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THE SPECIFIC ALPHA ACTIVITIES AND HALF LIVES OF U234, U235, AND U236

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THE SPECIFIC ALPHA ACTIVITIES AND HALF-LIVES
OF U^{234} , U^{235} , AND U^{236}

Edward Homer Fleming, Jr.

(Thesis)

June, 1952

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THE SPECIFIC ALPHA ACTIVITIES AND HALF-LIVES

OF U²³⁴, U²³⁵, AND U²³⁶

Edward Homer Fleming, Jr.
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June, 1952

ABSTRACT

The specific alpha activities and half-lives of U²³⁴, U²³⁵, and U²³⁶ have been determined. The material used for each determination was uranium very highly enriched in the isotope under investigation.

Accurate volume aliquots of U²³⁵ were electrodeposited quantitatively onto platinum disks and were counted in a medium geometry chamber. Accurate weight aliquots of U²³⁴ and of U²³⁶ were pipetted onto platinum disks, evaporated to dryness in an induction furnace, and counted in a medium geometry chamber.

The specific activities and half-lives found are as follows:

Isotope	Specific activity (d/m/mg)	Half-life (years)
U ²³⁴	$(1.370 \pm 0.009) \times 10^7$	$(2.475 \pm 0.016) \times 10^5$
U ²³⁵	$(4.74 \pm 0.10) \times 10^3$	$(7.13 \pm 0.16) \times 10^8$
U ²³⁶	$(1.406 \pm 0.011) \times 10^5$	$(2.391 \pm 0.018) \times 10^7$

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I. INTRODUCTION

In 1939, Nier¹ determined the half-life of U²³⁵ by establishing the activity ratio of the AcU series to the U_I series in natural uranium from mass spectrographic analyses of radiogenic lead samples. About five years later, Clark and co-workers² determined the half-life of this nuclide by counting and pulse analyzing uranium slightly enriched in U²³⁵. The two values were in disagreement by about 25 percent.

After Nier had published his work, A. Holmes³ devised a method for calculating the age of the earth, using Nier's mass spectrographic data, including his value for the half-life of U²³⁵. The method looked very promising from the beginning, and Holmes succeeded in deriving a value for the age of the earth of about 3.3 billion years. With the appearance of Clark's value, however, the figure became somewhat suspect. The decay constant of U²³⁵ appeared in the calculations as an exponential, and an error in this decay constant would alter the age calculation by many factors of the error.

Because of the wide-spread interest in an accurate value for the age of the earth, it was hoped that an accurate redetermination of the half-life of U²³⁵ could be made. Rapid development of

electromagnetic separation equipment has made it possible to obtain elements very highly enriched in isotopes which occur in nature only in low abundance. Consequently, uranium has become obtainable as 99.94 percent isotopically pure U^{235} . The use of such highly enriched materials has made it possible to eliminate or minimize several uncertainties associated with previous half-life determinations.

In 1949 this laboratory was privileged to procure samples of uranium oxide highly enriched not only in U^{235} , but also in U^{234} and U^{236} , from Dr. C. E. Larson, Y-12 Plant, Carbide and Carbon Chemicals Division, Oak Ridge, Tennessee. Thus, the opportunity for making more accurate determinations of the specific activities and half-lives of each of the isotopes was presented.

In the report of this work which follows, an effort has been made to present in a realistic fashion the difficulties encountered, particularly where the precise determination of alpha disintegration rates is involved.

II. CHEMICAL PURIFICATION OF THE MATERIALS

The oxides of two of the three isotopes, namely $U_3^{236}O_8$ and $U_3^{234}O_8$, were found to be contaminated with chemical impurities, chiefly iron, calcium, aluminum and magnesium, to the order of 2-4 percent.

It was necessary to reduce the amount of contamination in each of these samples to the order of 0.1 percent, since spectrographic analysis by the copper spark method ordinarily yields an over-all estimation of the impurities no better than a factor of 2.

The following method was found to be reasonably efficient and rapid, and was therefore employed:

(1) The oxide was dissolved in a minimum of hot, concentrated HNO_3 , and the solution was brought to a pH of about 5 by neutralization with NH_4OH .

(2) The solution was chilled in an ice bath, and upon the addition of 30 percent hydrogen peroxide, uranium peroxide precipitated upon standing.

(3) The mixture was centrifuged, and the supernatant liquid was poured off to be treated once again as in step (2). About 95 percent of the uranium was precipitated with the first addition of peroxide.

(4) The precipitate was then washed with about three times its volume of 10 percent H_2O_2 by stirring, and the mixture was centrifuged. The supernatant liquid was removed with a transfer pipet. The precipitate was washed four more times in this same manner.

(5) After the fifth washing, enough 10 percent H_2O_2 was added to permit efficient slurring, and the precipitate was transferred

to a clean platinum crucible. The crucible was then placed under a heat lamp, and the contents were taken slowly to dryness. Baking in air, at a temperature of 850-975° C, caused the peroxide salt to be converted to the oxide, U_3O_8 , with an over-all yield of 85-90 percent. A sample of the oxide was then analyzed spectrographically.

Results of Spectrographic Analyses

Isotope	% Fe_2O_3	% CaO	% Al_2O_3	% MgO	% Others	% Purity	Method
234	<0.01	<0.01	0.01	<0.01	<0.01	>99.95	Cu spark
235*	<0.04	<0.002	<0.001	<0.001	<0.1	>99.90	gallium oxide
236	0.14	<0.01	0.04	0.02	<0.01	>99.8	Cu spark

* $U_3^{235}O_8$ was found to contain the amounts of impurities as shown when received, and no effort was made to purify it further.

In order to be sure that baking the peroxide under the conditions described would convert the sample to U_3O_8 , since the samples were to be weighed as such, a sample of natural uranium was purified as described and subjected to an x-ray analysis. A sample of the $U_3^{235}O_8$ from Oak Ridge was analyzed in the same manner. The lattice constants of each were consistent, and deviated very slightly from those reported in the literature for $UO_{2.667}$. It is not possible to make an accurate calculation of composition from x-ray data alone, since the positions of the lines are so insensitive to a change in composition over the solid solution range. However, by plotting composition vs. partial pressure of oxygen at various temperatures, according to data

compiled by Biltz and Müller,⁴ a simple interpolation shows that the composition range lies between $\text{UO}_{2.655}$ and $\text{UO}_{2.665}$, when the oxide is prepared under these conditions. Consequently, in order to set limits of error on the composition of the oxides a composition range was assumed from $\text{UO}_{2.65}$ to $\text{UO}_{2.67}$. The limits of error associated with such a range are ± 0.06 percent, and any error due to a deviation of composition from U_3O_8 was considered to be negligible.

III. URANIUM 235

A. Mass and Pulse Analysis

The Y-12 Mass Spectrometer Laboratory at Oak Ridge analyzed all the isotopically enriched uranium samples used in this work. The mass percentage of the isotopes in the uranium sample whose principal isotope is U²³⁵ is as follows:

Percentage of isotope	Limits of error
235 - 99.94	±0.010
238 - 0.038	±0.009
234 - 0.022	±0.005

Since the specific activity of U²³⁴ is about 3000 times that of U²³⁵, the activity contribution of U²³⁴ is very significant in the above sample; therefore, it was necessary to determine the percentage of activity contributed by U²³⁴. The 48 channel linear differential pulse height analyzer was used for this purpose.⁵ Pulse analysis showed that (65.3 ± 1.3) percent of the disintegrations were emitted from U²³⁵ and 34.7 percent from U²³⁴.

B. Preparation of the Standard Solution

The balance used for weighing the oxide was an American Balance Corporation chainomatic semimicro analytical balance, with a load capacity of 200 g and a sensibility of about 25 µg. The weights and rider were calibrated against National Bureau of Standards calibrated weights. About 63 mg of the oxide were weighed in a clean porcelain crucible, which previously had been tare weighed. The uncertainty

in weighing was conservatively estimated as $<\pm 0.1$ percent.

The oxide was dissolved in 2 ml of warm concentrated HNO_3 . The solution was cooled, 2 ml of concentrated H_2SO_4 added, and the solution heated to drive off the HNO_3 . After recooling, the solution was quantitatively transferred from the crucible to a calibrated 10 ml volumetric flask, and distilled water was added until the solution was up to the mark. After thorough mixing, the standard solution was transferred to a 30 ml bottle, the glass stopper of which fitted over the outside of the neck. All volume aliquots were taken from this bottle, and each time care was taken to avoid touching the inside of the neck with the wet tip of the micropipet. The resulting concentration of the standard solution was 5.312 ± 0.010 mg of pure uranium per ml of solution.

The volumetric flask was calibrated with distilled water at 24°C , and the standard solution was prepared within one degree of this temperature. Since a difference of about 5°C is required to produce an error of 0.1 percent due to thermal expansion of water at this temperature, any error of this sort was estimated to be less than 0.05 percent.

A check on the concentration of the standard solution after standing over a one year period indicated that any change in concentration due to evaporation was less than 0.1 percent during the short period when the electrodepositions were made.

C. Electrodeposition of the Material

Each uranium sample was prepared for counting by an electrodeposition technique described in detail by Hufford and Scott.⁶

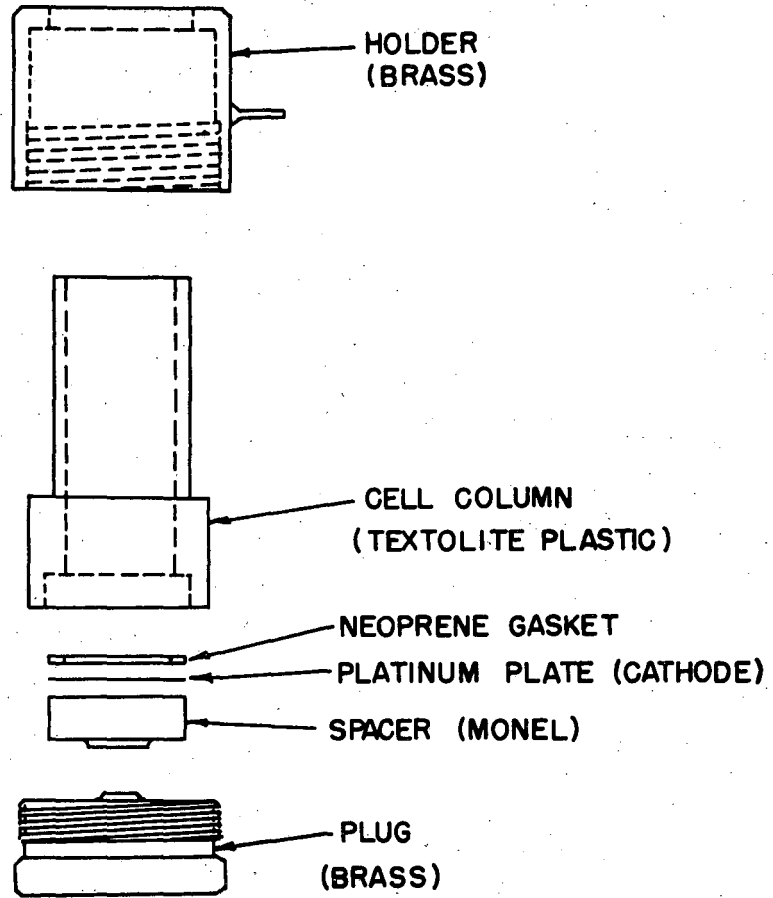
Fig. 1 shows the component parts of the electrolysis cell used for most of the electrodepositions. The cell is assembled by placing the neoprene gasket inside the cell column, inserting a 2 mil platinum plate one inch in diameter under the gasket, placing the monel spacer under the plate, bringing the holder down over the cell column, and screwing the brass plug tightly into the holder by hand. Each platinum plate was cleaned, prior to assembling the cell, by boiling in hot concentrated HNO_3 , rinsing with distilled water, and drying and annealing over a small bunsen flame.

