JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY
(Registered in U. S. Patent Office)
VOLUME 71 MAY 19, 1949 NUMBER 5

[CONTRIBUTION FROM THE METALLURGICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# The First Isolation of Plutonium

BY B. B. CUNNINGHAM[1] AND L. B. WERNER[1]

Following the discovery of $_{94}Pu^{239}$ in 1941, for about a year and one-half the investigations[2] of this isotope of plutonium were performed using compositions which contained $_{94}Pu^{239}$ in only very small proportion.

It is the purpose of the present paper to describe the first experiments in which plutonium was isolated and studied in the form of pure compounds, or in pure solutions at ordinary concentrations ($10^{-3}$–$10^{-1}$ $M$). The principal objectives of this work were the following: (a) to demonstrate a chemical process by means of which plutonium could be separated from uranium and fission products and be obtained in the form of pure compounds, (b) to determine the specific alpha disintegration rate of $Pu^{239}$,[3] and (c) to establish some of the chemical properties of pure plutonium compounds by direct observation.

At the time that most of the work described in this paper was done it had not yet been shown that a self-sustaining nuclear reaction, leading to the production of substantial amounts of $_{94}Pu^{239}$ could be achieved. All of the plutonium used in the work described herein was made by the reaction of natural uranium with neutrons produced by bombarding beryllium with cyclotron-accelerated deuterons of about 12-Mev energy. This method of producing $Pu^{239}$ has been described in some detail by Seaborg and Wahl.[2] The cyclotron of Washington University at St. Louis contributed most heavily to this program. Substantial amounts of plutonium were manufactured also by the 60-inch cyclotron of the University of California at Berkeley.

Since only a very low neutron flux could be obtained in this way the concentration of plutonium in the irradiated uranium, even after weeks of bombardment, did not exceed 0.003 p.p.m. A major part of the problem of isolating plutonium from this product, therefore, consisted of the separation of a great bulk of uranium. This work was made more difficult by the presence of high levels of radioactivity associated with the fission products of $U^{235}$.

For the most part, these bulk separations were carried out by A. H. Jaffey, T. P. Kohman, D. E. Koshland, Jr., and E. H. Turk at Chicago and by A. C. Wahl and J. W. Gofman at Berkeley.

Further work involved a progressive reduction in the scale of operations employing first laboratory apparatus of conventional size and finally extremely small equipment suitable to the so-called "ultra-micro" scale.

The "fluoride cycle" method of separating plutonium from uranium and fission products and of concentrating the element with successively smaller amounts of rare-earth carrier was based on the discovery by Seaborg and Wahl[2] that plutonium in its oxidized form is not carried by rare-earth fluoride precipitates, but is carried in its reduced state(s).

The separation of plutonium from neptunium (largely $Np^{239}$ in the case of our work) similarly was based on the work of these authors, who found that neptunium, but not plutonium, is oxidized to a "fluoride soluble" state by bromate in 1 $M$ sulfuric acid at room temperature.

In all of our work with fluoride solutions such solutions have been contained in "lusteroid," platinum or wax-coated glass apparatus.

---

(1) Present address: Department of Chemistry and Radiation Laboratory, University of California.

(2) G. T. Seaborg and A. C. Wahl, THIS JOURNAL, **70**, 1128 (1948).

(3) A knowledge of this constant was necessary in order to compute accurately the quantity of plutonium (as $Pu^{239}$) present in various experiments, and in particular in the measurements of the thermal neutron fission cross section of the isotope. It had been shown previously by Seaborg and Wahl that the half-life of the isotope $Pu^{239}$ was 25,000 ± 5000 years.

In the final stages of isolation of plutonium and in the preparation and identification of its compounds extensive use was made of the microgram-scale techniques developed by P. L. Kirk[4] and associates and by M. Cefola[5] and A. A. Benedetti-Pichler.[6]

A preliminary isolation of about one microgram of $_{94}\mathrm{Pu}^{239}$ was carried through during the latter part of August, 1942, and in September a second isolation was made from material containing about thirty micrograms of the element. Gravimetric operations were carried out on a two to five microgram scale, using plutonium obtained in the second isolation. It is interesting to note that this was the first time that an element made by synthetic means had been isolated and weighed as a pure compound.

## Experimental

**Isolation of One Microgram of Plutonium as the Fluoride.**—One microgram of $\mathrm{Pu}^{239}$ was produced in 5 kg. of uranyl nitrate hexahydrate by irradiation with neutrons produced by a d,n reaction on beryllium, using 12-Mev. deuterons from the Berkeley 60-inch cyclotron. The plutonium was separated from uranium, neptunium, and fission products and concentrated with 5 mg. of cerium and 5 mg. of lanthanum in 15 cc. of 0.5 *M* sulfuric acid solution by a series of "fluoride cycles" carried out by Wahl, Gofman and others at the University of California. Further concentration and ultimate isolation of the plutonium was carried out at Chicago.

The solution received from Berkeley was concentrated by evaporation in platinum to a volume of 8 cc. and was then transferred to a 15 cc. "lusteroid"[7] tube.

Two cc. of 27 *M* hydrofluoric acid and five drops of 5 *M* potassium fluoride were added to precipitate the cerium and lanthanum, together with the plutonium, as fluorides. The precipitate of mixed fluorides was separated from the solution by centrifugation, decantation and washing. Of the 70,000 alpha counts/minute[8] of $_{94}\mathrm{Pu}^{239}$ present in the original solution only 300 failed to precipitate with the rare earth fluorides.

The precipitate was transferred by washing to a 20 cc. platinum evaporating dish, treated with 0.3 cc. of 18 *M* sulfuric acid, and heated until fumes of sulfuric acid appeared. This sufficed to convert the insoluble lanthanum and cerium fluorides to soluble sulfates.

