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University of California



LOS ALAMOS SCIENTIFIC LABORATORY

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S. -T. Hsue
T. E. Sampson
J. L. Parker
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PLUTONIUM ISOTOPIC COMPOSITION BY GAMMA-RAY SPECTROSCOPY

by

S.-T. Hsue, T. E. Sampson, J. L. Parker, S. S. Johnson, and D. F. Bowersox

ABSTRACT

We discuss the general approach, computerized data analysis methods, and results of measurements to determine the isotopic composition of plutonium by gamma-ray spectroscopy. The simple techniques are designed to be applicable to samples of arbitrary size, geometry, chemical and isotopic composition that have attained ^{241}Pu - ^{237}U equilibrium. The combination of the gamma spectroscopic measurement of isotopic composition coupled with calorimetric measurement of total sample power is shown to give a totally nondestructive determination of sample Pu mass with a precision of 0.6% for 1000-g samples of PuO_2 with 12% ^{240}Pu content. The precision of isotopic measurements depends upon many factors including sample size, sample geometry, and isotopic content. Typical ranges are found to be ^{238}Pu , < 1-10%; ^{239}Pu , 0.1-0.5%; ^{240}Pu , 2-5%; ^{241}Pu , 0.3-0.7%; ^{242}Pu (determined by isotopic correlation); and ^{241}Am , 0.2-10%.

I. INTRODUCTION

Work at Los Alamos Scientific Laboratory (LASL) in the area of plutonium isotopic analysis by gamma-ray spectroscopy started in 1974 when J. L. Parker and T. D. Reilly outlined a method using ratios of neighboring peaks with relative efficiency corrections determined from the spectrum under study.¹ These techniques have received wide acceptance and have been put into routine use at several laboratories.^{2,3} Results from an interlaboratory comparison have been published.⁴ Different laboratories generally use the same techniques with the main difference being the methods used for determining photopeak areas.

A somewhat different approach has been used by Gunnirk⁵ who fits the complex 100-keV region with response functions of each isotope. This method has been used very successfully for the case of dilute solutions for which attenuation corrections are small.

Gunnirk and coworkers,^{6,7} and Cowder et al.,⁸ have used gamma rays in the < 60-keV region for isotopic analysis on freshly separated solutions in the 100 to 300-g/g range. Use of gamma rays in the

< 60-keV region has also been discussed by Umezawa et al.⁹

Techniques similar to Reference 1 have been described by Draznev and coworkers,¹⁰⁻¹² and Reilly et al.¹³

At LASL the press of other projects has prevented us from fully developing the methods proposed over six years ago. Only in the past year has there been a mandate to refine these techniques for application at LASL. The work reported here will enable routine application of this method for verification of Pu isotopic composition and determination of Pu isotopic composition for proper interpretation of total Pu measurements by calorimetry or neutron coincidence counting.

The procedures to be described require no peak fitting thus minimizing computer core and speed requirements. Little training is needed for the method to be routinely used by technicians. The method represents a simple, and perhaps the most versatile single detector approach to Pu isotopics.

In addition to the Pu isotopic fractions the procedure also computes specific power for interpretation of calorimetry measurements, and effective ^{240}Pu for neutron coincidence counter applications.

Algorithms are included that produce reasonably good estimates of the statistical precision of these quantities.

II. GENERAL APPROACH

The philosophy that has governed this approach is one of simplicity. We wish to see how far this technique can be taken using the simplest data acquisition and analysis techniques and yet have the widest applicability to arbitrary sample configurations.

The atom ratio of isotopes 1 and 2 is determined from a gamma ray spectrum by means of

$$\frac{N_1}{N_2} = \frac{C_1}{C_2} \times \frac{T_{1/2}(1)}{T_{1/2}(2)} \times \frac{B_2}{B_1} \times \frac{RE_2}{RE_1}, \quad (1)$$

where

- N - Number of atoms of indicated isotope
- C - Photopeak counts from selected gamma ray from indicated isotope
- $T_{1/2}$ - Half-life of indicated isotope
- B - Branching ratio of selected gamma ray from indicated isotope
- RE - Relative efficiency at selected gamma ray energy including geometry, sample self absorption, attenuation, and detector efficiency.

Half lives and branching ratios are taken from the literature.^{14,15} The relative efficiency is determined from the spectrum under study by determining the quotient of the photopeak counts and the branching ratio for a series of gamma rays from one of the isotopes in the sample. ^{239}Pu , ^{241}Pu , and ^{241}Pu - ^{237}U gamma rays are used in this method with the ^{241}Pu and ^{241}Pu - ^{237}U relative efficiency points being normalized to those from ^{239}Pu .

Photopeak areas are determined by region of interest (ROI) summation.¹⁶ Background regions are selected above and below each photopeak. A linear background is interpolated under the photopeak from the centroids of the background regions. Background regions are carefully selected to avoid neighboring peak interferences, particularly from ^{241}Am which can vary greatly from sample to sample.

Digital gain and zero stabilization is used in the data acquisition electronics. This is important

to ensure that the peaks don't wander out of their assigned ROIs. The 129.3 keV and 413.7 keV peaks of ^{239}Pu are used for zero and gain stabilization.

The ROI summation method puts great emphasis on good detector resolution in order to be able to resolve the peaks of interest from close lying neighbors. A high resolution planar detector of $\sim 200 \text{ mm}^2 \times 10 \text{ mm}$ deep is used for these measurements. Detectors of this type can have resolutions of $< 500 \text{ eV}$ at 122 keV although the detector used in this program has a resolution of 540 eV. The best possible resolution should be utilized. The major disadvantage to this detector type is its low efficiency at higher energies. With such a planar detector one is unable to utilize the potentially useful 600 keV region.

