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THE SPECIFIC ACTIVITY AND HALF-LIFE OF VARIOUS ISOTOPES OF PLUTONIUM

James C. Wallmann

Thesis

April 30, 1951

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Naval Radiological Defense Laboratory	45
Naval Research Laboratory	46
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New Operations Office	48
New York Operations Office	49-50
North American Aviation, Inc.	51
Oak Ridge National Laboratory, X-10 Site	52-57
Patent Branch, Washington	58
Technical Information Service, Oak Ridge	59-73
UCLA Medical Research Laboratory (Warren)	74
University of California Radiation Laboratory	75-78
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Total	80

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TABLE OF CONTENTS

	Page
INTRODUCTION	5
EXPERIMENTAL PROCEDURE AND APPARATUS	9
Isotopic Composition of the Material	10
Preparation of the Plutonium Compound	10
The Mass of Material Dissolved	14
Dissolution of the PuF_3	15
Plating of Solution Aliquots	16
Low Geometry Counter	17
Counting of the Plates	18
RESULTS AND DISCUSSION	20
ACKNOWLEDGMENTS	26
REFERENCES	27

LIST OF TABLES

Table		Page
1.	Apparent specific activity of Pu^{240} in various samples of neutron irradiated plutonium assuming a constant specific activity of Pu^{239} = 70,700 c/m/μg	7
2.	Loss in weight of PuF_3 samples	12
3.	Isotopic abundances of four plutonium samples	20
4.	Spectrographic analysis of plutonium samples (Aluminum impurity expressed as percentage of total sample)	21
5.	Observed specific activity of four plutonium samples	23
6.	Corrected specific activities of various plutonium samples and the specific activity of Pu^{240}	24
7.	The half-life of Pu^{239} and Pu^{240}	25

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THE SPECIFIC ACTIVITY AND HALF-LIFE OF VARIOUS ISOTOPES OF PLUTONIUM

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ABSTRACT

Accurate specific alpha activity measurements have been carried out on several samples of plutonium containing various proportions of Pu^{238}, Pu^{239}, Pu^{240}, Pu^{241}, and Pu^{242}. The last two isotopes were present to a significant extent in only one of the samples examined. The specific activity figures have been combined with mass analysis and alpha pulse analysis data on the same materials to obtain values for the specific activities of the isotopes Pu^{239} and Pu^{240}. Based on the work reported here, the specific activities of these isotopes (in terms of counts per minute per microgram at 52 percent counting yield) are 70,880 and 255,400 respectively. These figures correspond to half-lives of 24,360 years and 6,760 years. It is believed that the error in these values cannot exceed ± 0.4 percent.

THE SPECIFIC ACTIVITY AND HALF-LIFE OF VARIOUS ISOTOPES OF PLUTONIUM

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INTRODUCTION

Eleven isotopes of element 94, plutonium, are known: they are all radioactive with half-lives varying from 26 minutes up to 5×10^5 years. The nuclides normally available in greatest quantity are those of mass 239 and mass 240, both alpha particle emitters. Plutonium 239 is produced in uranium chain reactors by the reaction sequence: $U^{238}(n,\gamma)U^{239} \xrightarrow[23.5\ m]{\beta^-} Np^{239} \xrightarrow[2.33\ d]{\beta^-} Pu^{239}$; further neutron irradiation of Pu^{239} results in an n,γ reaction creating Pu^{240}. Detectable quantities of the masses 241-243 are produced by additional neutron captures when neutron irradiation is continued for a sufficiently long time.

The half-life of Pu^{239} can be determined most accurately by means of a specific activity measurement; the number of alpha particle disintegrations per unit time and unit mass of material is determined and this figure utilized for calculating the half-life. Measurement of the specific activity for Pu^{240} is complicated by the fact that the nuclide does not exist isotopically pure, as does Pu^{239}; in addition to the number of disintegrations per unit time and mass for the sample, the relative isotopic abundances of all the plutonium isotopes present must be known. These data allow calculation of the Pu^{240} half-life if the specific activity of Pu^{239} is known.

The first accurate value for the half-life of Pu^{239} was obtained by Cunningham and Werner[1] who weighed microgram quantities of pure plutonium dioxide and counted the alpha particles from the material, obtaining a half-life of 24,300 years. The limiting factor in these experiments was not the accuracy of weighing and volumetric aliquoting, but rather the uncertainty in the alpha counting yield of the counting instruments. Westrum, Hindman, and Greenlee[2] in a redetermination of the Pu^{239} half-life weighed plutonium metal, plutonium trichloride, and plutonium tribromide. A specific disintegration rate of 136,060 ± 400 disintegrations/min/μg, corresponding to a half-life of 24,400 ± 70 years, was obtained. Farwell, Roberts, Spane, and Wahl[3] also determined the half-life to be 24,400 years. The rate of energy production of a 120 gram sphere of Pu^{239} measured calorimetrically by the comparison of the rate of evaporation of liquid nitrogen by the sphere and by the input of electrical energy was found by Jones and Stout[4] to be 1.923 (± 1 percent) absolute watts/gm. Combining this value with the disintegration energy of the alpha decay, 5.23 mev, the half-life with respect to alpha emission was calculated to be 24,110 ± 240 years.

