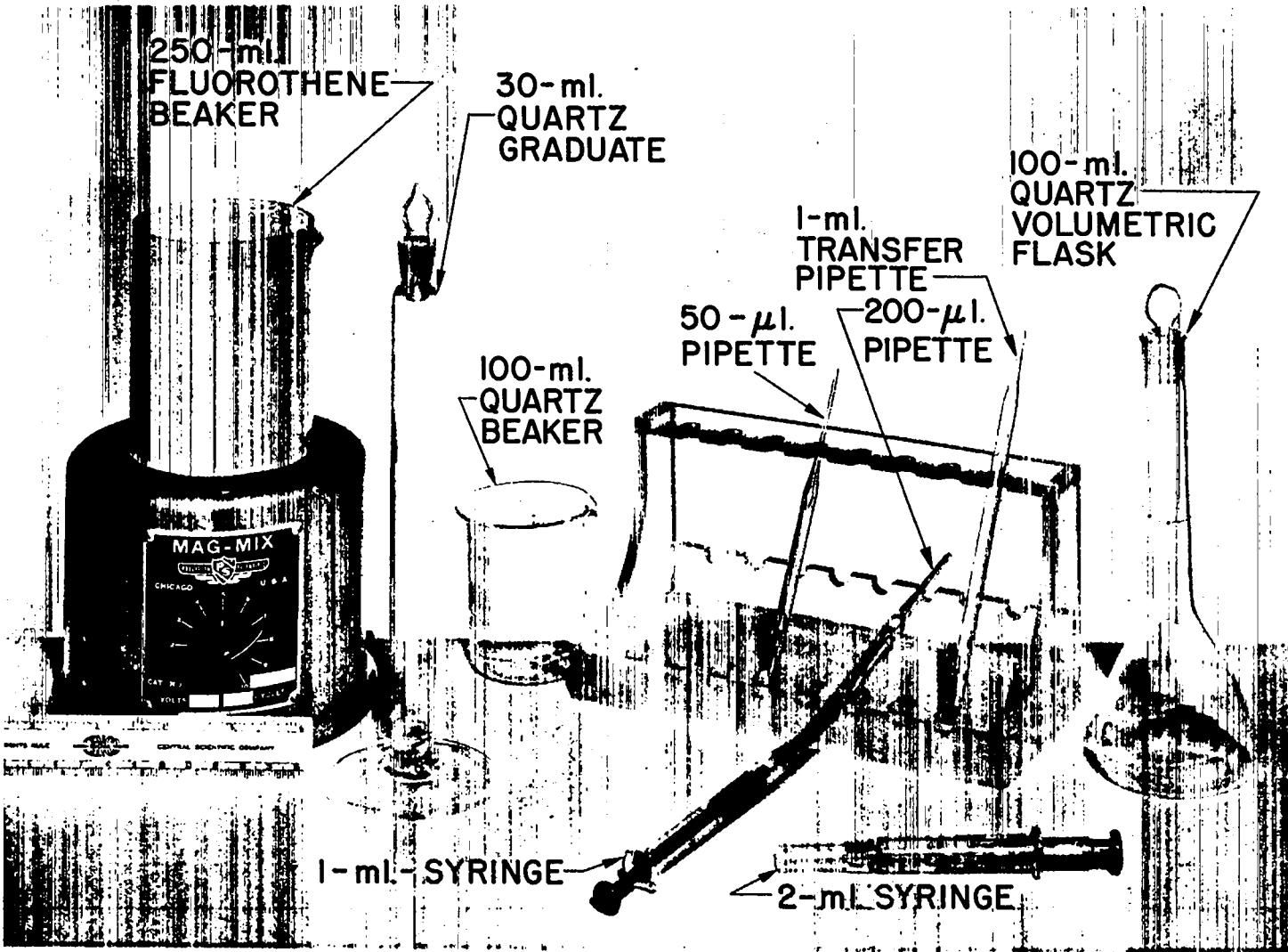


Figure 2. Precipitation Apparatus

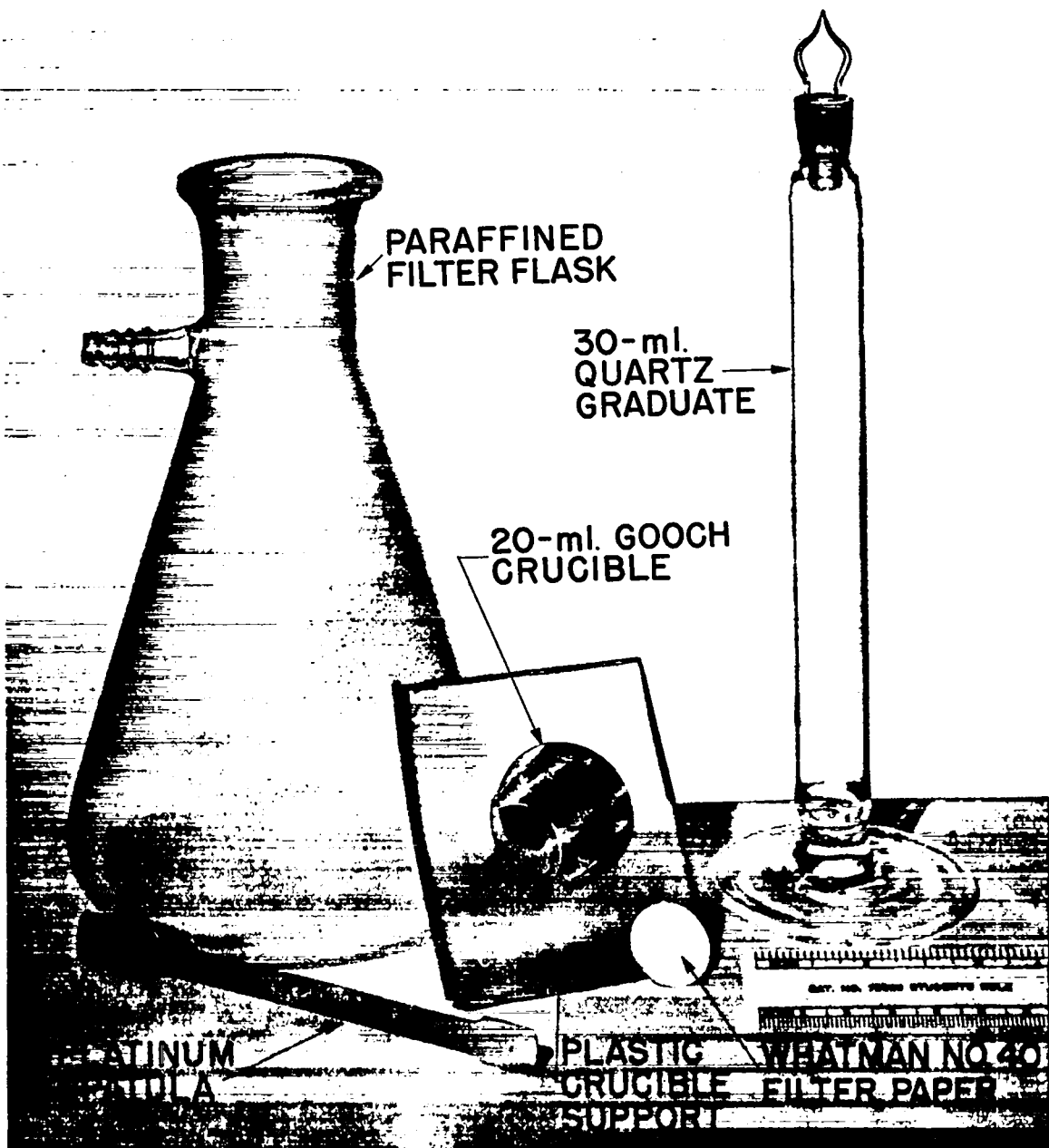


Figure 3. Filtration Apparatus

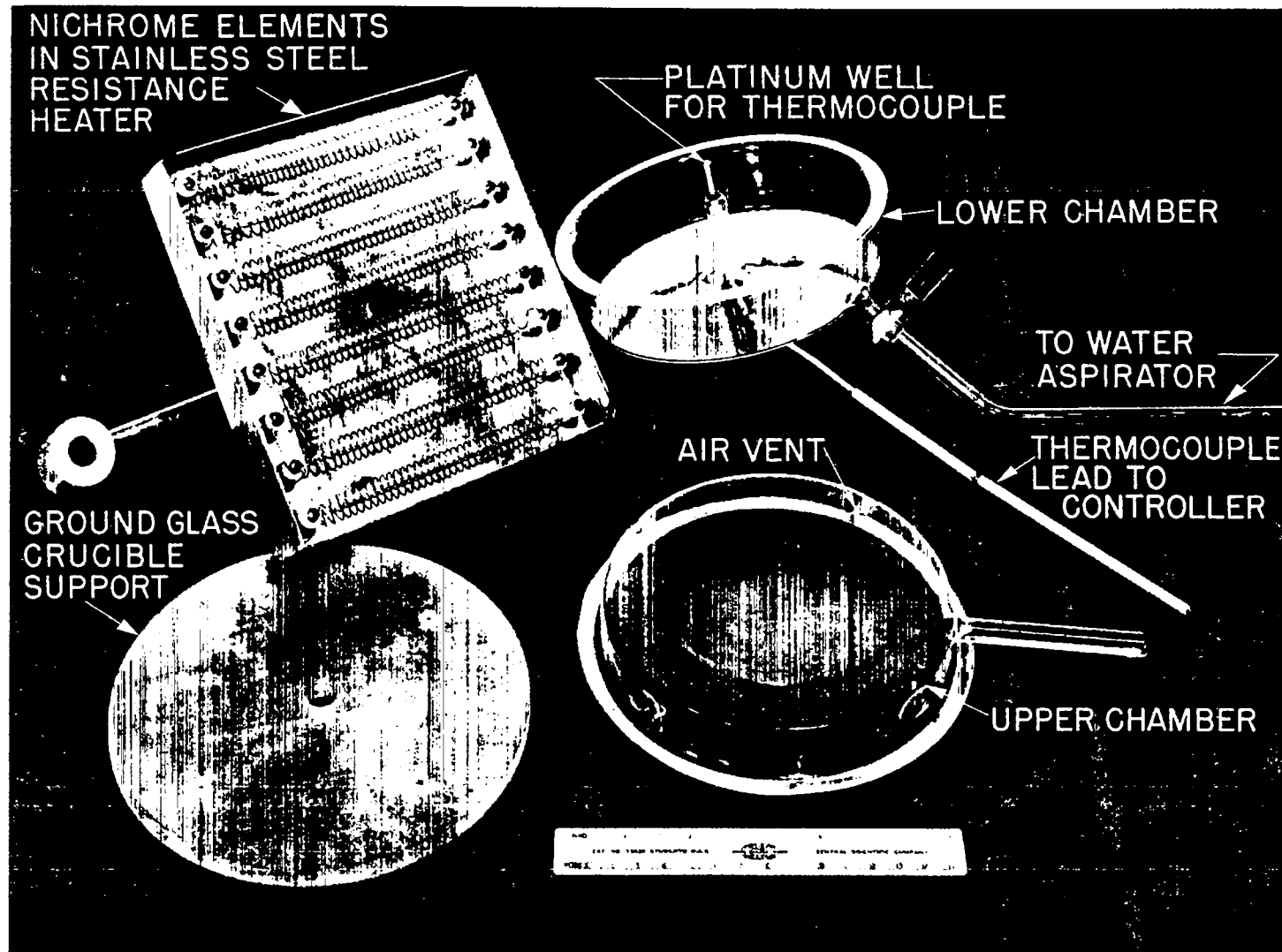


Figure 4. Drying Chamber

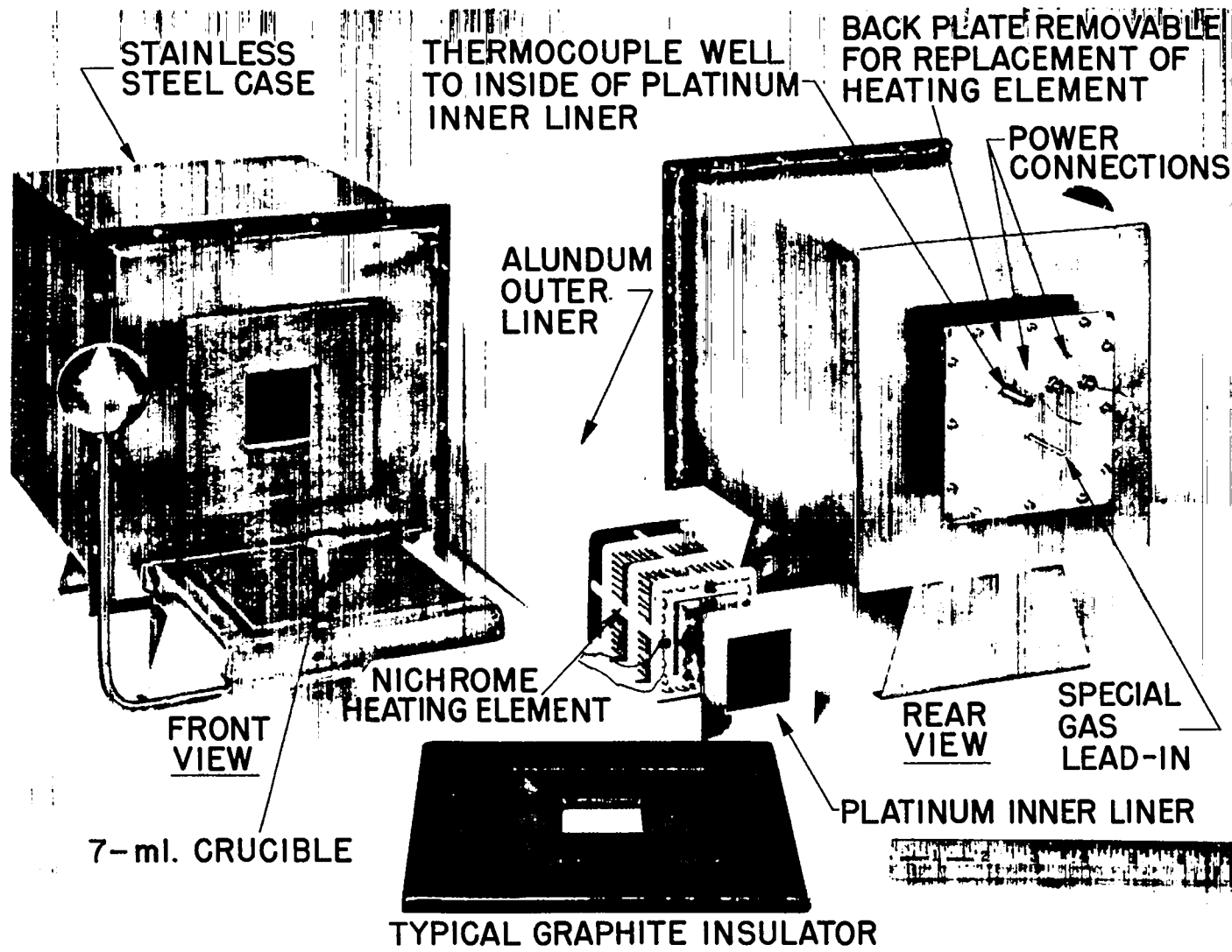


Figure 5. Ignition Furnace

EXPERIMENTAL RESULTS AND DISCUSSION

The mercury cathode cell (Figure 1) was tested to determine its efficiency in removing sub-microgram quantities of certain elements from hydrochloric acid solution. The elements listed in Table I were chosen for investigation since they are usually present as impurities in plutonium metal (starting material for preparation of the products described in this report) and are also known to be removed at the sub-milligram level. Four separate electrolyses were made, two with 1 gram of plutonium present and two in its absence. The other factors for all four electrolyses were identical as follows: (1) 50 milliliters of 1 N hydrochloric acid as the electrolyte, (2) 5-ampere constant current, (3) 45 to 50° C. electrolyte temperature, and (4) 1-hour total electrolysis. The current was maintained constant by adding 1-milliliter aliquots of quartz-distilled hydrochloric acid every 5 minutes and by increasing the power output of the direct current source. The electrolyte temperature was controlled by the flow of cooling water through the cell jacket. The rate of removal of the elements from the electrolyte was determined by spectrochemically analyzing aliquots taken from the cell at time intervals. The copper spark method ⁽³⁾ was used for those aliquots free of plutonium and the cupferron method ⁽¹⁰⁾ (using special standards) for those aliquots containing plutonium. The results of these analyses are summarized in Table I.