The analysis routines propagate the statistical uncertainties in the photopeak areas to give the statistical uncertainties in the final Pu isotopics. Because the isotopic ratios are not completely independent, the error propagation may not be rigorously exact. It has proven, however, to be a useful estimate of the observed precision of repeated runs on the same sample.

The techniques discussed here are applicable to a very wide range of sample types. Sample size is only limited by count rate and counting time considerations. Samples as small as 0.25 g have been measured; however, a few grams seems to be a more practical minimum size. Sample geometry has a great influence on count rate and can be more important than Pu mass alone. Samples can be as large as criticality considerations allow. For large samples count rates are tailored by choice of a suitable collimator. We attempt to keep count rates at about 10 kHz as a compromise between optimal data collection rates (higher than 10 kHz) and best resolution (lower). Counting times are influenced by the statistical precision desired and the ultimate application of the isotopic results. Simple verifications of, say, the $^{239}/^{241}$ ratio may take only a few minutes. Applications that require the ^{238}Pu and/or ^{240}Pu isotopics generally require at least several hours.

Cd and Ta filters are used to reduce the count rate from ^{241}Am at 59.5 keV and the 100 keV x-ray complex in order to remove any pile up peaks from the 150-165 keV region.

The specific algorithms discussed in this report apply only to samples which have attained ^{241}Pu - ^{237}U equilibrium. The 6.75 day half life of ^{237}U controls this time with 99% of equilibrium being reached 45 days after chemical separation of the ^{237}U . Similar analysis methods can be used for non-equilibrium materials but are not discussed here.

The methods are applicable to samples of arbitrary composition and geometry containing Am and up to $\sim 10 \mu\text{Ci/g}$ Pu of fission products. We have not yet examined mixed U-Pu samples. Some modifications to these methods may be necessary if significant amounts of ^{235}U are present.

One additional requirement for this method is that the isotopic distribution of all Pu in the sample must be homogeneous. The sample itself may contain a nonhomogeneous Pu distribution, but all Pu should have the same isotopic composition.

One weakness of the current methods is that the low efficiency of the planar detector does not enable one to use the information available from the 600-keV region. This region can potentially provide increased precision for ^{240}Pu in larger samples, a needed improvement for calorimetry and coincidence counting applications. The precision of the determination of low concentrations of ^{241}Am would also improve using the 600-keV region; however, this is not vital for calorimetry interpretation because Am contributes only a few per cent of the total power for concentrations below 1000 ppm. Use of a second, larger detector² violates our ground rules of simplicity and low cost. A single large detector could measure both the high energy and low energy regions simultaneously, but the poorer resolution of a larger detector makes the simple ROI summation method less applicable to the low energy data from a large detector than that from a higher resolution planar.

The algorithms to be described represent a simple, and perhaps the most versatile single detector approach to Pu isotopics. Even if the 600 keV region were utilized it would not be applicable to samples with incomplete fission product separation, because of gamma ray interferences, or to small samples, because of intensity problems.

III. ANALYSIS METHOD

Data is accumulated in Canberra Series 80 MCA interfaced to a PDP-11 series computer operating under RT-11 version 38. All analysis routines are written in FORTRAN, and are integrated into a versatile user-oriented package suitable for either production or R and D work.

Relative efficiency values are calculated from peak area/branching ratio for ^{239}Pu lines at 129.3, 143.4 + 144.2, 171.3, 179.2, 189.3, 195.7, 203.5, 255.4, 297.5, 345.0, 375.0, and 413.7 keV. All relative efficiencies are normalized to a value of 1.0 at 413.7 keV. Not all of these points are used in the subsequent analysis.

Next the ^{239}Pu relative efficiency values at 345.0 and 375.0 keV are linearly extrapolated to give values at 332.4 and 335.4 keV. The peak complexes at 332 and 335 keV contain contributions from ^{241}Pu - ^{237}U , ^{241}Am , and ^{239}Pu . The ^{239}Pu component is subtracted from both complexes using the 345.0-keV ^{239}Pu line. The remaining peak areas at 332 and 335 keV contain contributions from ^{241}Pu - ^{237}U and ^{241}Am . Assuming ^{241}Pu - ^{237}U equilibrium the two peak areas and two isotopic unknowns are used to solve for the $^{241}\text{Am}/^{241}\text{Pu}$ ratio.¹ This $^{241}\text{Am}/^{241}\text{Pu}$ ratio is used to correct other ^{241}Pu - ^{237}U peaks at 164.6, 208.0, 267.5, 332.4, 335.4, 368.6, and 370.9 keV for their ^{241}Am content.¹ The magnitude of this correction as a function of time since chemical separation of ^{241}Am and ^{237}U is shown in Fig. 1. Relative efficiency values at 148.6 keV from ^{241}Pu and at 164.6, 208.0, 267.5, and 332.4 keV from ^{241}Pu - ^{237}U are normalized to the ^{239}Pu values at 332.4 keV. The resulting relative efficiency curves for two sample sizes and a 200 mm² x 10 mm planar detector, are shown in Fig. 2.

In keeping with our goal of simplicity, we do not attempt to fit the entire curve. Interpolation and extrapolation over limited ranges are used to calculate the needed relative efficiency values.