The stirring anode used was a platinum disk 10 mils thick and $5/8$ inch in diameter, riveted to a tantalum shaft $1/8$ inch in diameter. The shaft was placed securely in the chuck of a variable speed stirring motor, which was set to run at 500 rpm. Further control on the stirring speed was afforded by a variac interposed between the house line and the stirring motor.

The power supply was built in this laboratory (see Fig. 2).

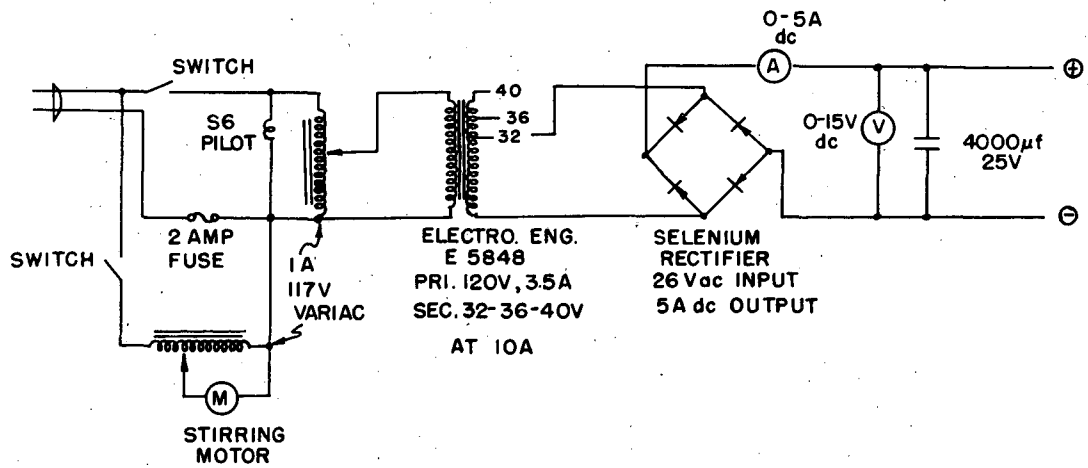
After the cell was assembled, an accurate volume aliquot was removed from the standard solution with a calibrated* micropipet

* Each micropipet was calibrated at least twice with mercury. The precision error in calibrating any one pipet was less than 0.06 percent. Apparently there is some evidence to indicate that mercury gives erroneous calibration values, probably because of its great convex meniscus. In most calibrations here it was possible, by careful manipulation, to eliminate the meniscus altogether, thereby eliminating this possible error. At any rate it is felt that the error in calibration of each micropipet was less than ± 0.1 percent.



MU 3459

Fig. 1. Electrolysis cell.



MU3460

Fig. 2. Power supply for electrolysis cell.

and transferred to the cell. The pipet was rinsed five times to ensure complete transfer. Four ml of 0.4 M ammonium oxalate solution was added as the electrolyte. The cell was placed in a water bath on a hot plate and the cathode lead was connected to the screw on the side of the cell column holder. The anode and stirring motor were placed so that the anode disk was a few mm beneath the surface of the solution. The anode lead was clipped to an uninsulated portion of the stirring motor. After the water bath reached a temperature of about 80° C, the power supply was turned on and the electrodeposition begun. Five volts were required to produce a current of 0.4 - 0.5 amperes in the circuit, the current used for all depositions with the cell described. After 15 or 20 minutes the current would drop, and addition of a few ammonium oxalate crystals caused the current to rise to its former value.

After the deposition was complete, the cell was filled with distilled water at about 80° C, and half the solution pipetted out. This procedure was repeated twice. The current was broken, the anode was removed from the cell, and the remaining solution was poured out. Three rapid rinses with cold water sufficed to rid the cell of any oxalate, and the deposit was allowed to dry in the cell. After drying, the plate was removed from the cell and flamed. The resulting film was adherent and uniformly distributed.

The time for essentially complete deposition was shown to be about 30 minutes by experiment, but each deposition of U²³⁵ was run for about 90 minutes to ensure that 99.9+ percent of the uranium was deposited. That such was the case was proven by the following

experiment. A quantity of uranium in solution was electrodeposited and the electrolytic solution was assayed for activity. Less than 0.1 percent of the original activity was found. The sample was placed in a 2π alpha counting chamber and the counting rate determined accurately. Then about 98 percent of the uranium was removed from the plate and redeposited on another plate. Both the first and second plates were then counted, and the sum of their counting rates was exactly equivalent to the counting rate of the first deposition.

Further proof that each deposition was quantitative was afforded by a plot of the specific counting rate for each sample versus the thickness of the sample (see Fig. 3). The maximum deviation of any point from the curve is less than 0.1 percent. This figure will be discussed further in Section V.

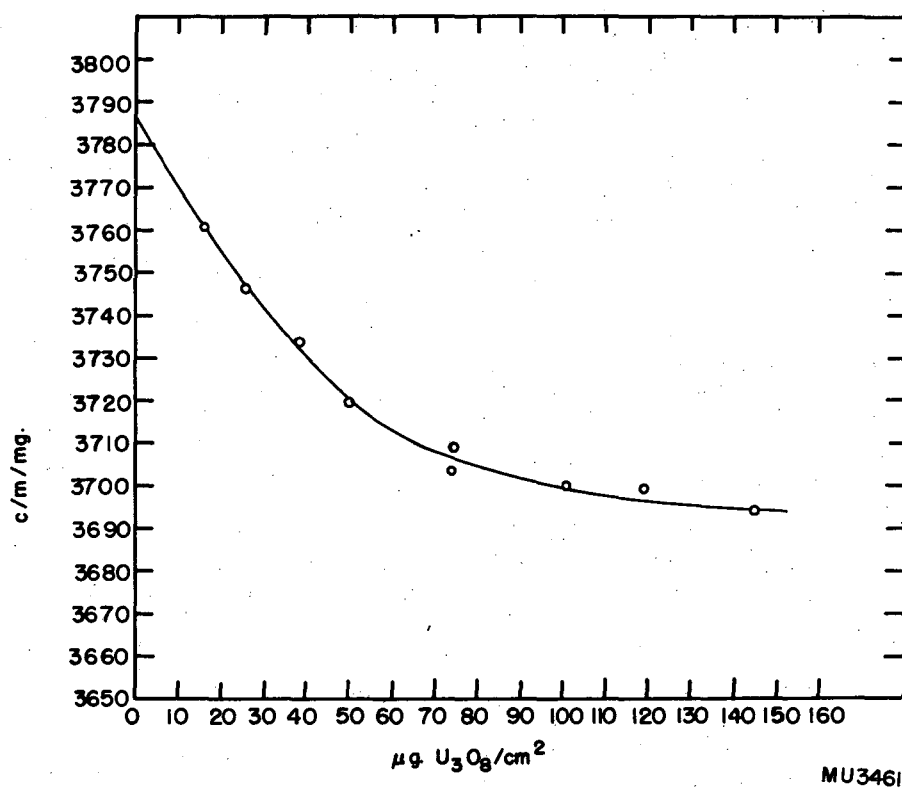


Fig. 3. Plot of specific counting rate vs film thickness in 2π alpha counting chamber.

IV. URANIUM 234 AND URANIUM 236

The experimental procedures used in preparing samples of U^{234} and U^{236} for counting were essentially the same and therefore will be discussed in the same section.

A. Mass and Pulse Analyses

The mass analyses reported by the Y-12 Mass Spectrometer Laboratory are as follows:

Principal isotope	Mass % of isotopes	Limits of error
U^{234}	234 - 95.99	± 0.07
	235 - 3.02	± 0.03
	238 - 0.98	± 0.05
U^{236}	236 - 96.65	± 0.07
	235 - 3.09	± 0.03
	234 - 0.05	± 0.01
	238 - 0.21	± 0.02

The sample whose principal isotope is U^{234} was not pulse analyzed, since the isotopes in small abundance had such comparatively low specific activities that any activity contribution by them was entirely negligible. For example, U^{235} would contribute about 0.001 percent to the total activity.

Pulse analysis* of the U²³⁶ sample showed the following activity percentages:

Activity % of isotope	Limits of error
236 - 97.7	±0.5
234 - 2.2	±0.5
235 - 0.1	±0.01

B. Weight Measurements

The uranium oxide used to prepare each plate was weighed on a quartz fiber torsion balance of the type described by Cunningham.⁷ The balance used was manufactured by the Ryerson Instrument Shop, University of Chicago, and is a modification of the Kirk, Craig, Gullberg, Boyer design. It has a maximum net load of about 3.4 mg, and a sensibility of 0.02 µg (see Fig. 4 and 5).

The torsion balance was calibrated by weighing directly on the balance two 2 mg weights, each standardized by the National Bureau of Standards. The true masses of these weights were known to ±0.05 µg. The calibration factors determined were 0.3424 and 0.3425 µg per division of the torsion wheel scale.

Since 1/20th part of a division could be detected with the vernier scale of the torsion wheel, as little as 20 µg could be

*The activity percentage of U²³⁵ was calculated from the mass percentage and the approximate specific activities of U²³⁴ and U²³⁵.