The value 6240 ± 120 years for the half-life of Pu^{240} was obtained in early experiments by Westrum, et al.,[2] as a result of the direct comparison of specific activity and isotopic abundance measurements, on several samples of plutonium which had received intense neutron irradiations. Another value for the Pu^{240} half-life has more recently been reported by Inghram, Hess, Fields, and Pyle:[5] 6580 ± 40 years. This measurement was made by observing the rate of growth of the uranium

daughters U^{235} and U^{236} from a plutonium sample containing Pu^{239} and Pu^{240} and used 24,410 years as the half-life of Pu^{239}.

While the existing data regarding the half-life of Pu^{240} show discrepancies greater than the estimated probable errors involved, an even more significant fact is noted if the specific activity of Pu^{240} is correlated with increasing time of exposure of Pu^{239} to neutron irradiation, i.e., with increasing percentage of Pu^{240} in the material. Cunningham, Thompson, and Ghiorso[6] determined the specific alpha activity of a highly irradiated sample of plutonium which contained 34 atom percent Pu^{240} and concluded on the basis of their measurement and earlier measurements on different material by Westrum[2] that the observed specific activities and mass abundance ratios of the samples were not consistent with a constant specific activity for Pu^{240}. The data are presented in Table 1.

Table 1

Apparent specific activity of Pu^{240} in various samples of neutron irradiated plutonium assuming a constant specific activity of Pu^{239} = 70,700 c/m/μg.

Pu^{239} (atom percent)	Pu^{240} (atom percent)	Pu^{238} (% by activity)	Observed sp. act. c/m/μg**	Pu^{240} sp. act.* c/m/μg**
99.98	0.02	----	70,798	----
98.65	1.30	0.51	74.123	304,900
98.08	1.82	0.72	75,124	283,300
95.37	4.43	negligible	80,064	285,300
92.76	6.86	0.2	84,634	277,700
58.1	34.0	8.3	140,000†	254,800

*assuming a constant specific activity of 70,700 c/m/μg for Pu^{239}
**at 52 percent counting yield
†Pu^{241} and Pu^{242} contribute ~300 c/m/μg of sample

The deviations shown are consistent in that the apparent specific activity of Pu^{240} decreases regularly with increasing abundance of the nuclide. Any of several possible suggestions could explain the discrepancy. If the value for the specific activity of Pu^{239} is in error and low by 1 percent a more consistent value for the specific activity of Pu^{240} could be assigned. However, such a conclusion would necessitate assigning what appear to be unreasonably large errors in the determination of the specific activity of essentially isotopically pure Pu^{239}.

The apparent specific activity of Pu^{240} in material of relatively low Pu^{240} abundance is an extremely sensitive function of both the observed specific activity of the sample and the specific activity of Pu^{239}; thus if the observed counts/min/μg for any material of low Pu^{240} content were in error by only a few tenths of one percent, the supposed increase of half-life of Pu^{240} would be experimentally baseless.

An alternate suggestion is that the effect is a true one and the specific alpha activity of either or both of the nuclides Pu^{239} and Pu^{240} is not constant but changes with neutron irradiation due to the formation of a excited isomeric state or states. Such a possibility is of sufficient importance to warrent further experimentation. The data on which the preceding discussion is based are the result of the efforts of several teams of workers using different techniques and counting instruments and mass spectrographs; a more internally consistent set of data should be obtained by making all the necessary determinations for several samples of plutonium at one laboratory. Such a series of specific activity determinations has been carried out using plutoniumtrifluoride and the compound weighed.

EXPERIMENTAL PROCEDURE AND APPARATUS

Before successful specific activity determinations were made with plutonium trifluoride, plutonium metal had been used for the determinations. The metal proved unsatisfactory for the purpose because the pieces of metal did not always dissolve completely; varied conditions of solution were tried but often microgram quantities of material did not dissolve regardless of the acids used or speed of solution of the metal. An additional problem arose when the metal was examined spectrographically for impurities; the percentage of impurity, often beryllium, was difficult to reduce to less than 0.1 - 0.2 percent. In the light of subsequent impurity difficulties with PuF_3 this problem does not seem insurmountable, but at that time the impurity corrections appeared large. Plutonium metal was made by reducing PuF_4 with barium metal in vacuum at high temperatures. Beryllia crucibles of the type described by Fried and Davidson[7] were used with a tungsten coil furnace for heating the assembly to about 1250°C. Over twice as many specific activity determinations were made with the metal as with the trifluoride before it was decided to use PuF_3: all these metal results were 1 - 2 percent below the specific activity figures ultimately determined with PuF_3 and this is of course to be expected if not all the weighed material dissolves.

The specific alpha activity of four different samples of plutonium has been determined using the following procedure: the mass of a plutonium(III) compound of known purity and isotopic composition was measured, all of the compound was dissolved in a known weight of solution, and weighed aliquots of this solution were plated on platinum plates and

counted in an alpha particle counter of known counting yield. For the purposes of a more detailed discussion this procedure will be separated into seven units of consideration.

Isotopic Composition of the Material

The relative abundances of the masses present in each plutonium sample were determined in a single focussing mass spectrograph utilizing a thermal source. Inghram and Hess at the Argonne National Laboratory determined[8] the abundance ratios in one sample of high Pu^{240} content as a check on the accuracy of the values measured in this laboratory. A summary of the mass analyses and estimated errors is presented in Table 3.

The presence of isotopes other than those found by mass analysis was detected by alpha pulse analysis of each sample. Such analysis revealed the percentage of the total plutonium alphas emitted having the 5.51 mev energy of Pu^{238} alpha particles. The uncertainty in this determination was of the order of 0.2 percent.

