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The Specific Alpha-Activities and Half-Lives of U^{234}, U^{235}, and U^{236}†

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The specific alpha-activities and half-lives of U^{234}, U^{235}, and U^{236} have been determined. The material used for each determination was uranium very highly enriched in the isotope under investigation.

Accurate volume aliquots of U^{235} were electrodeposited quantitatively onto platinum disks and were counted in a medium geometry chamber. Accurate weight aliquots of U^{234} and of U^{236} 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 (disint/min mg)	Half-life (years)
U^{234}	$(1.370\pm0.009)\times10^7$	$(2.475\pm0.016)\times10^5$
U^{235}	$(4.74\pm0.10)\times10^3$	$(7.13\pm0.16)\times10^8$
U^{236}	$(1.406\pm0.011)\times10^5$	$(2.391\pm0.018)\times10^7$

I. INTRODUCTION

In 1939, Nier[1] determined the half-life of U^{235} 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-workers[2] determined the half-life of this nuclide by counting and pulse analyzing uranium slightly enriched in U^{235}. The two values were in disagreement by about 25 percent.

After Nier had published his work, Holmes[3] devised a method for calculating the age of the earth, using Nier's mass spectrographic data, including his value for the half-life of U^{235}. Holmes derived a value for the age of the earth of about 3.3 billion years. With the appearance of Clark's value, this figure became somewhat suspect, especially since the decay constant of U^{235} appeared in the calculations as an exponential.

Because of the widespread interest in an accurate value for the age of the earth, it was hoped that an accurate redetermination of the half-life of U^{235} 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 corrections based on spectrographic analysis by the copper spark method ordinarily are uncertain by about a factor of 2.

The following method of purification was 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 slurrying, 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

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† This work was performed under the auspices of the AEC.

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[1] A. O. Nier, Phys. Rev. 55, 150, 153 (1939).

[2] Clark, Spencer-Palmer, and Woodward, Imperial Chemical Industries Limited, Research Department Declassified Report BR-522, unpublished (October, 1944).

[3] A. Holmes, Nature 157, 680 (1946).

yield of 85–90 percent. A sample of the oxide was then analyzed spectrographically. Results of the several spectrographic analyses of the purified oxides are given in Table I.

The oxide composition, U_3O_8, was verified as follows: A sample of natural uranium purified as described above and a sample of the $(U^{235})_3O_8$ from Oak Ridge were subjected to an x-ray analysis. The compounds were found to be isostructural with identical lattice constants, which 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 the x-ray data alone, since the lattice constants are not sensitive to slight changes in composition over the solid solution range. However, by plotting composition *versus* partial pressure of oxygen at various temperatures, according to data compiled by Biltz and Müller,[4] a simple interpolation shows that the composition lies between $UO_{2.655}$ and $UO_{2.665}$, when the oxide is prepared under our conditions. The corresponding uncertainty in the uranium content of the oxides is ±0.06 percent, and the deviation from the composition 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 percentages of the isotopes in the uranium sample whose principal isotope is U^{235} are given in Table II.

Since the specific activity of U^{234} is about 3000 times that of U^{235}, the activity contribution of U^{234} is very significant in the above sample; therefore, it was necessary to determine the percentage of activity contributed by U^{234}. 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 U^{235} and 34.7 percent from U^{234}.

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, chain, 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 <±0.1 percent.

TABLE I. Spectrographic analyses of uranium oxide samples.

Oxide	% Fe_2O_3	% CaO	% Al_2O_3	% MgO	% others	% purity	Method
$(U^{234})_3O_8$	<0.01	<0.01	0.01	<0.01	<0.01	>99.95	Cu spark
$(U^{235})_3O_8$[a]	<0.04	<0.01	<0.01	<0.01	<0.1	>99.90	gallium oxide
$(U^{236})_3O_8$	0.14	<0.01	0.04	0.02	<0.01	>99.8	Cu spark

[a] $(U^{235})_3O_8$ was found to contain the amounts of impurities as shown when received, and no effort was made to purify it further.

TABLE II. Isotopic analysis of enriched uranium sample.

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

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. The resulting concentration of the standard solution was 5.312±0.010 mg of pure uranium per ml of solution. 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.

Calibration, dilution to the standard volume, and subsequent removals of volume aliquots were all carried out at 24±1°C.

