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ISOTOPE-DILUTION MASS SPECTROMETRY IN THE MEASUREMENT OF PLUTONIUM ISOTOPE HALF-LIVES

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ABSTRACT

Isotope-dilution mass spectrometry has been used at Los Alamos to measure the half-lives of ^{239}Pu, ^{240}Pu, and ^{241}Pu. The latter was determined by measuring the rate of decrease of the [illegible]Pu/[illegible]Pu ratio in an appropriate isotopic mixture over a period of several years. The half-lives of the two lighter isotopes are too long to be determined in this manner. They were determined by measuring the rate of production of the uranium daughter relative to a known added ^{233}U spike. Experimental procedures were designed to control sources of error and to permit a detailed statistical treatment which included all known sources of error and accounted for all covariances. The uncertainties, at the 95% confidence level, associated with the measured half-lives were less than 0.4% for ^{241}Pu and less than 0.2% for ^{239}Pu and ^{240}Pu.

INTRODUCTION

The half-life values of the plutonium isotopes are necessary for many nuclear measurements and calculations such as calorimetric assays, alpha-particle counting measurements, and decay corrections of plutonium inventories and reference materials. Substantial differences have existed in published values for plutonium isotopes. To resolve some of these discrepancies, the Division of Safeguards and Security, DOE, convened a Half-Life Evaluation Committee consisting of six member laboratories. The Committee agreed to re-measure several plutonium isotope half-lives by as wide a variety of techniques as possible to reduce the effect of technique dependent systematic errors. The goal was half-life values with a relative standard deviation of 0.1%. Initially, three techniques were to be used to measure the half-life of ^{239}Pu. Each technique (alpha-particle counting, calorimetry, and mass spectrometry) was to be used by at least two laboratories. The results of that initial effort have been published.(1) It is the intent of this paper to describe the evaluation of the isotope-dilution mass spectrometry procedures used at Los Alamos as a part of that effort and for the ^{240}Pu measurement, and the different procedure used for the ^{241}Pu measurement. Isotope dilution mass spectrometry can be a very useful quantitative analytical tool when it is properly applied. This problem furnishes a classical application and illustrates both the unique advantages and many of the critical operations.

EXPERIMENTAL PLAN FOR ^{240}Pu HALF-LIFE MEASUREMENT

The same basic experimental plan was used for the half-life measurements of ^{239}Pu and ^{240}Pu. This plan was established after a statistical evaluation of all steps involved, to ensure an appropriate distribution of effort.

The fundamental decay equation, in the form most useful for this calculation, is

$$(1) \qquad \frac{N_{236}}{N^0_{240}} = 1 - \exp -[\ln(2)\Delta t/H_{240}]$$

Since each decay of a ^{240}Pu atom produces an atom of ^{236}U, which is measured relative to an internal standard of ^{233}U added in a known atom ratio to the initial ^{240}Pu, the equation becomes

$$(2) \qquad \left(\frac{N_{236}}{N_{233}}\right)\left(\frac{N_{233}}{N^0_{240}}\right) = 1 - \exp -[\ln(2)\Delta t/H_{240}]$$

The experimental measurements to be controlled are (a) $\Delta(N_{236}/N_{233})$ to be measured by mass spectrometry (b) the initial number of ^{233}U atoms (c) the initial number of ^{240}Pu atoms and (d) Δt. If the initial uranium content of the plutonium can be made sufficiently small, $\Delta(N_{236}/N_{233})$ approaches the final measured value. For decay times of a year or longer, the error in measuring Δt is insignificant in the error propagation. The measurements requiring greatest care then are the make-up values N^0_{240} and N_{233}, and the ratio N_{236}/N_{233} measured by mass spectrometry.