The sulfates were dissolved in 2 cc. of 2 *M* nitric acid, the solution was transferred to a Lusteroid tube and several mg. of solid argentic oxide were added to oxidize the plutonium to the "fluoride soluble" oxidation state. The solution was then made 2 *M* in hydrofluoric acid. The rare earth fluoride precipitate was packed in the bottom of the tube by centrifugation. The supernatant solution, containing plutonium in the oxidized "fluoride soluble" state, was separated from the precipitate with a 0.1 cc. wax-coated syringe-controlled micropipet of the type developed by Kirk.[9] Assay for alpha activity showed 95% of the plutonium to be in the supernatant solution. This was transferred to a 20-cc. platinum dish and evaporated on a hot-plate until fumes of sulfuric acid began to appear. In this operation plutonium is reduced to a fluoride insoluble state.[2] The residue was diluted with water to a volume of 2 cc. and transferred to a 15-cc. lusteroid tube. One-half milligram each of lanthanum and cerium were added as solutions of the nitrates in 50 μl[10] volumes of dilute nitric acid. The lanthanum, cerium and plutonium were precipitated by the addition of 100 μl of 27 *M* hydrofluoric acid. The supernatant liquid was removed and the precipitate washed once with one cc. of water.

In all subsequent operations with this sample of plutonium special attention was paid to the purity of the reagents. The water, nitric, hydrochloric and sulfuric acids used were distilled twice in an all-pyrex still. Other reagents used were of the best grade obtainable.

The fluoride precipitate was transferred by washing with redistilled water into a 20-cc. platinum evaporating dish, and the fluorides were converted to sulfates by heating with 0.1 cc. of 18 *M* sulfuric acid. The residue was dissolved in one cc. of water. This solution was made 2 *M* in nitric acid, transferred to a 15 cc. lusteroid tube and treated with enough solid argentic oxide to impart a deep brown color to the solution. The rare earths were precipitated by the addition of 100 μl of 27 *M* hydrofluoric acid. The supernatant solution was separated from the lanthanum–cerium fluoride precipitate with a wax-coated micropipet as described previously. Assay for alpha-activity showed the solution to contain 58,000 c./m. of $\mathrm{Pu}^{239}$.

Twenty microliters of 18 *M* sulfuric acid was added to the solution from a micropipet and the solution was then heated on a hot-plate until the acid began to fume strongly. The residue was diluted with 150 μl of water and transferred to a previously prepared 15-cc. lusteroid tube having a specially formed conical bottom. This tube was formed on a wooden mould from an ordinary round-bottom tube by first heating the lusteroid in a bath of boiling glycerol.

Twenty-five microliters of 0.05 *M* lanthanum nitrate in 0.1 *M* nitric acid was added to the plutonium solution. The solution was stirred and was then made 3 *M* in hydrofluoric acid by adding 25 μl of 27 *M* hydrofluoric acid from a wax-coated micropipet. The precipitate (containing lanthanum and plutonium fluorides at a weight ratio of about 20:1) was packed in the tip of the cone by centrifugation. The supernatant solution was removed and the precipitate was washed once with 50 μl of 2 *M* hydrofluoric acid. Examination of the combined supernatant and wash liquids for alpha activity showed that about 7% of the plutonium was not precipitated in this step. The washed precipitate was suspended in 50 μl of water by twirling a small loop of fine platinum wire in the mixture. The suspension was transferred with a micropipet to a 1 cc. platinum crucible and 10 μl of sulfuric acid was added to the suspension. The crucible was heated carefully on an electric hot-plate until fumes of sulfuric acid were just visible. The residue was allowed to cool and was then diluted with 15 μl of 2 *M* nitric acid. The solution was transferred to the tip of a wax-coated 200 μl microcone[11] by using a capillary pipet mounted on a micromanipulator[12] as shown in Fig. 1. The pieces were brought into alignment and the delivery operation was observed through a 30 power stereoscopic binocular microscope.[13]

All subsequent chemical operations with this sample of plutonium were performed with this same assembly.

The plutonium was oxidized to the "fluoride soluble" state by adding sufficient solid silver nitrate and potassium peroxydisulfate to impart a brown color to the solution

---

(4) P. L. Kirk, *Ann. Rev. Biochem.*, **9**, 593 (1940).

(5) M. Cefola, Ph.D. Thesis, New York University, 1941.

(6) A. A. Benedetti-Pichler, "Microtechnique of Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942.

(7) A transparent fluoride resistant plastic manufactured by the Lusteroid Container Corporation of 50 Parker Avenue, South Orange, N. J.

(8) All counts were made in a $2\pi$ geometry alpha counter in which the counting yield was 50 ± 5%.

(9) The construction, calibration and use of micropipets for measuring liquid volumes in the range 5 μl to 100 μl is described in a series of papers by Kirk and Associates. See, for example, R. C. Sisco, B. B. Cunningham and P. L. Kirk, *J. Biol. Chem.*, **139**, 1 (1941).

(10) μl = microliter = $10^{-6}$ l.

(11) Manufactured by Microchemical Specialties Company, Berkeley, California.

(12) Gamma manipulator manufactured by the Gamma Scientific Company, New York, New York.

(13) The microscopes used by us have been either the Bausch and Lomb Model SKW or the Spencer Model 29LF, equipped with a heavy metal base.

and the lanthanum was precipitated by the addition of about 2 μl of 27 *M* hydrofluoric acid. The precipitate was packed in the tip of the cone by centrifuging in a small air-driven centrifuge.[8] The supernatant solution was transferred to a second wax-coated microcone and the silver precipitated by the addition of one microliter of 12 *M* hydrochloric acid. The supernatant solution was transferred to a 1 cc. platinum crucible and heated until the residual sulfuric acid began to fume strongly. The residue was diluted with about 30 μl of water and this solution was transferred into a 200 μl cone. Five microliters of 0.1 *M* nitric acid containing five micrograms of lanthanum were added and the lanthanum and plutonium were precipitated together as the "hydroxides" by making the solution alkaline with 8 *M* ammonium hydroxide.

The precipitate of lanthanum and plutonium hydroxides was washed three times with 15 μl portions of freshly prepared 2 *M* ammonium hydroxide and was then dissolved in 30 μl of 2 *M* nitric acid.