A check on the concentration of the standard solution after one year 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. Electrodepositon of the Material

Each uranium sample was prepared for counting by an electrodeposition technique described in detail by Hufford and Scott.[6] Figure 1 shows the component parts of the electrolysis cell used for most of the electrodepositions. 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 $\frac{5}{8}$ inch in diameter, riveted to a tantalum shaft $\frac{1}{8}$ 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.

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

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[4] W. Biltz and H. Müller, Z. anorg. u. allgem. Chem. **163**, 257 (1927).

[5] Ghiorso, Jaffey, Robinson, and 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, Div. IV.

[6] D. L. Hufford and B. F. Scott, *The Transuranium Elements: Research Papers* (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 16.1.

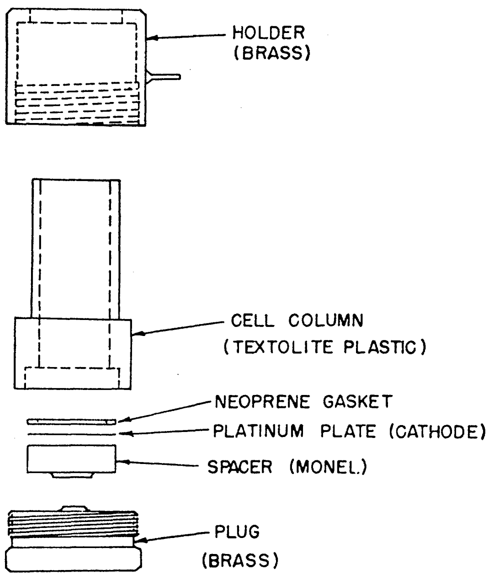

FIG. 1. Electrolysis cell.

calibrated[7] micropipet and transferred to the cell. The pipet was rinsed five times to ensure complete transfer. Then the deposition was carried out as described in reference 6.

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 U^{235} 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 deposited 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.

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 summarized in Table III.

The sample whose principal isotope is U^{234} was not pulse analyzed, since the activity contributions of U^{235} and U^{238} were entirely negligible.

Pulse analysis of the U^{236} sample showed that 97.7 ± 0.5 percent of the activity was contributed by U^{236} and 2.2 percent by U^{234}. The remaining 0.1 percent contributed by U^{235} was calculated from the mass percentage and the approximate specific activities of U^{234} and U^{235}.

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.[8] 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 load capacity of about 20 mg, a weighing range of about 3.4 mg, and a sensibility of 0.02 μg.

The balance was calibrated directly by weighing separately two 2 mg weights standardized to ± 0.03 percent by the National Bureau of Standards. The factors obtained in the two calibrations were 0.3424 and 0.3425 μg per division of the torsion wheel scale. Weighings were reproducible to ± 0.05 division read from the vernier scale of the torsion wheel. All samples weighed exceeded a mass of 100 μg, and thus were weighed with a precision of better than ± 0.02 percent and an over-all uncertainty of 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 diameter to the side of the tube

TABLE III. Mass analyses of the U^{234} and U^{236} samples.

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

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[7] Each micropipet was calibrated for content with mercury. The calibration error, including the uncertainty in the correction for the meniscus effect, was less than ± 0.1 percent.

[8] B. B. Cunningham, Nucleonics **5**, 62 (1949).

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 micromanipulator. A small microfunnel drawn from $\frac{1}{4}$-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 $\frac{1}{3}$ 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.

C. Dissolution and Plating of the Materials

After weighing as described, the weighing tube with sample was placed in a clean 10-ml glass stoppered volumetric flask. Flask and contents were then weighed on the semimicro balance described in Sec. III. The flask was then tipped causing most of the oxide powder to fall out of the weighing tube into the bottom of the flask, and 350 μl 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.

