Half-life of ^{241}Pu

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The half-life of ^{241}Pu was determined by periodically observing the decrease in isotope abundance of ^{241}Pu relative to other isotopes of plutonium with a thermal ionization mass spectrometer. A synthetic mixture of plutonium isotopes with initial values of ^{241}Pu/^{239}Pu, ^{241}Pu/^{240}Pu, and ^{241}Pu/^{242}Pu isotope ratios close to unity was prepared. This was done with the objective of achieving high precision (better than 0.1%) in the isotope ratio measurements. The decrease in the isotope ratio was measured at intervals of 6 months over a period of about 5 yr. A value of 14.38±0.02 yr was obtained using the double ratio method which eliminates variable systematic error due to isotope fractionation. The value obtained in the present work supports the results reported earlier by the daughter growth method from this laboratory and is in good agreement with the values reported recently by other laboratories during the course of our investigations.

I. INTRODUCTION

In view of the large discrepancy[1] between various published values for the half-life of ^{241}Pu, which range from 14—15 yr, various laboratories[2–8] are measuring the half-life using different methods and instruments. The half-life of ^{241}Pu has also been determined in this laboratory by a variety of methods. Earlier from this laboratory, the results obtained by the daughter growth method[9–12] employing α spectrometry,[9,10] α proportional counting,[10] isotope dilution alpha spectrometry,[11] and isotope dilution mass spectrometry[12] in independent sets of experiments for measuring the ingrowth of ^{241}Am had been reported. This paper presents a ^{241}Pu half-life value obtained by periodically measuring the change in abundance of ^{241}Pu relative to other isotopes of plutonium through thermal ionization mass spectrometry. The method demands a precise measurement of the small change (about 1% in three months) in the atom ratio of ^{241}Pu relative to other isotopes of plutonium.

In thermal ionization mass spectrometry, the observed isotope ratios in a single run change with time due to isotope fractionation in the ion source. The extent of isotope fractionation depends upon a number of parameters such as sample composition and size, sample purity, sample acidity, sample loading procedure, heating temperatures of the vaporization and ionization filaments, and the time of measurement, and is proportional to the mass difference between the two isotopes. This makes it difficult to achieve high accuracy in the half-life of ^{241}Pu using a single ratio (^{241}Pu/^{239}Pu, ^{241}Pu/^{240}Pu, or ^{241}Pu/^{242}Pu) unless the experimental conditions are strictly controlled and reproduced over the entire period of the experiment, which may be as long as 5—10 yr. The difficulty is evident from the half-life values reported by Zeigler and Ferris[13] in which six different American laboratories participated in a sample exchange program; the ^{241}Pu half-life values from these laboratories varied from 14.50 to 15.06 yr. The effect of isotope fractionation can be circumvented by using the double ratio method (also referred to as the ratio of ratios method), provided the isotope ratios are measured with high precision (external standard deviation better than 0.1%). The latter argument is evident from the data reported by Wilkins,[14] who in spite of using the double ratio method obtained the poor half-life value of 15.02±0.10 yr, due to poor precision (0.5—1%) in the isotope ratio measurements.

In the present work, a synthetic mixture of plutonium isotopes was used with initial ^{241}Pu/^{239}Pu, ^{241}Pu/^{240}Pu, and ^{241}Pu/^{242}Pu isotope ratios close to unity. The experimental conditions were strictly controlled and carefully reproduced over the entire period of the experiment. Both factors led to high external precision (better than 0.1%) in the isotope ratio measurements. The isotope fractionation effect was eliminated by using the ratio of ratios method for calculating the half-life. To obtain a change of at least 2% in the isotope ratios, measurements were made at six month intervals.

II. PRINCIPLE OF THE METHOD

The method involved the mass spectrometric determination of ^{241}Pu/^{239}Pu, ^{241}Pu/^{240}Pu, and ^{241}Pu/^{242}Pu isotope ratios over a period of five years. If $R(t)$ denotes one of the isotope ratios at a time "t" and $R(0)$ is the value at zero time, then

$$\ln[R(0)/R(t)]=\lambda(^{241}\mathrm{Pu})t \ . \quad (1)$$

A least squares analysis yields a half-life value for ^{241}Pu. A corresponding equation was used for calculating the half-life with the double ratio method. The double ratios used in the present work were (^{241}Pu/^{239}Pu)/(^{242}Pu/^{240}Pu), (^{241}Pu/^{240}Pu)/(^{240}Pu/^{239}Pu), and (^{241}Pu/^{242}Pu)/(^{240}Pu/^{241}Pu).

