

New determination of the half-life of ^{233}U

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Combining different methods, all based on the measurement of the specific activity of a large number of samples from two different batches of uranium oxides, both enriched to nearly 100% ^{233}U , a new determination of the half-life of ^{233}U was made. The activities of the samples were determined by α counting techniques: low geometry, liquid scintillation, and 4π -proportional counting. The uranium content of the samples was determined by mass spectrometric isotope dilution techniques and by controlled potential coulometry. The half-life was measured as $(1.5925 \pm 0.0040) \times 10^5$ yr. The uncertainty quoted is the over-all uncertainty at the 99.7% confidence level, taking into account both statistical and systematic effects. This result is in close agreement with the value published recently by Jaffey *et al.* and with the new recommended value, evaluated by Lemmel.

[RADIOACTIVITY ^{233}U ; measured $T_{1/2}$.]

I. INTRODUCTION

In this paper we present a new measurement of the half-life of ^{233}U which is important for several reasons. For example, it plays an important role in the evaluation of some fission constants since its value can influence the final evaluated values of the constants.^{1,2} Furthermore, ^{233}U may be used to spike uranium samples of low specific activity for the purpose of quantitative analysis,³ and here also an accurate knowledge of the half-life is essential since the amount of the spike material is determined by α counting.

Unfortunately, the spread of the published values is many times larger than that expected from the accuracies claimed. Hanna *et al.* (Ref. 1, 1969) estimated from the published data a best value of $(1.593 \pm 0.024) \times 10^5$ yr. However, this value was based on six results published between 1952 and 1967,⁴⁻⁹ all determined by α counting techniques, giving a mean value of $(1.617 \pm 0.008) \times 10^5$ yr, and two results in 1967-1968 giving a mean of $(1.554 \pm 0.003) \times 10^5$ yr.^{10, 11} One of the latter two results was obtained by α counting, the other by calorimetric techniques, and therefore the difference of 4% between the two mean values cannot be attributed solely to the apparent systematic discrepancy between half-life values obtained by α counting and by calorimetry.^{2, 10, 12}

In an attempt to resolve the problem, a careful new determination has been carried out recently at Argonne National Laboratory.¹³ These measurements gave a value of $(1.5911 \pm 0.0015) \times 10^5$ yr, where the quoted uncertainty is only statistical (standard error of the mean). A measurement at Atomic Energy of Canada, Ltd., giving a value

of $(1.583 \pm 0.007) \times 10^5$ yr has also been reported.¹⁴

A compilation of the values reported up to 1974 has been given elsewhere.¹⁵ Recently, Lemmel (Ref. 2, 1975) recommended the value of $(1.5900 \pm 0.0020) \times 10^5$ yr, where the uncertainty quoted is the standard error of the mean. This value was evaluated from all available data, including the result presented in this paper.

Here we report a new determination made at the Central Bureau for Nuclear Measurements. Different methods were applied using two materials: one with (99.762 ± 0.004) at.% ^{233}U [CBNM (Central Bureau for Nuclear Measurements) reference number 161], the other on loan from Oak Ridge National Laboratory, with (99.9986 ± 0.0002) at.% ^{233}U (CBNM reference number 278).

II. PRINCIPLE OF THE MEASUREMENTS

The basis of the measurements is the equation for radioactive decay:

$$-\frac{dN}{dt} = \lambda N,$$

where λ is the decay constant of the isotope under investigation, here ^{233}U , and N is the number of atoms of this isotope present in the sample. This number N can be determined by adding to the sample a known number of atoms of another uranium isotope, e. g., ^{238}U , and making an accurate measurement of the ratio ^{233}U to this added (spike) isotope by mass spectrometry. It can also be deduced from a determination of the total uranium content of the sample by element assay (e. g. chemical techniques) and subsequent isotope analysis by mass spectrometry. The ^{233}U activity

dN/dt of the sample can be obtained by a measurement of the total α activity of the sample and by applying a correction for the contribution to the count rate from all other radionuclides: other uranium isotopes, daughter products, and radionuclidic impurities.