About 100 μg[14] of solid ammonium peroxydisulfate and 40 μg of silver nitrate were added and the solution was stirred and allowed to stand for ten minutes to permit complete oxidation of the plutonium. One microliter of 27 *M* hydrofluoric acid was added, the solution was stirred and the precipitated lanthanum fluoride centrifuged out. The supernatant solution was transferred to a one cc. platinum dish, treated with 5 μl of 18 *M* sulfuric acid and heated until fumes of sulfuric acid appeared. The residue was diluted with 25 μl of water and the diluted solution was transferred to a 200 μl microcone.

One microliter of 27 *M* hydrofluoric acid was added to precipitate the plutonium as the fluoride, and the solution was centrifuged immediately. A fluoride precipitate, barely visible to the naked eye, but easily visible under 30 × magnification was observed in the tip of the microcone. This precipitate was semi-gelatinous and flocculent in appearance, similar to the fluorides of thorium or tetra positive cerium. This first isolation of plutonium took place on August 18, 1942.

About fifteen minutes after centrifuging the precipitated plutonium fluoride a 0.25 μl aliquot of the supernatant solution was removed, dried and assayed for alpha activity. Seventy-five alpha counts per minute were found to be present in the aliquot. On the assumption that the half-life of $Pu^{239}$ was 30,000 years the solubility of the plutonium fluoride was calculated to be about 5 mg. of plutonium per liter. Shortly after this determination was completed a precipitate of ammonium fluosilicate started to form in the microcone.

Although the procedure outlined above was not satisfactory in its final stages, for the isolation of plutonium of high purity for gravimetric work, it served to demonstrate that the fluoride-cycle method of concentration and purification of plutonium was applicable at all relative concentrations of lanthanum and plutonium.

**Preparation of Twenty Micrograms of Plutonium Nitrate.**—While the preliminary isolation of plutonium just described was being carried out 90 kg. of uranyl nitrate hexahydrate was being irradiated with neutrons from a bombardment of beryllium with 12-Mev. deuterons produced in the Washington University cyclotron at St. Louis. Chemical operations designed to isolate the plutonium from this material were begun at Chicago in the latter part of August. The procedure used was as follows:

The 90 kg. of uranyl nitrate hexahydrate was dissolved in 100 l. of diethyl ether to yield 8 l. of aqueous phase (containing all of the neptunium and plutonium, most of the fission products and 6.5 kg. of uranyl nitrate hexahydrate and 120 l. of ether phase containing 83.5 kg. of uranyl nitrate hexahydrate).

The aqueous phase was evaporated on a steam-bath until its composition was approximately that of uranyl nitrate hexahydrate. The residue was treated with 7.1 l. of ether to yield a second aqueous phase of 0.6 l. volume, containing about 500 g. of the hexahydrate, together with the plutonium, neptunium and fission products.

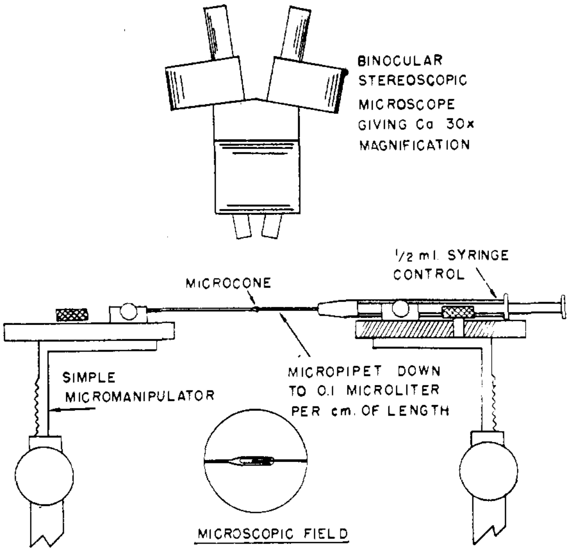

Fig. 1.—Apparatus used for chemical operations on the microgram scale.

This solution was diluted to 2.0 l. with 2 *M* nitric acid and made 0.0014 *M* in lanthanum nitrate. Lanthanum fluoride was precipitated by making the solution 4 *M* in hydrofluoric acid. The supernatant solution, containing all of the uranium and about 25% of the fission products was discarded.

The lanthanum fluoride precipitate was converted to lanthanum sulfate by heating in a platinum dish with 18 *M* sulfuric acid. The residue was dissolved in 200 cc. of 2 *M* nitric acid. To this solution were added 20 g. of potassium peroxydisulfate and 0.25 g. of silver nitrate and the solution was stirred until the brown color of argentic ion was clearly evident. Lanthanum was precipitated as the fluoride by making the solution 4 *M* in hydrofluoric acid. Plutonium and neptunium, in their higher oxidation stages, remained in the supernatant solution. All but about 1% of the remaining fission product activity precipitated with the lanthanum fluoride, which was discarded.

The plutonium and neptunium in the supernatant solution were reduced to their fluoride insoluble states by adding sufficient 6% sulfur dioxide solution to discharge the color of the argentic ion.

The reduced plutonium and neptunium were carried from solution on a preformed lanthanum fluoride precipitate by the slow addition with stirring of 50 mg. of lanthanum as lanthanum nitrate solution.

The lanthanum fluoride was separated and converted to lanthanum sulfate by heating with sulfuric acid. The residue was diluted to 100 ml. with a 2 *M* nitric acid and 10 g. of potassium peroxydisulfate and 0.1 g. of silver nitrate were added. After allowing ten minutes for complete oxidation of the plutonium and neptunium the lanthanum was precipitated by hydrofluoric acid in the usual way.

The plutonium and neptunium in the separated supernatant solution were reduced with an excess of 6% sulfur dioxide solution, and were carried from solution by adding 30 mg. of lanthanum (in nitric acid solution) slowly, with stirring. The lanthanum fluoride precipitate was separated and fumed to dryness with concentrated sulfuric acid.

The residue was dissolved in 40 cc. of 1.5 *M* sulfuric acid, made 0.1 *M* in potassium bromate and allowed to stand at room temperature for thirty minutes. The fluoride precipitate, containing all of the plutonium, was separated. The supernatant solution, containing 90% of the neptunium, was discarded.