Preparation of the Plutonium Compound

Stock solutions of four samples of plutonium were available in the laboratory. These solutions were submitted for spectroscopic examination and found to contain no impurities which would not be removed by precipitation of plutonium peroxide. Consequently, in each case a plutonium nitrate solution containing about 5 - 10 mg of plutonium was treated with 30 percent hydrogen peroxide to precipitate plutonium peroxide. Optimum conditions for the precipitation of the olive green plutonium peroxide were final acidities of 1 - 3 M and 5 percent final

peroxide concentration: these conditions agree with those stated by Cunningham.[9] Two washes of the precipitate in 1.5 M HCl were followed by dissolution of the precipitate by heating in concentrated HCl in the presence of a platinum wire. From this solution, after dilution and then centrifugation to remove any insoluble impurities, plutonium peroside was again precipitated and washed twice with dilute hydrochloric acid. Dissolution of the precipitate was repeated under the same conditions used previously. The diluted and centrifuged solution was then transferred to an HF resistant lusteroid cone and gaseous nitrogen bubbled through the solution to remove any oxygen gas. This and all subsequent operations were carried out in a nitrogen atmosphere. After the solution was treated with nitrogen, gaseous sulfur dioxide was bubbled through the solution for a minimum of 20 minutes to insure the complete reduction of plutonium(IV) to plutonium(III). While sulfur dioxide was still bubbling through the plutonium(III) solution, several drops of hydrofluoric acid were added to precipitate plutonium trifluoride. A lavender precipitate appeared immediately upon adding the hydrofluoric acid; sulfur dioxide treatment was continued for an additional period of 15 minutes and then the cone was sealed with "parafilm" and the solution centrifuged. The plutonium trifluoride was washed twice with distilled water: sulfur dioxide was bubbled through each wash solution for 3 - 5 minutes. After the second washing, the precipitate was slurried with distilled water onto a platinum filter. Washing was continued with 2 - 4 ml each of distilled water, absolute methanol, and diethyl ether in that order, the platinum filter being held in a suction flask.

Only in the case of the plutonium sample designated "12B" did the preparation of plutonium trifluoride differ from that outlined above. There was less than 500 μg of sample "12B" available and instead of being transferred to the platinum filter, the trifluoride was washed with alcohol and ether in a pyrex centrifuge cone.

The plutonium trifluoride which was prepared by the method outlined proved ideal for specific activity measurements. It dissolved within 15 minutes in dilute nitric acid with only gentle heating necessary. Every portion before weighing and dissolution was heated in vacuum, $<1 \times 10^{-6}$ mm Hg, (as detected by an RCA 1949 ion gauge tube) at 200°C or 300°C for 30 minutes in a vacuum apparatus of the type described by Lohr:[10] that this treatment completely removed easily volatilized impurities is shown by the fact that a 1.2 mg sample of plutonium trifluoride lost only an addition 0.19 μg in weight upon being heated at 300°C after an original treatment at 200°C. Each of the four separate plutonium trifluoride preparations lost weight upon heating in vacuum. The loss in weight of representative samples of each preparation is shown in Table 2.

Table 2

Loss in Weight of PuF_3 Samples

Preparation	Loss in weight on heating in vacuum (%)
T	3.14
C	2.21
HC	3.65
12B	3.22

It is not to be expected that the loss in weight in each preparation would be the same since the quantity of material prepared was not equal in each case, the amount of washing on the platinum suction filter was not the same, and in the preparation of "12B" the actual method of washing was different.

In addition to the precautions taken to prevent oxidation of plutonium(III) to plutonium(IV), e.g., exclusion of oxygen from the plutonium solutions, there is other evidence to indicate that plutonium trifluoride was the precipitated compound. A sample of "C" preparation of plutonium trifluoride was submitted for x-ray identification after heating the material in vacuum: the crystal structure was hexagonal and the lattice constants were found to be in agreement with the published data of Zachariasen.[11,12] The color of the plutonium trifluoride was lavender, and showed no traces of any inhomogenity.

All four plutonium trifluoride preparations were submitted for spectrographic analysis for impurities after having been heated in vacuum. The analyses were made with a Baird Eagle Mount Spectrograph: results of the spectrographic analyses are presented later in this paper.

The Mass of Material Dissolved

The mass of plutonium trifluoride dissolved for each independent specific activity measurement was determined by weighing the PuF_3 in a cone on a quartz torsion fiber microbalance. The balance used was designed by the Ryerson Instrument Shop, University of Chicago, and is a modification of the type described by Kirk, Craig, Gullberg, and Boyer.[13] The essential features of the balance may be seen in Figure 1. The beam is constructed of fine quartz fibers and is fused to a torsion fiber perpendicular to the beam. The rear of the torsion fiber (to the right in Figure 1) is fused to a quartz bow. The front of the torsion fiber is mounted on the axis of the torsion wheel which is calibrated in arbitrary units. Just visible in Figure 1 are the hangdown fibers which hang from the ends of the beam down into the pan wells and which are provided with small hooks on the ends from which a cone or counterweights can be suspended. Addition of weight to one side of the balance is compensated for by rotation of the torsion wheel. An optical system similar to that of a comparison microscope focuses on portions of a fine index fiber, which is above and parallel to the beam, and projects the images on a ground glass screen on the two sides of a split field. The null point is found by bringing the two index fiber images into apposition.