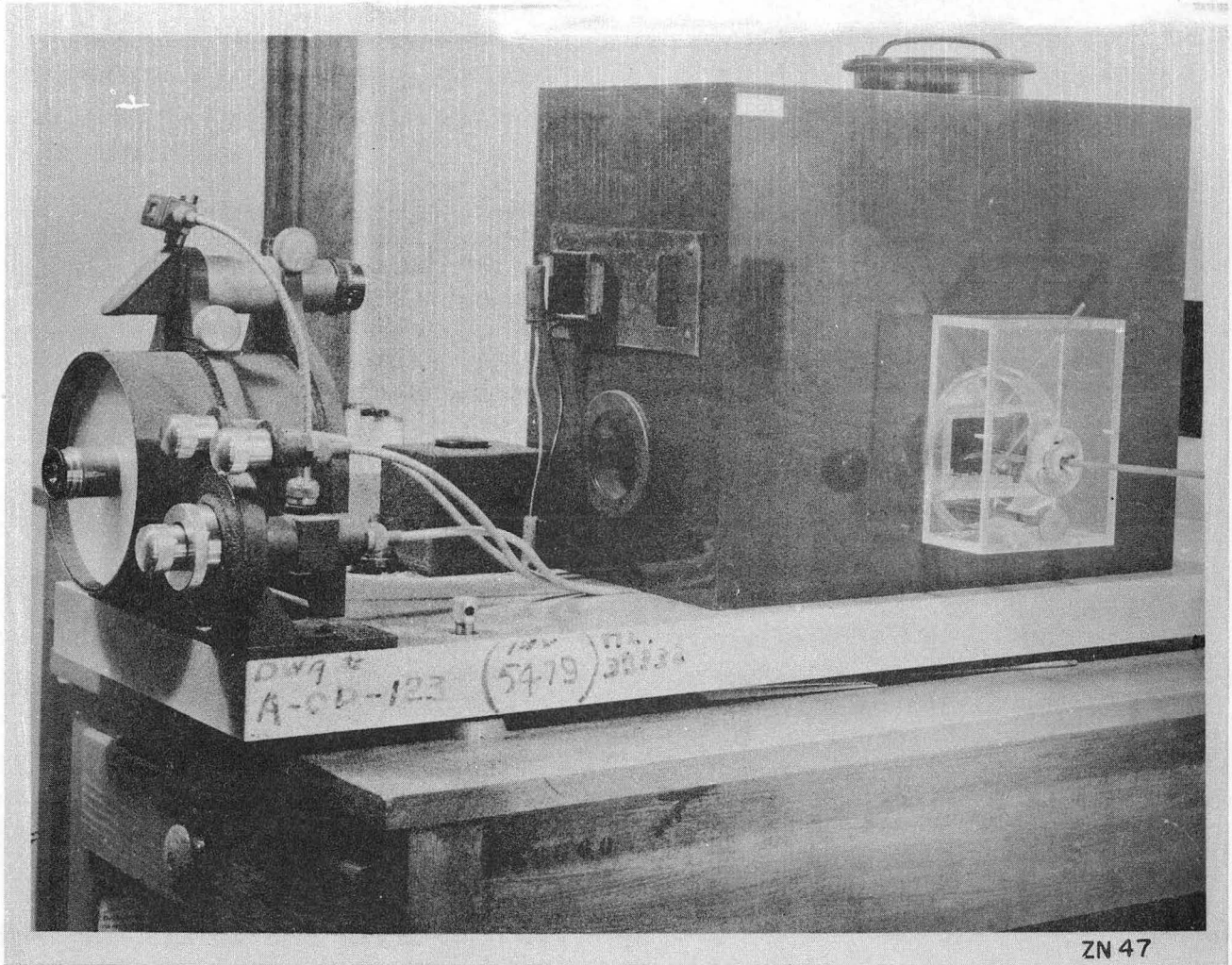


Fig. 4. Quartz fiber torsion balance - exterior view.

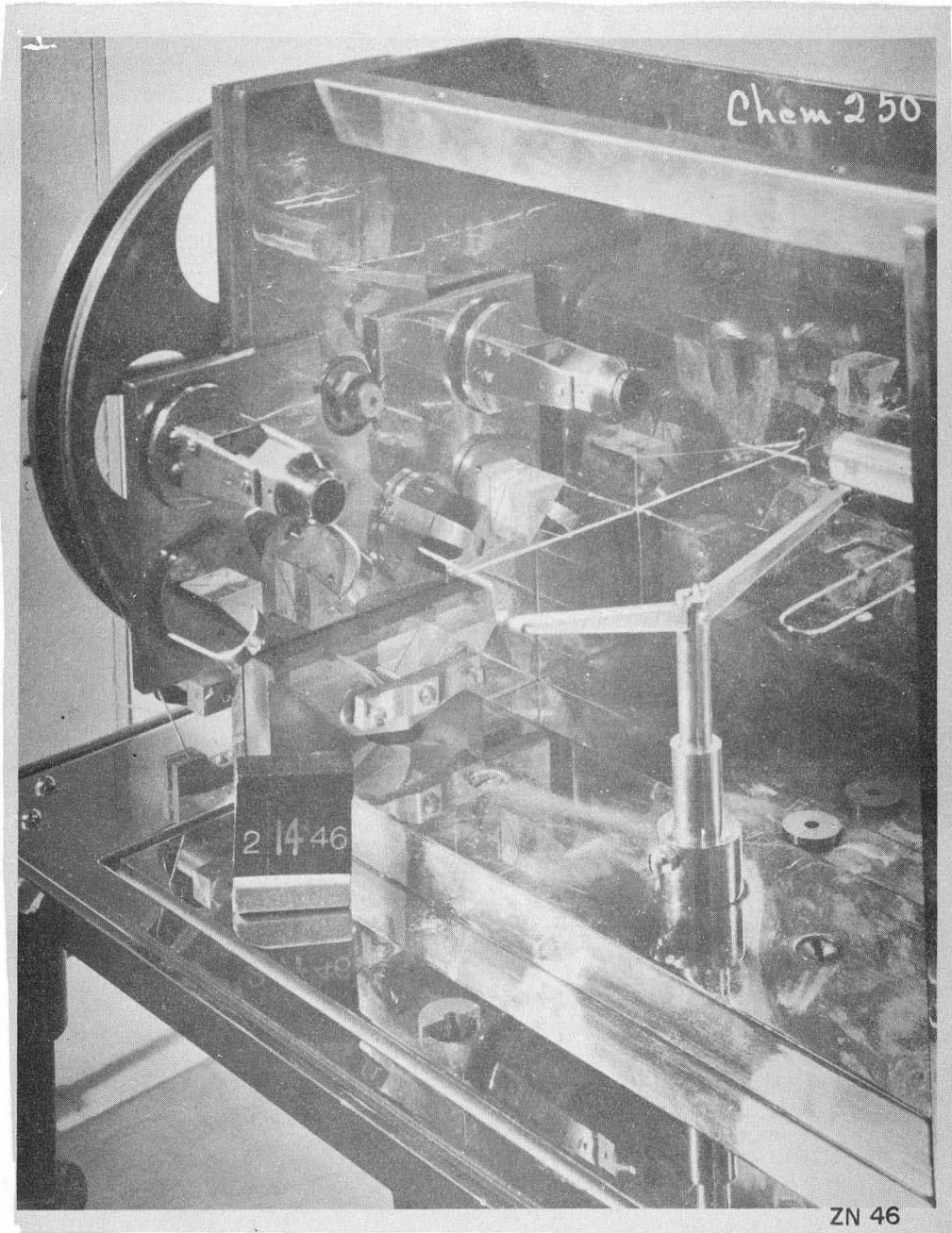


Fig. 5. Quartz fiber torsion balance - interior view.

weighed with an error of ± 0.1 percent. However, all samples weighed exceeded a mass of 100 μg , and thus were weighed with a reproducibility within 0.02 percent. The over-all uncertainty in weighing for any sample was less than 0.05 percent.

For each sample of oxide to be weighed, a weighing container was prepared from thin-walled quartz tubing of about 1 mm i.d., by sealing one end of the tubing in the flame of a microtorch, cutting the tubing about 4 mm from the sealed end, and fusing a quartz fiber of about 100 microns in diameter to the side of the tube near the opening. The fiber was bent to form a hook so that it could be suspended on the hang-down fiber of the torsion balance. The tube was cleaned in boiling nitric acid, distilled water, and dried in a clean covered beaker in an oven. Tubes of this size weighed approximately 6 mg.

After tare weighing on the torsion balance, a tube was mounted in a pair of screw-controlled cork-tipped forceps held in a micro-manipulator. A small micro-funnel drawn from 1/4 inch pyrex tubing was held by a clamp above the weighing tube. The weighing tube was carefully positioned directly under the stem of the funnel and brought upward until the stem of the funnel was inserted about 1/3 of the way into the tube. The required amount of oxide was poured into the funnel, and it dropped neatly to the bottom of the weighing tube. The tube and sample were then weighed on the torsion balance.

Extra precautions were taken in handling U^{234} because of the high specific activity of this isotope. It is calculated that about 1 μg of U^{234} should cause an early demise of one who ingests that quantity into the lungs. The purification of this material while

in solution was performed in an open fume hood, but converting the peroxide slurry to powdered U_3O_8 and loading the weighing tubes with this powder were done in a closed box.⁷ The loaded weighing tubes were transferred from the closed box to the torsion balance in a transfer box shown in Fig. 6.

C. Dissolution and Plating of the Materials

After determining the weight of a sample with the torsion balance, the weighing tube with sample was transferred to a clean 10 ml glass-stoppered volumetric flask. The flask and sample were weighed on the American Balance Corporation balance described in Section III. The flask was tipped so that most of the oxide powder fell out of the weighing tube into the bottom of the flask, and 350 μ l of concentrated HNO_3 were added. After standing for about 6 hours in the cold, all the oxide was dissolved. Then 2.6 ml of 5.6 M H_2SO_4 was added, and the flask was heated gently and shaken for about 20 minutes to ensure homogeneity of the solution.

The flask was reweighed and the concentration of uranium in μ /g of liquid was calculated.

A clean 2 mil platinum disk one inch in diameter was tare weighed on the same analytical balance. The disk rested on the bottom of a small porcelain titration disk inverted in a porcelain crystallizing dish 1 1/2 inches in diameter. About 100 μ l of liquid of known uranium concentration was transferred in a micropipet to the platinum plate, and the liquid and plate weighed. A solution 5 M in H_2SO_4 has a vapor pressure such that loss of liquid by evaporation was approximately 1/5 mg/min in our laboratory. By taking successive