III. EXPERIMENTAL

A. Preparation and purification of synthetic mixture

A synthetic mixture of plutonium isotopes was prepared by using solutions of ^{241}Pu (enriched), ^{242}Pu (en-

TABLE I. An illustration of mass spectrometric data.

Filament loading No.	Run No.	Isotope ratio $^{241}Pu/^{239}Pu$	$^{241}Pu/^{240}Pu$	$^{241}Pu/^{242}Pu$	$^{240}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
1	(i)	0.471 960	0.924 772	0.694 667	0.510 319	0.679 353
		±0.000 22[a]	±0.000 20[a]	±0.000 09[a]	±0.000 12[a]	±0.000 37[a]
	(ii)	0.472 326	0.925 074	0.694 668	0.510 541	0.679 821
		±0.000 11	±0.000 11	±0.000 16	±0.000 03	±0.000 17
	(iii)	0.472 675	0.925 518	0.694 539	0.510 717	0.680 556
		±0.000 11	±0.000 10	±0.000 03	±0.000 10	±0.000 12
	Mean	0.472 320	0.925 121	0.694 625	0.510 526	0.679 910
		±0.000 36[b]	±0.000 37[b]	±0.000 07[b]	±0.000 20[b]	±0.000 61[b]
2	Mean	0.471 868	0.924 750	0.695 034	0.510 253	0.678 904
		±0.000 11	±0.000 07	±0.000 01	±0.000 05	±0.000 17
3	Mean	0.471 746	0.924 499	0.695 035	0.510 274	0.678 654
		±0.000 27	±0.000 14	±0.000 11	±0.000 21	±0.000 30
Mean of means		0.471 98	0.924 79	0.694 90	0.510 35	0.679 16
		±0.000 30[b]	±0.000 31[b]	±0.000 24[b]	±0.000 15[b]	±0.000 66[b]

[a]Internal standard deviation
[b]External standard deviation.

TABLE II. Summary of data on isotope ratio measurements.

	Decay period (d)	Isotope ratio $^{241}Pu/^{239}Pu$	$^{241}Pu/^{240}Pu$	$^{241}Pu/^{242}Pu$	$^{240}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
1	0	0.572 28	1.117 45	0.841 52	0.512 13	0.680 05
		±0.000 14[a]	±0.000 63[a]	±0.000 24[a]	±0.000 14[a]	±0.000 41[a]
2	231	0.552 89	1.084 46	0.814 51	0.509 83	0.678 81
		±0.000 32	±0.000 82	±0.000 64	±0.000 25	±0.00094
3	430	0.537 87	1.054 78	0.794 97	0.509 93	0.676 59
		±0.000 68	±0.001 00	±0.000 56	±0.000 24	±0.000 72
4[c]	883	0.510 10	0.994 00	0.752 93	0.513 17	0.677 49
		±0.000 71	±0.000 38	±0.001 50	±0.001 80	±0.001 80
5	1269	0.482 63	0.945 71	0.710 49	0.510 34	0.679 30
		±0.000 26	±0.000 31	±0.000 30	±0.000 10	±0.000 68
6	1436	0.471 98	0.924 79	0.694 90	0.510 35	0.679 16
		±0.000 30	±0.000 31	±0.000 24	±0.000 15	±0.000 66
7	1871	0.445 82	0.873 46	0.655 95	0.510 37	0.679 65
		±0.000 07	±0.000 08	±0.000 03	±0.000 05	±0.000 16
				Means of means	0.51087	0.67872
					±0.0005[b]	±0.0005[b]

[a]External standard deviation s calculated from

$$s^2=\sum_{i=1}^{n}(x_i-\bar{x})^2/(n-1)\,,$$

where x_i is a replicate mass spectrometric analysis and n is their number.
[b]Standard error of the mean of means calculated as $s/\sqrt{n}$, where

$$s^2=\sum_{i=1}^{n}(x_i-\bar{x})^2/(n-1)$$

with $n=7$, where x_i is the isotope ratio at each decay period.
[c]Not considered for calculation of the half-life due to poor precision on the isotope ratios measured.