The inner balance case is enclosed by two additional covers, the outermost of which is visible in Figure 2. At the left in Figure 2 are the ground glass screen with a telescope mounted in the center for reading the scale and vernier on the torsion wheel. The three controls

and cables operate the torsion wheel, optical system and beam arrest. Shown fitted to the side port of the outer case is the lucite transfer box used for loading and unloading radioactive samples. Figure 3 is a closeup of the lucite transfer box showing one of the loader fittings on the end of the probe. The loader fitting actually used for the PuF_3 weighings was a length of copper tubing bent vertically at the end, and of proper size to accomodate the sample cone.

The sample cones themselves were made of thin-walled quartz tubes, sealed at one end and with a small quartz hook fused to the opposite end. A typical tube weighed 2 - 5 mg, was 7 mm in length and had an inside diameter of ~1 mm.

Two methods were used to calibrate the balance. Two 2 mg weights standardized by the National Bureau of Standards were weighed directly on the microbalance. The true mass of these weights was known to 0.05 percent and the factors obtained were 0.3536 and 0.3535 μg/division of the torsion wheel scale. A second calibration was made by weighing five platinum wires together on an Ainsworth knife-edge microbalance, and then weighing each wire separately on the torsion microbalance; the factor obtained, also with an accuracy of 0.05 percent, was 0.3534 μg/division. The balance factor used for all weighings was 0.3535 μg/division, an average of the three calibrations.

Dissolution of the PuF_3

After the plutonium trifluoride was weighed on the microbalance in a quartz cone, it was removed with the transfer box manipulator pictured in Figure 3, placed in a 10 ml flask and the flask plus contents were

weighed. Then by turning the flask on its side all of the pieces of trifluoride could be made to fall out of the wide-mouthed weighing cone; enough 4 M H_2SO_4 - 2 M HNO_3 solution was then added so that the plutonium when dissolved had a concentration of about 17 μg/100λ of solution (one lambda = 10^{-6} liter). Dissolution of the material occurred in less than 20 minutes time when the flask was placed under a heat lamp. After the plutonium trifluoride had dissolved and the flask had cooled the solution was thoroughly shaken, care being taken to prevent liquid from wetting the ground glass stopper and thus exposing the solution to evaporation losses. The flask and solution were then weighed. All weighings of the empty flask or flask plus contents were performed on an American Balance Corporation chainomatic analytical balance with a load capacity of 200 g and sensitivity of about 0.03 mg. This pair of weighings determined the weight of solution containing a known quantity of plutonium.

Complete dissolution of the plutonium trifluoride appeared to take place, for centrifugation of the solution showed no residue. After several flasks had remained undisturbed for about five weeks they were empties of their contents and checked for absorbed radioactivity: none was detected.

Plating of Solution Aliquots

The solution added to the plutonium trifluoride was 4 M H_2SO_4 - 2 M HNO_3. A 100 λ aliquot of this solution after dissolution of the PuF_3, etc., was delivered by micropipette to a platinum plate contained in a light dish with removable cover. This system was weighed both

before and after delivering the aliquot on the American Balance Corporation analytical balance used for weighing the flask and contents. Care was taken to pipette the solution quickly so that the time of exposure to air was only about 20 seconds. Under these conditions the need of corrections for evaporation losses was eliminated since presence of the sulfuric acid reduced the partial pressure of the water: e.g., one hundred lambdas of a typical solution exposed to the air for 5 minutes showed a gain in weight of 50 μg. A similar technique has been described by Westrum.[14]

Aliquots delivered in this way were evaporated to dryness in an induction heater and flamed to eliminate any volatile residues. Unflamed plates had a counting rate 1 - 5 percent below the rate observed after flaming.

Low Geometry Counter

A vacuum low geometry chamber, of the type discussed by Jaffey,[15] and a Higinbotham scaling circuit were used to count the alpha particles emitted from the known quantity of plutonium on the platinum plate. The equation used for calculating the geometry factor of the chamber was the following: $\frac{4d^2}{h^2} + 3 + 3\frac{a^2}{h^2} - \frac{a^4}{4h^2d^2} + \frac{9a^2 - h^2}{4d^2}$ = geom. factor to give 52% counting yield

where a = radius of the sample

h = radius of the collimator

d = distance from sample to collimator.

The geometry factor of the chamber actually used was ~686, i.e., the geometry factor times the observed counting rate equals 52 percent of the total disintegrations.

A low geometry chamber was chosen for the measurement of the alpha particle activity on the plates because backscattering and coincidence losses become negligible, i.e. the alpha counting yield (ratio of counts to disintegrations) is known accurately. This quantity is needed to convert the observed alpha particle counting rate of the plates to the absolute alpha disintegration rate. Cunningham, Ghiorso, and Hindman[16] noted that in a parallel-plate ionization chamber the alpha particle counting yield may be greater than 50 percent due to backscattering of some of the particles from the sample mount. The calculations of Crawford[17] indicate that normal to the surface of the plate there are virtually no backscattered particles and with the collimating aperture in a low geometry chamber normal to the plane of the sample mount, the counting yield is identical to the geometry and can be calculated by geometrical measurements.

The dimensions of the chamber were determined by the Radiation Laboratory machine shop when the chamber was constructed and were subsequently checked in the laboratory by the use of a Gaertner cathetometer. The probable error in the geometry measurement of the chamber is <0.1 percent.

Counting of the Plates

In the actual counting of the plutonium alpha particles several factors must be considered: statistical accuracy of the counts taken, self-absorption of the sample, backscattering, coincidence corrections, background correction, and determination of the plateau; Jaffey, Kohman, and Crawford[18] offer a discussion of most of these factors.