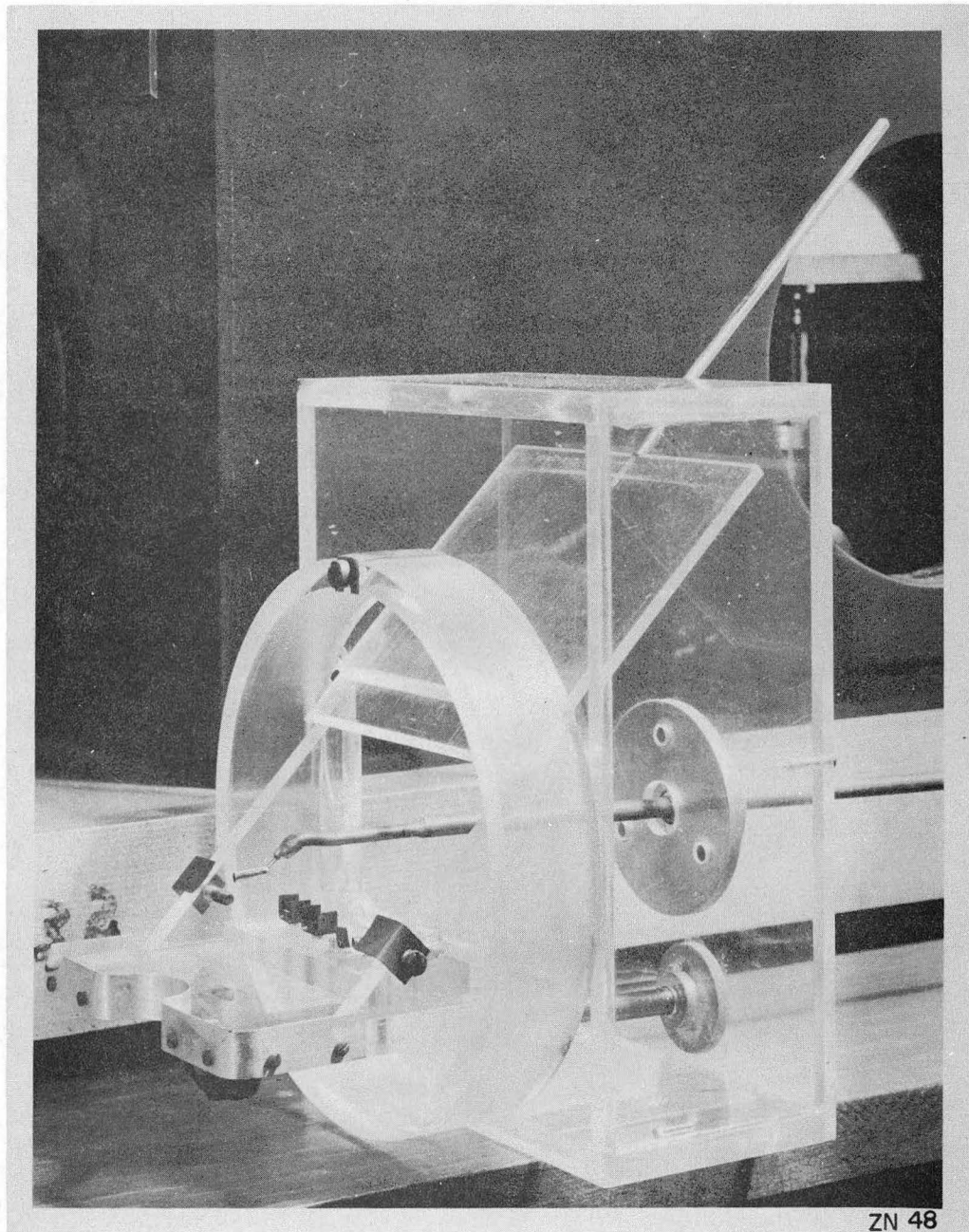


Fig. 6. Lucite transfer box.

weighings using a stop watch and extrapolating to the time when the 2-3 drops were placed on the plate, the weight of liquid could be obtained with an error $< \pm 0.1$ percent. A typical set of weighings is given, to show the magnitude of masses used, and to demonstrate a typical extrapolation shown in Fig. 7.

Torsion Balance Weighing

1779.55 div. - sample + tube
-939.75 div. - tare
839.80 div. - sample

$$839.80 \times 0.34245 = 287.59 \mu\text{g oxide}$$

$$287.59 \times 0.8458 = 243.24 \mu\text{g uranium}$$

$$243.24 \times 0.9599 = 233.49 \mu\text{g U}^{234}$$

Analytical Balance Weighing

12.89913 g flask + tube + oxide
-0.00029 oxide
12.89884 g flask + tube

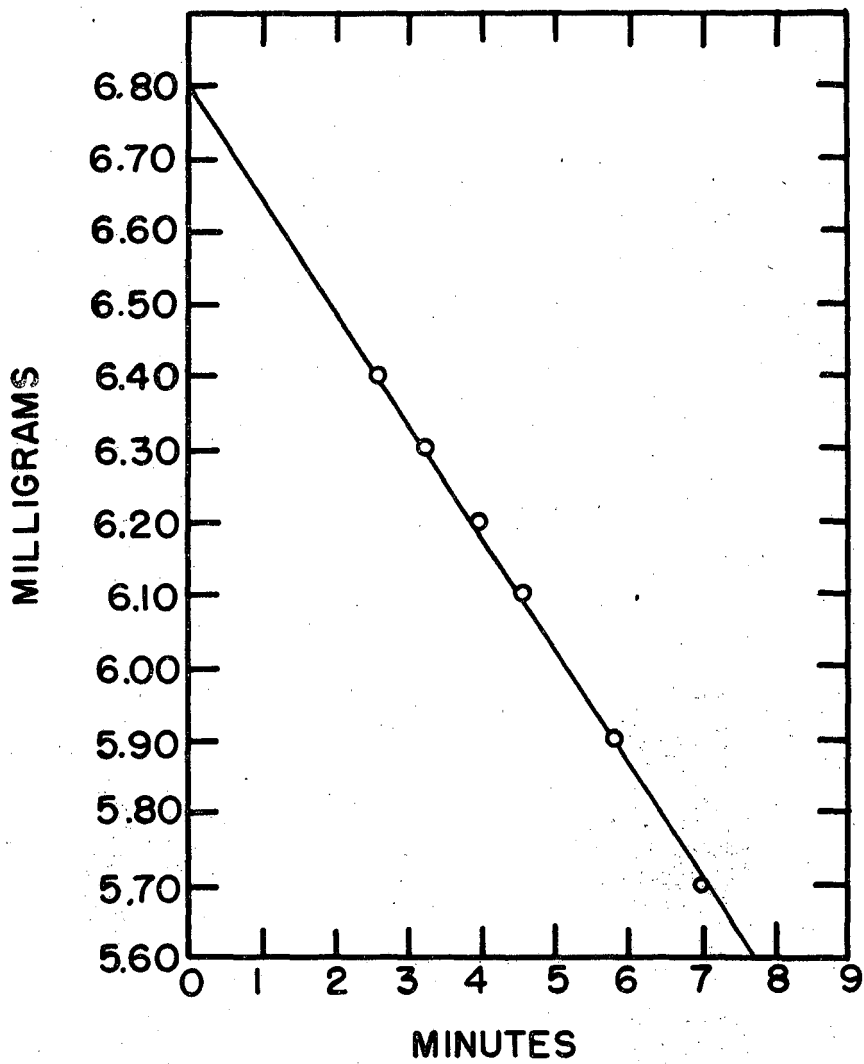
16.85258 g flask + tube + liquid
-12.89884 flask + tube
-3.95374 g liquid

$$\frac{233.49}{3.95374} = 59.055 \mu\text{g U}^{234}/\text{g liquid}$$

Plate 24-21

15.29680 g plate + support + liquid (zero time extrapolation - see Fig. 7)
15.16079 plate + support
0.13601 g liquid

$$0.13601 \times 59.055 = 8.032 \mu\text{g U}^{234} \text{ plated}$$



MU 3462

Fig. 7. Plot of change in weight vs time for analytical balance weighing.

Flask Reweighed: 16.71343 g

16.71343
12.89884

3.81459 g liquid remain

16.85258
16.71343

0.13915 g liquid removed

$$0.13915 \times 59.055 = 8.218 \mu\text{g U}^{234} \text{ removed}$$

233.49
8.22

225.27 $\mu\text{g U}^{234}$ remain

$$\frac{225.27}{3.81459} = 59.055 \mu\text{g U}^{234}/\text{g liquid (concentration check)}$$

After weighing the liquid on the platinum plate, the crystallizing dish and contents were placed in an induction furnace. As the furnace increased the temperature of the plate, the drop of liquid began to evaporate slowly, with no bubbling or spattering. When only H_2SO_4 remained as solvent, by carefully controlling the furnace a series of fairly concentric rings was formed as the droplet was reduced in size. After complete evaporation, the plate was brought to a dull red heat over a microburner, and the plate was ready for counting.

V. COUNTING OF THE SAMPLES

If the reader has been in the unfavorable position in which the precise determination of alpha disintegration rates is necessary, he need not be reminded that accurate results are not easily attained. There are many factors which affect such determinations, some of which are quite difficult to control. Many of these factors are discussed by Jaffey, Kohman, and Crawford in their Manual on the Measurement of Radioactivity.⁸ However, a detailed discussion of all the problems is not to be found in any one place in the literature. The major considerations will be discussed below.

When an alpha-radioactive substance is mounted on a polished backing material such as platinum, 50 percent of the alpha disintegrations are emitted such that one component of their paths is normal to and toward the plate. None of these particles would be detected in a conventional 50 percent geometry (2π) ionization chamber were it not that a finite number entering the plate at low angles are backscattered out with sufficient residual range to be counted. J. A. Crawford⁹ has made theoretical calculations which indicate that alpha particles with a range of 3.68 cm in air are backscattered from platinum to the extent of 3 - 3.5 percent. Cunningham, Ghiorso, and Hindman¹⁰ found that the apparent specific activity of Pu²³⁹ was 4 percent higher when counted in a 50 percent geometry chamber than when counted in a 0.04 percent geometry chamber, and they attributed the difference to the detection of backscattered particles in the 2π chamber. Cunningham, Ghiorso, and Jaffey¹¹ observed that 3.1 percent of the alpha particles emitted from natural uranium were

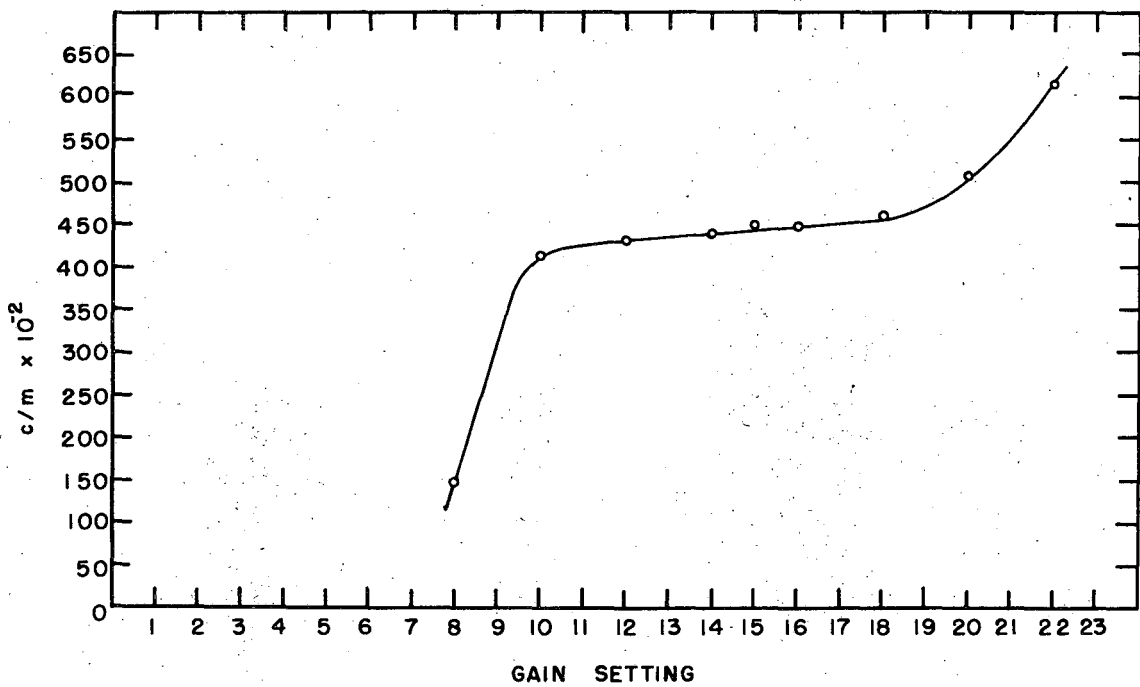
effectively backscattered from platinum, neglecting self-absorption.

Crawford's calculations further indicate that the amount of backscattering should depend on the atomic number of the backing material and the range (energy) of the alpha particle. The former requirement has been partially verified by experiment.^{11,12}

Theoretically, for "weightless" samples, a correction for the geometry factor of a 2π chamber can be derived from Crawford's work. However, if a sample is not weightless, an appreciable number of the backscattered particles are self-absorbed by the radioactive substance, so that the specific counting rate decreases with increasing film thickness.¹³ This fact is demonstrated by Fig. 3. By extrapolating to zero film thickness, at which no self-absorption takes place, the theoretical calculation can still be made.