To achieve a final accuracy of 0.2 to 0.3% on the half-life, the main quantities N and dN/dt should be determined with accuracies of about 0.05%. We used two independent methods for each determination in order to detect and to eliminate, as far as possible, any systematic effects.

III. MEASUREMENT PROCEDURE

Nine series of measurements were performed between 1969 and 1974. For the first five series of measurements liquid samples were prepared by dissolving the uranium oxide in nitric acid and by diluting to concentrations of about 1 mg uranium, per ml of 1 *M* nitric acid. Accurately weighed aliquots of these solutions were distributed for the uranium determinations (Sec. IV) by isotope dilution mass spectrometry, by controlled potential coulometry, and for the activity measurements using a low-geometry counter, a liquid scintillation counter, and a 4π proportional counter (Sec. V). Sampling and dilution problems for such measurements have been described earlier.¹⁶ Further aliquots were used for the mass spectrometric measurement of the isotopic composition of the uranium and for the determination of the contribution of other radionuclides to the total activity by γ -ray spectrometry (Sec. VI).

For the other series of measurements, solid samples were prepared by electro-spraying^{17, 18} of an acetate solution onto platinum coated quartz plates, the active area of the samples being about 20 cm² and the uranium amount varying between 2 and 15 mg. The activity was measured in a low-geometry counter and the layers were then completely dissolved in nitric acid and aliquots were distributed for liquid scintillation, isotope dilution mass spectrometry, coulometry, and γ -ray spectrometry. A further thin electro-sprayed source of about 8 $\mu\text{g U/cm}^2$ was used for α -ray spectrometry.

In earlier work on ²³⁴U,¹⁹ it was observed that changes in the uranium isotopic composition during the preparation of the acetate solution and the electro-spraying were smaller than 0.05%. But, since one can expect a nearly complete separation of the thorium from the uranium parent (e.g., the ²²⁹Th grown from the ²³³U) during the preparation of the acetate solution, it is necessary to determine the thorium content both for the dissolved uranium oxide and for the

electrosprayed layers. That such a separation happens is shown on the 440 keV γ -ray peak of ²¹³Bi, in secular equilibrium with ²²⁹Th, in Fig. 1, spectrum 2, and spectrum 3. Both spectra were measured, at the same time, on the same original uranium material; spectrum 2 on the dissolved uranium oxide and spectrum 3 on one of the dissolved electro-sprayed layers.

IV. DETERMINATION OF THE ²³³U CONTENT

For the determination of the ²³³U content of the samples, two independent methods have been applied.

The mass spectrometric isotope dilution technique^{20, 21} was used for all the samples. The measurements were performed on thermal ionization mass spectrometers using the National Bureau of Standards (NBS) 950a U₃O₈ reference material as spike. This material is certified to contain, after a standardized ignition, (99.94 \pm 0.02)% stoichiometric U₃O₈. In a high precision mass spectrometric ratio measurement the ²³³U content of the sample was compared directly to the main isotope of the spike material: (99.2745 \pm 0.0008)% ²³⁸U. The precision of the ratio measurements was generally better than \pm 0.05%. From calibration procedures of ratio measurements by means of the National Bureau of Standards suite of isotopic standards covering isotope ratios in the range 100/1 to 1/1, systematic errors were carefully determined and corrected for. The maximum systematic uncertainty associated with these corrections was estimated as \pm 0.05%. By progressing in the careful standardizing of the samples for isotope ratio measurements with respect to concentration, chemical purity, acidity, and size of the samples loaded into the mass spectrometer, the overall accuracy of the measurements could be improved from \pm 0.3% in 1969 to \pm 0.12% for the more recent determinations.

For samples where at least about 10 mg of material was available, controlled potential coulometry^{22, 23} was applied for the uranium content determinations. Using these uranium content values and the isotopic composition of the samples, the ²³³U content was calculated. With the limited amounts of material available only 10 mg uranium aliquots could be used for each measurement and the precision obtained was \pm 0.05%. The over-all uncertainty was \pm 0.2% for the measurements on the solutions and \pm 0.3% for the layers where the systematic uncertainty was somewhat greater, due to the fact that even less than 10 mg was available for coulometry.

