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***Calorimetry for Safeguards
Purposes***

***DETERMINATION OF PLUTONIUM IN
REACTOR FEED MATERIAL***

***F. A. O'Hara
J. D. Nutter
~~W. W. Rodenburg~~
M. L. Dinsmore***

January 5, 1972

AEC Research and Development Report

MOUND LABORATORY

Miamisburg, Ohio
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FOREWORD

This progress report contains detailed information on the technical contribution made by Mound Laboratory to the Safeguards Program of the U. S. Atomic Energy Commission. Questions regarding information in this report should be directed to Dr. J. D. Nutter or Dr. F. A. O'Hara, Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio 45342.

ABSTRACT

This report is the first of a series of reports covering work performed at Mound Laboratory at the request of the AEC Office of Safeguards and Materials Management. The purpose of this work is to test the feasibility and applicability of calorimetric assay of radioactive materials involved in the reactor fuel cycle, primarily plutonium.

Included is a brief history of calorimetry, a description of the instrumentation and techniques used, and the results of the calorimetric assay of two reactor-fuel samples. These samples each contained approximately 1 kg of plutonium oxide feed material with isotopic compositions typical of plutonium from fast breeder reactors and light water reactors.

INTRODUCTION

Early in 1970, the AEC/Office of Safeguards and Materials Management requested Mound Laboratory to determine the feasibility of the calorimetric assay technique for Safeguards situations. The following features are some of the advantages of this technique:

- The assay is nondestructive.
- The calorimetric technique is highly precise and, where the isotopic composition of sample is known, highly accurate.
- Calorimeters can be adapted to an automatic data processing system or operated by a technician.
- The total power of a sample can be determined without sampling or aliquotting.
- Calorimetry can discriminate between the fissile isotopes ^{235}U and ^{239}Pu because of the difference in half-lives.
- The measurements are based on primary electrical standards which in general are more reliable than counting standards.

BACKGROUND

A calorimeter is an instrument for measuring heat. All chemical and physical processes involve energy changes. The direct evaluation of these changes is the goal of the methods of calorimetry. Calorimetric measurements are almost completely based on temperature measurements, and in many cases involve problems of temperature control.

The modern calorimetric method is essentially the measurement of the amount of electrical energy necessary to duplicate the thermal effect accompanying a physical or chemical change. Modern calorimetric data are, therefore, primarily expressed in units of electrical energy.

Radionuclide calorimeters are used to measure materials emitting alpha, beta, or gamma radiation. The principal difference between radionuclide calorimetry and other fields of calorimetry is the emission of an almost constant rate of heat (power) due to absorption of the emitted particles by the calorimeter during decay of the isotope present in the sample. In other types of calorimeters, a burst of heat is usually measured. Calorimetry was one of the earliest techniques used for the quantitative determination of radioactivity. In 1903, Pierre Curie and A. Laborde were able to estimate the energy released from radium bromide by utilizing a calorimeter.¹ Rutherford and Barnes, also in 1903, determined the heat produced by 1 g of radium in equilibrium with its short half-life daughters.²

If a sample of radioactive material is known to contain only one radioisotope, the following equation applies:

$$W = \frac{2.11933 \times 10^3 Qm}{T_{\frac{1}{2}} A} \quad (1)$$

where

W = watts measured in calorimeter;

Q = disintegration energy of isotope in million electron volts (MeV),

m = mass of isotope present in grams;

$T_{\frac{1}{2}}$ = half-life of the isotope in years;

A = atomic weight of isotope in grams.

If the disintegration energy and the half-life of the isotope are known, the mass of the isotope present in the sample can be determined. The calorimeter thus serves as an assay instrument. If the mass and disintegration energy are known, calorimetry gives the power and hence the half-life may be determined. If the half-life is short enough, the

change with time of the power of the sample may be measured calorimetrically and is sufficient to determine the half-life of the nuclide. The most precisely known half-lives have been determined by this method.

Equation (1) can also be expressed in the form:

$$W = 1.60210 \times 10^{-13} Q \lambda N, \quad (2)$$

or

$$W = 1.60210 \times 10^{-13} Q \lambda N_0 e^{-\lambda t}, \quad (3)$$

where

N = number of atoms of isotope at time, t ,

N_0 = number of atoms of isotope at time, $t = 0$,

λ = decay constant of isotope in second^{-1} .

In actual practice, equations (1) and (2) can be simplified to

$$W = mF, \quad (4)$$

where

m = grams of isotope,

F = specific power of isotope in watt/gram.

The specific power of an isotope can be calculated from equation (1), or determined experimentally utilizing equation (4).

The calorimetrically determined wattage (W) in equations (1) through (4) assumes that no significant amount of the energy of radioactive decay escapes undetected from the calorimeter and that the daughter isotope is stable.