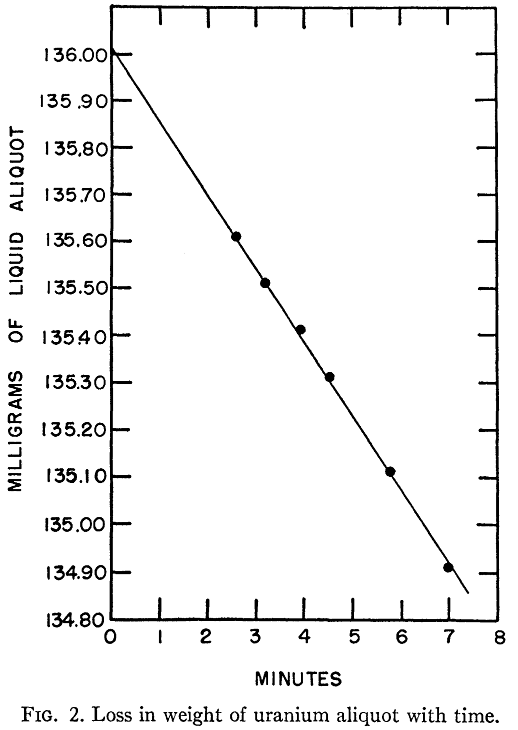

Fig. 2. Loss in weight of uranium aliquot with time.

The flask was reweighed and the concentration of uranium in μg/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 $1\frac{1}{2}$ inches in diameter. About 100 μl of liquid of known uranium concentration was transferred with a micropipet to the platinum plate, and the liquid and plate weighed. Loss of liquid by evaporation was corrected for by taking successive weighings using a stop watch and extrapolating to the time when the 2–3 drops were placed on the plate as shown in Fig. 2. A typical set of weighings is given below.

Torsion Balance Weighing

1779.55 div.—sample+tube
−939.75 div.—tare
839.80 div.—sample

839.80×0.34245 = 287.59 μg oxide
287.59×0.8458 = 243.24 μg uranium
243.24×0.9599 = 233.49 μg 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. 2)
15.16079 plate+support
0.13601 g liquid

0.13601×59.055 = 8.032 μg U^{234} plated

Flask Reweighed: 16.71343 g

16.71343
−12.89884
3.81459 g liquid remain

16.85258
−16.71343
0.13915 g liquid removed

0.13915×59.055 = 8.218 μg U^{234} removed

233.49
−8.22
225.27 μg 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 temperature of the plate rose, the drop of liquid began to evaporate slowly, with no bubbling or spattering. When only H_2SO_4 remained as

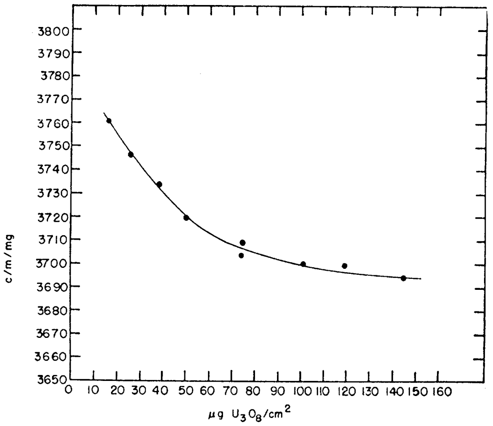

FIG. 3. Specific counting rate *vs* film thickness for samples in 2π-alpha-counting chamber.

solvent, careful control of the furnace resulted in the formation of a series of fairly concentric rings 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

Precise determinations of alpha-disintegration rates are subject to a number of errors, 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.*[9] 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.

A thin sample of an alpha-radioactive substance mounted on a flat polished backing material emits 50 percent of its alpha-particles with a direction component toward the backing plate. In a conventional 50-percent geometry (2π) ionization chamber a significant fraction of these particles suffer multiple scattering by the atoms of the backing plate in such a way that they emerge from the plate in the direction of the sensitive volume of the counter. Cunningham, Ghiorso, and Hindman[10] found experimentally that the apparent specific activity of Pu^{239} was 4-percent higher when counted in a 50-percent geometry chamber than when counted in a 0.04-percent geometry chamber, and Cunningham, Ghiorso, and Jaffey[11] observed that 3.1 percent of the alpha-particles emitted from natural uranium were effectively backscattered from platinum, neglecting self-absorption.

Theoretical calculations by Crawford[12] 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, in good agreement with experiment. Moreover, they show that the amount of backscattering should depend on the atomic number of the backing material and the range (energy) of the alpha-particle. The dependency on atomic number has been partially verified by experiment.[11, 13]

For "weightless" samples, a correction for the geometry factor of a 2π-chamber can be derived from Crawford's formulas, but 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.[14] 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, the plateau is usually found to have a linear slope of from 2–4 percent over the range of the plateau, as is shown in Fig. 4. Undoubtedly such slopes are caused principally by an increase in the number of backscattered particles detected with increased gain. Then the counting rate for a sample in such a chamber is arbitrary, since knowledge of the gain setting is insufficient for accurate evaluation of the counting yield.