V. DETERMINATION OF THE ACTIVITY

Three different methods were used for the determination of the α activity of the samples. Two of them have been developed to a high degree of accuracy: α counting under defined low-geometry solid angle,^{24,25} and liquid scintillation α counting.^{26,27} For the actual measurements the precision of both methods was generally of the same order as the counting statistics of about $\pm 0.05\%$. The accuracy of the methods was estimated, from comparisons of several methods for α counting, to be $\pm 0.1\%$ or even better.^{25,27,28} A third method, using a 4π proportional counter, was appreciably less accurate than both other methods, mainly because of the uncertainty on the *correction* for self-absorption; nevertheless it has been applied in about half of the determinations.

VI. DETERMINATION OF THE ISOTOPIC COMPOSITION AND CONTRIBUTION OF OTHER NUCLIDES TO THE TOTAL COUNT RATE

Mass spectrometric isotope analysis was performed several times on both materials used. The uncertainty on the measured ratio ^{233}U to total uranium was less than $\pm 0.05\%$. From the isotopic composition of both materials (99.762 and 99.9986 at. % ^{233}U , respectively), it was obvious that the contribution of the other long-lived uranium isotopes to the α -count rate was extremely small. Any contribution of short-lived nuclides, e. g., ^{232}U and its daughter products, the ^{228}Th decay chain, and the daughter products of ^{233}U , the ^{229}Th decay chain, can only be determined with sufficient accuracy by α - or γ -ray spectrometry. Originally, we tried to determine this contribution by α -ray spectrometry, using solid state detectors. Because of pileup effects and bad counting statistics the results were rather inaccurate. The ratio of the γ activity of the ^{228}Th and ^{229}Th daughter products to that of the respective uranium parents being orders of magnitude higher than the respective α activity ratios, one could expect a better accuracy from γ -ray spectrometry, and, finally, we applied this technique using calibrated NaI(Tl) and Ge(Li) detectors. If the time elapsed since the separation is known, or determined experimentally from a measurement of the ^{229}Th grown from the ^{233}U , the ^{232}U content can be determined with a good accuracy from the ingrowth of ^{228}Th . For example, the 0.3 ppm ^{232}U in material 161 was determined from the count rate in the 583 keV γ -ray peak of ^{208}Tl , in secular equilibrium with ^{228}Th (See Fig. 1, spectrum 1). The contribution of ^{232}U plus daughter products and ^{229}Th plus daughter products

to the α -count rate was, respectively: material 161, $(0.20 \pm 0.04)\%$; material 278, $(0.10 \pm 0.01)\%$ (1972); material 278, $(0.17 \pm 0.01)\%$ (1973); material 278, $(0.08 \pm 0.01)\%$ (1974, electrosprayed layers).

VII. RESULTS

The results of the measurements are given in Table I. Combining, for the nine series of measurements, the different methods of uranium determinations and activity measurements, 36 individual results were obtained. The uncertainties quoted for the individual results were obtained by taking three times the standard error plus the linear sum of the systematic uncertainties. The mean of the 36 results, obtained by weighting these results with the squared reciprocals of their uncertainties, is $(1.5925 \pm 0.0007) \times 10^5$ yr. The quoted deviation is the weighted standard error of the mean. The ratio of the internal to the external consistency, that for 36 observations should be equal to (1 ± 0.12) ,²⁹ is 0.92 and does thereby not differ significantly from unity; hence, the mode of weighting used is acceptable. Since the 36 individual results were obtained from a considerably greater number of measurements,