N^0_{240} Makeup Measurement. Six solutions were prepared from one batch of ^{240}Pu oxide used by all participating laboratories with chemical and isotopic characterization done by four of the laboratories. Three weighed portions were dissolved in HF-HBr and separated from uranium by ion exchange.(2) Weighed aliquots of a calibrated ^{233}U solution were added to two weighed portions of each of the three purified plutonium solutions, providing six mixtures containing measured quantities of [illegible]Pu and ^{233}U. The quantities of ^{233}U added were approximately equal to the amount of ^{236}U expected to be produced by [illegible]Pu decay in one year.

Mass Makeup Measurement. A solution was prepared by dissolving 99.996% enriched $^{233}U_3O_8$ in nitric acid and calibrating by mass spectrometry. Calibration solutions were prepared from weighed portions of NBS SRM 960 natural uranium metal and of a high-purity enriched uranium metal that had been extensively characterized at Los Alamos. Six weighed aliquots of each solution were combined with weighed aliquots of the ^{233}U solution, and the twelve resulting mixtures were analyzed by mass spectrometry to provide the ^{233}U concentrations. The factors entering into the calculation of the concentration of the SRM-960 calibration solution are:

Table I. Computed Concentration of SRM 960 Calibration Solution and Associated Uncertainty

Variable	Value	%RSD
[illegible] SRM-960 metal	2 g	0.015
[illegible] chemical purity	0.9998	0.009
[illegible] isotopic enrichment	0.99275	negl.
Avogadro's constant	6.022 E23	0.0005
Atomic weight	238.051	negl.
[illegible] initial solution	120 g	0.0005
[illegible] first dilution aliquot	2 g	0.030
[illegible] first dilution solution	120 g	0.0005
[illegible] second dilution aliquot	2 g	0.030
[illegible] second dilution solution	120 g	0.0005
[illegible] of final solution	1.4 E16 atoms/g	0.046

The controlling error is associated with the delivery and weighing of the 2-g aliquots for dilution, with a smaller component in the initial weighing. The factors entering into the calculation of the make-up ratio N_{233}/N^{0}_{240} are given in Table II.

Table II. Variables and Assigned Errors Affecting the N_{236}/N^0_{240} ratio.

Variable	Value	% RSD
N^0_{240} (typical)	~ 1.9 E21 atoms	0.023
^{238}U Conc (SRM 960)	~ 1.4 E16 atoms/g	0.046
^{235}U Conc (LA metal)	~ 1.2 E16 atoms/g	0.052
^{233}U Conc (vs 238)	1.31473 E16	0.062
^{233}U Conc (vs 235)	1.31495 E16	0.063
^{233}U Conc (avg)	1.31484 E16	0.044
N_{236}/N^0_{240}	~ 9.6 E-5	0.049

The error associated with N^0_{240} results from about equal contributions from the uncertainty in the assigned purity of the starting material and the weighing error. That associated with the ^{235}U calibrating solution is similar to the illustration for the SRM 960 solution except for a larger uncertainty in the assigned purity. The propagated values for the ^{233}U solution include the assigned RSD of the two calibrating solutions and the random error of the mass spectrometric measurement. The agreement between the two values is gratifying in that most of the mass spectrometry bias would be expected to be mass-dependent and brought out by the 3-mass difference in the calibration standard.

Mass Spectrometry. For the mass spectrometric measurement of $^{236}U/^{233}U$ ratio, the uranium fraction was separated by ion exchange from portions of each of the six mixtures. Four portions of each were analyzed soon after mixing to provide the t^0 values. At four elapsed times from 0.95 to 1.1 yr, two portions of each of the six solutions were analyzed for the 236/233 ratio. Their averages provided 24 separate calculations of the half-life. The mass spectrometers used were AVCO/[illegible] instruments using an electron multiplier detector as a current amplifier and operated under computer control. The program scans each peak magnetically and jumps to the next peak. The peak center is located and measurements from the center of the peak top are averaged. A measurement sequence consists of nine sweeps through the spectrum. Atom fractions are calculated from each consecutive pair of sweeps, giving eight calculations and an average and internal standard deviation. Mass discrimination of the system was established by multiple analyses of NBS SRM U-500. The uncertainty associated with the correction factor of 1.0024 per AMU was estimated to be 0.064%, resulting about equally from the random measurement error and the stated uncertainty in the NBS certified value. It should be noted that this error should be largely nullified through the use of this factor for the calibration of the ^{233}U solutions as well as the grow-in measurements.