In the case of parent-daughter decay in the sample,

$$N_1 = N_0 e^{-\lambda_1 t} \quad (5)$$

$$N_2 = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1} \left[e^{-\lambda_1 t} - e^{-\lambda_2 t} \right] \quad (6)$$

where the subscripts 1 and 2 refer to the parent and daughter, respectively, and N_0 = number of atoms of the parent at $t = 0$.

The wattage of the sample can then be calculated by adding the wattages of the parent and daughter obtained and by combining equation (2) with equations (5) and (6) as follows:

$$W_s = W_1 + W_2$$

$$= 1.60210 \times 10^{-3} \lambda_1 N_0 \left[Q_1 e^{-\lambda_1 t} + \frac{Q_2 \lambda_2}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \right]. \quad (7)$$

Alpha and beta radiation are completely absorbed by a calorimeter. Gamma radiation is much more penetrating, and the calorimeter must be constructed of sufficiently thick walls in order that only a small fraction of the energy may escape. The escaped energy can be calculated or measured with gamma detectors. From these results, corrections may be applied to the observed powers. However, for the materials involved in the reactor fuel cycle, no such corrections are necessary.

Reactor-grade plutonium consists of various amounts of the isotopes ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{242}Pu and ^{241}Am , depending on the neutron spectrum of the reactor in which it was produced, the extent of fuel burnup, and the length of time from americium separation.

When a sample contains a mixture of isotopes, such as reactor fuels, the heat is merely the total of the individual constituents, which may be expressed as follows:

$$W_s = \sum_{i=1}^n W_i = \sum_{i=1}^n m_i F_i. \quad (8)$$

If the plutonium concentration and isotopic ratios of the material in a sample are known, the quantity of each isotope can be determined. Substituting $R_i m_{total}$ for m_i (mass of a particular isotope) in equation (8) as follows:

$$W_s = m_t \sum_{i=1}^n R_i F_i, \quad (9)$$

where m_t = the total weight of all isotopes (grams), and

R_i = the isotopic ratio of the i^{th} isotope.

The mass of a particular isotope can be obtained by rearranging equation (9) as follows:

$$m_i = \frac{R_i W_s}{R_1 F_1 + R_2 F_2 + \dots + R_n F_n}. \quad (10)$$

If the isotopic analysis and calorimetry date are within one month of each other, it is not necessary to compute the decay of the isotopic ratios. Normally, the uncertainties in the isotopic ratios will be larger than the amount of decay. However, when greater lengths of time are required (or to obtain better accuracy when large fractions of ^{241}Pu are present), it is necessary that the isotopic ratios be decayed.

Generally, the precision of the calorimeter measurement is greater than the uncertainty associated with the mass spectrometric determination, which is no better than 0.3% for isotopes with concentrations greater than 10%. For isotopes whose concentration lies between 0.1 and 1%, the minimum error is 1%. Concentrations less than 0.1% may have errors from 5% to as much as 100% for concentrations in the range of 0.0010%.³ Therefore, it would be advantageous to compare the sample power at any time to the predicted value based on earlier calorimetric determinations.

There are two components of heat generation in which the specific power is greater than that of ^{239}Pu . These are ^{238}Pu and ^{241}Am . The more serious of these is ^{238}Pu for two reasons. First, it is the next lowest mass isotope to ^{239}Pu , and for this reason, errors in the isotopic determination due to spectrum "toe-tailing", (interference) from the major peak would tend to affect the already low abundance sensitivity of the minor ^{238}Pu peak. Second, this potential error is compounded by the shorter alpha half-life of ^{238}Pu , which gives a specific power 250 times that of ^{239}Pu . Although this is partially offset by the difference in the abundance ratios, it is not unusual for the component of heat generated by the decay of ^{238}Pu to almost equal that of the ^{239}Pu . This effect is less pronounced in fast reactor plutonium than in light water reactor plutonium, due to the lower fraction of ^{238}Pu present in the sample. The other instance of an isotope with greater specific power than ^{239}Pu is americium. In this case, ^{241}Am , which emits an alpha particle with a 432 yr half-life, is produced from the decay of ^{241}Pu . For this reason, a determination of the americium content of the sample is required, preferably at the time of mass spectrometric analysis. Because of the ingrowth of americium, the thermal output of reactor fuel samples will be observed to grow. The rate of this growth offers a method of verifying the ^{241}Pu content.

As an aid in the determination of the quantity of ^{238}Pu and ^{241}Am in the sample, it has been suggested that the neutrons, both spontaneous and those emitted from the α -n reaction, be measured simultaneously with the calorimetric determination.⁴ Also, gamma-ray spectroscopy could be used for an accurate and nondestructive determination of plutonium isotopic abundances.^{5,6}

THE DESIGN OF RADIONUCLIDE CALORIMETERS

The subject of calorimetry is extensive and its techniques are usually involved and complicated.^{1,2} In general, a calorimeter is designed to accomplish a specific task or measurement. The concept of a "universal calorimeter" has never become a reality. The three main types of radionuclide calorimeters and their uses are as follows:

- (1) Isothermal - temperature of the calorimeter remains constant during a reaction or calibration measurement. The heat output of the reaction or calibration measurement is determined by the time integrated heat exchange between calorimeter and its environment.
- (2) Adiabatic - ideally, no heat exchange between calorimeter and environment.
- (3) Isothermal Jacketed - the environment is temperature controlled, and the heat exchange between calorimeter and environment is a correction which must be applied to results.