Efficiencies at 152.7 (^{238}Pu), 160.3 (^{240}Pu), and 161.5 keV (^{239}Pu) are determined by linear interpolation between 148.6 and 164.6 keV. The efficiency at 169.6 keV (^{241}Am) is set equal to that at 171.3. Efficiency points at 208.0, 267.5, and 332.4 keV are fit with a quadratic equation and the fit is extrapolated to recompute the efficiency

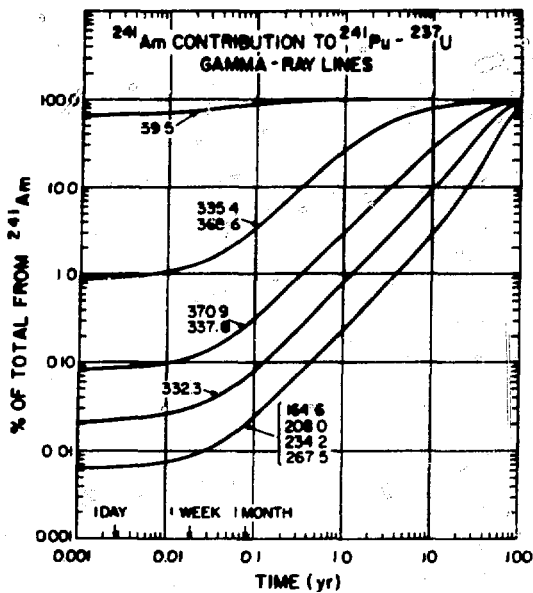


Fig. 1. ^{241}Am contribution to ^{241}Pu - ^{237}U gamma-ray lines as a function of time after chemical separation. Parameters are line energies in kiloelectron volts.

at 203.5 keV. The efficiency for ^{241}Am at 125.3 keV is determined by linear extrapolation from 148.6 and 129.3 keV.

The isotopic ratios are calculated next. The $^{238}\text{Pu}/^{241}\text{Pu}$ ratio is calculated from clean single lines at 152.7 keV (^{238}Pu) and 148.6 keV (^{241}Pu).

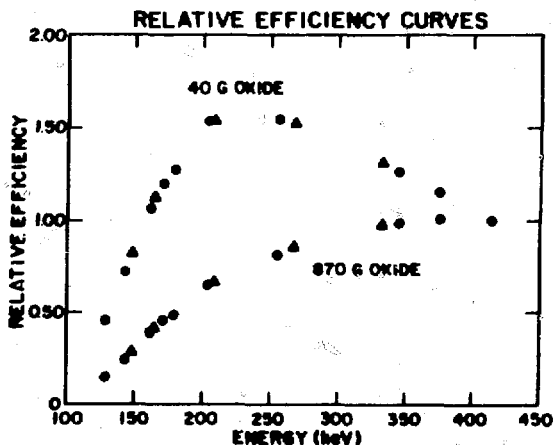


Fig. 2. Typical relative efficiency curves for two sample sizes using a $200\text{-mm}^2 \times 10\text{-mm}$ deep planar detector. Solid circles are points from ^{239}Pu . Triangles are points from ^{241}Pu and ^{241}Pu - ^{237}U normalized to ^{239}Pu points at 332 keV.

Two values are calculated for the $^{239}\text{Pu}/^{241}\text{Pu}$ ratio, first from the 345.0 keV (^{239}Pu) and 332.4 keV (^{241}Pu - ^{237}U) lines and second, from the 203.5-keV (^{239}Pu) and 208.0-keV (^{241}Pu - ^{237}U) lines. The final value for the $^{239}\text{Pu}/^{241}\text{Pu}$ ratio is determined from a weighted average of the two ratios. The 203/208 ratio gives more precise results for low burnup Pu while the 345/332 ratio is better for reactor grade Pu.

The $^{240}\text{Pu}/^{241}\text{Pu}$ ratio is calculated from the 160.3 keV (^{240}Pu) and 164.6 keV (^{241}Pu - ^{237}U) lines. The 160.3 keV ^{240}Pu line is isolated from the 160 keV complex by stripping out the ^{241}Pu component at 160.0 keV with the 164.6 keV ^{241}Pu - ^{237}U line and stripping out the small ^{239}Pu component 160.2 keV with the 161.5 keV ^{239}Pu line.

The $^{241}\text{Am}/^{239}\text{Pu}$ ratio is calculated two ways. The first uses the 125.3 keV ^{241}Am line and the 129.3 keV ^{239}Pu line with ^{239}Pu interferences at 124.5 and 125.2 keV being stripped using the 129.3 keV ^{239}Pu line. The second ratio uses the clean single lines at 169.5 keV (^{241}Am) and 171.3 keV (^{239}Pu). The latter ratio is not useful below ^{241}Am concentrations of about 1 000 ppm because the 169.5 keV ^{241}Am line is not visible. The 125/129 ratio can give $^{241}\text{Am}/^{239}\text{Pu}$ ratios down to a few hundred ppm Am concentrations. The final $^{241}\text{Am}/^{239}\text{Pu}$ ratio is calculated from a weighted average of the two ratios.

The statistical errors in the peak areas associated with each ratio are propagated to give the estimated statistical precision of each ratio. These statistical errors are used as the weighting factors in the weighted averages used to compute the final values for the ^{239}Pu and ^{241}Am ratios.

All ratios contain one (or more depending on the algebraic form) adjustable constant(s) which are "tweaked" slightly using measurements with known standards. These adjustable constants correct for several effects. One effect is possible errors in the branching ratios.⁴ Other effects can arise from systematic errors introduced by the specific peak area analysis and relative efficiency interpolations and extrapolations used. Adjustments are a few per cent, typically.