When the counting rate of a weightless sample in a 2π chamber is measured as a function of the gain setting of the scaling circuit, a plateau is found, varying in slope from 2-4 percent over the range of the plateau. A typical plateau of such a system is shown in Fig. 8. Such slopes are undoubtedly caused principally by an increase in the number of backscattered particles detected with increased gain.

Obviously then, the counting rate for a sample in such a chamber will be arbitrary. Moreover, two different scaling circuits, with gain settings at the same approximate position from the left knee of the plateaus, might yield counting rates for a single sample differing by several tenths of percent. There is no reason to believe that identical counting rates would not be obtained were the



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Fig. 8. Plot of counting rate vs gain for
2π alpha counting chamber.

gain settings in exactly the same relative position, but it is extremely difficult to make such adjustments.

This variation of counting rate with gain makes the absolute evaluation of a precise disintegration rate measured in a 2π chamber very unreliable. All other parameters may be evaluated in an absolute fashion in some way, but no method has been devised which permits accurate correction for this deviation, other than calibration against a counting chamber of accurately known geometry. Even then, the calibration is accurate only for a particular system at a unique gain setting.

The best that can be said for use of the 50 percent geometry chamber is that it affords a very convenient means for determining precise relative data, provided the samples are reasonably uniform in thickness and have the same backing material and alpha decay energy. It is also adequate for the determination of absolute disintegration rates with an uncertainty of the order of ± 3 percent.

Fortunately, there is a method by which precise determinations of alpha disintegration rates is made more feasible. Jaffey¹⁴ has demonstrated experimentally that the backscattered particles detected in a 2π chamber are those caused by low angle scattering and are emitted at an angle less than about 35° with reference to the backing plate. Hence, chambers have been designed to eliminate the detection of all low angle backscattered particles, by detecting only those particles which are emitted from the backing plate with an angle usually of about 85° or more. These are termed "low geometry chambers." When the samples used in the preparation of

Fig. 3 were counted in a low geometry chamber, no such ordered variation in the counting rate with gain occurred.

Fig. 9 shows a schematic diagram of a typical low geometry chamber used in this laboratory. The aperture at the top (often called a "collimator") is covered with a mica window $1\frac{1}{2}$ - 2 mg/cm^2 in thickness, with a very thin film of aluminum evaporated on the top side of the mica to make the window surface conducting. During operation, the chamber is evacuated so that the alpha particles emitted in the proper direction from the sample travel freely up to the window, pass through it and are detected in the argon-filled region above the window in the conventional manner.

Fig. 10 illustrates a plateau measured for such a chamber. It is seen that no ambiguity in counting rate is involved.

If we let

c = radius of the aperture,

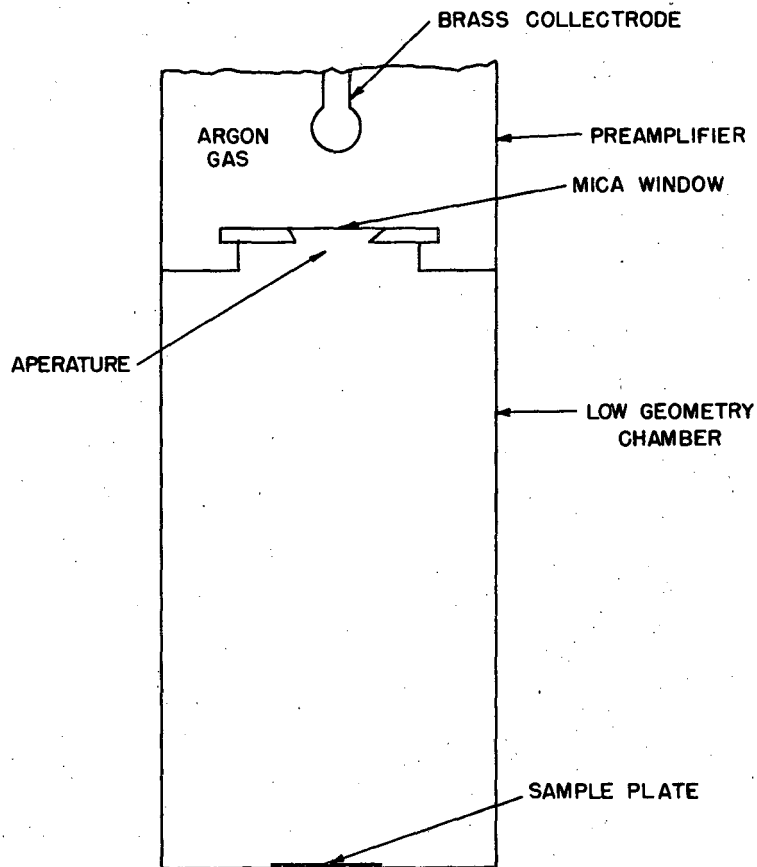
h = distance from the sample to the plane
of the aperture, and

s = radius of a uniformly distributed sample
coaxial with and parallel to the plane of
the aperture,

for the case where $s = 0$, the point source geometry factor

$$G_p = 1/2 \left[1 - \frac{h}{\sqrt{h^2 + c^2}} \right] = \frac{c^2}{2(h^2 + c^2 + h\sqrt{h^2 + c^2})}$$

This is called the Point Source Equation.



MU3464

Fig. 9. Diagram of low geometry alpha counting chamber.

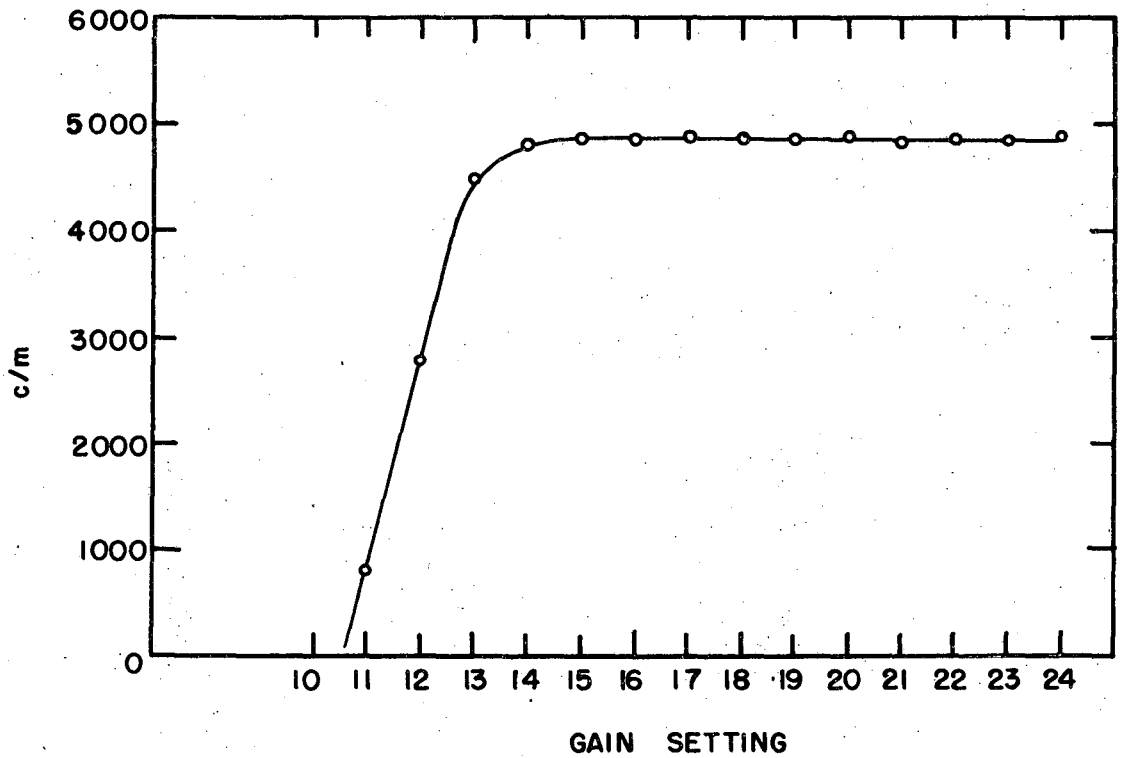


Fig. 10. Plot of counting rate vs gain for low geometry alpha counting chamber.

When c/h and $s/h \ll 1$, the following equation holds approximately:

$$F = \frac{1}{G_s} \approx 4 \frac{h^2}{c^2} + 3 + 3 \frac{s^2}{c^2} - \frac{s^4}{4c^2h^2} + \frac{9s^2 - c^2}{4h^2}$$

where G_s is the geometry factor for samples of significant radius.

The last equation was developed by H. P. Robinson in this laboratory, by considering corrections involving the inverse square law and the cosine of the angle at the aperture subtended by the vertical axis of the chamber and an element of sample surface away from the center of the sample. It is accurate to within ± 0.1 percent for

$$s/h < \begin{cases} 0.15 \\ 0.2 \\ 0.5 \end{cases} \text{ and } c/h < \begin{cases} 0.19 \\ 0.14 \\ 0.07 \end{cases}$$

and is entirely adequate for low geometry chambers of conventional size.

For cases where s/h and c/h are greater than these corresponding values, accurate calculations of the geometry factors are very laborious. Tables have been prepared in the computer laboratory at the University of California which list values of G_s as a function of s/h from 0 to 2 and c/h from 0.01 to 4. The computations were made using as a basis the integral shown below. It is similar to the one described by Kovarik and Adams.¹⁵ The intervals of s/h and c/h are such that, for most cases, G_s can be determined with an error $< \pm 0.05$ percent by a first order interpolation. In extreme cases, a second order interpolation is necessary.

Let us now distinguish between what has been called the geometry factor, G_s , and the counting yield, Y . The geometry factor G_s is

defined by the integral

$$\frac{1}{A} \int_A \Omega(G_p) dA$$

where A is the area of the sample and $\Omega(G_p)$ is the solid angle subtended by the aperture and any point on the sample surface; or, in another sense, it is the probability that the alpha particles at a distance h from the aperture will emerge through the aperture, on purely geometrical grounds.