TABLE III. Half-life of ^{241}Pu calculated from changes in isotope ratios. Footnotes a–d were calculated for each method separately.

Data points used	$T_{1/2}$ (yr) by single ratio method			$T_{1/2}$ (yr) by double ratio method		
	$\frac{^{241}Pu}{^{239}Pu}$ (X)	$\frac{^{241}Pu}{^{240}Pu}$ (Y)	$\frac{^{241}Pu}{^{242}Pu}$ (Z)	$\frac{^{241}Pu}{^{239}Pu}\cdot\frac{^{240}Pu}{^{242}Pu}$ (X)	$\frac{^{241}Pu}{^{240}Pu}\cdot\frac{^{239}Pu}{^{240}Pu}$ (Y)	$\frac{^{241}Pu}{^{242}Pu}\cdot\frac{^{241}Pu}{^{240}Pu}$ (Z)
(1,5)	14.143	14.441	14.236	13.941	14.753	14.338
(2,6)	14.463	14.369	14.405	14.503	14.277	14.386
(3,7)	14.567	14.496	14.224	14.289	14.431	14.360
Mean	14.391 ±0.22[a]	14.435 ±0.064[a]	14.289 ±0.10[a]	14.244 ±0.28[a]	14.487 ±0.24[a]	14.361 ±0.024[a]
Variance for x,y,z	0.048	0.004	0.010	0.080	0.059	0.0006
Covariance for xy,yz,zx	0.0022[b]	−0.0060[b]	0.0051[b]	−0.0687[b]	−0.0057[b]	0.0068[b]
Mean of means		14.371 ±0.085[c]			14.364 ±0.023[c]	
Least squares analysis	14.515 ±0.055	14.433 ±0.053	14.337 ±0.050	14.396 ±0.072	14.357 ±0.053	14.376 ±0.014
Mean		14.428 ±0.089[d]			14.376 ±0.019[d]	

[a]Standard deviation σ calculated from

$$\sigma^2=\sum_{i=1}^{n}(x_i-\bar{x})^2/(n-1)$$

with $n=3$.

[b]Covariance $\sigma(xy,\ yz,$ or $zx)$ calculated from expressions of the type

$$\sigma_{xy}=\frac{1}{n-1}\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})$$

with $n=3$.

[c]Error calculated considering variance and covariance

$$\text{Total error}=\frac{1}{n}(\sigma_x^2+\sigma_y^2+\sigma_z^2+2\sigma_{xy}+2\sigma_{yz}+2\sigma_{zx})^{1/2}\ .$$

[d]External standard deviation s calculated from

$$s^2=\sum_{i=1}^{n}(x_i-\bar{x})^2/(n-1)$$

with $n=3$.

TABLE IV. Isotope fractionation factors calculated for different isotope ratios.

	Isotope ratio (single)	Fractionation[a] factor	Isotope ratio (double)	Fractionation[a] factor
1	$\frac{^{241}Pu}{^{239}Pu}$	1.004 18	$\frac{^{241}Pu}{^{239}Pu}\cdot\frac{^{240}Pu}{^{242}Pu}$	1.000 017
2	$\frac{^{241}Pu}{^{240}Pu}$	1.002 09	$\frac{^{241}Pu}{^{240}Pu}\cdot\frac{^{239}Pu}{^{240}Pu}$	0.999 993
3	$\frac{^{241}Pu}{^{242}Pu}$	0.997 93	$\frac{^{241}Pu}{^{242}Pu}\cdot\frac{^{241}Pu}{^{240}Pu}$	1.000 010

[a]Represent the boundary values on Langmuir's equation and calculated as $\sqrt{m_1/m_2}$, where m_1 and m_2 are the nuclide masses of the isotopes 1 and 2, respectively.

TABLE V. Comparison of various ^{241}Pu half-life values.