The ratios of ^{238}Pu , ^{239}Pu , and ^{240}Pu to ^{241}Pu are converted to weight fractions of those isotopes. The ^{242}Pu fraction is determined by

isotopic correlation techniques. The Pu isotopic weight fractions are then recomputed incorporating the ^{242}Pu value. The ^{241}Am content is computed from the measured $^{241}\text{Am}/^{239}\text{Pu}$ ratio and the final ^{239}Pu weight fraction. Statistical precision estimates are propagated from the estimates for the individual isotopic ratios.

For interpretation of calorimetry, the sample specific power (watts/g Pu) can be computed from the measured isotopic composition.¹⁴ Neutron coincidence counting can be interpreted with the computation of the effective ^{240}Pu mass which utilizes the ^{238}Pu , ^{240}Pu , and ^{242}Pu isotopic results.¹⁷

IV. CALIBRATION

The basic expression for isotopic ratios from gamma spectroscopy (Eq. 1) produces results using published fundamental constants that, in principle, can be used without recourse to standards. We have incorporated adjustable calibration constants into these ratios to adjust for branching ratio errors and biases in peak area and relative efficiency algorithms. By calibration we mean the adjustment of these constants to give the best agreement with measurements on known standards.

Obtaining "known standards" is more difficult than it may seem. There are known problems with even the NBS Standard reference material.⁴ First of all, the ^{238}Pu must be determined by alpha spectrometry and not mass spectrometry. For low ^{238}Pu concentrations (<0.1%) sample and filament contamination with environmental ^{238}U is a problem. For higher ^{238}Pu concentrations alpha spectrometry and mass spectrometry seem to agree well. The determination of ^{241}Am concentrations in many of the samples available to us is not as precise as desired. Uncertainties of 2-3% are quoted whereas standards with uncertainties of <0.5% are needed. We find that the best ^{241}Am values, for our purposes, are obtained by allowing the ^{241}Am to grow into a high ^{241}Pu content sample and calculating the ^{241}Am knowing the half lives and chemical separation date.

The constants are adjusted by comparing the measured isotopic ratios determined from repeated high precision long runs with those ratios determined from the best appropriate chemical techniques.

Such calibration results are shown in Table I. Here a wide range of sample sizes and types were counted. The samples range from multi-hundred gram (PEO series) to 0.25 g (NBS) with the P2 series being ~2 g and SAL series being 1 g. The ^{240}Pu content ranged from 6 to 18%. The best values for the calibration constants were used to recompute the isotopics. It is the recomputed isotopics, after adjustment of the calibration constants, that are displayed in Table I. The fact that the mean values are not 1.0 illustrates the difficulty in making these adjustments for such a wide range of isotopics, especially for ^{240}Pu which has three terms in its $^{240}\text{Pu}/^{241}\text{Pu}$ ratio expression. The effect of a constants adjustment on the $^{240}\text{Pu}/^{241}\text{Pu}$ ratio is illustrated graphically in Fig. 3. (These are different data than Table I.) There would appear to be still a small slope as a function of ^{240}Pu content, even after the constants adjustment.

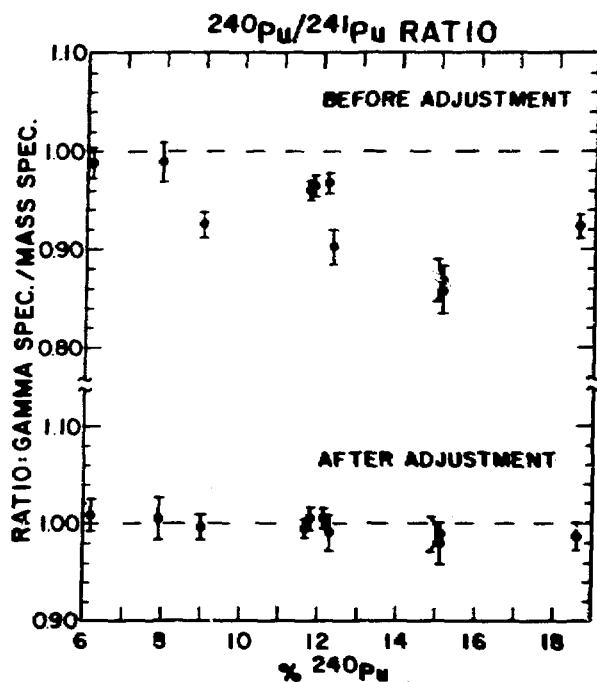


Fig. 3. Effect of adjustments of calibration constants on $^{240}\text{Pu}/^{241}\text{Pu}$ ratio. The before adjustment data show results using only fundamental constants with all calibration constants equal to 1.0.