As will be discussed later, the design of a calorimeter system may employ one or a combination of any or all of the three main types described above.

Some of the factors which influence the design of a radionuclide calorimeter are listed as follows:

- (1) The Sample - Normally, the amount of sample power, physical size and types of radiation determine the physical dimensions of the calorimeter. In general, large high wattage samples require "heavy" calorimeters, while low wattage samples require "light", highly sensitive microcalorimeters which are capable of measuring fractions of microwatts. Thus, the concept of a universal calorimeter is limited because a trade-off must be made between larger sample sizes and higher calorimeter sensitivity. The thickness of the walls and the types of radiation involved will determine the fraction of heat which escapes from the calorimeter undetected. This fraction is normally quite low and can be accurately calculated so that it is only a minor consideration.

- (2) Calibration Method Used - Two methods are available for calibration: the first, use of a known radioactive sample or heat standard; the second, electrical heating or calibration. In both cases, the observed power of the sample is traceable to the primary electrical standards at the National Bureau of Standards.
- (3) Time Per Assay - A complete assay involves both the sample run and calibration run. The time required to accomplish this is a complex function of all the following factors:
- a. type of calorimeter - isothermal, adiabatic or isothermal jacketed;
 - b. thermal conductivities and heat capacities of all the materials in the sample and calorimeter; and
 - c. construction techniques - precision machining is necessary to assure the uniform and constant thermal paths which are essential for reliable performance.
- (4) The Level of Accuracy Desired - Accuracy is dependent upon the following:
- a. items outlined above under "Time Per Assay";
 - b. accuracy of the analysis of the relative abundance of isotopes present in the sample;
 - c. high precision in all measurements;
 - d. accuracy in correcting for the power not detected by the calorimeter.

In addition to the above design factors, consideration must be given to the environment in which the calorimeter will be used. For example, in-line or assay calorimeters are normally designed to be rugged, reliable and easy to operate while maintaining the specified accuracy.

Again, the concept of a specified calorimeter of a single design to cover all aspects of radionuclide calorimetry is not practical or economical when one considers all the factors which go into the design. Since 1949, many types of calorimeters have been used at this Laboratory. However, no other design has surpassed the precision, accuracy and ease of operation of the isothermal twin-type for radionuclide studies.

Figure 1 shows a cut-away of an isothermal twin-bridge calorimeter. It consists of two identical thermels (thermal elements), each separated from the inner wall of a brass submarine jacket by an annular space. This "air gap" serves as a thermal resistance to heat produced in the sample area. Each thermel has a four terminal calibration heater bifilarly wound on an aluminum can which serves as the sample area. Plastic ends serve as supports for the sample area and reduce axial heat loss. Two nickel resistance thermometers are wound over the entire length of each thermel, and the four windings are connected as a transposed-arm wheatstone bridge supplied with constant current (see Figure 2). The bridge potential (BP) is thus directly proportional to the temperature difference between the two sides of the calorimeter.

The calorimeter is operated in a constant temperature environmental bath. The twin design reduces the effect of environmental temperature fluctuations. For example, a temperature difference of a microdegree between the two sides can be measured even though the environmental bath is controlled to only a millidegree.

FIGURE 1 - Cross section of a typical isothermal twin-bridge calorimeter.

DIAGRAM OF BRIDGE CIRCUIT

DIAGRAM OF HEATER CALIBRATION CIRCUIT

FIGURE 2 - Simplified sketches of the isothermal calorimeter circuitry.

The construction of a precise heat flux calorimeter requires that (1) the thermal paths from the sample chamber to the environmental bath remain constant or reproducible; (2) the temperature of the environment remain constant; and (3) the temperature measured is representative of the sample (i.e., no matter where the sample is located in the sample chamber, top, bottom, or middle, the temperature rise observed is the same). The latter effect is often referred to as "heat distribution" error. The resistance thermometer may be considered as a heat flux averager. Assuming uniformity in the wire winding and the air gap, the resistance change of the section of the thermometer covering any surface is proportional to the temperature gradient, and hence, the heat flux through that element. Thus, the Mound-designed calorimeter has the effect of minimizing "heat distribution" errors.

With the calorimeter empty, a small bridge potential, BP_0 , may be observed. The BP_0 is due to small differences in the resistances of each arm and small variations in the thickness of the air gap.

When a radioactive sample is placed into the sample chamber, the temperature rises inside the sample chamber until the heat losses through the nickel thermometer and across the air gap to the jacket and environmental bath equals the heat being generated by the sample. When this steady-state condition exists, the temperature rise, observed by reading the potential across the wheatstone bridge is proportional to the amount of heat being generated. Axial heat losses through the plastic ends and insulating materials are considered negligible or reproducible during calibration of the calorimeters.