The fluoride precipitate was fumed to dryness with an excess of sulfuric acid and the bromate oxidation repeated.

---

[14] μg = microgram = $10^{-6}$ g.

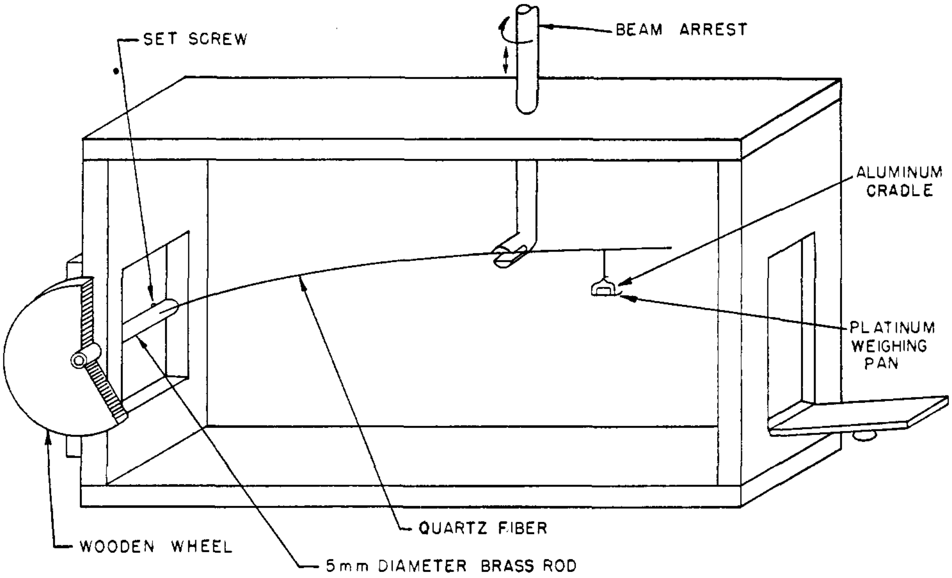

Fig. 2.—Salvioni balance.

These two cycles sufficed to separate all but 1% of the neptunium originally present with the plutonium.

The fluoride precipitate was again fumed to dryness with sulfuric acid and was then dissolved in 40 cc. of 1 *M* nitric acid. Assay of the solution for alpha activity showed it to contain $5.1 \times 10^6$ c./m. of $Pu^{239}$. Half of this solution was set aside for nuclear work.

To the remainder of the solution was added 2 g. of ammonium peroxydisulfate and 35 mg. of silver nitrate. After five minutes 5 cc. of 27 *M* hydrofluoric acid was added and ten minutes later the solution was centrifuged. The plutonium in the separated supernatant solution was reduced by the addition of one cc. of 6% sulfur dioxide solution and was carried from solution by the slow addition of one mg. of lanthanum (in 0.1 *M* nitric acid). The solution was stirred for ten minutes and then centrifuged. The supernatant solution was set aside.

The lanthanum fluoride was heated with sulfuric acid, dissolved in one cc. of 1 *M* nitric acid. The plutonium was oxidized by the addition of 0.1 g. of ammonium peroxydisulfate and 2 mg. of silver nitrate. After ten minutes, the lanthanum was precipitated by the addition of 0.2 cc. of hydrofluoric acid. After an additional ten minutes the solution was centrifuged.

The plutonium was reduced to its "fluoride insoluble" oxidation state by the addition of 0.1 cc. of 30% hydrogen peroxide solution. The plutonium was precipitated from solution by the addition of 0.1 mg. of lanthanum (as a nitrate solution).

After thirty minutes the solution was centrifuged and the fluoride precipitate was separated and transferred to a 1 cc. platinum crucible. The mixed fluorides of plutonium and lanthanum were treated with 25 μl of concentrated sulfuric acid, evaporated to dryness and dissolved in 100 μl of 2 *M* nitric acid solution. Ten milligrams of ammonium peroxydisulfate and 0.2 mg. of silver nitrate were added to oxidize the plutonium. The lanthanum was separated from the oxidized plutonium by precipitation with hydrofluoric acid.

The supernatant solution, containing plutonium in the oxidized state, was transferred to a one cc. platinum crucible and evaporated to dryness. The residue was dissolved in 100 μl of 1 *M* nitric acid, transferred to a 200 μl microcone and made alkaline with freshly prepared ammonium hydroxide.

The flocculent yellow-green precipitate was centrifuged and washed three times with 20-μl portions of 1 *M* ammonium hydroxide solution. The volume of the centrifuged precipitate was estimated to be about 7 μl.

The crude plutonium hydroxide precipitate was dissolved in 50 μl of 1 *M* nitric acid solution. The solution was then made 0.5 *M* in potassium iodate. This resulted in the separation of a buff-colored precipitate of plutonium iodate.

The iodate was metathesized to the hydroxide by treatment with four successive 20 μl portions of 10 *M* ammonium hydroxide solution.

The hydroxide was washed three times with 20 μl portions of 1 *M* ammonium hydroxide, dissolved in 10 μl of 6 *M* nitric acid, and precipitated as the iodate by the addition of 10 μl of 0.5 *M* potassium iodate–6 *M* nitric acid solution. After twenty minutes the precipitate was washed twice with 10 μl portions of 6 *M* nitric acid–0.5 *M* potassium iodate solution.

The precipitation and washing of the iodate with strongly acid solution was carried out to remove the last traces of lanthanum from the plutonium.

The iodate was metathesized to the hydroxide by four successive treatments with freshly distilled 10 *M* ammonium hydroxide. The "hydroxide" was dissolved in 10 μl of 2 *M* nitric acid to give a pale yellow-green solution approximately 0.01 *M* in plutonium.

A portion of this solution was used to determine the specific alpha activity of $Pu^{239}$, as outlined in the succeeding section.

**Construction of a Microbalance Having a Sensitivity of 0.01 μg.**—The determination of the specific alpha activity of $Pu^{239}$ required the prior construction of a balance capable of weighing a few micrograms of a pure plutonium compound with an error not exceeding about ±0.03 μg.