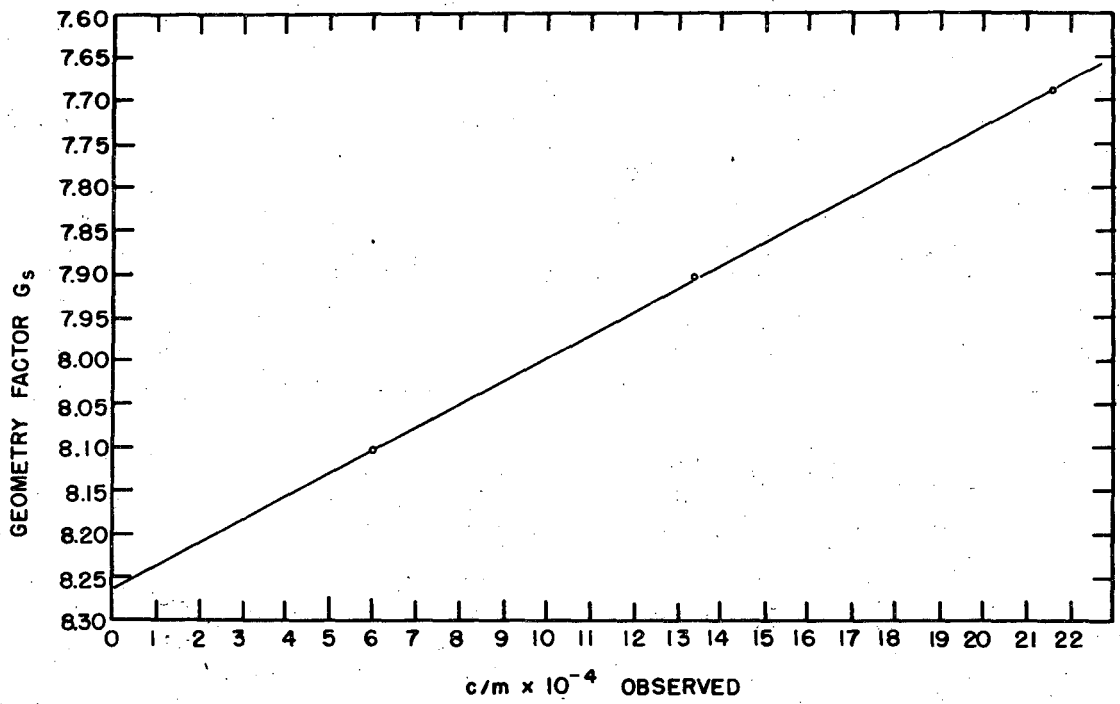
The counting yield is the ratio of the number of particles registered by the scaling circuit to the number emitted in all directions from the sample. Seldom, if ever, does $Y = G_s$, for the following reasons:

- (1) G_s is roughly proportional to c^2 and to h^2 . Therefore, the diameter of the aperture and the distance from the aperture to the sample each must be measured with an error no greater than ± 0.03 percent if the over-all error of G_s is to be no greater than ± 0.1 percent. It is usually easier to measure h more accurately than to measure $d = 2c$, since h is usually larger and d is an internal diameter. For example, the low geometry chamber used for calibration work mentioned later has a diameter of about 0.75 inch. 0.03 percent of 0.75 inch is about 0.2 mil. For this chamber h is about 5.4 inches. 0.03 percent of 5.4 inches is about 1.5 mils.
- (2) Alpha particles have a finite range through the material from which the aperture ring is constructed. Hence, the diameter used for calculating the geometry factor must be somewhat

larger than that actually measured. This effect may be serious under certain conditions. For example, if 6 Mev alpha particles were defined by an aperture ring made of aluminum having an edge beveled at an angle of 30° and an aperture of 0.2000 inch diameter, the effective diameter would be 0.2036 inch, and the error in the geometry factor calculated from the measured diameter would be about 3 1/2 percent.*

- (3) Since alpha particles enter the ionization chamber at random intervals, there is a probability that two or more particles will enter within an interval shorter than the resolving time of the scaling circuit. Should this occur, only one of the two or more particles will be registered. This process is termed a coincidence. Coincidence losses increase with counting rate, and must be corrected for when they become appreciable. Fig. 11 illustrates the coincidence calibration curve for the chamber used for counting all the samples prepared for this work. The uncertainty in the coincidence correction read from this curve is of the order of 3 percent. Since the coincidence correction itself is about 3 percent per 10^5 c/m, the uncertainty contributed by the coincidence correction to counting rates in the region of 10^5 c/m is about ± 0.1 percent, and is lower for lower counting rates.

*For this work, the aperture ring of the low geometry chamber was made of stainless steel and had a bevel of 60° . The aperture was about 3/4 inch in diameter. The error due to a greater effective diameter was about 0.06 percent. The same error for the medium geometry chamber was about 0.006 percent.



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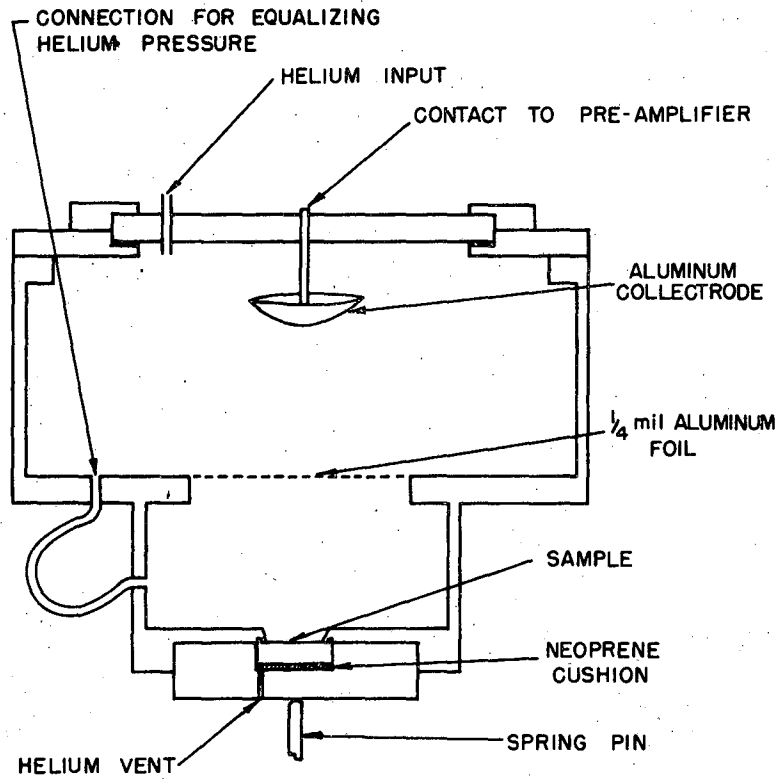
Fig. 11. Coincidence loss curve - plot of geometry factor vs counting rate for medium geometry counter.

- (4) The sample must be distributed as a perfectly uniform film thin enough so that self-absorption is negligible, if G_s is to equal Y , and it must be perfectly coaxial with the aperture and must be parallel to the plane of the aperture. Errors due to the last two requirements can easily be made insignificant, and errors due to the first can be made insignificant if the sample is prepared with care.*

Since the specific activity of U^{235} is relatively low, a low geometry chamber of the type described previously is not suitable for counting the alpha particles emitted by this isotope. For example, if 1 mg of the uranium enriched in U^{235} were to be counted in the low geometry chamber in this laboratory which gives the highest counting rate for a given sample ($G_s \approx 1/800$ for this chamber), the counting rate would be approximately 9 c/m plus background. About two months would be required to determine the gross counting rate with a standard (two-thirds) error of ± 0.1 percent.

In light of this impracticality, a chamber which has a G_s value of about 8 percent was designed by A. Ghiorso. A diagram of the chamber is shown in Fig. 12 ($c \approx 2$ inches and $h \approx 3$ inches). Aluminum leaf about 0.1 mil thick, or about 0.7 mg/cm^2 , is fixed across the aperture, and serves as the window. The entire chamber is filled with helium gas during operation. Because of the high relative geometry, this chamber has been named a "medium geometry chamber."

*An experimental check was made with a sample of 40 mm diameter which had a visually bad distribution compared to those used for specific activity measurements. Error due to nonuniformity was shown to be < 0.05 percent for this sample.



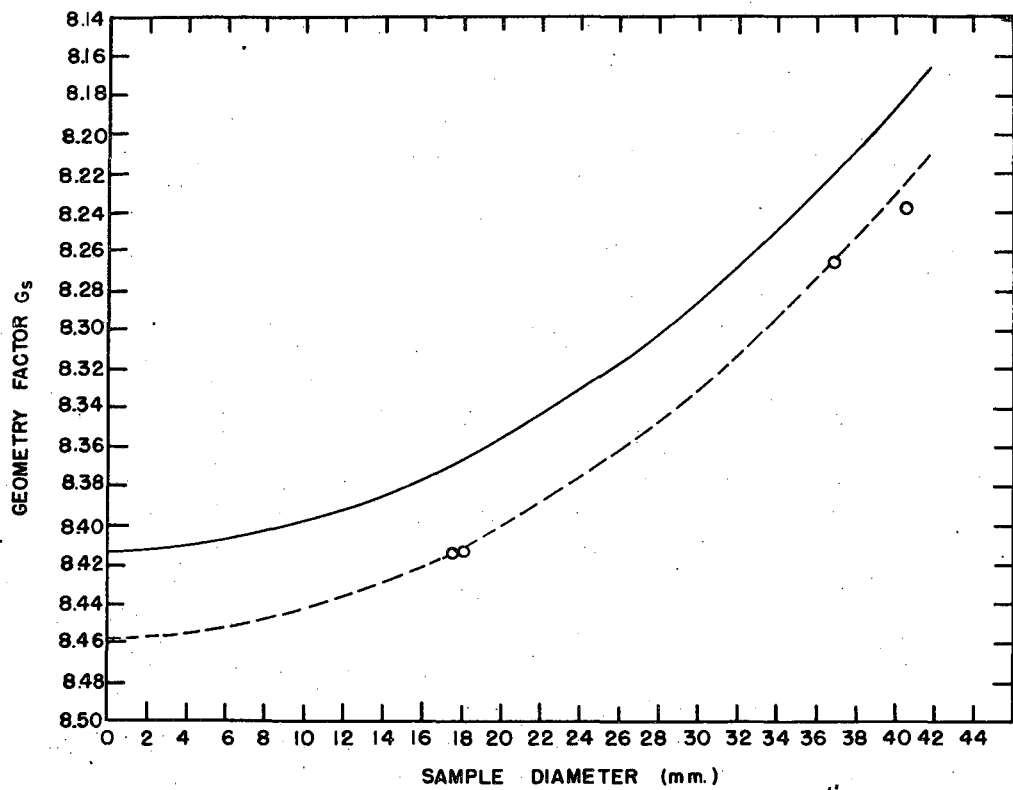
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Fig. 12. Diagram of medium geometry alpha counting chamber.

Fig. 13 shows a plot of geometry factor vs sample diameter for this chamber calculated with the use of the geometry tables mentioned previously in this section. The four points seen in the figure represent calibration points taken by counting samples of the diameter shown and correcting for coincidence losses. The absolute disintegration rates of each of these samples were measured previously by counting in the low geometry chamber of $G_s \approx 1/800$. The point at diameter 36.9 mm represents the value of the geometry factor for three samples of this diameter given by the extrapolation to zero counting rate shown in Fig. 11.

It is seen from Fig. 13 that the calibration points differ from the calculated curve by about 1/2 percent. About 3/5 of the difference could be accounted for by the probable error due to the uncertainties involved in determinations of the c and h values for the low and medium geometry chambers, in counting of the calibration samples and in the coincidence corrections. It is improbable that each of these determinations is in error to its limit and in the proper direction to serve as the sole cause for the discrepancy.

The medium geometry chamber was used to count all samples of U^{234} , U^{235} , and U^{236} . The background of the chamber remained at (14.9 ± 0.1) c/m throughout the work. The counting rates of the samples in this chamber ranged from 7000 to 12,000 c/m for the various U^{234} samples, from 400 to 800 c/m for U^{235} samples, and from 200 to 400 c/m for those of U^{236} .