Table I

REMOVAL OF CERTAIN ELEMENTS BY MERCURY CATHODE ELECTROLYSIS

	<u>Without Plutonium</u>			<u>With Plutonium</u>		
	<u>µg./ML. Added</u>	<u>Removal Time,* Min.</u>	<u>µg./ML. after 1 Hr.</u>	<u>P.P.M.** Added</u>	<u>Removal Time,* Min.</u>	<u>P.P.M.** after 1 Hr.</u>
Cr	0.5	15	< 0.005	25	20	< 0.5
Co	0.5	10	< 0.005	25	15	< 0.5
Fe	2.5	15	< 0.025	125		****
Pb	0.5	5	< 0.01	25	10	< 1
Mn	2.5	30	< 0.01	125	30***	2
Ni	2.5	15	< 0.01	125	20	1
Sn	0.5	5	< 0.1	25		****
Zn	0.5	5	< 0.25	25		****

*Element no longer detected in aliquot.

**With reference to the plutonium content.

***Remained at 2 p.p.m. after 30 minutes.

****Not determinable by the cupferron method.

These results indicated that the mercury cathode effectively removed submicrogram amounts of certain impurity elements from hydrochloric acid solutions whether or not plutonium was present. A decrease in the removal efficiency caused by the presence of plutonium in the electrolyte was observed only for manganese, and then to a minor degree. Although the iron, tin, and zinc could not be determined in the presence of plutonium by the analytical methods used, it is concluded from the

purity of the final product that they were essentially as effectively removed as in the absence of plutonium. Additional electrolysis experiments showed that increase of the plutonium concentration of the electrolyte had no significant effect on the removal of the impurity elements and that 8 grams of plutonium could be processed with the results listed in Table I.

Attention was next centered on developing a method whereby the light elements (mainly those of atomic number less than 21) would be removed from the electrolyzed plutonium solutions. The separation processes investigated were organic solvent extraction of plutonium cupferrate, ammonium hydroxide precipitation, and hydrogen peroxide precipitation. Only the last one proved successful; however, a brief discussion will be made on the findings of the other two processes.

The electrolysis yielded a plutonium solution containing the (III) and (IV) oxidation states which was readily and completely chelated by cupferron. After quantitative extraction into such solvents as benzene, hexone, and toluene, the plutonium cupferrate was recovered and ignited to the dioxide at 500° C. About 25 purifications were carried out and in every case the product was contaminated with 20 to 100 parts per million of copper, iron, and silicon. The main cause of the contamination was traced to the cupferron which could not be purified by either reprecipitation or sublimation. Varying the pH of the chelation was also tried without significant success.

Six separate ammonium hydroxide precipitations were made on aliquots of an electrolyzed plutonium solution. The precipitates were ignited to the dioxide and when analyzed were found to contain 25 to 200 parts per million of magnesium, calcium, and silicon. These impurity elements were traced to the electrolyzed solutions as being non-removed by the mercury cathode and which coprecipitated with the plutonium hydroxide even under controlled precipitations at pH values less than 5.

The first experiments using hydrogen peroxide as the precipitant were conducted with thorium as a stand-in for plutonium. Substantial purification from the light elements was obtained. It was also observed that precipitations from strong acid gave purer products than those made at controlled pH values of 1.0 and 1.5, and that a scavenger precipitate containing 10 to 20 percent of the thorium carried with it the greater proportion of the precipitable impurity elements.