TABLE I
NONDESTRUCTIVE GAMMA-RAY MEASUREMENTS OF PU ISOTOPICS

(R = Gamma-ray assay/chemical assay)

| Pu Isotopics Sample I.D. | ²³⁸ Pu | | ²³⁹ Pu | | ²⁴⁰ Pu | | ²⁴¹ Pu | | ²⁴² Pu | |
|-----------------------------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|
| | Chem(%) | R | Chem(%) | R | Chem(%) | R | Chem(%) | R | Chem(%) | R |
| PE0381 | 0.037* | 0.849 | 88.684 | 0.999 | 10.321 | 1.013 | 0.838 | 0.999 | 0.120 | 1.027 |
| PE0382 | 0.029* | 0.875 | 89.491 | 0.999 | 9.665 | 1.013 | 0.704 | 1.027 | 0.110 | 0.883 |
| PE0385 | 0.029* | 0.778 | 90.019 | 0.998 | 9.262 | 1.018 | 0.595 | 0.994 | 0.094 | 0.806 |
| PE0447 | 0.044* | 0.865 | 88.842 | 1.000 | 10.120 | 1.005 | 0.837 | 0.999 | 0.157 | 0.754 |
| NBS946 | 0.233 | 1.033 | 84.204 | 1.000 | 12.269 | 1.003 | 2.713 | 1.005 | 0.580 | 0.898 |
| NBS947 | 0.279 | 1.040 | 76.801 | 1.002 | 18.620 | 0.998 | 3.089 | 1.009 | 1.211 | 0.888 |
| NBS948 | 0.010 | 1.040 | 91.677 | 0.999 | 7.951 | 1.007 | 0.328 | 0.999 | 0.033 | 1.040 |
| P20116 | 0.386 | 0.984 | 78.512 | 0.995 | 15.216 | 1.004 | 4.854 | 1.005 | 1.033 | 1.296 |
| P20117 | 0.016 | 0.906 | 93.479 | 0.999 | 6.151 | 1.022 | 0.317 | 0.995 | 0.039 | 0.641 |
| P20118 | 0.028 | 0.949 | 90.168 | 0.999 | 8.983 | 1.014 | 0.717 | 1.003 | 0.104 | 0.853 |
| P20119 | 0.040 | 1.011 | 86.936 | 0.996 | 11.748 | 1.026 | 1.106 | 0.999 | 0.170 | 1.148 |
| P20120 | 0.386 | 0.985 | 78.515 | 0.997 | 15.216 | 0.997 | 4.850 | 1.006 | 1.033 | 1.288 |
| ASQMET | 0.015* | 0.855 | 93.649 | 1.000 | 5.948 | 1.006 | 0.354 | 0.997 | 0.033 | 0.753 |
| SAL639 | 0.051 | 1.009 | 86.642 | 0.999 | 11.849 | 1.001 | 1.241 | 0.988 | 0.218 | 0.992 |
| SAL640 | 0.052 | 1.020 | 86.266 | 1.000 | 12.239 | 1.002 | 1.223 | 0.992 | 0.221 | 0.997 |
| Average | | 0.998 | | 0.999 | | 1.009 | | 1.001 | | 0.954 |
| S.D. | | 0.043 | | 0.002 | | 0.008 | | 0.009 | | 0.187 |

*²³⁸Pu determined by mass spectrometry. Not used in calculating the average.

Over a wide range of sample sizes, configurations, and isotopics, the isotopics measured by gamma-ray spectroscopy show essentially no bias. Poor alpha spectrometer determinations of ²³⁸Pu may contribute to the relatively poor precision observed in Table I for that isotope. The extent of this contribution is not known. The bias and imprecision for ²⁴²Pu is not significant because of its small weight fraction in most Pu mixes.

V. PU MASS MEASUREMENTS WITH CALORIMETRY-GAMMA RAY SPECTROSCOPY

The isotopics calibration that produced the results in Table I was used with gamma ray spectroscopy measurements of fourteen 870-g Pu samples of FFTF oxide and one 500-g sample of weapons grade metal. All samples were also measured in a calorimeter. The plutonium isotopic composition determined from the gamma-ray measurement was used to determine the sample's specific power in watts/g Pu, which was combined with the calorimeter measurement of sample power in watts to give the sample

mass in g Pu.¹⁴ The results for the plutonium mass are compared with the accepted values determined by destructive chemical analysis for g Pu/g sample, ignition for moisture content, weighing, and mass spectrometry for isotopic composition.

This combination technique is not new, having been in use at Mound Laboratory¹⁸ and Rockwell-Henford³ for some time. This is, however, the first application of this powerful combination of NDA techniques at LASL.

The FFTF oxide had nominal isotopic composition of 0.06% ²³⁸Pu, 86.6% ²³⁹Pu, 11.6% ²⁴⁰Pu, 1.3% ²⁴¹Pu, 0.2% ²⁴²Pu, and 600 ppm ²⁴¹Am.

In Table II the 4-h gamma-ray isotopic measurements are ratioed to the mass spectrometry values. The ratios for ^{239,240,241}Pu are also displayed in Fig. 4. Agreement is seen to be excellent for the major plutonium isotopes with the exception of ²³⁸Pu. Here ²³⁸U contamination is always a problem for mass spectrometry and can produce large errors at these relatively low concentrations (0.05 to 0.07%). The gamma spectroscopy results are more reliable than these mass spectrometry