Several balances having the required degree of sensitivity have been described in the literature.[15,16,17,18]

Because of the extreme simplicity of its construction, however, we chose to attempt a refinement of the Salvioni[19] "balance." It was hoped that the considerable

---

(15) B. D. Steele and K. Grant, *Proc. Roy. Soc.* (*London*), **A82**, 580 (1909).

(16) Hans Pettersson, "A New Microbalance and Its Use," Ph.D. thesis, the University of Stockholm, 1914. Published by Wald, Zachrissons Boktryckeri A.-B., Göteborg, 1914.

(17) W. Ramsey and R. Whytlaw-Gray, *Proc. Roy. Soc.* (*London*), **A84**, 536 (1911).

(18) F. Emich in Abderhalden's "Handbuch der biologischen Arbeitsmethoden," Abt. I, T. 3, p. 268, Vienna and Berlin, Urban und Schwarzenberg, 1921.

(19) E. Salvioni, Misura di mase comprese fra g. $10^{-1}$ a g. $10^{-6}$, Messina, 1901.

delay required by the construction of one of the more elaborate instruments might thus be avoided.

The construction of the Salvioni balances used by us is shown in Fig. 2. These balances, which consist of nothing more than a fine horizontal fiber of quartz, mounted rigidly at one end, and suitably protected from air currents, required only a few hours to construct.

The sensitivity (deflection of the free end of the fiber per unitload) is readily calculable from the relation

$$d = \frac{Fa^2(^1/_2l - l/6a)}{EI}$$

where $d$ is the deflection in cm., $F$ the applied force at a distance $a$ cm. from the fixed end, $l$ the length of the fiber from the fixed end to the tip of the pointer, $E$ is Young's modulus and $I$ the moment of inertia of a section of the fiber about its diameter.

By using a twenty-two power Leitz horizontal microscope equipped with a filar micrometer, deflections of the free end of the fiber could be read to ±0.0005 mm. Setting this as approximately equal to the required sensitivity of ±0.03 μg, choosing 12 and 10 cm. as convenient lengths for $l$ and $a$, respectively, the required diameter was calculated as 0.106 mm.

Several fibers of appropriate length and about 0.1 mm. in diameter were drawn from clear quartz rod. The most uniform was selected and one end drawn out to a fine point. A small quartz hook was fused to the fiber at a point two centimeters from the end of the pointer.

The fiber was then mounted in a protective housing as shown in Fig. 2. The case was constructed of wood with glass sides. The fixed end of the fiber was mounted in a small hole drilled perpendicular to the axis of a 5 mm. diameter brass rod, and clamped in place by a set screw as shown. Coarse adjustment of the horizontal position of the free end of the fiber could be made by rotating the brass rod by means of a wheel outside the case. A beam arrest for holding the fiber in a fixed position while loading or unloading was made from an L-shaped piece of 5 mm. brass rod. The vertical arm of this rod projected through a tightly fitting hole in the top of the balance case. By rotation and vertical movement of the rod a notch in the end of the horizontal member could be caused to engage the beam in any desired position.

Materials to be weighed were placed on a small platinum weighing pan of the size and shape shown in Fig. 3. The weighing pan was then placed in an aluminum cradle which could be attached to the beam of the balance as indicated.

Pan and cradle were cut by hand from very thin metal foil, laid on a smooth block of soft pine. A fragment of razor blade was used as a cutting tool. The cutting operation was observed with a thirty-power stereoscopic binocular microscope. The cut foils were shaped into the desired forms by rubbing the metal with a tiny glass rod.

The weighing pans were made from 0.1 mil platinum foil and had a weight of about 200 μg. The weight of the aluminum cradle was roughly the same.

These pieces were attached and detached from the balance with the aid of a micromanipulator.

A useful kind of forceps for holding the weighing pan while material was being added to it was made by providing platinum tips for a small ruling pen. By turning the knurled nut on the ruling pen the jaws of the forceps were brought together to clamp and hold the tail of the pan.

Since the balance case and reading microscope were mounted separately some effect was to be anticipated from differences in expansion of the separate mountings during changes in room temperature. Such an effect was expected to appear as a slow apparent drift in the position of the quartz fiber in the field of the microscope. The effect was investigated on several occasions. Typical data are shown in Table I.

On most occasions the rate of drift was considerably less than that illustrated in Table I. However, for any pair of weighings made more than a few minutes apart, it was obviously necessary to correct for the drift. This was done by immediately reloading the balance with a second pan of nearly the same weight and correcting for the observed drift in the interval between successive weighings.

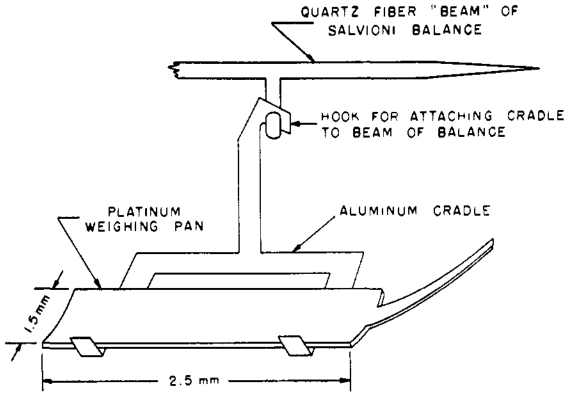

Fig. 3.—Weighing pan and pan cradle for the Salvioni balance.

TABLE I

APPARENT CHANGE IN POSITION OF BEAM UNDER CONSTANT LOAD

| Time | Beam position, scale reading |
|---|---|
| 1:15 p.m. | 48.1 |
| 1:20 p.m. | 47.2 |
| 1:30 p.m. | 46.2 |
| 1:40 p.m. | 44.7 |
| 1:50 p.m. | 43.5 |
| 2:00 p.m. | 42.5 |
| 3:00 p.m. | 36.5 |

The balance was calibrated by two independent methods, the first of which involved the construction of two additional Salvioni balances of lesser sensitivity. The relation between load and displacement for the first of these was established by using a standard one milligram weight to produce a deflection of several hundred scale divisions. This balance was used to weigh a smaller weight (piece of fine platinum wire) which was used to calibrate the second more sensitive balance. The second balance was in turn used to weigh a piece of fine quartz fiber of about 10 micrograms weight which was used to calibrate the most sensitive balance.