The optimum solvent composition for the precipitation of plutonium peroxide was established by making precipitations of 100-milligram aliquots of an electrolyzed plutonium solution with different hydrochloric acid, nitric acid, and sulfuric acid ratios. The best solvent, from the standpoint of both filterability and product purity, was composed of 1.5 N hydrochloric acid and 0.4 N sulfuric acid. Spectrochemical analyses of the ignited peroxide precipitates obtained from such solvents indicated only traces of impurity elements (< 5 p.p.m.) except for 100 to 500 parts per million of tin. The source of tin was

traced to the analytical reagent grades of hydrogen peroxide. The process was then scaled to the 8-gram plutonium level with tin-free hydrogen peroxide.

The merits of making a 10 to 20 percent scavenger precipitate were clearly demonstrated by analyses which showed that these precipitates contained most of the precipitable impurity elements which had remained in the electrolyzed solutions. The purity of these scavenger precipitates as well as the final ignited peroxide precipitates are shown in Table II.

It now became extremely simple to prepare high-purity plutonium(III) chloride solution by the direct dissolution, with heating, of plutonium peroxide in hydrochloric acid. Several batches of final peroxide precipitate, when so treated and analyzed by the cupferron method, showed that less than the spectrochemical sensitivity limits were present for the elements lithium, sodium, potassium, beryllium, magnesium, calcium, aluminum and lanthanum. Such solutions are used for the preparation of comparison and control standards in the cupferron method.⁽¹⁰⁾

Table II

PURITY OF PLUTONIUM DIOXIDE AND PLUTONIUM(III)
CHLORIDE SOLUTION PREPARED BY MERCURY CATHODE ELECTROLYSIS
AND PEROXIDE PRECIPITATION

	<u>Original Metal</u>	<u>Scavenger Precipitate</u>	<u>Purified Product</u>
Ag	ND (< 1)	ND (< 1)	ND (< 1)
Al	15	ND (< 5)	ND (< 5)
B	1	0.2	ND (< 0.1)
Be	ND (< 0.1)	ND (< 0.1)	ND (< 0.1)
Ca	ND (< 5)	ND (< 5)	ND (< 5)
Cd	ND (< 5)	ND (< 5)	ND (< 5)
Co	ND (< 5)	ND (< 5)	ND (< 5)
Cr	7	ND (< 2)	ND (< 2)
Cu	20	2	< 1
Fe	150	< 1	< 1
La	ND (< 10)	ND (< 10)	ND (< 10)
Li	ND (< 0.1)	ND (< 0.1)	ND (< 0.1)
Mg	3	2	< 1
Mn	30	5	2
Na	ND (< 5)	ND (< 5)	ND (< 5)
Ni	30	2	< 1
Pb	1	2	< 1
Si	40	25	< 1
Sn	1	< 1	< 1
Zn	ND (< 20)	ND (< 20)	ND (< 20)

ND - Not detected, therefore less than the spectrochemical sensitivity limit as listed. Metallic elements omitted from the table were not detected.

Impurity concentration is expressed as parts per million of element in plutonium.

Analysis of the dioxide product was made by the carrier-distillation method using U_3O_8 -matrix standards.

RECOMMENDED PROCEDURE

Caution

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

A. Preparation of High-Purity Plutonium Dioxide

1. Dissolve 8 ± 0.5 grams of plutonium metal with the minimum quantity of quartz-distilled hydrochloric acid in a 50-ml. quartz volumetric flask. Add 5 ml. of quartz-distilled hydrochloric acid and make to volume with quartz-distilled water.
2. Transfer the solution to the electrolysis cell. Electrolyze for 1 hour at 5 amp. Control the current by adding 1 ml. of quartz-distilled hydrochloric acid at 5-minute intervals and by adjusting the power output of the source. Maintain the electrolyte temperature within the range of 45 to 50° C. by the flow of cooling water in the cell jacket.
3. Transfer the electrolyzed solution to a 100 ml. quartz volumetric flask, add 20 ml.* of quartz-distilled hydrochloric acid and 1.25 ml. of quartz-distilled sulfuric acid. Make to volume with quartz-distilled water.
4. Transfer the solution to a 250-ml. fluorothene beaker. Slowly add 5 ml. of fresh 30 percent hydrogen peroxide (more, if not fresh) to effect a precipitate of 1 to 1.5 grams. The solution should be agitated by the plastic-covered magnet during the addition of the hydrogen peroxide.
5. Filter the precipitate with Whatman No. 40 paper supported in a 20-ml. platinum Gooch crucible, collecting the filtrate in a 500-ml. paraffined suction flask. Save the precipitate for plutonium recovery.