The time required to reach this steady-state condition is proportional to the heat capacity of the sample and sample chamber, and the thermal conductivities of the materials between the sample and the environmental bath (this includes the air-gap, thermel form and the packaging of the sample). Inasmuch as the calorimeter is fabricated to have constant or reproducible thermal paths, the packaging of the sample in most cases is the factor which controls the required time to reach steady-state temperature equilibrium.

After the sample has reached equilibrium and the bridge potential, BP_s , is read using a potentiometer (or high input impedance digital voltmeter), the sample is removed from the calorimeter and the calorimeter is calibrated electrically. A highly regulated dc power supply is used to supply power to the four terminal calibration heaters built into the calorimeter. Figure 2 shows a wiring schematic of the heater calibration circuit. The heaters are fabricated from low temperature coefficient wire such as manganin with copper heater leads.

The heater lead problem (i.e., power generated in leads) normally inherent in single sided calorimeter design is minimized in the twin calorimeter. This is accomplished by utilizing a heater circuit with identical leads to heaters in both the sample and reference sides. When the heater on the sample side is used, current passes through two leads on the sample side and two leads on the reference side of the calorimeter. Thus, the differential calorimeter design compensates for the heat in the leads since both sides have identical power in leads (see Figure 2).

The power dissipated in the heater is expressed by

$$W_h = EI, \quad (11)$$

where

W_h = watts in heater

E = voltage across heater

I = current in amperes through heater.

The current through the heater is determined by measuring the voltage across a standard resistor:

$$I = \frac{HI}{R_s} \quad (12)$$

where I = current in amperes through standard resistor

HI = voltage across the standard resistor (Figure 2)

R_s = value of standard resistor in ohms.

The voltage across the heater is determined indirectly by using a voltage divider and subtracting the voltage drops in the heater leads (HPL1 and HPL2). The following equation applies:

$$E = \left(\frac{R'_s + R''_s}{R'_s} \right) HP - HPL_1 - HPL_2 \quad (13)$$

where

E = voltage across the heater

$\frac{R'_s + R''_s}{R'_s}$ = ratio of voltage divider

HP = voltage across resistor R'_s

HPL₁ = voltage drop in lead one (see Figure 2)

HPL₂ = voltage drop in lead two (see Figure 2)

thus

$$W_h = \left[\left(\frac{R'_s + R'_{s'}}{R'_s} \right) HP - HPL_1 - HPL_2 \right] \frac{HI}{R_s} \quad (4)$$

When steady-state temperature equilibrium is reached with electrical heating, the bridge potential BP_h, is measured.

The electrical calibration is carried out to duplicate the thermal output of the sample. The following equation is used to calculate sample power:

$$W_s = W_h + \frac{BP_s - BP_h}{S} \quad (5)$$

where

W_s = watts in sample

W_h = watts in heater

BP_s = bridge potential with sample (μV)

BP_h = bridge potential with heater (μV)

S = sensitivity of the calorimeter (μV/watt)

The sensitivity is essentially constant over increments of 0.1 to 0.2 watts and thus exact duplication of power is not necessary providing power levels are within 5%. The sensitivity of the calorimeter, S, is determined using electrical calibration or standardized radioisotopic heat sources. The following equation is used to determine the calorimeter sensitivity and may be checked at each electrical calibration of the calorimeter:

$$S = \frac{BP_h - BP_o}{W_h} \quad (6)$$

The foregoing description of operating the calorimeter is called the Replacement Method. In general terms, the sample power is replaced with electrical power. There are two other methods of operating the calorimeter; the Differential Method, and the Isothermal Method.⁷

In the Differential Method, electrical heat in the reference side of the calorimeter is compared directly to the sample heat. This method allows determinations in about half the time required for the "replacement method" since the sample and heater run are effectively made simultaneously. However, operation in this mode requires a foreknowledge of the sample to within about 1% and is normally most useful when many samples of approximately the same size are measured. For unknown samples, this method is only slightly faster than the replacement method. When using this method, the sample power is calculated from the following equation:

$$W_s = W_h + \frac{BP_s - BP_m}{S} \quad (17)$$

where the slope correction (BP_m) is equal to the slope factor (m) times the watts in the heater (W_h), or

$$BP_m = mW_h \quad (18)$$

In the Differential Method the quantity $BP_s - BP_m$ will be zero if the power in the reference side exactly matches the sample power.

The quantity BP_m compensates for small differences in the two sides of the calorimeter and is determined by running current through the sample and reference heaters connected electrically in series. The resulting bridge off-balance is then plotted versus the power in the sample side which generally results in a straight line.