	Authors	Year	Method	Half-life (yr)
1	Seaborg *et al.* (Ref. 15)	1949		10
2	Thompson *et al.* (Ref. 16)	1950	ingrowth of ^{241}Am	15.37[a]
3	Mackenzie *et al.* (Ref. 17)	1953	ingrowth of ^{241}Am by α counting	14.12±0.2[a]
4	Rose *et al.* (Ref. 18)	1956	ingrowth of ^{241}Am by γ counting	13.87±0.28[a]
5	Brown *et al.* (Ref. 19)	1960	ingrowth of ^{241}Am by α counting	14.12±0.24[a]
6	Smith (Ref. 20)	1961	α/β branching ratio	13.3±0.3
7	French *et al.* (Ref. 21)	1966	change in isotopic ratios by mass spectrometry	13.59±0.46
8	Nisle and Stepan (Ref. 22)	1970	change in reactivity	14.63±0.27
9	Shields (Ref. 23)	1970	change in isotopic ratios by mass spectrometry	14.6±0.4
10	Whitehead *et al.* (Ref. 24)	1972	ingrowth of ^{241}Am	14.96±0.15[a]
11	Zeigler and Ferris (Ref. 13)	1973	change in isotopic ratios by mass spectrometry (mean of six laboratories)	14.89±0.11
12	Strohm and Jordan (Ref. 25)	1974	calorimetric determination of power decay	14.355±0.007
13	Wilkins (Ref. 14)	1974	change in isotopic ratios by mass spectrometry	15.02±0.10
14	Whitehead (Ref. 2)	1977	ingrowth of ^{241}Am	14.56±0.10
15	Crouch (Ref. 3)	1978	change in isotopic ratios by mass spectrometry on different samples	14.24—14.53
16	Garner (Ref. 4)	1978	change in ^{241}Pu/^{240}Pu isotopic ratios by mass spectrometry on different samples	14.38±0.07
17	Vaninbroukx (Ref. 5)	1978	(a) change in ^{241}Pu/^{240}Pu isotopic ratios by mass spectrometry	14.30±0.14
			(b) ingrowth of ^{241}Am by γ and α counting	14.60±0.10
18	Aggarwal and Jain (Ref. 9)	1979	ingrowth of ^{241}Am by α spectrometry, taking ^{239}Pu and ^{240}Pu as reference isotopes	14.42±0.09
19	Aggarwal *et al.* (Ref. 10)	1980	(a) ingrowth of ^{241}Am by α spectrometry, taking ^{242}Pu as a reference isotope	14.37±0.09
			(b) ingrowth of ^{241}Am by α proportional counting; Pu determination by isotope dilution mass spectrometry	14.50±0.08
20	Marsh *et al.* (Ref. 6)	1980	change in ^{241}Pu/^{242}Pu isotope ratios by mass spectrometry	14.32—14.43
21	Aggarwal *et al.* (Ref. 11)	1981	ingrowth of ^{241}Am by isotope dilution α spectrometry	14.52±0.08
22	Aggarwal *et al.* (Ref. 12)	1982	ingrowth of ^{241}Am by isotope dilution mass spectrometry	14.32±0.11

TABLE V. (*Continued*).

	Authors	Year	Method	Half-life (yr)
23	De Bievre *et al.* (Ref. 8)	1983	changes in ^{241}Pu/^{240}Pu isotope ratios by mass spectrometry	14.33±0.02
24	Present work	1984	changes in ^{241}Pu/^{239}Pu, ^{241}Pu/^{240}Pu, and ^{241}Pu/^{242}Pu isotope ratios by mass spectrometry	
			(a) single ratio method	14.43±0.08
			(b) double ratio method	14.38±0.02

[a]Half-life of ^{241}Pu recalculated using $T_{1/2}$ for ^{241}Am=432.6 yr.

riched), and ^{239}Pu. Enriched ^{241}Pu was obtained from Oak Ridge National Laboratory in 1969. Chemical exchange between the plutonium isotopes was ensured by using H_2O_2 in 3*M* HNO_3 as the redox reagent. The plutonium solution was evaporated to near dryness, treated with concentrated HNO_3 twice to break the polymer, if present, and was finally taken up in 7*M* HNO_3. It was subjected to a redox cycle once more and purified from ^{241}Am with a double stage anion exchange procedure. The plutonium solution in 7*M* HNO_3 was loaded into the (60 °C) column containing Dowex 1×8 resin (200—400 mesh). Americium was washed down with 3*M* HNO_3 and plutonium was eluted with 0.35*M* HNO_3. The purified plutonium solution (referred to as the synthetic mixture) was transferred to a clean and dry volumetric flask using 1*M* HNO_3. The radiochemical purity of the synthetic mixture was checked by γ spectrometry and was found to be free of ^{241}Am (by checking for the 60 keV peak on an intrinsic germanium detector).