Determination of the plateau of the counter was accomplished by counting a very radioactive sample for short periods. The proper gain setting to use to minimize any effects due to line voltage fluctuations was thus made evident.

The counting of an unknown number of backscattered alpha particles was avoided by using a low geometry chamber, as mentioned in the preceding section. Determination of the coincidence correction by counting paired plates showed it to be <0.1 percent at the counting rates used.

Self-absorption was avoided by plating small enough quantities of plutonium so that even if some pile-up of the material did occur, self-absorption would be $\ll 0.1$ percent. In several cases plates were made with twice as much material on them as other plates from the same solution had been given: no discrepancy in the counting rates was observed which indicates that self-absorption was absent. In addition, the pulse heights of the alpha particles from each plate were observed in an oscilloscope and always found to be of equal height.

All counts were corrected for the background of the chamber and amplifying circuit. These background corrections were completely reproducable except when other laboratory personnel used the chamber to count very radioactive samples; in general even this acquired background could be cleaned off the chamber.

The statistical error of the counts taken on each plate was <0.1 percent. Expressed mathematically, if ρ is the fractional error and W the probability of making an actual error less than ρ, then $\rho = \frac{K}{\sqrt{M}}$

where M is the total number of counts taken and K depends on W. The "standard fractional error" in which K = 1.0 and the percentage probability of making an actual fractional error less than $\rho = \frac{K}{M} = 68.3\%$ was used for computing the number of counts necessary to give statistics better than 0.1 percent.

RESULTS AND DISCUSSION

The specific activities of four different samples of plutonium have been determined by weighing plutonium trifluoride. Table 3 summarizes the isotopic abundances for each of the four samples; all the values are from mass spectrographic analyses except the figures for Pu^{238} which were determined by alpha particle pulse analysis of the samples. In general, the probable error for abundances of 1 - 10 percent is ± 5 percent, for abundances <1 percent, ± 5 - 10 percent.

Table 3

Isotopic abundances of four plutonium samples

Sample designation	Pu^{238} (% by activity)	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
		(.....atom percent.....)			
T	—	100.0	—	—	—
C	0.57	98.55±0.5	1.37±0.07	0.098±0.01	—
HC	1.69	95.6±0.15	4.08±0.20	0.23±0.02	<0.02
12B	8.84	58.1±0.48	34.0±0.48	6.8±0.32	1.02±0.11
12B*	—	57.6±0.21	34.4±0.2	6.66±0.07	1.25±0.02

*abundances determined by Inghram and Hess[8]

Each of the four plutonium samples was precipitated as PuF_3 and before any material from the four preparations was weighed it was heated in vacuum to constant weight. Portions of each of the four plutonium trifluoride preparations were treated in this fashion and submitted for spectrographic analysis. No impurities except aluminum were detected but the amount of aluminum impurity detected was so inconsistent that Table 4 is presented for purposes of discussion.

Table 4

Spectrographic analysis of plutonium samples
(Aluminum impurity expressed as percentage of total sample)

Sample Analysis No.:	1	2	3	4	5
T	—	0.1	0.8	0.1	0.22
C	0.0	—	0.7	0.4	1.0
HC	—	—	0.3	1	0.23
12B	—	—	—	1	0.00

The irregularities observed in the spectrographic analyses are of importance because of the necessity of knowing exactly what impurity corrections to make in the observed specific activities. One possible conclusion about the material is that each preparation has in it inhomogeneously distributed aluminum. The stock solution of plutonium nitrate in each case showed <0.1 percent aluminum impurity, however, and the hydrogen peroxide and hydrofluoric acid reagents and distilled water were analysed spectrographically and found to be free of aluminum: introduction of aluminum into the sample during preparation of the

plutonium trifluoride is difficult to explain. In addition, the agreement of the observed specific activities of two samples from the same PuF_3 preparation is strong evidence for homogenity of the PuF_3.

For analyses 1, 2, and 3, about 200 μg of the desired sample was dissolved in 200 μl of 1 percent hydrochloric acid spectrographic solution. The solutions for analysis No. 3 were allowed to stand undisturbed for 24 hours, which is about ten times longer than normal: some correlation is noted between higher aluminum content of the solution containing dissolved PuF_3 and longer period of contact of this solution with the pyrex cone. To verify this effect solutions of 50 μl of 27 M HF in 50 ml of 1 percent hydrochloric acid solution of known impurity content were made up 24 and 2 hours before spectrographic analysis. The older solution showed an increase of aluminum content from 2 μg aluminum/100 λ solution to 3 - 4 μg aluminum/100 λ solution. One judges from this that the fluoride ion present due to dissolution of the PuF_3 is reacting with the pyrex cone to a slight extent. There is also an increase of the sensitivity for detection of aluminum in the presence of fluoride ion, because a solution of known aluminum concentration showed an increased aluminum concentration, greater than could be accounted for by the previously determined amount of reaction of the fluoride ion with the pyrex cone.

Analyses 4 and 5 indicate that the preparations probably contain some aluminum. Analysis four was run on material which was handled only in quartz and thus should not have picked up any aluminum from the sample tube. Analysis five was obtained by placing a known quantity of solid PuF_3 on the copper electrodes and dissolving it right on the

electrode with dilute hydrochloric acid. The frequent results indicating a low percentage of impurity do, however, cause one to question whether the same material when showing high percentage impurity might have become contaminated during the process of drying the solution on the electrodes. For the purposes of correcting the specific activity figures, the impurities found in analysis No. 5 are accepted as most nearly correct. Preparation "C" was considered to have a 0.2 percent impurity; this is not unreasonable since "C" did not show any impurities in analysis No. 1 and was prepared in the same way and with the same reagents as the other samples.