This variation of counting rate with gain makes the absolute evaluation of a precise disintegration rate measured in a conventional 2π-chamber very unreliable. 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.

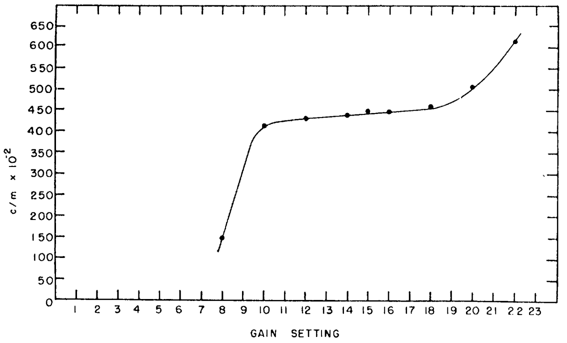

FIG. 4. Counting rate *vs* gain for sample in 2π-alpha-counter.

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[9] Jaffey, Kohman, and Crawford, Metallurgical Laboratory Declassified Report M-CC-1602, unpublished (January, 1944).

[10] Cunningham, Ghiorso, and Hindman, *The Transuranium Elements: Research Papers* (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 16.3.

[11] Cunningham, Ghiroso, and Jaffey, *The Transuranium Elements: Research Papers* (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 16.6.

[12] J. A. Crawford, *The Transuranium Elements: Research Papers* (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 16.55.

[13] C. A. Kienberger, Phys. Rev. **76**, 1561 (1949).

[14] B. F. Scott, reported in Metallurgical Laboratory Report CN-1764, unpublished (July, 1944).

However, such chambers do afford convenient means for determining precise relative data, provided the samples are reasonable uniform in thickness and have the same backing material and alpha-decay energy. They also are adequate for the determination of absolute disintegration rates with an uncertainty of the order of ±3 percent.

Fortunately, precise determinations of alpha-disintegration rates are feasible. Jaffey[15] 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, low geometry chambers effectively eliminate the detection of all backscattered particles, by detecting only those particles which are emitted from the backing plate with an angle of about 85° or more. When the samples used in the preparation of Fig. 3 were counted in a low geometry chamber, the slope of the plateau decreased to zero.

Figure 5 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.

Figure 6 illustrates a plateau measured for such a chamber. It is seen that no ambiguity in counting rate is involved.

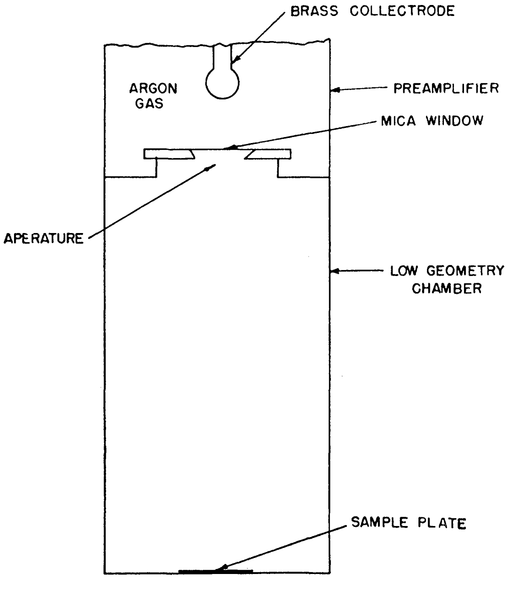

FIG. 5. Schematic diagram of low geometry chamber.

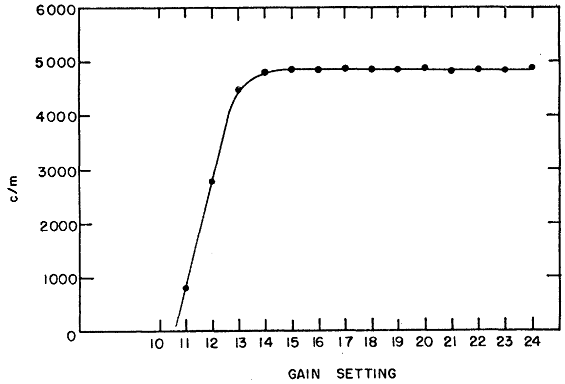

FIG. 6. Counting rate *vs* gain for sample in low geometry counter.