TABLE II
PLUTONIUM ISOTOPIC BY GAMMA-RAY SPECTROSCOPY

| Sample | Ratio: $\frac{\text{Gamma Spectroscopy (4 h)}}{\text{Mass Spectrometry}}$ | | | | | |
|----------------------------|---|-------------------|-------------------|-------------------|-------------------|-------------------|
| | ^{238}Pu | ^{239}Pu | ^{240}Pu | ^{241}Pu | ^{242}Pu | ^{241}Am |
| FFTF Oxide | | | | | | |
| LA013AC1 | 0.8738 | 0.9986 | 1.0090 | 0.9934 | 1.171 | 0.994 |
| LA013AC2 | 0.8486 | 1.0022 | 0.9825 | 0.9986 | 1.138 | 0.932 |
| LA013AC3 | 0.8850 | 0.9998 | 1.0000 | 0.9954 | 1.155 | 1.036 |
| LA013AC4 | 0.8810 | 0.9992 | 1.0042 | 0.9965 | 1.167 | 1.003 |
| LA013AC5 | 0.8292 | 0.9975 | 1.0169 | 0.9946 | 1.184 | 0.989 |
| LA013AC6 | 0.8746 | 0.9972 | 1.0191 | 0.9943 | 1.187 | 1.037 |
| LA013AC8 | 0.9052 | 0.9987 | 1.0074 | 0.9996 | 1.173 | 1.117 |
| LA0135CB | 0.9729 | 0.9945 | 1.0398 | 0.9998 | 1.129 | 1.047 |
| LA0146C3 | 0.8990 | 0.9965 | 1.0243 | 0.9945 | 1.169 | 0.843 |
| LA0148C3 | 0.7331 | 1.0077 | 0.9402 | 1.0122 | 1.200 | 1.239 |
| LA0153C3 | 0.8149 | 0.9955 | 1.0324 | 1.0071 | 1.091 | 1.239 |
| LA0154C3 | 0.9152 | 1.0012 | 0.9951 | 0.9991 | 1.229 | 1.221 |
| LA0150C3 | 0.9587 | 0.9964 | 1.0231 | 0.9942 | 1.224 | 1.031 |
| Weapons Grade Metal | | | | | | |
| J001325 | 0.3437** | 1.0014 | 0.9844 | 0.9955 | 0.689** | 1.114 |
| mean (bias) | 0.8762 | 0.9990 | 1.0056 | 0.9982 | 1.171 | 1.060 |
| observed std dev | 0.062 | 0.0034 | 0.025 | 0.0054 | 0.037 | 0.116 |
| predicted std dev | 0.031 | 0.0037 | 0.027 | 0.0057 | -- | 0.071 |

*Am determined by radioanalytical techniques

**omitted from average

values. If reliable ^{238}Pu results are needed from mass spectrometry for low ^{238}Pu values, the user should request the ^{238}Pu be determined by alpha spectroscopy. Even in small concentrations, the high specific power of ^{238}Pu contributes significantly to the total sample power. Its accurate determination is essential for proper interpretation of calorimetric measurements.

The bias in the ^{242}Pu results arises from the isotopic correlation technique used. For a wide range of sample isotopics, the ^{242}Pu results will fluctuate. Over a narrow burnup range the bias may be substantially reduced by choosing a different correlation. In any case, this bias is not significant for total plutonium determination because ^{242}Pu contributes negligibly to the plutonium specific power.

The relatively large bias and standard deviation for ^{241}Am is caused by the poor statistical precision of the gamma spectroscopy measurement at these lower americium levels (300 to 700 ppm) and the imprecision of the radioanalytical techniques used to determine the "standard" values. For these low americium content samples, the americium

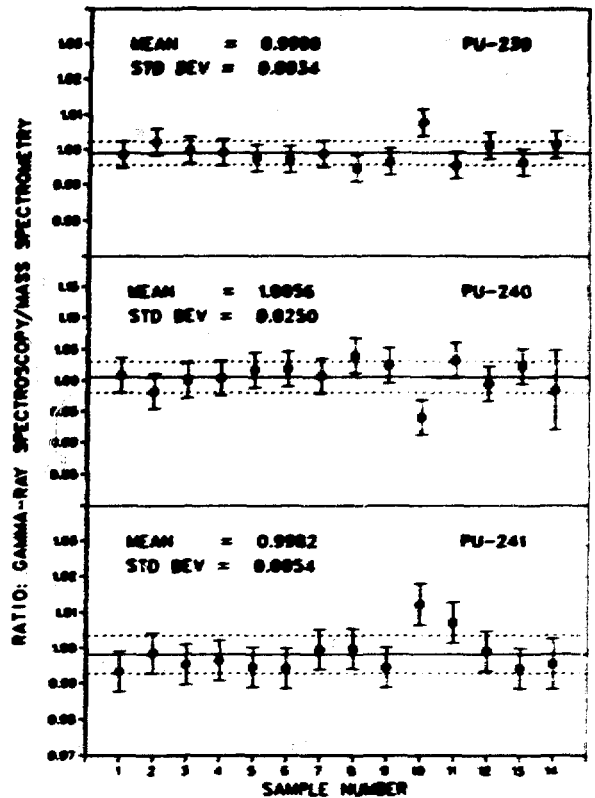


Fig. 4. Gamma-ray isotopics compared to mass spectrometry values. Samples 1-13 are 1000-g PuO_2 with nominal 0.06% ^{238}Pu , 86.6% ^{239}Pu , 11.8% ^{240}Pu , 1.0% ^{241}Pu , and 0.2% ^{242}Pu . Sample 14 is 500-g of weapons grade Pu metal with nominal 0.01% ^{238}Pu , 93.8% ^{239}Pu , 5.9% ^{240}Pu , 0.27% ^{241}Pu , and 0.05% ^{242}Pu .

contributes only a minor portion (1 to 2%) of the sample power. Fortunately the gamma measurement precision improves for higher americium concentrations, which can contribute significantly to the sample power. For high americium the accuracy of the gamma-spectrometry measurement of americium is limited by the unavailability of sub-1% accuracy for the americium content of plutonium standards.