Table 5 summarizes the specific activity data for each plutonium sample. The determinations shown for a given sample represent independent weighings and vacuum-heat treatments on separate portions of the prepared PuF_3. Two plates were made for every run with the exception of one run on sample "C". The uncertainties indicated are the standard deviations of a single determination.

Table 5

Observed specific activity of four plutonium samples

Sample	Wt of PuF used (μg)	Observed c/m/μg	Average c/m/μg
T	1119	70720 70750	70730 ± 30 (0.05%)
T	1045	70750 70680	
C	429	73640 73620	
C	1014	73520 73450	73600 ± 100 (0.14%)

The data in Table 6 indicate that the specific activity of plutonium does not decrease with increasing isotopic abundance. The two most reliable determinations are T and 12B, since the error in the mass analysis is least in these cases and the impurity corrections appear valid; these samples agree closely with the previous determination of Westrum[2] and Cunningham.[6] The two intermediate samples show a specific activity for Pu^{240} of nearly the same value as 12B; this is acceptable agreement when the sensitivity of the Pu^{240} specific activity to changes in the values for these samples is noted. The specific activity of 70,880 c/m/μg for Pu^{239} corresponds to a half-life of 24,360 years and the half-life of Pu^{240} is calculated to be 6760 years. The probable error for both of these values if ± 0.4 percent.

In Table 7 is presented a summary of all the reported half-life determinations for Pu^{239} and Pu^{240}.

Table 7
The half-life of Pu^{239} and Pu^{240}

Nuclide	Half-life (years)	Reference
Pu^{239}	24300	1
Pu^{239}	24400	2
Pu^{239}	24400	3
Pu^{239}	24110	4
Pu^{239}	24360	this paper
Pu^{240}	6240	2
Pu^{240}	6300	3
Pu^{240}	6580	5
Pu^{240}	6780	6
Pu^{240}	6760	this paper

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REFERENCES

1. B. B. Cunningham and L. B. Werner, J. Am. Chem. Soc. 71, 1521 (1949).
2. E. F. Westrum, Jr., J. C. Hindman, and R. W. Greenlee, Metallurgical Laboratory Report CC-3894 (November, 1946).
3. G. W. Farwell, J. E. Roberts, A. Spane, and A. C. Wahl, Los Alamos Scientific Laboratory Report LAMS-293 (October 11, 1945).
4. W. M. Jones and J. W. Stout, Los Alamos Scientific Laboratory Report LA-347 (August 17, 1945); Phys. Rev. 71, 582 (1947).
5. M. G. Inghram, D. C. Hess, Jr., P. R. Fields, and G. L. Pyle, Argonne National Laboratory Memorandum ANL-WMM-647 (1950).
6. B. B. Cunningham, S. G. Thompson, and A. Ghiorso, University of California Radiation Laboratory Memorandum MB-IP-425 (October 14, 1949).
7. S. Fried and N. R. Davidson, J. Am. Chem. Soc. 70, 3539 (1948).
8. M. G. Inghram and D. C. Hess, Jr., private communication to F. L. Reynolds.
9. B. B. Cunningham, University of California Radiation Laboratory Memorandum MB-GTS-78 (February 26, 1951).
10. H. R. Lohr, L. Eyring, and B. B. Cunningham, University of California Radiation Laboratory Report UCRL-791 (July, 1950).
11. W. H. Zachariasen, National Nuclear Energy Series Plutonium Project Record 14B, Paper 20.5 (1949).
12. W. H. Zachariasen, Acta Cryst. 2, 388 (1949).
13. P. L. Kirk, R. Craig, J. E. Gullberg, and R. Q. Boyer, Ind. and Eng. Chem. Anal. Ed. 19, 427 (1947).
14. E. F. Westrum, Jr., National Nuclear Energy Series Plutonium Project Record 14B, Paper 16.2 (1949).