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, then for the case where $s=0$,

$$G_P=\frac{1}{2}\left[1-\frac{h}{(h^2+c^2)^{\frac{1}{2}}}\right]=\frac{c^2}{2[h^2+c^2+h(h^2+c^2)^{\frac{1}{2}}]},$$

where G_P = the "point source" geometry factor.

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

$$1/G_s \cong 4h^2/c^2+3+3s^2/c^2-s^4/4c^2h^2+(9s^2-c^2)/4h^2,$$

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

The approximate 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 ±0.1 percent for such values as $s/h<0.15$, 0.2, 0.5, when $c/h<0.19$, 0.14, 0.07, respectively. It is entirely adequate for low geometry chambers of conventional dimensions.

When s/h and c/h are greater than values such as those given, 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 based on the integral shown above, which is similar to the one described by Kovarik and Adams.[16] The inter-

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[15] A. H. Jaffey, unpublished work.

[16] A. F. Kovarik and N. I. Adams, Phys. Rev. **40**, 718 (1932).

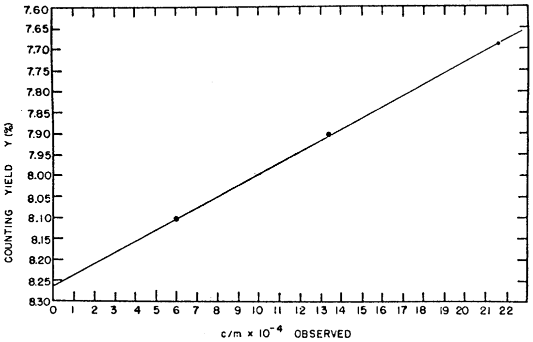

FIG. 7. Counting yield *vs* counting rate for samples in medium geometry counter.

vals of s/h and c/h are such that, for most cases, G_s can be determined with an error $<\pm0.05$ percent by a first order interpolation. In extreme cases, a second order interpolation is necessary.

A distinction must now be made between the geometry factor, G_s, and the counting yield, Y. G_s was defined accurately above, and is, in one sense, 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 does $Y=G_s$, for the following reasons:

(1) The evaluation of G_s requires experimental measurements of chamber and aperture dimensions and is subject to error. In the case of the low geometry chamber used for calibration work mentioned later, evaluation of G_s to ±0.1 percent required that $d=2c$ be measured to ±0.2 mil and h to ±1.5 mils since d and h were 0.75 and 5.4 inches, respectively.

(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. 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 3.5 percent.[17]

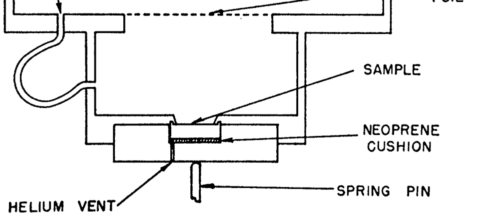

FIG. 8. Schematic diagram of medium geometry chamber.

(3) Two or more alpha-particles entering the ionization chamber within an interval shorter than the resolving time of the scaling circuit register as a single event. Figure 7 gives the coincidence correction 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 counts/min, the uncertainty contributed by the coincidence correction to counting rates in the region of 10^5 counts/min is about ±0.1 percent, and is lower for lower counting rates.

(4) The calculation of G_s assumes that the sample is distributed as a perfectly uniform film, that no self-absorption occurs and that the sample is perfectly coaxial with the aperture and 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.[18]

The low geometry chamber of the type described previously was not suitable for counting the alpha-particles emitted by U^{235}, since the specific counting rate amounted to only 9 counts/min per mg of the isotope. A chamber of intermediate geometry ($G_s \cong 8$ percent) was designed by A. Ghiorso, especially for counting U^{235}. A diagram of the chamber is shown in Fig. 8 ($c \simeq 2$ inches and $h \simeq 3$ 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."

The bold line in Fig. 9 shows the geometry factor *versus* 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, and the dotted line is the experimental counting

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[17] 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 ¾ 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.

[18] 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.

yield. The absolute disintegration rates of each of these samples were measured previously by counting in the low geometry chamber of $G_s \simeq 1/800$. The point at diameter 36.9 mm represents the value of the counting yield for three samples of this diameter given by the extrapolation to zero counting rate shown in Fig. 7.