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Fig. 13. Plot of geometry factor vs sample diameter for medium geometry alpha counting chamber.

VI. RESULTS AND DISCUSSION

Summary of Limits of Errors (in percent)

Uranium isotope	No. of samples counted	Std. dev. for all samples	Pulse analysis	Mass analysis	Sol'n conc.	Geom. factors	Chem. purity	Over-all error
234	9	± 0.38	--	± 0.07	± 0.1	± 0.50	± 0.10	± 0.65
235	9	± 0.84	± 2.0	± 0.01	± 0.2	± 0.50	± 0.10	± 2.2
236	3	± 0.14	± 0.50	± 0.07	± 0.1	± 0.50	± 0.20	± 0.79

The table above summarizes all the known sources of error involved in the determinations of the specific activities by the procedures used. The uncertainties in the pulse analysis values are standard (two-thirds) errors. The values for geometry factors were those determined by the dotted line of Fig. 13, which is based on the calibrated geometry of the medium geometry chamber. The uncertainties of the other values have been discussed in previous sections.

The over-all limits of error for the specific activity of each isotope are the square root of the sum of the squares of the other errors listed. They represent standard errors.

Results

Uranium isotope	Specific activity (d/m/mg)	Half-life (years)
234	$(1.370 \pm 0.009) \times 10^7$	$(2.475 \pm 0.016) \times 10^5$
235	$(4.74 \pm 0.10) \times 10^3$	$(7.13 \pm 0.16) \times 10^8$
236	$(1.406 \pm 0.011) \times 10^5$	$(2.391 \pm 0.018) \times 10^7$

Jaffey and co-workers¹⁶ have measured the half-life of U^{236} by counting samples of uranium enriched in U^{236} , for which mass and pulse analyses were determined. The weight of each sample was determined indirectly by counting neutron-induced fissions produced in the U^{235} present. The value found was 2.457×10^7 yr. No limits of error are stated for the final value, but the principal author has stated privately that the value should lie within ± 2 percent of this figure. Therefore, their value is in agreement with the value quoted in this thesis.

Because of the wide interest in the various specific activities, half-lives, mass ratios and activity ratios of the three isotopes comprising natural uranium, a table is presented which contains most of these values found in the literature of the past fifteen years. An analysis of each set of values is not always straightforward, since many are calculated from other values which are determined experimentally, often by indirect measurement. Furthermore, many of the published papers are written with so few details that an objective analysis for sources of error is often impossible. Nevertheless, an attempt has been made to evaluate the data so that "best" values may be stated which are themselves internally consistent. That such a task is subject to bias has been kept in mind throughout this evaluation; consequently, conservative limits of error have been set for these "best" values. It has not been feasible to present all the reasons for each selection, but the principal reasons have been stated briefly.

Values Reported Within the Past Twenty Years

t_{234} (yr) $\times 10^{-5}$	Sp. Act. ₂₃₄ (d/m/mg) $\times 10^{-7}$	t_{235} (yr) $\times 10^{-8}$	Sp. Act. ₂₃₅ (d/m/mg) $\times 10^{-3}$	Ref.
2.7 \pm 0.27	1.3 \pm 0.13	7.06 \pm 0.21 (recalc.)	4.78 \pm 0.14	1
2.29 \pm 0.14	1.48 \pm 0.09			17
2.35 \pm 0.14	1.44 \pm 0.09			17
2.522 \pm 0.008	1.345 \pm 0.004	8.8 \pm 1.1	3.82 \pm 0.49	12
2.67 \pm 0.04	1.27 \pm 0.02			19
2.475 \pm 0.016	1.370 \pm 0.009	7.13 \pm 0.16	4.74 \pm 0.10	(This work)
		8.91		2
		7.53 \pm 0.23	4.48 \pm 0.14	22
2.48 \pm 0.02	1.37 \pm 0.01	7.13 \pm 0.14	4.74 \pm 0.09	"Best" values

Values Reported Within the Past Twenty Years (Cont.)

t_{238} (yr) $\times 10^{-9}$	Sp. Act. ²³⁸ (d/m/mg)	t_{natural} (yr) $\times 10^{-9}$	Sp. Act. ^{natural} (d/m/mg)	Ref.
		2.221 ± 0.008	1501 ± 6	20
		2.221 ± 0.004	1501 ± 3	23
4.49 ± 0.01	742.7 ± 1.6	2.220 ± 0.002	1502 ± 1.5	12
4.51 ± 0.01	738.8 ± 1.6	2.221 ± 0.004	1501 ± 3	"Best" values

N_{238}/N_{235}	N_{238}/N_{234}	N_{234}/N_n (%)	$R = \frac{A_{235}}{A_{238}}$ (%)	$\frac{A_{234}}{N_n} = \frac{A_{238}}{N_n}$	A_{235}/N_n	Ref.
138.9 ± 1.4	$16,800 \pm 10\%$	0.00591 ± 0.00059	4.6 ± 0.1			1
139	$19,700 \pm 6\%$					17
137.0 ± 0.7						18
138.0 ± 0.3						18
		0.005481 ± 0.000012		737.4 ± 1.6	27.2 ± 3.5	12
			3.63 ± 0.03			2
138.0 ± 1.0	$18,400 \pm 1\%$	0.00539 ± 0.00004	4.6 ± 0.1	733.5 ± 1.6	34.1 ± 0.8	"Best" values

The mass ratio U^{238}/U^{235} in natural uranium has been measured with mass spectrographs by at least three different groups. In 1932, Nier¹ reported a value of 139 ± 1 percent. He showed further that there is no significant variation of the ratio with the age of the mineral in which the uranium is contained, by finding the same ratio, within limits of error, for minerals varying in age from 10^3 to 10^9 years.

In 1946, Chamberlain and co-workers¹⁷ found the same value. During the same year, Fox and Rustad¹⁸ determined a value of 137.0 ± 0.7 , a weighted average of 14 sets of readings, with an electron bombardment source. With a thermal source they found a value of 138.0 ± 0.3 , a weighted average of nine sets. The resolution corrections were much smaller with the latter source, mainly because metal ions, rather than UF_5^+ ions were detected.

It is seen that a value of 137.7 falls within the limits of error of all values reported. However, since Nier and Chamberlain each independently found the ratio to be 139, and since the average of the resolution corrections used in determining the value 137.0 was 1.7 percent, it is felt that a best value for the mass ratio U^{238}/U^{235} in natural uranium is 138 ± 1 percent.

The values quoted for the half-life of U^{234} vary from 2.29 to 2.7×10^5 yr, an average spread of about 16 percent. The value 2.7×10^5 yr ± 10 percent (Nier),¹ was derived by determining the mass ratio of U^{238} to U^{234} in natural uranium, and assuming that radioactive equilibrium exists between these isotopes in natural uranium. Then using the half-life 4.5×10^9 yr for U^{238} , the half-life of U^{234} was calculated from the equation:

$$\lambda_{234}N_{234} = \lambda_{238}N_{238}, \text{ or}$$

$$\frac{N_{234}}{T_{234}} = \frac{N_{238}}{T_{238}}.$$

The value 2.29×10^5 yr ± 6 percent (Chamberlain, et al.),¹⁷ was determined in the same manner as was Nier's, but a mass spectrograph having a higher resolving power was used. This value and that of Nier agree within the limits set by each author.

The value 2.35×10^5 yr ± 6 percent (Chamberlain, et al.),¹⁷ was determined by measuring the specific activity of uranium enriched in U^{234} and U^{235} by counting in a 2π chamber, determining the mass abundances of each isotope in the enriched samples, and subtracting the activity contributions of U^{235} and U^{238} calculated from specific activities for these isotopes determined elsewhere. The counting yield of the 2π chamber was determined by counting "thin samples" of known weight of natural uranium and dividing the specific counting rates by the specific activity of natural uranium as determined by Kienberger.¹²

The value 2.522×10^5 yr ± 0.3 percent (Kienberger),¹² was determined in a manner similar to that used by Chamberlain, et al. to obtain their latter value of 2.35×10^5 yr, again counting each sample in a 2π chamber. From a single material, samples of varying thickness were prepared, and counted, and a specific counting rate at zero film thickness was found by extrapolation. A value for backscattering from the nickel backing material was calculated from Crawford's⁹ work, and the counting yield of the chamber was computed.

From these values, the specific activity of the material was computed. The values of Kienberger and Chamberlain almost agree within quoted limits, each determined by the same method in principle.

The value $2.67 \times 10^5 \text{ yr} \pm 1.3 \text{ percent}$ (Goldin, et al.)¹⁹ was determined by genetic means. U^{234} was allowed to grow in by two beta particle emissions from UX_1 (Th^{234}), which originally decayed from U^{238} by alpha emission. The weight of U^{234} was calculated from the weight of the parent U^{238} , the several decay periods involved, and the decay constants of U^{238} and the intermediate isotopes. The work was extremely complex experimentally, requiring a great many operations subject to error. The description of the work was insufficiently detailed to permit independent evaluation of these errors. However, one is forced to conclude that such a method is extremely unlikely to yield results in error less than a few percent. Almost certainly the 1.3 percent quoted is unrealistic. Furthermore, the value determined is outside of agreement with the weighted mean of the other values by some $7 \frac{1}{2}$ percent.

The value $2.475 \times 10^5 \text{ yr} \pm 0.7 \text{ percent}$ was discussed in detail in previous sections. It is the only value determined by direct means, with very highly enriched uranium, and is independent of any constants of other isotopes or isotope ratios.

By weighting each value reported, considering the directness of each method, the method of counting, and the limits of error quoted by each author, a best value for the half-life of U^{234} is computed as $2.48 \times 10^5 \text{ yr} \pm 1 \text{ percent}$, with a concomitant specific activity of $1.37 \times 10^7 \text{ d/m/mg}$. Considering limits of error, all

values quoted in the table are in agreement with this value except Chamberlain's first value of 2.29×10^5 yr and Goldin's value of 2.67×10^5 yr.

Nier¹ was among the first to determine a value for the half-life of U^{235} , viz., 7.06×10^8 yr (recalculated in accordance with reference 20). The half-life was calculated with the equation:

$$R = \frac{\lambda_{235} N_{235}}{\lambda_{238} N_{238}} = \frac{AcU}{U_I}$$

assuming everything known except λ_{235} . For the ratio N_{238}/N_{235} , he used the value 139. λ_{238} was computed from the specific activity of natural uranium²⁰ and $N_{238}/N_{\text{natural}} = 0.9928$. R was determined by measuring the Pb^{207}/Pb^{206} ratio with a mass spectrometer for several radiogenic lead ores of known age, and utilizing the equation:

$$\frac{N_{207}}{N_{206}} = \frac{1}{139} \frac{\exp(139R\lambda_{238}t) - 1}{\exp(\lambda_{238}t) - 1}$$

where t is the age of the ore.

R was found by graphical means to be 0.046 ± 2 percent. A 1 percent error in the ratio N_{238}/N_{235} has practically no effect on the value of R. Therefore, his value of the half-life of U^{235} should be in error no greater than about 3 percent. This assumption is strengthened by the beautiful consistency of his data.