The other mode of operation, which is sometimes used to speed up the time per assay, is the Isothermal Method. In this method, the temperature of the calorimeter is maintained several degrees above the temperature of the bath by a servo-controller (see Figure 3). This is accomplished by shunting one arm of the bridge such that it is at balance when there is W_o watts of power on the sample side of the calorimeter. The amount of power supplied to the empty calorimeter, W_o , is measured by means of a current squared to voltage transducer placed in series with the calorimeter heater. This device averages the fluctuations of the servo-controller output and supplies a dc voltage proportional to the heat input to the calorimeter. When a sample is placed in the calorimeter, the control power drops to a lower level, W_o' . The power of the sample is merely the difference between the two readings, or

$$W_s = W_o - W_o' \quad (19)$$

No correction is needed here since the temperature, and hence the power input, is kept constant by means of the controller. The isothermal method eliminates the time constant of the calorimeter entirely so that the time to reach equilibrium depends only on the time constant of the sample itself. This time limitation can be reduced still further by pre-equilibrating the sample in a "thermalizing well" in the same environmental water bath (see Figure 4).

FIGURE 3 - Circuitry arrangement for the Isothermal Method of operation.

The effect of packaging, automatic servo-control, pre-equilibration and desired accuracy on the equilibrium time has been investigated.

When a calorimeter is automated, the temperature of the sample chamber is held constant. Since the overriding constraint on thermal equilibrium of the sample is packaging, pre-equilibrating the sample to the calorimeter temperature, can greatly reduce the equilibrium time in the calorimeter.* In this case, the only thermal disturbance which must be undergone will occur during transfer of the sample from the thermalizing well to the calorimeter.

In an attempt to illustrate some of the trade-offs in time and accuracy, a series of experiments were performed in order to incorporate the factors mentioned above. These included the following cases:

1. Unautomated calorimeter and empty sample adaptor can;
2. Unautomated calorimeter, sample in adaptor can spaced with plastic bags and shot;
3. Automated calorimeter, sample in adaptor can;
4. Automated calorimeter, sample can previously in thermalizing well controlled to within 0.007°C of calorimeter chamber;
5. Ideal case: sample at equilibrium, removed and reinserted;
6. Case 2 (above), with copper shot between sample and adaptor.

The results of these experiments are shown in Table 1. It can be seen that if less precise results can be tolerated, the necessary equilibrium time can be significantly reduced. Also, faster equilibrium times may be achieved with the addition of automatic temperature controllers and equilibration tubes.

*This is especially useful when a calorimeter is automated and the temperature of the sample chamber is held constant.

Table 1

TIME TO REACH DESIRED EQUILIBRIUM

Case	Time (hr)			Comments
	0.01% Equilibrium	0.1% Equilibrium	1.0% Equilibrium	
1	4.8	3.6	2.8	Heater only, no sample
2	13.1	10.2	8.1	Poorly packaged sample in unautomated calorimeter
3	8.0	6.1	4.7	Same as Case 2 with calorimeter automated
4	3.0	1.6	0.8	Same as Case 3 with sample pre-equilibrated within 0.007°C
5	3.0	1.3	0.4	Ideal case; sample at exact calorimeter temperature
6	8.0	6.3	5.2	Same as Case 2 with improved packaging

The calorimeter system (shown in Figure 4) includes a calorimeter, a regulated power supply, an environmental bath, a control panel, and a readout device (potentiometer or digital voltmeter). The control panel selects heater circuitry and contains the standard resistor for measuring current through the heater as well as a voltage divider network to measure the voltage drop across the heater. Additional equipment may include a recorder, a servo-controller and integrator (for isothermal operation), a master control panel for selection when several calorimeters are being operated and a calculator. Figure 4 also shows a typical console for operating two calorimeters in the isothermal mode. The calorimeter and environmental bath may be located adjacent to the console or as much as 100 ft away in a different area. Figure 5 shows an arrangement of several calorimeters located at various distances from the master control console for an actual installation.

ENVIRONMENTAL BATH

CONSOLE ARRANGEMENT

FIGURE 4 - Components used in a typical isothermal calorimeter system.

FIGURE 5 - Calorimeter installations in Mound Laboratory's plutonium processing building.

EXPERIMENTAL

The loan of the two samples from Atlantic Richfield Hanford Company (ARHCO) was arranged by the AEC/Office of Safeguards and Materials Management (OSMM) through the Richland Operations Office. The isotopic composition of the samples used were characteristic of feed material produced in light water reactors and fast breeder reactors.

The oxide was packaged in a sealed "tuna fish can", two sealed plastic bags and an outer can with Drierite between the bags and outer can. Details on the composition of these samples are given in Table 2. The only assay requested other than that normally provided was an americium analysis.

A series of measurements were made over a time span of 48 days to approximate the time scale of a typical shipper-receiver exchange.