It is seen from Fig. 9 that the calibration points differ from the calculated curve by about 0.5 percent. A complete explanation for this systematic difference has not been found.

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) counts/min throughout the work. The counting rates of the samples in this chamber ranged from 7000 to 12,000 counts/min for the various U^{234} samples, from 400 to 800 counts/min for U^{235} samples, and from 200 to 400 counts/min for those of U^{236}.

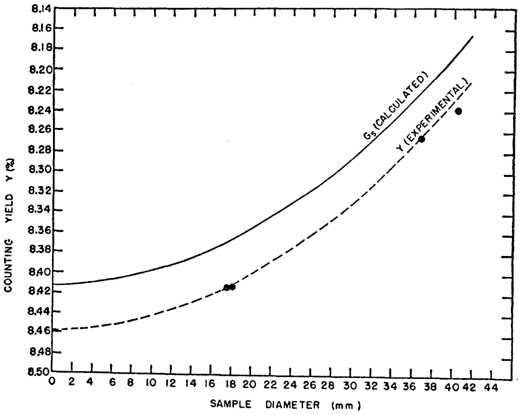

FIG. 9. G_s and Y *vs* sample diameter for medium geometry chamber.

VI. RESULTS AND DISCUSSION

Table IV summarized 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. 9, which is based on the experimentally measured geometry of the medium geometry chamber. The uncertainties of the other values have been discussed in previous sections.

The results of this work are given in Table V.

Jaffey and co-workers[19] have measured the half-life of U^{236} by counting mass and pulse analyzed samples of uranium enriched in U^{236}. The weight of each sample was determined indirectly by counting neutron-induced fissions produced in the U^{235} present. The value found for the half-life of U^{236} was 2.457×10^7 yr. No limits of error were given for this figure, but in a private communication the principal author has set limits of ±2 percent. The value is thus in agreement with that found by us.

TABLE IV. 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 standard 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

Because of the wide interest in the three isotopes comprising natural uranium, Table VI is presented which summarizes the various specific activities, half-lives, mass ratios, and activity ratios reported in the literature of the past fifteen years. Unfortunately, many of the published papers are written with so few details that a critical analysis for sources of error is impossible. Nevertheless, an attempt has been made to evaluate the data so that "best" values may be stated which are themselves internally consistent. It has not been feasible to present all the reasons for each selection, but the principal reasons have been stated briefly. Conservative limits of error have been set for these "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, Nier[1] reported a value of 139 ± 1.4. He showed further that the ratio was the same, within limits of error, for minerals varying in age from 10^3 to 10^9 years.

In 1946, Chamberlain and co-workers[20] found the same value, and in the same year Fox and Rustad[21] obtained a ratio of 137.0 ± 0.7 from a weighted average of 14 sets of readings, using an electron bombardment source. With a thermal source they found a value of 138.0 ± 0.3 from 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.

A "best value" for the mass ratio U^{238}/U^{235} in natural uranium of 138 ± 1.4 is estimated from these data.

The values quoted for the half-life of U^{234} vary from 2.29 to 2.7×10^5 yr. The values 2.7×10^5 yr ±10 percent (Nier),[1] and 2.29×10^5 yr ±6 percent (Chamberlain, *et al.*),[20] were derived by measuring the mass ratio of U^{238} to U^{234} in natural uranium and assuming radioactive equilibrium between the isotopes. Using 4.5×10^9

TABLE V. Specific activities and half-lives of U^{234}, U^{235}, and U^{236}.

Uranium isotope	Specific activity (disint/min 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	$(1.406 \pm 0.011) \times 10^5$	$(2.391 \pm 0.018) \times 10^7$

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[19] Jaffey, Diamond, Hirsch, and Mech, Phys. Rev. **84**, 785 (1951).

[20] Chamberlain, Williams, and Yuster, Phys. Rev. **70**, 580 (1946).

[21] M. Fox and B. Rustad, Carbide and Carbon Chemicals Corporation Report BD-R-88, unpublished (January, 1946).

TABLE VI. Recent values of natural constants for the common uranium isotopes.