15. A. H. Jaffey, Argonne National Laboratory Report CC-3771 (February 6, 1947).

16. B. B. Cunningham, A. Ghiorso, and J. C. Hindman, Metallurgical Laboratory Report CN-1241 (January 5, 1944).

17. J. A. Crawford, Metallurgical Laboratory Report CC-1342 (February 1, 1944).

18. A. H. Jaffey, T. P. Kohman, and J. A. Crawford, Metallurgical Laboratory Report M-CC-1602 (January, 1944).

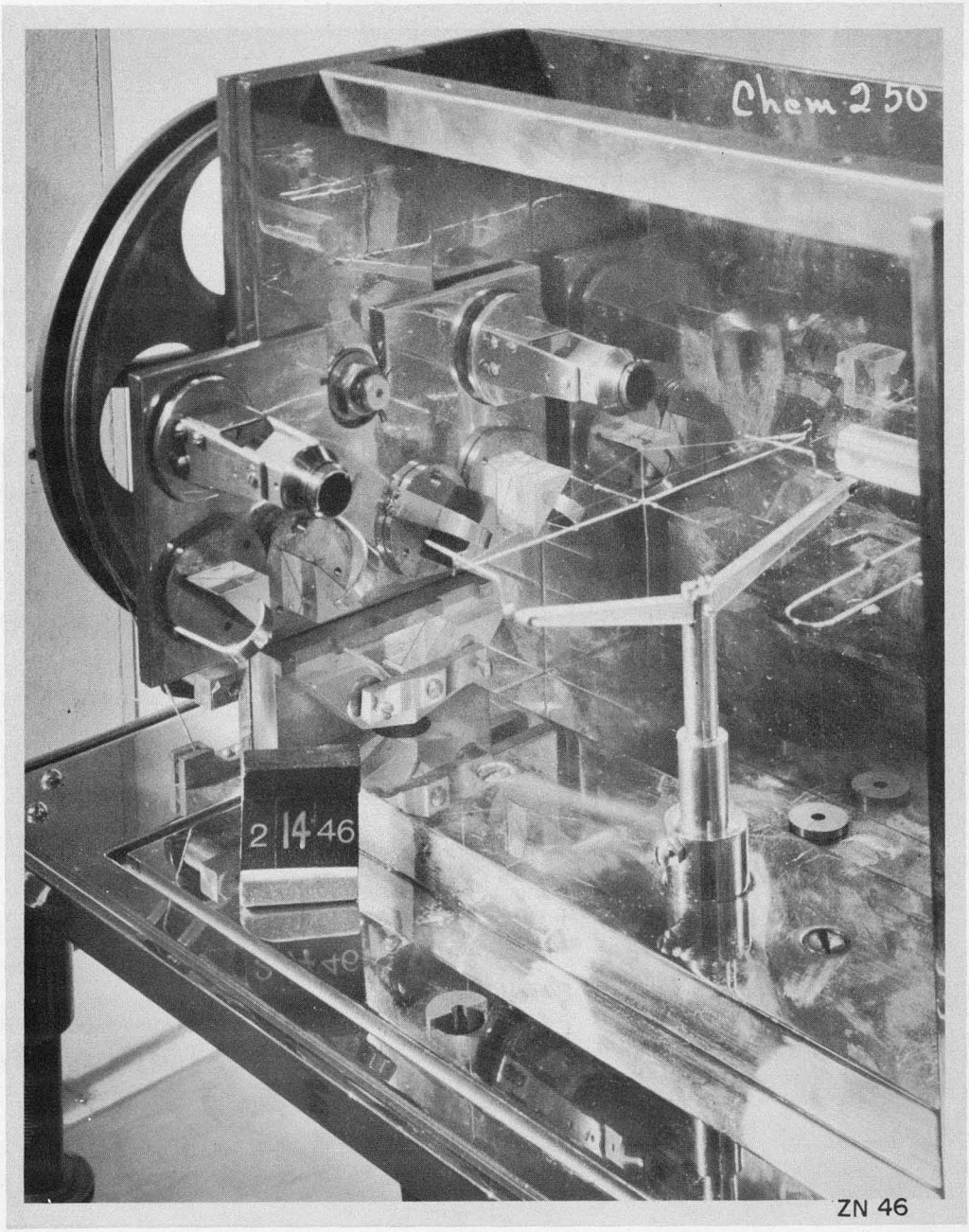

Fig. 1

Quartz Microbalance

(Interior View)