RESULTS OF ^{240}Pu and ^{239}Pu HALF-LIFE MEASUREMENT

The value of HL_{240} and its associated standard deviation were estimated by a computation which included covariances. The resulting value of HL_{240} is 6574 yr, with a standard deviation (mean) of 6.2 yr. The 95% confidence limits are 6574 ± 12.8 yr. Values from the other member laboratories are not yet available for comparison.

This experimental plan is basically the same as that used for the earlier HL_{239} measurement. Our value of HL_{239} was 24,164 yr, with a standard deviation (mean) of 14 yr, calculated by the variance-covariance procedure. In comparison, simple averaging yielded 24,162 yr, with a standard deviation of the mean of 2.6 yr. The results of the interlaboratory effort are given in Table III.

Table III. Values of the Half-Life of ^{239}Pu Measured by Member Laboratories of the Half-Life Evaluation Committee

Laboratory	Technique	Measured HL (yr)
Mound	Calorimetry	24,101
[illegible]	Calorimetry	24,102
[illegible]	α-particle counting	24,112
[illegible]	α-particle counting	24,124
[illegible]	Mass spectrometry	24,164
[illegible]	Mass spectrometry	24,089
[illegible]	Mass spectrometry	24,139
	Average	24,119 ± 26

HALF-LIFE MEASUREMENT OF ^{241}Pu

This very direct experiment involved the measurement of the decreased amount of ^{241}Pu relative to long-lived ^{242}Pu. From the fundamental decay equation, $-dN_{241}/dt = \lambda_{241} N_{241}$, the computational relationship is $HL = -(\ln 2)(\Delta t)/\ln(R_t/R_0)$

in which R_t and R_0 are the ^{241}Pu/^{242}Pu atom ratios at times t and t_0. A single mixture of enriched ^{241}Pu and ^{242}Pu isotopes in strong hydrochloric acid was used in which the ^{241}Pu/^{242}Pu ratio approached unity in 3 years. The ^{241}Pu/^{242}Pu atom ratios were measured on two portions of the mixture at t_0 and on four portions at each of three elapsed times of 2.5, 2.9 and 3.6 years. All mass spectrometric measurements were done on at least duplicate filament loadings of each separated portion within 2 days following ion-exchange separation of ^{241}Am. The measured half-life value is 14.379 years with a 95% confidence interval of 14.32 to 14.43 years.

DISCUSSION OF FACTORS AFFECTING ISOTOPE-DILUTION MASS SPECTROMETRY

The determination of plutonium half lives by measuring uranium daughters illustrates the strength of the isotope-dilution mass spectrometric technique. The uranium daughter is determined accurately in 10^5 times as much plutonium following a chemical separation that need not provide its quantitative recovery. Various factors must be considered to attain high reliability. These include chemical treatment that guarantees isotopic exchange of sample and added (spike) isotopes, use of spikes that are calibrated accurately preferably relative to primary reference materials, and mass spectrometric measurements that are bias-free. Even the small uncertainty associated with the certified value of primary reference materials can be significant.

Reflecting on our experiments, several changes would have improved measurement reliability. These include more measurements at the t_0 times, use of more accurate NBS-developed techniques for delivering weight aliquots of solutions, and greater replication of measurements for those factors that contributed the larger uncertainties.

For the ^{241}Pu half-life measurement, both ^{241}Pu and ^{242}Pu would be added isotopes. This would virtually eliminate isotopic fractionation and mass discrimination uncertainties.

REFERENCES

1. W. W. Strohm, International Journal of Applied Radiation and Isotopes 29, 481-483 (August 1978).

2. S. F. Marsh, Los Alamos National Laboratory Report LA-8399 (August 1980).