B. Mass spectrometry

The ^{241}Pu/^{239}Pu, ^{241}Pu/^{240}Pu, and ^{241}Pu/^{242}Pu isotope ratios were determined periodically after separating ^{241}Am from an aliquot of the solution of the synthetic mixture with the procedure mentioned in Sec. III A. A CH-5 mass spectrometer was used for the first four measurements and a MAT-261 mass spectrometer for the latter three. Rhenium ribbons (0.04×0.7×8 mm) served as the vaporization and ionization filaments in the double filament assembly. The various parameters like sample loading conditions (2 A for 5 min), sample size (1 μg of plutonium), sample acidity (0.5*M* HNO_3), heating temperatures of the vaporization and ionization filaments (2 A and 6 A, respectively), and the time of data acquisition were kept constant over the entire experiment. Temperatures of the ionization and vaporization filaments were fixed by monitoring $^{187}Re^+$ ion current (3×10^{-12} A) and $^{239}Pu^+$ ion current (1×10^{-11} A), respectively. At each interval, three independent filament loadings were used, and each mass spectrometric analysis consisted of two or three runs of isotope ratios, each run containing a set of 11 isotope ratios. Mass spectrometric measurements were completed within 24 h from the time of purification. An illustration of the mass spectrometric data obtained is given in Table I. A summary of data on isotope ratio measurements over a period of 1871 d is shown in Table II.

IV. RESULTS AND DISCUSSION

The results obtained for the half-life of ^{241}Pu using single ratios as well as double ratios are shown in Table III. The ^{241}Pu signal used in each of the ratios (single or double) was from the same mass spectrometric determination, and hence the different isotope ratios were not independent. For assigning an error on half-life, the half-life values were calculated from the data points given in Table II, viz., (1,5), (2,6), and (3,7); each pair considering a decay period of about 3 yr. A value of 14.37±0.08 yr was obtained using a single ratio, whereas the use of a double ratio gave a half-life value of 14.36±0.02 yr. For arriving at the best estimate of the half-life, a least squares analysis of the isotope ratios determined at different decay periods was performed. Values of 14.43±0.09 and 14.38±0.02 yr were obtained by the single ratio method and the double ratio method, respectively. Here the errors specified represent the external standard deviation. It may be mentioned that the first approach gives the best estimate of error while the second approach gives the best estimate of the half-life value. Hence the half-life values recommended from the present work are 14.43±0.08 and 14.38±0.02 yr by the single ratio method and the double ratio method, respectively.

As can be seen from the boundary values of the isotope fractionation factors given in Table IV, the use of the double ratio eliminates the variable systematic error which can arise due to isotope fractionation in the ion source. Thus the use of the double ratio method can yield an accurate value for the half-life of ^{241}Pu as compared to the single ratio method. We believe that in the present work, due to our efforts to reproduce the different experimental parameters over the entire period and the high precision in the isotope ratio measurements, the use of the single ratio has also yielded a value which is close to that obtained by the double ratio method. But the use of the double ratio method along with the high precision in the isotope ratio measurements certainly leads to higher precision and accuracy in the half-life value.

A comparison of the various ^{241}Pu half-life values published so far is presented in Table V. It is evident that the value obtained in the present work by the parent decay method supports the values reported earlier from this laboratory by the daughter growth method.[9–12] Furthermore, the present value is in good agreement with the re-

sults reported recently by other international laboratories during the course of our investigations. It may be mentioned that the work reported in this paper is the first experiment of its kind in that the half-life of ^{241}Pu has been evaluated using all the possible single isotope ratios as well as double isotope ratios, whereas in the studies reported recently by other international laboratories, only one isotope ratio, ^{241}Pu/^{240}Pu, or ^{241}Pu/^{242}Pu, was used.

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