At the bottom of Table II the observed bias, observed standard deviation, and expected or predicted standard deviation are listed. The expected or predicted standard deviations are propagated from counting statistics, a nontrivial feature of the analysis software. The fact that the various isotopic ratios are not completely independent causes the estimates to be not rigorously exact. They are intended to give the user a reasonably good precision estimate. The excellent agreement

between the observed and predicted precisions for the major isotopes is, perhaps, somewhat fortuitous.

The gamma-spectrometer isotopics were used to interpret a calorimetry measurement on each sample. A comparison of total plutonium mass from calorimetry-gamma spectroscopy is shown in Col. 2 of Table III. The same comparison is made for calorimetry-mass spectrometry in Col. 3 of Table III. Calorimetry-gamma spectroscopy shows a bias of 0.2% with an observed precision of $\sim 0.6\%$. The larger bias of 1.5% for calorimetry-mass spectrometry is attributed to poor ^{238}Pu mass spectrometer values. The calorimetry-gamma spectroscopy comparison with chemical analysis is also shown graphically in Fig. 5. The observed precision of $\sim 0.6\%$ for the Pu mass determination comparison in Table III will also contain a contribution from the precision of the weighing and destructive chemical analysis techniques used to determine the "accepted" chemical analysis values. Experience indicates that this precision may be $\sim 0.1-0.2\%$ ¹⁸

TABLE III
TOTAL PLUTONIUM CONTENT

| Ratio: | Calorimetry-Gamma Spectroscopy (4 h) | Calorimetry-Mass Spectrometry |
|---------------------|--------------------------------------|-------------------------------|
| | Destructive Chemical Analysis | Destructive Chemical Analysis |
| FFTF Oxide | | |
| LA0134C1 | 1.0046 | 0.9893 |
| LA0134C2 | 1.0151 | 0.9894 |
| LA0134C3 | 1.0045 | 0.9897 |
| LA0134C4 | 1.0045 | 0.9894 |
| LA0134C5 | 1.0044 | 0.9693 |
| LA0134C6 | 1.0017 | 0.9893 |
| LA0134C8 | 0.9982 | 0.9698 |
| LA0135C8 | 0.9982 | 1.0048 |
| LA0146C3 | 1.0055 | 0.9930 |
| LA0148C3 | 1.0107 | 0.9698 |
| LA0153C3 | 0.9927 | 0.9749 |
| LA0154C3 | 0.9952 | 0.9884 |
| LA0150C3 | 0.9968 | 0.9974 |
| Weapons-grade Metal | | |
| J001325 | 0.9957 | 0.9942 |
| mean (bias) | 1.0020 | 0.9849 |
| observed std dev | 0.0063 | 0.0168 |
| predicted std dev | 0.0093 | -- |

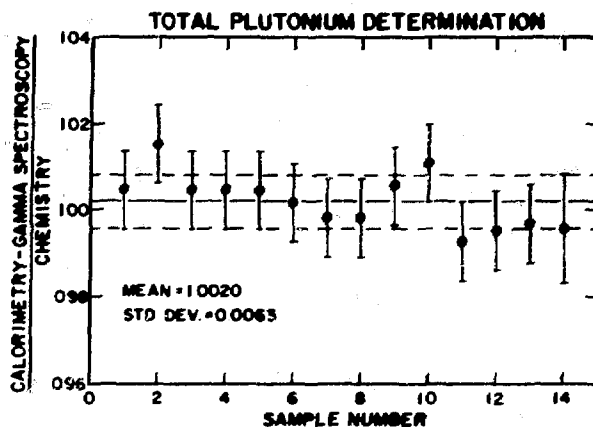


Fig. 5. Total plutonium determination by combination of calorimetry and gamma spectroscopy compared to conventional chemistry techniques. Error bars are predicted uncertainties arising from gamma-ray isotopic determination.

The uncertainties predicted for the gamma spectroscopy results can be used to predict the precision of the sample's specific power and hence the precision of the plutonium mass determination. Uncertainties in the calorimeter power measurement are negligible compared to the isotopic determination. Under the assumption of uncorrelated uncertainties in the gamma-ray isotopics, a representative curve of precision vs counting time, as in Fig. 6, can be generated. These curves are specific to each experiment and depend on the sample size and geometry, count rate, detector type, and sample isotopic including ^{241}Am , as well as counting time. The curves in Fig. 6 are for an 870-g Pu FFTF PuO_2 sample and a 500-g weapons grade metal sample counted at 10 kHz with a $2\text{-cm}^2 \times 10\text{-mm}$ -deep planar detector. The assumption of uncorrelated gamma-ray isotopic results is not rigorously valid and there is evidence that the observed precision is even better than that predicted by error propagation by a factor of two.

In Table IV we summarize some of the precisions that have been observed on measurements on three different sample types. The first entries for FFTF oxide summarize the measurements already discussed. The other two entries (reactor-grade oxide and weapons-grade oxide) summarize the results of repeated measurements of the specific power from gamma-ray isotopics. These two samples did not have enough sample mass or a precise enough Pu mass value to