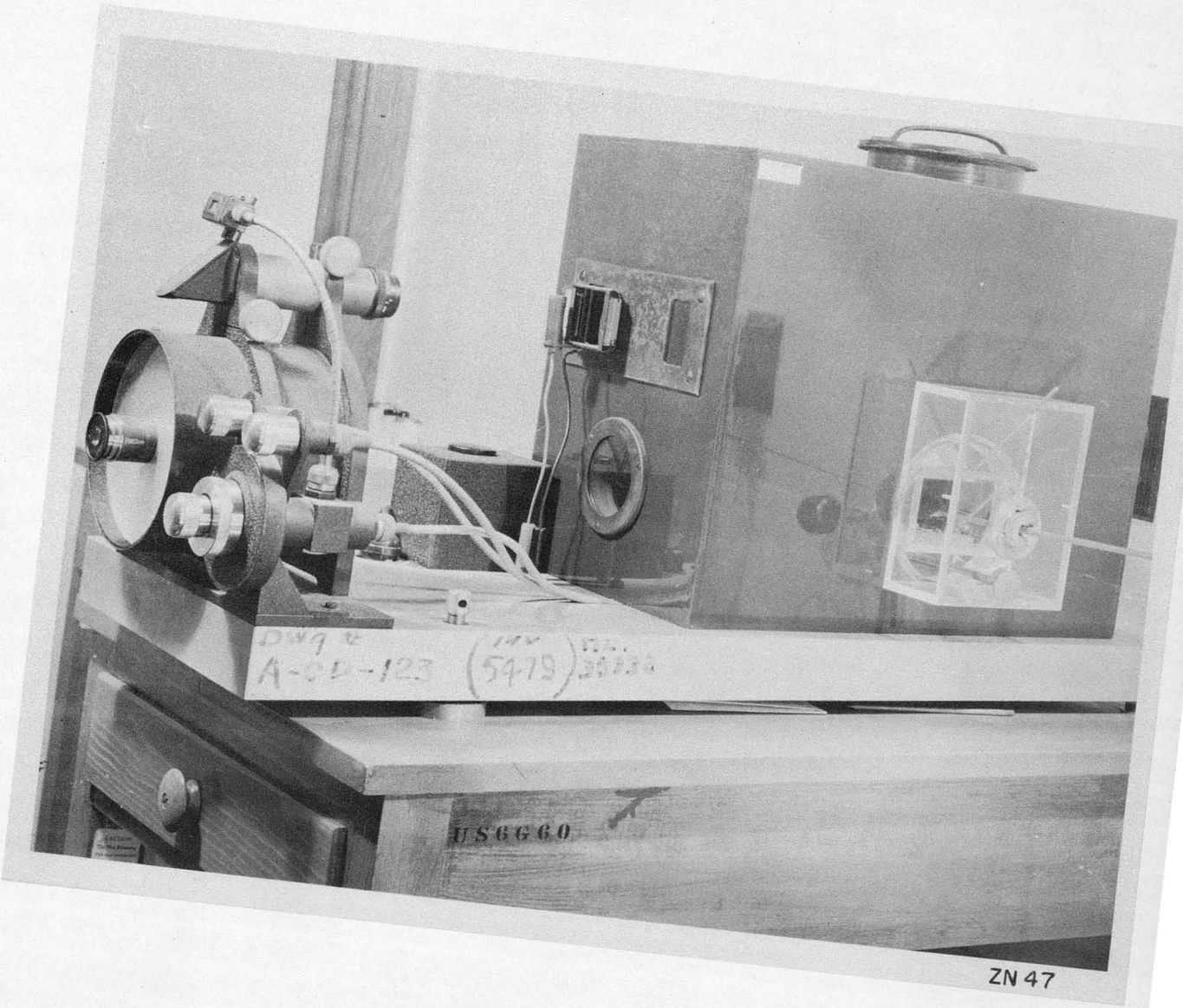

Fig. 2

Quartz Microbalance

(Exterior View)

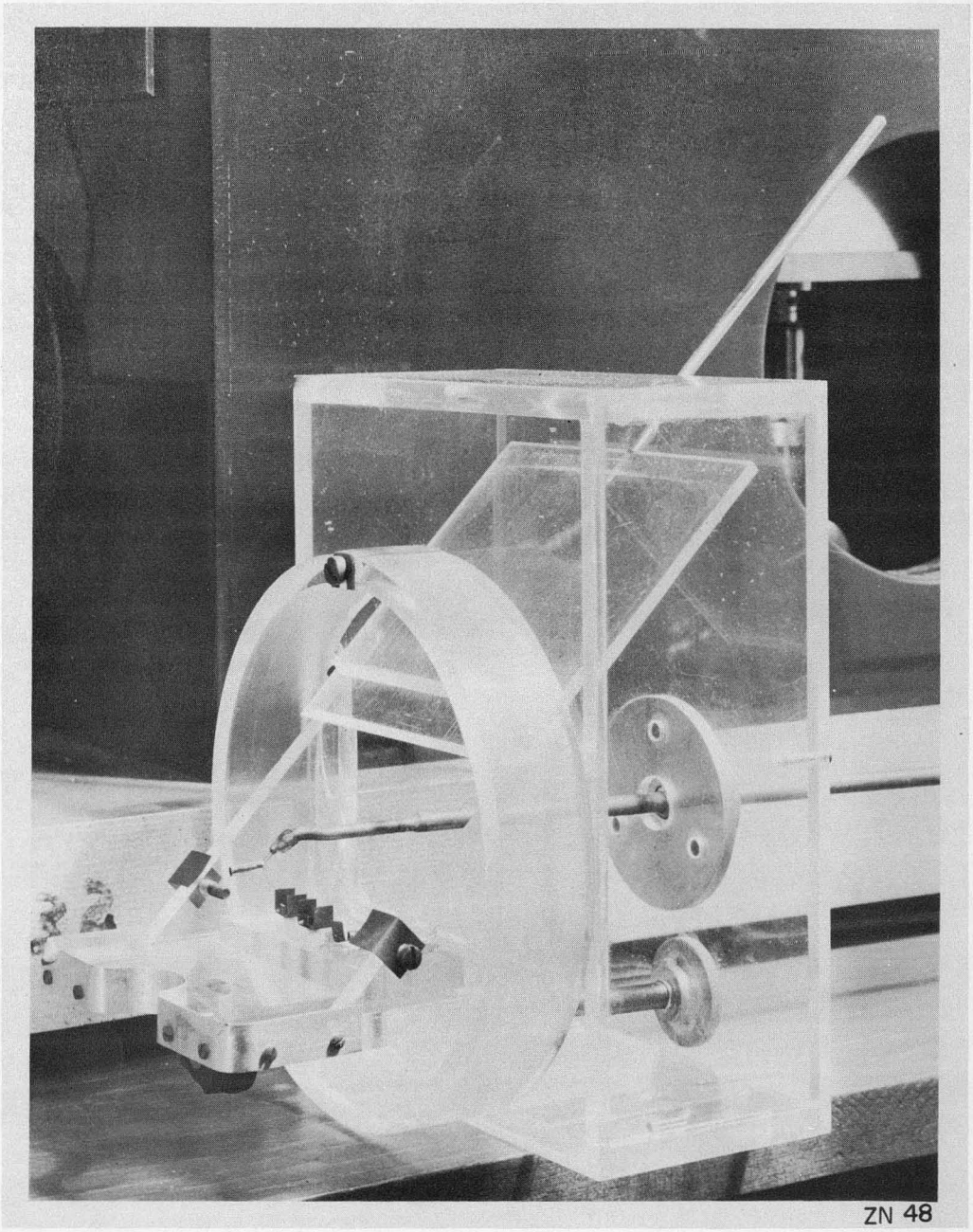

Fig. 3

Lucite Transfer Box

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