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

t_{238} (yr) $\times 10^{-9}$	Sp. Act.$_{238}$ (disint/min mg)	t_{natural} (yr) $\times 10^{-9}$	Sp. Act.$_{\text{natural}}$ (disint/min 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 (%)	$R=A_{235}/A_{238}$ (%)	$A_{234}/N_n=A_{238}/N_n$	A_{235}/N_n	Ref.
138.9±1.4	16,800±10%	0.00591 ±0.00059	4.6 ±0.1			1
139	19,700±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±1%	0.00539 ±0.00004	4.6 ±0.1	733.5±1.6	34.1±0.8	"Best" values

yr for the half-life of U^{238},

$$T_{234}=4.5\times 10^9 (N_{234}/N_{238}) \text{ yr}.$$

Chamberlain's mass spectrograph gave better resolution than that used by Nier.

The value 2.35×10^5 yr±6 percent (Chamberlain, *et al.*)[20] was computed from measurements of the specific activity of uranium enriched in U^{234} and U^{235}, using 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.[13]

The value 2.522×10^5 yr±0.3 percent (Kienberger)[13] was determined in a similar manner, 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's[10] work. The specific activity of the material was computed from these data. The values of Kienberger and Chamberlain based on the same principle of measurement agree nearly within quoted limits of error.

The value 2.67×10^5 yr±1.3 percent (Goldin *et al.*)[22] was determined by genetic relationships. 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} (determined by counting), the several decay periods involved, and the decay constants of U^{238} and the intermediate isotopes. The method required many operations subject to error, including a chemical yield and separation of Th^{234} from natural uranium, which was assumed to be quantitative. 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. The limits of error of ±1.3 percent quoted seems unrealistic. Furthermore, the value determined is outside of agreement with the weighted mean of the other values by some 7.5 percent.

The value 2.475×10^5 yr±0.7 percent found by us 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 of counting, and the limits of error quoted by each author, a best value for the half-life of U^{234} is computed as 2.48×10^5 yr±1 percent, with a concomitant specific activity of 1.37×10^7 disint/min 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.

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[22] Goldin, Knight, Macklin, and Macklin, Phys. Rev. **76**, 336 (1949).

Nier[1] 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 the work of Kovarik and Adams[23]). The half-life was calculated from the relation

$$R=\frac{\lambda_{235}N_{235}}{\lambda_{238}N_{238}}=\frac{\text{Activity of } U^{235}}{\text{Activity of } U^{238}}.$$

For the ratio N_{238}/N_{235}, he used the value 139. λ_{238} was computed from the specific activity of natural uranium[20] and $N_{238}/N_{\mathrm{natural}}=0.9928$. 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, Nier's value of the half-life of U^{235} should be in error by less than about 3 percent. This assumption is strengthened by the beautiful consistency of his data.

Kienberger[13] reports a value of 8.8×10^8 yr±12.5 percent for the half-life of U^{235}, 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 4.5 percent.

Clark and co-workers[2] reported a figure for the half-life of U^{235} of 8.91×10^8 yr, based on a value of 0.0363 for R, computed from pulse analyses of natural uranium. It is now known[24] that their value for R is about 15-percent low, since they were unable to resolve high and low energy alpha-groups comprising about 15 percent of the alpha-spectrum of U^{235}. Correcting for this error gives $R=0.0425$, and a half-life of 7.64×10^8 yr. A further discrepancy of 7 percent compared to Nier's values remains unexplained.

A value of 7.53×10^8 yr±3 percent was obtained by Knight,[25] who measured the specific activity of a portion of the same highly enriched U^{235} used for our work, and found a specific disintegration rate of 7279±23 disint/min mg, in good agreement with our value of 7257±70 disint/min mg. Knight's pulse analysis, made with a one-channel pulse-height analyzer, indicated that about 61.6 percent of the disintegrations were those of U^{235}, giving 4484 disint/min mg of U^{235}.

Careful pulse analysis of this material made with the 48-channel differential pulse analyzer in this laboratory gave 65.3±1.3 percent for the U^{235} contribution. Knight's gross specific activity multiplied by 0.653 gives a half-life of 7.10×10^8 yr.

From the values discussed above, a weighted average gives a best value of 7.13×10^8 yr±2 percent for the half-life of U^{235}, with a corresponding specific activity of 4.74×10^3 disint/min mg.

Kovarik and Adams[23] 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. They obtained 1501 disint/min mg for the specific activity of natural uranium.