Calibration by this method was carried out twice using different sets of weights. The factors 0.0630 and 0.0634 μg/scale division, respectively, were obtained. The linear relation between load and deflection, over the range of weights used, was checked by the method of combining weights.

The calibration of the balance established by the method outlined above was checked independently as follows:

A liter of thorium nitrate solution in pure 0.2 $M$ nitric acid was prepared to contain about 2 g. of thorium per liter. The residue obtained by evaporating a 10.00 ml. aliquot of the solution on platinum and igniting to thorium dioxide was found to weigh 23.0 ± 0.1 mg.

A micropipet of about 1 μl volume was constructed from fine capillary tubing and calibrated for content by determining the weight of mercury contained by the filled pipet. The weight, determined as the mean of three weighings on an ordinary analytical balance was found to be 17.2 ± 0.1 mg. Using the appropriate value for the density of mercury, the volume of the pipet was calculated to be 1.27 ± 0.01 μl.

This pipet was mounted in a micromanipulator and used to deliver 1.27 μl of the standardized thorium solution onto the platinum weighing pan, as shown in Fig. 4.

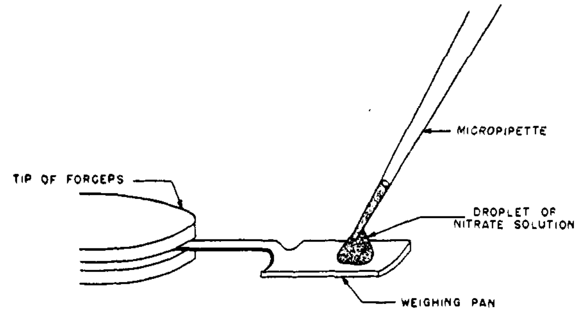

Fig. 4.—Transfer of a solution to the weighing pan of the Salvioni balance.

The pipet was rinsed twice and the rinsings delivered onto the pan also. The solution on the pan was dried slowly under a heat lamp and then the pan was transferred to the micromuffle furnace illustrated in Fig. 5. The muffle was heated to about 800°, maintained at this temperature for fifteen minutes and then allowed to cool. The pan was replaced on the balance and the increased deflection produced by the thorium dioxide residue noted. From the standardization of the thorium solution it was known that the weight of thorium dioxide added to the micro weighing pan was $1.27 \times 2.30 = 2.92$ $\mu$g. The increased deflection of the beam produced by this added load was observed to be 46.6 divisions, from which it was calculated that the factor: micrograms/scale divisions was $2.92/46.6 = 0.0626$.

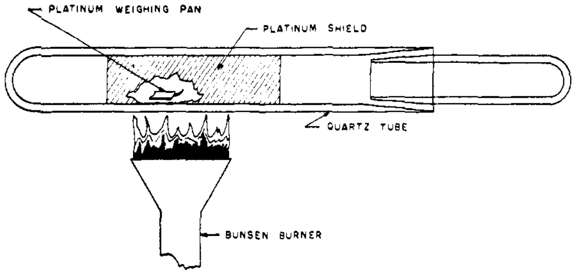

Fig. 5.—Micromuffle.

The value for the balance factor was taken as the average of the three determinations:

$$\frac{0.0630 + 0.0634 + 0.0626}{3} = 0.0630\ \mu\text{g/scale div.}$$

with a mean deviation of $\pm 0.0003$ $\mu$g/scale division.

Since the position of the beam could be read to $\pm 0.2$ of a scale division this corresponded to a sensitivity of $\pm 0.00126$ $\mu$g.

**Determination of the Specific Alpha Activity of $Pu^{239}$.**—A 2.5-$\mu$l aliquot of the solution of pure plutonium nitrate in nitric acid was delivered onto the previously weighed platinum weighing pan, dried, and the residue ignited to plutonium oxide. The technique used to transfer the plutonium solution to the weighing pan, to dry it and ignite the residue to plutonium oxide was the same as that which had been shown to be satisfactory in the case of a thorium nitrate solution. The conditions of ignition were the same as those used to obtain thorium dioxide.

In the first weighing of plutonium oxide, on September 10, 1942, the additional deflection produced by the plutonium oxide added to the pan was found to be 440 scale divisions, corresponding to a weight of oxide of $44.0 \times 0.0630 = 2.77$ $\mu$g.

The oxide deposit on the boat was examined microscopically and observed to have a clear yellow color. This first weighed sample of a compound of pure plutonium was preserved by sealing the boat and oxide deposit in a glass tube.

On the following day a somewhat larger aliquot of the plutonium nitrate solution was used to prepare a larger sample of oxide for weighing. The deflection produced by the second sample of oxide was 70.8 scale divisions corresponding to a weight of 4.55 $\mu$g.

Because of uncertainties in the alpha counting yield caused by self absorption and curvature of the boat, no attempt was made to determine the alpha activity of the oxide deposit directly. Instead, the boat was immersed in 100 $\mu$l of concentrated sulfuric acid in the bottom of a small platinum dish and the acid was heated to fuming. Occasional microscopic examination of the boat showed the oxide deposit was dissolving slowly, and after about two hours had dissolved completely. The sulfuric acid solution was diluted to 10.00 ml. and a $9.81 \pm 0.03$ $\mu$l aliquot of this solution evaporated to dryness on a 1-inch diameter platinum disc. The alpha activity of this fraction was found to be 296 alpha counts per minute corresponding to a total alpha activity of the 4.45 $\mu$g of oxide of $(296 \times 10 \times 10^3)/9.81 = 302{,}000$ counts per minute. The calculated specific activity of plutonium oxide was: $302{,}000/4.45 = 67.900$ c./m./$\mu$g.

It was considered probable that the formula of the oxide weighed was $PuO_2$. This was inferred from the extreme difficulty of dissolving the oxide, in which respect it resembled the strongly ignited dioxides of thorium and cerium, rather than the more readily soluble sesquioxides of the rare earths. The specific activity of $Pu^{239}$ was calculated as: $67{,}900 \times 271/239 = 77{,}000$ counts per minute per microgram.