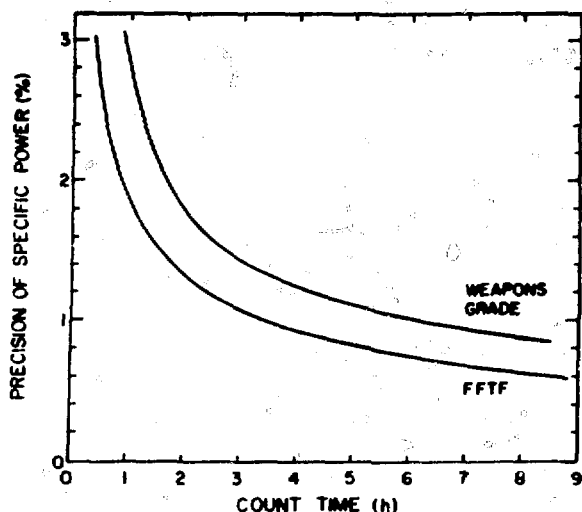


Fig. 6. Predicted precision of specific power for 500-g weapons grade metal and 1000-g FFTF PuO_2 sample counted at 10 kHz with $200\text{-mm}^2 \times 10\text{-mm}$ deep planar detector. Curves are specific to each experiment and are not of general applicability. See Table IV for illustration that observed precision is even better than that predicted.

enable them to give a meaningful calorimeter measurement.

The Table IV entries illustrate how the precision of the specific power can vary, especially as a function of the isotopic composition. For low A_m samples the uncertainty in the ^{240}Pu isotopic dominates the predicted precision. As the A_m content increases, the ^{240}Pu power contribution becomes less important and results in improved overall precision. There is evidence in Table IV that the observed precision from repeated measurements is significantly better than that predicted by error propagation.

VI. ONGOING RESEARCH

We are investigating the extension to nonequilibrium (^{241}Pu - ^{237}U) materials. For these materials one can not use the 148.6 keV ^{241}Pu line and the ^{241}Pu - ^{237}U lines interchangeably. We are investigating taking all ratios with respect to the 148.6 ^{241}Pu line using the 129.3 ^{239}Pu , 152.7 ^{238}Pu , and 160.3 ^{240}Pu lines. For some types of samples the <60 keV region may be accessible. We are looking into using this region for $^{238}\text{Pu}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ ratios while using the 120-150-keV region for

$^{241}\text{Pu}/^{239}\text{Pu}$. This is similar to work already done on solutions⁶⁻⁸ but the relative efficiency corrections are more difficult for the arbitrary sample.

The alternate combination of gamma-spectroscopy with neutron coincidence counting for the determination of total plutonium is also being pursued.

VII. CONCLUSIONS

We have described the computerized implementation of algorithms for the determination of isotopic ratios by gamma-ray spectroscopy for plutonium samples of arbitrary geometry and composition.

The results have been compared with values determined from mass spectrometry. For 4-h measurements on 870-g Pu FFTF oxide samples, we find precisions of $\sim 3\%$ for ^{238}Pu , 0.4% for ^{239}Pu , 2.7% for ^{240}Pu , and 0.6% for ^{241}Pu . When these measurements are combined with calorimetric measurements of the total sample power we are able to make a completely nondestructive determination of total Pu content with a bias of 0.2% (comparable to precision of destructive chemistry techniques) and a precision of 0.6%. The precision of the total Pu determination can be even better for different sample types and experimental conditions.

The techniques described here coupled with ongoing research can be applied to the majority of samples found in the fuel cycle.

TABLE IV

PRECISION OF DETERMINATION OF SPECIFIC POWER
USING GAMMA-RAY SPECTROSCOPY

| | <u>238</u> | <u>239</u> | <u>240</u> | <u>241</u> | <u>242</u> | <u>Am</u> |
|---|------------|------------|------------|------------|------------|------------|
| FFTF Oxide (Low Am) | | | | | | |
| Typical Isotopic (wt %) | 0.061 | 86.58 | 11.79 | 1.35 | 0.20 | 595 ppm |
| Typical Isotopic Precision | | | | | | |
| 4-h Measurement (%) | 3.5 | 0.38 | 2.8 | 0.57 | -- | 6.3 |
| % Total Power | 11.7 | 56.3 | 28.2 | 1.5 | 0.01 | 2.3 |
| Specific Power = 0.00298 w/g Pu | | | | | | |
| Predicted Precision of Specific Power (4-h Measurement) = 0.9% | | | | | | |
| Observed Precision-Repeated Measurements = 0.6% | | | | | | |
| <hr/> | | | | | | |
| Reactor-Grade Oxide (High Am) | | | | | | |
| Typical Isotopic (wt %) | 0.24 | 84.10 | 12.36 | 2.77 | 0.53 | 16 000 ppm |
| Typical Isotopic Precision | | | | | | |
| 7.4-h Measurement (%) | 0.70 | 0.24 | 1.70 | 0.54 | -- | 0.15 |
| % Total Power | 23.6 | 28.3 | 14.6 | 1.6 | 0.01 | 31.9 |
| Specific Power = 0.00577 w/g Pu | | | | | | |
| Predicted Precision of Specific Power (7.4-h Measurement) = 0.31% | | | | | | |
| Observed Precision-Repeated Measurements = 0.15% | | | | | | |
| <hr/> | | | | | | |
| Weapons-Grade Oxide (Low Am) | | | | | | |
| Typical Isotopic wt % | 0.014 | 93.34 | 6.30 | 0.32 | 0.026 | 189 ppm |
| Typical Isotopic Precision | | | | | | |
| 5.9-h Measurement (%) | 5.0 | 0.14 | 2.2 | 0.31 | -- | 5.5 |
| % Total Power | 3.3 | 76.5 | 18.7 | 0.46 | 0.001 | 1.07 |
| Specific Power = 0.00235 w/g Pu | | | | | | |
| Predicted Precision of Specific Power (5.9-h Measurement) = 0.45% | | | | | | |

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