Curtiss and co-workers[26] 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 particles backscattered from the backing material. Therefore, a plot of specific counting rate *versus* film thickness yielded a straight line, and an extrapolated value of 750.6 disint/min mg at zero film thickness. The counting yield was considered to be 0.5 and the specific activity equal to 1501 disint/min mg±0.2 percent.

Kienberger[13] counted electrodeposited samples of natural uranium in a 2π-chamber and computed the counting yield of the chamber in the same manner as was done for his U^{234} work. He reports a value of 1502 disint/min mg±0.1 percent.

The excellent agreement among these three values probably is somewhat fortuitous. A best value is 1501 disint/min mg±0.2 percent for the specific activity of natural uranium, estimated from the data.

Kienberger,[13] using isotopically pure U^{238}, has determined a value of (742.7±1.6) disint/min mg for the specific activity of this isotope, 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.

This may be compared with the specific activity of U^{238} calculated from the best values quoted thus far.

Thus, $N_{235}/N_{238}=1/138=0.725$ percent, and $N_{234}/N_{238}=ca$ 0.0054 percent (see below). Therefore, $N_{235}/N_n=0.719$ percent and $N_{238}/N_n=99.28$ percent.

Specific activity of U^n:	1501±3.0 disint/min mg
Specific activity of U^{235} ×0.00719:	−34±0.8
Activity contribution of U^{234} and U^{238} in U^n:	1467±3.1 disint/min mg

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[23] A. F. Kovarik and N. I. Adams, J. Appl. Phys. **12**, 296 (1941).

[24] A. Ghiorso, Phys. Rev. **82**, 979 (1951).

[25] G. B. Knight, Oak Ridge National Laboratory Report K-663, unpublished (August, 1950).

[26] Curtiss, Stockman, and Brown, National Bureau of Standards Report A-80, unpublished (December, 1941).

Activity contribution of U^{238} in U^n:

$$\tfrac{1}{2}\times 1467 = 733.5 \pm 1.6 \text{ disint/min mg}$$

$$\frac{733.5}{0.9928} = 738.8 \pm 1.6 \text{ disint/min mg},$$

the specific activity of U^{238}.

A relatively large error in the specific activity of U^{235} has but little effect on that of U^{238} calculated in this way. If the value for the specific activity of natural uranium is accurate to ±0.2 percent, then the value 742.7 disint/min mg for U^{238} must be in error by at least 0.5 percent. Actually, the agreement seems surprisingly good.

The half-life corresponding to 738.8 disint/min mg is 4.51×10^9 yr. Although Nier[1] used the value 4.56×10^9 yr indirectly for the calculation of R, the difference has a negligible effect on R, and on the recalculated value of 7.06×10^8 yr for the half-life of U^{235}.

From the best values quoted thus far, $R=0.046 \pm 0.001$. U^{234}/U^n in natural uranium may be calculated as follows: Since U^{238} and U^{234} are in radioactive equilibrium, activity of U^{234} equals the activity of $U^{238} = 733.5\pm 1.6$ disint/min mg of U^n. Dividing by the specific activity of U^{234}, 1.37×10^7 disint/min mg±0.7 percent, the mass ratio U^{234}/U^n equals (0.00535 ± 0.00004) percent.

From mass spectrographic analysis, Nier[1] found the mass ratio U^{238}/U^{234} in natural uranium to be $16{,}800\pm 10$ percent. From this figure the mass ratio U^{234}/U^n is calculated to be (0.00591 ± 0.00059) percent.

Chamberlain and co-workers[20] found $19{,}700\pm 6$ percent for U^{238}/U^{234}, from which (0.00504 ± 0.00030) percent is calculated for U^{234}/U^n.

Kienberger 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 coworkers and the value calculated in this paper are in agreement, within quoted limits of errors, as is nearly the case with Kienberger's value if one considers his statement in the text of his paper that his value is good to at least 1 percent. From the relevant data discussed above, a "best value" for the mass ratio U^{234}/U^n is found to be (0.00539 ± 0.00005) percent.

In conclusion it seems worth while to point out that, with but few exceptions, the papers to which we have referred do not give the slightest information concerning a question of fundamental importance in much of the work, *viz.*, the chemical purity of the materials used. It would seem that this problem has been ignored by many workers in the past. Thus, the values reviewed above, where no mention of chemical purity is made, will stand in doubt merely because of this oversight.

Since Holmes[3] 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 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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