A second determination of the specific alpha activity of the oxide based on weighing a 2.20 $\mu$g sample gave a figure of 65,500 counts per minute per microgram, corresponding to a value of 74,200 counts per minute per microgram of $Pu^{239}$.

Additional determinations based on samples of similar weight yielded the values $7.3 \times 10^4$ and $7.2 \times 10^4$ c./m./$\mu$g, respectively. It is likely that the first two determinations yielded values somewhat too high because of counting errors from background effects. The counters used were of early design and proved to be highly microphonic. Insufficient attention was paid to correcting for this effect in the first measurements.

The average value of $7.4 \pm 0.3 \times 10^4$ alpha counts per minute per microgram was considered to be reliable to $\pm 5\%$.

Six months later a number of additional specific activity measurements were carried out in collaboration with A. Ghiorso and J. C. Hindman, employing a quartz fiber torsion balance of improved type designed and built by Kirk, R. E. Craig, J. E. Gullberg and R. Q. Boyer.[20] Employing samples of 20 to 50 micrograms weight, and alpha counters of improved operating characteristics, a more precise figure of $7.1 \pm 0.1 \times 10^4$ c./m./μg was established. A concurrent precise determination of the alpha counting yield of $Pu^{239}$ mounted in thin samples on platinum showed this to be $52 \pm 0.5\%$. From these figures the half life of $Pu^{239}$ was calculated as $24{,}300 \pm 370$ years.

**Proof of the Oxidation Number of Plutonium in Plutonium Iodate.**—Direct proof of the oxidation number of plutonium in a plutonium compound was obtained in October, 1942, in an experiment involving only a few micrograms of plutonium.

The experiment was carried out as follows:

About 3 micrograms of plutonium in 1 μl of 4 *M* nitric acid solution was precipitated as the iodate by the addition of excess iodic acid. (No reduction of iodate to iodine was observed to occur when the iodic acid was added to the plutonium solution.) The plutonium iodate precipitate was washed three times with 20 μl portions of distilled water. The washed iodate precipitate was suspended in a few microliters of distilled water and transferred by pipet onto a cleaned and weighed platinum weighing pan. The precipitate was dried for four hours at ~100° and the weight of the iodate determined on the Salvioni balance. The weight was found to be 1.70 μg (with a probable error of weighing of about ±0.03 μg). The precipitate was then dissolved in a little hydrochloric acid, diluted to 1 cc. volume and an aliquot of the solution placed on a counting plate for determination of the plutonium by alpha activity. The calculated alpha activity of the whole sample was 32,800 c./m. The weight of plutonium in the plutonium iodate was therefore $3.28 \times 10^4/7.4 \times 10^2 = 0.442$ μg. From these data the ratio moles $IO_3^-$/moles Pu in plutonium iodate was calculated as

$$\frac{\dfrac{1.70 - 0.442 \text{ micrograms iodate}}{175 \text{ (MW } IO_3^{--})}}{\dfrac{0.442 \text{ micrograms Pu}}{239 \text{ (AW Pu)}}} = \frac{7.20 \times 10^{-3}}{1.85 \times 10^{-3}} = 3.90$$

The value found was sufficiently close to that required for $Pu(IO_3)_4$ to establish the fact that the +4 state is one of the stable oxidation states of plutonium.

**Determination of the Approximate Solubilities of Some Plutonium Compounds.**—The establishment of a reasonably accurate value for the specific alpha activity of $Pu^{239}$ permitted the quantitative determination of extremely small amounts of plutonium by alpha-particle counting methods. As little as 10 c./m. could be determined with an error of only a few per cent., so that in effect as little as $10/74{,}000 = \sim 1.3 \times 10^{-4}$ μg could be analyzed for with an error of about ±5%. Advantage of this fact was taken to obtain data on the completeness of precipitation of plutonium by various reagents, after a fixed time interval. The results were of interest in connection with the problems of designing chemical methods for the large scale extraction, decontamination and purification of this element, and constituted rough solubility values for various plutonium compounds.

These measurements, which were carried out in collaboration with Dr. Michael Cefola, utilized only 0.1 μg of plutonium in the solid phase per determination. The following procedure was used:

Quartz microcones of about 1 cm. length were constructed from about 1 mm. diameter quartz tubing which had been pulled from larger tubing in an oxy-hydrogen flame. About 0.2 μl of a solution containing about 0.1 μg of plutonium in an appropriate concentration of nitric or sulfuric acid was introduced into the bottom of the cone by means of a syringe-controlled micropipet.

An appropriate quantity of a precipitating reagent was added in the same way, and the mixture was stirred, usually by introducing a fine glass thread attached to a magnetic vibrator. Either the open end of the cone was then closed with paraffin, or the cone was placed in a larger cone which was stoppered. The liquid and solid phases were allowed to remain in contact overnight at room temperature. The phases were then separated by centrifugation (the smaller cone being placed inside a larger tube for this purpose) and a sample of the supernatant liquid was withdrawn into a specially calibrated micropipet of $0.252 \pm 0.005$ μl volume. The contents of the pipet were delivered, with rinsing, onto a one inch diameter platinum disc, dried, and ignited. The alpha activity on the disc was determined in a $2\pi$ geometry counter and from this figure the concentration of plutonium per unit volume of supernatant solution was calculated. Typical data are summarized in Table II.