*The electrolysis depletes the hydrogen ion concentration. Analyses of electrolyzed solutions showed them to be 0.3 ± 0.1 N in hydrochloric acid.

6. Transfer the filtrate to a 250-ml. fluorothene beaker. Precipitate the remainder of the plutonium with an excess of 30 percent hydrogen peroxide added at the rate of 2 ml. per minute (40 ml. of fresh reagent are required).
7. Wash and stir the precipitate with 30 ml. of 1 N hydrochloric acid (prepared with 1 part quartz-distilled hydrochloric acid and 5 parts quartz-distilled water), and decant. Repeat four times, combining and saving the supernatants for plutonium recovery.
8. Collect the precipitate on Whatman No. 40 filter paper supported in a 20-ml. platinum Gooch crucible. Wash the precipitate five times with 10-ml. volumes of 1 N hydrochloric acid, saving the filtrates for plutonium recovery. Prevent channeling by lightly tamping the precipitate with a platinum spatula.
9. Transfer the precipitate to 7-ml. platinum crucibles and heat to dryness in the drying chamber.
10. Ignite to plutonium dioxide at a minimum temperature of 900° C. for 12 hours in a platinum-lined furnace.

B. Preparation of High-Purity Plutonium(III) Chloride Solutions

Steps 1 through 8. Same as Preparation A.

9. Transfer the precipitate to a 100-ml. quartz beaker and dissolve it with heat in excess quartz-distilled hydrochloric acid. Analyze aliquots for plutonium and free acid concentration.

10. Transfer to a quartz volumetric flask a volume of the solution which, upon the addition of the proper amount of quartz-distilled hydrochloric acid and quartz-distilled water to give a solution 1.87 N in hydrochloric acid, contains 50 mg. of plutonium per milliliter.

QUALITY OF PRODUCT

Only 2 of 15 preparations gave products exceeding the impurity element levels listed in Table II and these differed only by containing 4 to 6 parts per million of manganese. An average recovery of 7.2 grams of pure dioxide from 8 grams of metal indicated an 80 percent yield.

Elaborate precautions must be taken to keep contamination to a minimum. In addition to the techniques required for the actual chemical processing, the following should be observed: (1) Clean all apparatus by two separate washes in hot C.P. nitric acid, rinsing just prior to use with quartz-distilled water. (2) Wash rubber gloves with a low-ash detergent and completely remove traces of the detergent with distilled water. (3) Filter the air supply to the laboratory to remove atmospheric dust. (4) Heat new platinum ware with fused potassium bisulfate to remove polishing abrasives, such as aluminum oxide, that were used by the manufacturer. The last traces of the fusion are removed by repeated washings in hot nitric acid. Soak new quartz ware in hot nitric acid for at least 1 week. (5) Thoroughly wipe the interior of the dry-box as well as its contents once each week with medical gauze dampened with distilled water.

CONCLUSIONS

1. Mercury cathode electrolysis was found to be highly efficient in removing the heavy-element impurities from a hydrochloric acid solution of plutonium. The concentration of elements below manganese in the electromotive force series was decreased to less than 0.01 microgram per milliliter by this process.
2. Precipitation of plutonium as the peroxide separated it from the light-element impurities. The best solvent for precipitation, from the standpoint of filterability and product purity, was found to be

composed of 1.5 N hydrochloric acid and 0.4 N sulfuric acid. A scavenger precipitate of 10 to 20 percent of the plutonium was found to carry with it most of the precipitable metal impurities.

3. The combining of these purification processes yielded plutonium peroxide precipitates of extremely high purity which could either be ignited to high-purity plutonium dioxide or be dissolved in hydrochloric acid to give high-purity plutonium(III) solutions. Recommended procedures for such preparations are described.

4. Purification of plutonium by either extraction of its cupferrate into organic solvents or by precipitation of the hydroxide was not successful.

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