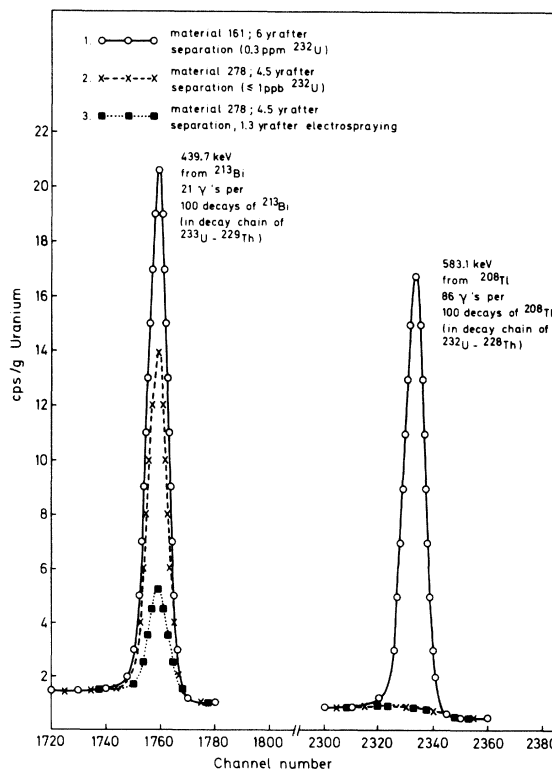


FIG. 1. ^{228}Th , ^{229}Th , and ^{232}U determination by γ -ray spectrometry using a Ge(Li) detector.

TABLE I. Results of the various series of measurements. Weighted mean and standard error for the individual determinations of the half-life of ^{233}U is $(1.5925 \pm 0.0007) \times 10^5$ yr; for the series, is $(1.5924 \pm 0.0008) \times 10^5$ yr.

Series (year of measurement)	Material: CBNM batch number	U-mass determination			Activity determination			^{233}U half-life ($\times 10^{-5}$ yr)			Weighted mean of the series and uncertainty
		Method	Number of determinations	Estimated systematic uncertainty $\pm\%$	Method	Number of determinations	Estimated systematic uncertainty $\pm\%$	Results of the individual determinations	Standard error $\pm\%$	Uncertainty $\pm\%$	
1 ^a (1969)	161	ID ^b	2	0.20	LG ^c	3	0.15	1.5975	0.10	0.7	1.5957 \pm 0.6%
								1.5887	0.05	0.5	
								1.5943	0.17	1.0	
2 ^a (1969)	161	CPC ^f	5	0.15	LG	3	0.15	1.6047	0.10	0.6	1.5952 \pm 0.6%
								1.5960	0.05	0.5	
								1.6015	0.17	1.0	
3 ^a (1972)	278	ID	2	0.20	LS	4	0.15	1.5915	0.13	0.7	1.5952 \pm 0.6%
								1.5908	0.06	0.5	
								1.5963	0.15	1.0	
4 ^a (1973)	278	CPC	5	0.15	LG	3	0.15	1.5982	0.13	0.7	1.5952 \pm 0.6%
								1.5976	0.06	0.5	
								1.6030	0.15	0.9	
5 ^a (1973)	278	ID	2	0.20	LS	11	0.20	1.5877	0.10	0.7	1.5878 \pm 0.6%
								1.5838	0.03	0.5	
								1.5832	0.15	1.0	
6 ^g (1974)	278	CPC	5	0.15	LG	4	0.15	1.5921	0.10	0.6	1.5894 \pm 0.4%
								1.5882	0.03	0.4	
								1.5876	0.15	0.9	
7 ^g (1974)	278	ID	2	0.10	LS	12	0.10	1.5872	0.05	0.4	1.5974 \pm 0.4%
								1.5917	0.05	0.4	
								1.5984	0.07	0.4	
8 ^g (1974)	278	ID	2	0.07	LS	16	0.10	1.5994	0.03	0.3	1.5920 \pm 0.4%
								1.5900	0.18	0.9	
								1.5959	0.07	0.5	
9 ^g (1974)	278	CPC	5	0.15	LS	16	0.10	1.5970	0.03	0.3	1.5914 \pm 0.4%
								1.5876	0.18	1.0	
								1.5920	0.05	0.4	
10 ^g (1974)	278	ID	3	0.07	LG	2	0.15	1.5914	0.05	0.4	1.5914 \pm 0.4%
								1.5914	0.05	0.4	
								1.5914	0.05	0.4	

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