TABLE II

APPROXIMATE SOLUBILITIES OF PLUTONIUM SALTS

| Solid phase | Color | Liquid phase | Solubility, g. Pu/l. |
|---|---|---|---|
| Plutonium iodate | Buff yellow | 0.5 *M* $KIO_3$ | 2.1 |
| Plutonium iodate | | 0.25 *M* $KIO_3$ | 1.8 |
| Plutonium iodate | | 0.5 *M* $KIO_3$-3 *M* $HNO_3$ | 4.8 |
| Plutonium iodate | | 0.5 *M* $KIO_3$-6 *M* $HNO_3$ | 6.2 |
| Ammonium (?) plutonium, fluoride | Pale green | $H_2O$ | 10.8 |
| | | 3 *M* HF-*ca.* 1 *M* $NH_4NO_3$ | 12.3 |
| | | 6 *M* HF-*ca.* 1 *M* $NH_4NO_3$ | 44.8 |
| Plutonium hydroxide | Bright green | $H_2O$ | 1.8 |
| | | 8 *M* $NH_4OH$ | 0.24 |
| Plutonium peroxide | Dark green | 1 *M* $HNO_3$-6 *M* $H_2O_2$ | 23 |

---

[20] P. L. Kirk, R. E. Craig, J. E. Gullberg and R. Q. Boyer, *Anal. Chem.*, **19**, 427 (1947).

**Acknowledgment.**—The work described above was carried out as part of the wartime research conducted by the Metallurgical Laboratory of the University of Chicago (now the Argonne National Laboratory) under Contract W-7401-eng-37. The work was done in the Transuranium Section of the Chemistry Division under the general direction of Professor G. T. Seaborg.

## Summary

1. The isolation of chemically pure plutonium and the preparation of the first pure compounds of this element are described.

2. Methods are described for the preparation and purification of plutonium compounds on a one to thirty microgram scale.

3. The specific alpha activity of $Pu^{239}$ was determined by weighing microgram samples of plutonium oxide, and the value $7.1 \pm 0.1 \times 10^4$ alpha counts per minute per microgram (in a $2\pi$ geometry counter) found.

4. The half life of the isotope $Pu^{239}$ has been computed from specific activity and counting yield measurements to be 24,300 ± 370 years.

5. It is shown that the +4 state is a stable oxidation state of plutonium.

6. Approximate solubilities of plutonium iodate, ammonium plutonium fluoride, plutonium "hydroxide" and plutonium peroxide have been determined. The colors of these compounds and of plutonium oxide have been noted.

RECEIVED JUNE 23, 1948

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

# Mechanism of the Disproportionation of Plutonium(V)[1]

BY ROBERT E. CONNICK

The +5 oxidation state of plutonium is unstable in moderately acidic solutions with respect to the reaction

$$2\mathrm{Pu(V)} = \mathrm{Pu(IV)} + \mathrm{Pu(VI)} \qquad (1)$$

This reaction proceeds sufficiently slowly in 0.5 *M* hydrochloric acid that it is possible to produce plutonium(V) in solution and then measure its rate of disproportionation. From a study of the rate law several interesting conclusions can be drawn as to the mechanism of disproportionation.

In a previous paper[1a] an experiment was described in which plutonium(VI) in solution in 0.5 *M* hydrochloric acid was approximately 50% reduced to the +5 oxidation state by electrolytic reduction at a platinum electrode. The solution was then transferred to a quartz cell and its absorption spectrum measured as a function of time at room temperature by means of a Beckman Spectrophotometer. By analysis of the absorption curve it was possible to determine the amounts of plutonium(III), plutonium(IV), plutonium(V) and plutonium(VI) present in the solution at all times. The present paper deals with the information obtained from this experiment relating to the kinetics of the disproportionation of plutonium(V).

A plot of the data is given in Fig. 1 and the data are given in Table I, both of which have been taken from reference (1). The first interesting point to be observed is that plutonium(VI) and plutonium(III) are produced in the initial stages of the disproportionation of plutonium(V), rather than plutonium(VI) and plutonium(IV), although the latter combination is thermodynamically more stable than the former.

TABLE I

RELATIVE CONCENTRATIONS OF VARIOUS OXIDATION STATES IN THE DISPROPORTIONATION OF PLUTONIUM(V)

| Time in hours | Plutonium oxidation states; per cent. of total plutonium | | | | |
|---|---|---|---|---|---|
| | Pu(VI) | Pu(V) | Pu(IV) | Pu(III) | Total |
| 1.0 | 48.1 | 45.3 | <1 | 2.4 | 95.8 |
| 3.0 | 55.2 | 39.0 | ~1 | 4.7 | 99.9 |
| 5.0 | 62.3 | 29.6 | 2.0 | 7.2 | 101.1 |
| 7.0 | 68.5 | 20.8 | 3.7 | 9.3 | 102.3 |
| 9.0 | 72.5 | 14.2 | 5.8 | 9.8 | 102.3 |
| 11.0 | 74.5 | 10.0 | 8.0 | 9.5 | 102.0 |
| 13.0 | 75.6 | 7.8 | 9.6 | 8.5 | 101.5 |
| 15.0 | 76.4 | 6.3 | 11.4 | 7.7 | 101.8 |
| 17.0 | 76.8 | 5.2 | 12.9 | 7.1 | 102.0 |
| 19.0 | 77.0 | 4.5 | 14.0 | 6.6 | 102.1 |
| 24.0 | 76.5 | 3.6 | 16.5 | 5.1 | 101.7 |
| 29.0 | 76.0 | 3.0 | 18.8 | 4.0 | 102.8 |
| 39.0 | 75.1 | 1.5 | 21.7 | 3.0 | 101.3 |

This phenomenon has been explained[1] as being due to the rapid reduction of plutonium(IV) by plutonium(V) according to the equation

$$\mathrm{Pu(IV)} + \mathrm{Pu(V)} = \mathrm{Pu(III)} + \mathrm{Pu(VI)} \qquad (2)$$

From the experimental data of reference (1) it is clear that the equilibrium of equation (2) was rapidly established and was maintained at all times during the experiment. The ease of establishment of the equilibrium is readily understood when the equation is written using the actual ionic species, since the reaction consists of the transfer of only an electron

$$\mathrm{Pu}^{+4} + \mathrm{PuO_2}^{+} = \mathrm{PuO_2}^{++} + \mathrm{Pu}^{+3} \qquad (3)$$

An average value of 8.5 was obtained for the equilibrium quotient of reaction (2) in 0.5 *M* hydro-

---

[1] This research was carried out under the auspices of the Manhattan District at the Chemistry Department of the University of California during the summer of 1944.

[1a] "The +5 Oxidation State of Plutonium," R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, MDDC-749, July 6, 1944.