Kienberger¹² reports a value of 8.8×10^8 yr ± 12 1/2 percent for the half-life of U^{235} , which was calculated by difference. He measured the specific activity of natural uranium and of U^{238} , and

computed the activity contribution of U^{238} in the former. By subtracting twice this contribution (U^{234} assumed to be in radioactive equilibrium with U^{238}) from the specific activity of natural uranium, the activity contribution of U^{235} is computed. Dividing this value by the mass abundance of U^{235} in natural uranium gives the specific activity of U^{235} . The figure is subject to great error because it is determined by a small difference between two large numbers. For example, if the value for the specific activity of natural uranium is in error by 0.1 percent, that for U^{235} would be in error by 4 1/2 percent.

Clark and co-workers² reported a figure for the half-life of U^{235} of 8.91×10^8 yr. They determined R (see page 50) by pulse analyzing natural uranium, and quoted a value of 0.0363 for R, from which they calculated the half-life in the manner previously described. It is now known²¹ that they were unable to resolve high and low energy alpha groups comprising about 15 percent of the alpha spectrum of U^{235} , and therefore found a value for R which is about 15 percent low. A recalculation on this basis leads to an R value of 0.0425, and a half-life of 7.64×10^8 yr, values which are still in error by 7 percent when compared to Nier's values. An explanation of this latter discrepancy has not been found.

A value of 7.53×10^8 yr \pm 3 percent has been determined by Knight,²² who measured the specific activity of a portion of the same highly enriched U^{235} used for work reported in this thesis, and found it to have 7279 ± 23 d/m/mg. A crude pulse analysis was made with the use of a one channel pulse height analyzer, which showed that about 61.6 percent of the disintegrations were those of U^{235} .

Thus, the specific activity of U^{235} was computed as 4484 d/m/mg.

The specific activity of the same material was measured in this laboratory and found to be 7257 ± 70 d/m/mg. The comparable figures are in disagreement by only 0.3 percent, which is very gratifying considering the limits of error set for each value. However, a very careful pulse analysis of this material was made here utilizing the 48 channel differential pulse analyzer, which resulted in the figure (65.3 ± 1.3) percent for the U^{235} contribution. Hence, when Knight's gross specific activity figure is multiplied by 0.653, the corresponding half-life value becomes 7.10×10^8 yr.

Considering the values discussed above, a weighted average provides a best value of 7.13×10^8 yr \pm 2 percent for the half-life of U^{235} , with a corresponding specific activity of 4.74×10^3 d/m/mg.

Kovarik and Adams²⁰ were the first workers to make a precise determination of the specific activity of natural uranium. They eliminated backscattering and self-absorption as sources of error by counting only those alpha particles which passed through the holes of a metal grid. The value reported for the specific activity is 1501 d/m/mg.

Curtiss and co-workers²³ counted samples of natural uranium of known weights and various thicknesses in a 2π chamber. The samples were thick enough to absorb essentially all of the backscattered particles. Therefore, a plot of specific counting rate vs film thickness yielded a straight line, and an extrapolated value to zero film thickness gave a specific counting rate of 750.6 c/m/mg. Since the backscattered particles were not detected, the counting yield was considered to be 50 percent. Thus, the specific activity

was computed as 1501 d/m/mg \pm 0.2 percent.

Kienberger¹² counted electrodeposited samples of natural uranium in a 2 π chamber, and computed the counting yield of the chamber in the same manner as was done for his U²³⁴ work. He reports a value of 1502 d/m/mg \pm 0.1 percent.

Disregarding the fact that it is highly improbable on statistical grounds that three values which are so difficult to determine and which are subject to so many sources of error are in agreement to better than 0.1 percent, one is forced to conclude that a best value is 1501 d/m/mg \pm 0.2 percent for the specific activity of natural uranium.

Kienberger,¹² using isotopically pure U²³⁸, has determined a value for the specific activity of this isotope, viz., (742.7 \pm 1.6) d/m/mg, by the same method used for his natural uranium work. It is the only value reported in recent years that has been determined by direct means.

However, with the best values quoted thus far, one is able to calculate the specific activity of U²³⁸. The calculation follows:

$$\frac{N_{235}}{N_{238}} = \frac{1}{138} = 0.725 \text{ percent}$$

$$\frac{N_{234}}{N_{238}} = \text{ca } 0.0054 \text{ percent (see below).}$$

$$\text{Therefore, } \frac{N_{235}}{N_n} = 0.719 \text{ percent and } \frac{N_{238}}{N_n} = 99.28 \text{ percent.}$$

Specific activity of U^n : 1501 ± 3.0 d/m/mg

Specific Activity of U^{235} x 0.00719: $- 34 \pm 0.8$

Activity contribution of U^{234} and U^{238} in U^n : 1467 ± 3.1 d/m/mg

Activity contribution of U^{238} in U^n : $1/2 \times 1467 = 733.5 \pm 1.6$ d/m/mg

$$\frac{733.5}{0.9928} = 738.8 \pm 1.6 \text{ d/m/mg, the specific activity of } U^{238}.$$

It is seen that a relatively large error in the specific activity of U^{235} has but little effect on that of U^{238} calculated in the way. Therefore, if we assume the value for the specific activity of natural uranium to lie within ± 0.2 percent, as the three reported values indicate, it must be concluded that the value 742.7 d/m/mg must be in error by at least $1/2$ percent. Actually, the agreement seems surprisingly good, considering the counting method used by Kienberger, and realizing the very low specific activity of this isotope.

The half-life concomitant with 738.8 d/m/mg is 4.51×10^9 yr. Although Nier¹ used the value 4.56×10^9 yr indirectly in his equations for the calculation of R, the difference results in a negligible change in R, and therefore a negligible change in the recalculated value 7.06×10^8 yr for the half-life of U^{235} . Furthermore, from the best values quoted thus far, R is

$$(4.6 \pm 0.1) \text{ percent} = \frac{AcU}{U_I}.$$

Another calculation can be made, which yields the mass ratio of U^{234}/U^n in natural uranium. Since it is assumed that U^{238} and U^{234}

are in radioactive equilibrium in natural uranium, the activity contribution of U^{234} is the same as that of U^{238} , viz., 733.5 ± 1.6 d/m of U^{234} per mg of U^n . Then, dividing by the specific activity of U^{234} , 1.37×10^7 d/m/mg ± 0.7 percent, the mass ratio U^{234}/U^n is calculated to be (0.00535 ± 0.00004) percent.

Nier¹ measured the mass ratio U^{238}/U^{234} in natural uranium spectrographically, and found an average value of $16,800 \pm 10$ percent. From this figure the value (0.00591 ± 0.00059) percent is calculated for the mass ratio U^{234}/U^n .

Chamberlain and co-workers¹⁷ report the value $19,700 \pm 6$ percent for U^{238}/U^{234} , from which the value (0.00504 ± 0.00030) percent for U^{234}/U^n is calculated.

Kienberger¹² determined the mass ratio U^{234}/U^n by analyzing samples of uranium highly enriched in U^{234} , and determining the specific activities of these samples. Using his values for the specific activities of U^{238} and U^n , he calculated the value (0.005481 ± 0.000012) percent.

The values of Nier and of Chamberlain and co-workers, and the value calculated in this thesis are all in agreement, when the limits of errors are recognized. However, Kienberger's value quoted above is in disagreement, unless one considers his statement that the value is good to at least 1 percent, in which case agreement is almost reached. Consequently, a best value for the mass ratio U^{234}/U^n is found to be (0.00539 ± 0.00005) percent.

It is alarming to note that, with but few exceptions, the papers published by the authors listed above do not give the slightest information concerning a most fundamental question which is associated

with all the experimental work discussed. Knowledge of the degree of chemical purity of the substances used is absolutely necessary if results are to be meaningful. That this problem has been completely ignored by many workers in the past becomes all too evident when the literature is read. It is not reasonable to expect a reader to assume that contaminants, which are ever-present even though in negligible amounts perhaps, have been determined and accounted for. Thus, the values reviewed above, where no mention of chemical purity is made, will stand in doubt merely because of this oversight.

Since A. Holmes³ used the value 7.13×10^8 yr for the half-life of U^{235} in his calculations of geological time, which has been found to be the best value to date, no correction can be claimed necessary for his value of the age of the earth on this basis alone.

It is to be hoped that sometime within the near future values which have been discussed at length here will be redetermined, particularly those associated with natural uranium and with U^{238} . The availability of uranium highly enriched in particular isotopes makes the task less formidable, and increases the possibility for accurate results. It is hoped further that especial attention be granted to the problems of determining precise alpha disintegration rates since within this realm undoubtedly lie the most bases for disagreement among the values reported in the literature.

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REFERENCES

1. A. O. Nier, Phys. Rev. 55, 150, 153 (1939).
2. F. L. Clark, H. J. Spencer-Palmer, and R. N. Woodward, Imperial Chemical Industries Limited, Research Department Declassified Report BR-522 (October, 1944).
3. A. Holmes, Nature 157, 680 (1946).
4. W. Biltz and H. Müller, Z. anorg. u. allgem. Chem. 163, 257 (1927).
5. A. Ghiorso, A. H. Jaffey, H. P. Robinson, and B. B. Weissbourd, The Transuranium Elements: Research Papers (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 16.8, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B.
6. D. L. Hufford and B. F. Scott, ibid., Paper No. 16.1.
7. B. B. Cunningham, Nucleonics 5, 62 (1949).
8. A. H. Jaffey, T. P. Kohman, and J. A. Crawford, Metallurgical Laboratory Declassified Report M-CC-1602 (January, 1944).
9. J. A. Crawford, The Transuranium Elements: Research Papers (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 16.55, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B.
10. B. B. Cunningham, A. Ghiorso, and J. C. Hindman, ibid., Paper No. 16.3.
11. B. B. Cunningham, A. Ghiorso, and A. H. Jaffey, ibid., Paper No. 16.6.
12. C. A. Kienberger, Phys. Rev. 76, 1561 (1949).
13. B. F. Scott, reported in Metallurgical Laboratory Classified Report CN-1764 (July, 1944).
14. A. H. Jaffey, unpublished work.

DECLASSIFIED
~~CONFIDENTIAL~~

15. A. F. Kovarik and N. I. Adams, Phys. Rev. 40, 718 (1932).
16. A. H. Jaffey, H. Diamond, A. Hirsch, and J. Mech, Phys. Rev. 84, 785 (1951).
17. O. Chamberlain, D. Williams, and P. Yuster, Phys. Rev. 70, 580 (1946).
18. M. Fox and B. Rustad, Carbide and Carbon Chemicals Corporation Classified Report BD-R-88 (January, 1946).
19. A. S. Goldin, G. B. Knight, P. A. Macklin, and R. L. Macklin, Phys. Rev. 76, 336 (1949).
20. A. F. Kovarik and N. I. Adams, J. Applied Phys. 12, 296 (1941).
21. A. Ghiorso, Phys. Rev. 82, 979 (1951).
22. G. B. Knight, Oak Ridge National Laboratory Classified Report K-663 (August, 1950).
23. L. F. Curtiss, L. L. Stockman, and B. W. Brown, National Bureau of Standards Classified Report A-80 (December, 1941).

~~CONFIDENTIAL~~

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