Table 2

SAMPLE DESCRIPTION

	<u>Light Water Reactor Sample</u>	<u>Fast Reactor Feed Sample</u>
Sample Designation	RL-101-0-30-3-2	RL-101-0-30-3-3
Net oxide weight (g)	1,037.8	1,136.0
Pu content (%) ^a	86.36	87.17
Pu content (g)	896.24	990.3
Isotopic analysis ^a (wt %)		
²³⁸ Pu	0.236	0.058
²³⁹ Pu	75.647	85.676
²⁴⁰ Pu	18.424	12.111
²⁴¹ Pu	4.585	1.940
²⁴² Pu	1.108	0.215
Am concentration ^b (ppm)		
(assumed to be ²⁴¹ Am)	6,334	1,376
Total metallic		
impurities ^a (ppm)	1,220	952

^aChemical assay 3/27/70.

^bAmericium analysis on 3/12/70.

The calorimeter used in this investigation was Mound Laboratory Model 102, Serial No. 104, which is of the isothermal twin bridge type described earlier. The sample chamber is 4.75 in. (12.07 cm) in diameter by 8.75 in. (22.23 cm) long. An aluminum calorimeter sample can, which fits snugly into the sample chamber, was used to load samples into the calorimeter. The wall and bottom thickness of this sample can are approximately 0.25 in. (0.64 cm) and reduce the usable volume of the sample cavity to 4.25 in. (10.80 cm) diameter by 8.5 in. (21.59 cm) long. The calorimeter was operated using the replacement method described above.

Both the precision and accuracy of the calorimeter were determined by using a Mound Laboratory two-watt standard heat source, the power of which was known accurately to $\pm 0.007\%$. On a series of twelve measurements the standard deviation from the known value was $\pm 0.02\%$ with an average bias of less than 0.01%. Thus, at the 95% confidence level, the accuracy of the calorimeter was slightly better than $\pm 0.05\%$.

An oxide sample was placed in the calorimeter sample can and the void space between the can and the packaged sample was filled with copper shot to assure good thermal contact between cans. The sample was loaded into the calorimeter and allowed to come to steady-state equilibrium. The time required to reach equilibrium was approximately six hours. A recording system was used which allows the operator to suppress all but a small fraction of the dc output from the calorimeter bridge and record this small fraction to have a visual trace of the equilibrium conditions (both empty and loaded) of the calorimeter (see Figure 6). After equilibrium was attained, the bridge potential was measured using a Guildline 9160-G potentiometer and a Leeds and Northrup 9834 null detector. The sample was removed and replaced with an empty oxide container. The calorimeter was then calibrated electrically by the replacement method which has been described in the Background section of this report.

Typically, one sample determination per day was run with a total operator time of one hour including calculations.

The calculation of the plutonium content from both the wattage and the isotopic data was performed by utilization of Mound Laboratory's "Plutonium Isotope Accountability Program (S025)". This is an IBM 360-50 compatible program which takes as input the isotopic ratios, specific powers, the time from americium separation to mass spectral determination (which can be determined from the ratio of ^{241}Pu to ^{241}Am found by chemical analysis), and the time from mass spectrometric analysis to calorimetric determinations. The total quantity of plutonium in grams at the date of the mass spectral analysis, the grams of each plutonium isotope, the power of each isotope on the date of the calorimetric analysis, and the total sample power by day for any period of time desired are calculated and printed out. The decay constants used in this program are given in Table 3, and an example of a manual calculation of each sample is given in the appendix.

Figure 6: Approach to Equilibrium for Feed Material Sample

Table 3

NUCLEAR CONSTANTS FOR ISOTOPES IN PLUTONIUM FUEL

Isotope	Average Total Disintegration Energy (MeV)	Type Decay	$T_{\frac{1}{2}}$ (yr)	Specific Power (W/g)
$^{238}\text{Pu}^{\text{a, b, c}}$	5.592	α	87.78	5.6642×10^{-1}
$^{239}\text{Pu}^{\text{d}}$	5.243	α	24,140	1.924×10^{-3}
$^{240}\text{Pu}^{\text{e}}$	5.255	α	6,538	7.089×10^{-3}
$^{241}\text{Pu}^{\text{c}}$	0.00721	β	14.39	3.389×10^{-3}
$^{242}\text{Pu}^{\text{a}}$	4.98	α	379,000	1.146×10^{-4}
$^{241}\text{Am}^{\text{e}}$	5.635	α	432.7	1.1450×10^{-1}

^a See reference 8.

^b See reference 9.

^c K. C. Jordan and W. A. Wellman, Mound Laboratory Memorandum (unpublished) to Los Alamos Scientific Laboratories on "Calorimetric Standardization of IASL ^{238}Pu $^{16}\text{O}_2$ Heat Source 30-C5," Aug. 1970.

^d See reference 10.

^e See reference 11.

RESULTS

A total of 27 runs were made on the two samples and the results are shown in Tables 4 and 5. Graphs of these results (see Figures 7 and 8) demonstrate the following two points: first, the precision of the measurements on the unknown was well within that determined on the standard heat source used to check the instrument ($2\sigma = 0.03\%$ versus 0.05%). Thus, the unknowns were as easy to reproduce as the known. The second point is the rate of growth of the power due to ^{241}Pu . When calorimetry is used as a comparison for shipper-receiver reports, tampering with the sample would be an extremely difficult task and could be detected by comparing both the total power and the rate of growth of the sample power (see Table 6). For example, in 8 days the power of the LWR sample grows 0.1% and for the FRF sample this change takes 11 days.

Table 4

LIGHT WATER REACTOR SAMPLE

<u>Run</u>	<u>Day</u>	<u>Date</u>	<u>Calorimeter Value (W)</u>	<u>Amount of Pu at time of Mass Spectrometry (g)</u>	<u>Deviation (g)</u>
I	1587	5/07/70	4.64799	905.80	-0.12
II	1588	5/08/70	4.64973	906.03	+0.11
III	1591	5/11/70	4.64973	905.70	-0.23
IV	1592	5/12/70	4.65160	905.95	+0.03
V	1593	5/13/70	4.65294	906.10	+0.18
VI	1594	5/14/70	4.65266	905.94	+0.02
VII	1595	5/15/70	4.65305	905.90	-0.02
VIII	1627	6/16/70	4.67109	905.88	-0.04
IX	1628	6/17/70	4.67159	905.86	-0.06
X	1629	6/18/70	4.67276	905.98	+0.06
XI	1630	6/19/70	4.67389	906.09	+0.17
XII	1633	6/22/70	4.67466	905.94	-0.01
XIII	1634	6/23/70	4.67471	905.81	-0.11

Mean 905.95

Average (for day 1611) = 3.05944 905.98

$$\sigma = \sqrt{\frac{\sum D^2}{n-1}} = 0.12 \text{ g}$$

$$2\sigma = 0.23 \text{ g} = 0.025\%$$

Table 5

FAST REACTOR FEED

<u>Run</u>	<u>Day</u>	<u>Date</u>	<u>Calorimeter Value (W)</u>	<u>Amount of Pu at time of Mass Spectrometry (g)</u>	<u>Deviation (g)</u>
I	1598	5/18/70	3.05552	985.15	-0.14
II	1599	5/19/70	3.05643	985.36	+0.07
III	1600	5/20/70	3.05631	985.24	-0.05
IV	1601	5/21/70	3.05709	985.40	+0.11
V	1602	5/22/70	3.05717	985.34	+0.05
VI	1605	5/25/70	3.05739	985.16	-0.13
VII	1606	5/26/70	3.05797	985.26	-0.03
VIII	1607	5/27/70	3.05826	985.27	-0.02
IX	1612	6/01/70	3.05964	985.29	0.00
X	1616	6/05/70	3.06082	985.33	+0.04
XI	1619	6/08/70	3.06095	985.12	-0.17
XII	1621	6/10/70	3.06235	985.40	+0.11
XIII	1635	6/24/70	3.06649	985.55	+0.26
XIV	1636	6/25/70	3.06573	985.22	-0.07

Mean 985.29

Average (for day 1609) = 4.66126

985.31

$$\sigma = \sqrt{\frac{\sum D^2}{n-1}} = 0.12 \text{ g}$$

$$2\sigma = 0.23 \text{ g} = 0.024\%$$

Figure 7 - Decay values for the LWR sample (also, see Table 3).

Figure 8 - Decay values for the FBR sample (also, see Table 4).

Table 6

CALCULATED LWR SAMPLE POWER AS A FUNCTION OF TIME

ALL INTERVALS ARE MEASURED FROM T(0)= 1/1/66
 MASS SPEC RATIOS ARE AS OF DAY 1545.69200

3-26-70

M1 = 0.213519018839006D 01 grams ^{238}Pu ALL VALUES AT DATE OF
 W1 = 0.120941442650790D 01 watts ^{238}Pu CALORIMETRY EXCEPT G
 M2 = 0.685343648041317D 03 grams ^{238}Pu
 W2 = 0.131860117883149D 01 watts ^{238}Pu
 M3 = 0.166914777120359D 03 grams ^{240}Pu
 W3 = 0.118325885500623D 01 watts ^{240}Pu
 M4 = 0.411952597097213D 02 grams ^{241}Pu
 W4 = 0.139610735156245D 00 watts ^{241}Pu
 C = 0.568884537810973D 01 C-D = watts of Am
 D = 0.474000897271995D 01
 M5 = 0.100382637860723D 02 grams ^{242}Pu
 W5 = 0.115018426460817D-02 grams ^{242}Pu
 G = 0.905980486107612D 03 grams total Pu at mass spectral analysis date

	Sample Power (W)	Time (Days from Jan. 1, 1966)
T = -0.240000000000000D 02	WS = 0.464761101296165D 01	1585
T = -0.230000000000000D 02	WS = 0.464818068144913D 01	
T = -0.220000000000000D 02	WS = 0.464875026994452D 01	
T = -0.210000000000000D 02	WS = 0.464931977845829D 01	
T = -0.200000000000000D 02	WS = 0.464988920700089D 01	
T = -0.190000000000000D 02	WS = 0.465045855558278D 01	1590
T = -0.180000000000000D 02	WS = 0.465102782421440D 01	
T = -0.170000000000000D 02	WS = 0.465159701290623D 01	
T = -0.160000000000000D 02	WS = 0.465216612166870D 01	
T = -0.150000000000000D 02	WS = 0.465273515051227D 01	
T = -0.140000000000000D 02	WS = 0.465330409944739D 01	1595
T = -0.130000000000000D 02	WS = 0.465387296848451D 01	
T = -0.120000000000000D 02	WS = 0.465444175763406D 01	
T = -0.110000000000000D 02	WS = 0.465501046690651D 01	
T = -0.100000000000000D 02	WS = 0.465557909631229D 01	
T = -0.900000000000000D 01	WS = 0.465614764586134D 01	1600
T = -0.800000000000000D 01	WS = 0.465671611556561D 01	
T = -0.700000000000000D 01	WS = 0.465728450543403D 01	
T = -0.600000000000000D 01	WS = 0.465785281547754D 01	
T = -0.500000000000000D 01	WS = 0.465842104570659D 01	
T = -0.400000000000000D 01	WS = 0.465898919613161D 01	1605
T = -0.300000000000000D 01	WS = 0.465955726676302D 01	
T = -0.200000000000000D 01	WS = 0.466012525761177D 01	
T = -0.999999999999999D 00	WS = 0.466069316868679D 01	
T = 0.0	WS = 0.466126100000000D 01	1609
T = 0.999999999999999D 00	WS = 0.466182875156134D 01	
T = 0.200000000000000D 01	WS = 0.466239642338173D 01	
T = 0.300000000000000D 01	WS = 0.466296401547010D 01	
T = 0.400000000000000D 01	WS = 0.466353152783838D 01	
T = 0.500000000000000D 01	WS = 0.466409896049648D 01	
T = 0.600000000000000D 01	WS = 0.466466631345483D 01	1615
T = 0.700000000000000D 01	WS = 0.466523358672386D 01	
T = 0.800000000000000D 01	WS = 0.466580078031397D 01	
T = 0.900000000000000D 01	WS = 0.466636789473559D 01	
T = 0.100000000000000D 02	WS = 0.466693492849914D 01	
T = 0.110000000000000D 02	WS = 0.466750188311503D 01	1620
T = 0.120000000000000D 02	WS = 0.466806875809368D 01	
T = 0.130000000000000D 02	WS = 0.466863555344549D 01	
T = 0.140000000000000D 02	WS = 0.466920226918089D 01	
T = 0.150000000000000D 02	WS = 0.466976890531027D 01	
T = 0.160000000000000D 02	WS = 0.467033546184405D 01	1625
T = 0.170000000000000D 02	WS = 0.467090193879264D 01	
T = 0.180000000000000D 02	WS = 0.467146833616644D 01	
T = 0.190000000000000D 02	WS = 0.467203465397585D 01	
T = 0.200000000000000D 02	WS = 0.467260089223128D 01	
T = 0.210000000000000D 02	WS = 0.467316705094314D 01	1630
T = 0.220000000000000D 02	WS = 0.467373313012182D 01	
T = 0.230000000000000D 02	WS = 0.467429912977771D 01	
T = 0.240000000000000D 02	WS = 0.467486504992123D 01	
T = 0.250000000000000D 02	WS = 0.467543089056276D 01	
T = 0.260000000000000D 02	WS = 0.467599665171271D 01	1635

Table 7

CALCULATED FAST REACTOR FEED SAMPLE POWER AS A FUNCTION OF TIME

ALL INTERVALS ARE MEASURED FROM T(0) = 1/1/66
 MASS SPEC RATIOS ARE AS OF DAY 1557.00000

4 -7-70

M1 = 0.570838586339664D 00 grams ^{238}Pu ALL VALUES AT DATE OF
 W1 = 0.323334392074512D 00 watts ^{238}Pu CALORIMETRY EXCEPT G

M2 = 0.844171852128744D 03 grams ^{239}Pu
 W2 = 0.162418664349570D 01 watts ^{239}Pu

M3 = 0.119329249199925D 03 grams ^{240}Pu
 W3 = 0.845925047578266D 00 watts ^{240}Pu

M4 = 0.189849401786979D 02 grams ^{241}Pu
 W4 = 0.643399622656072D -01 watts ^{241}Pu

C = 0.244627137521203D 01 C-D = watts of Am
 D = 0.218444518684134D 01

M5 = 0.211841927755174D 01 grams ^{242}Pu
 W5 = 0.242728480821878D -03 grams ^{242}Pu

G = 0.985311291884528D 03 grams total Pu at mass spectral analysis date

		Sample Power (W)		Time (Days from Jan. 1, 1966)
T = -0.130000000000000D 02	WS = 0.305600789609829D 01			
T = -0.120000000000000D 02	WS = 0.305627181468691D 01			
T = -0.110000000000000D 02	WS = 0.305653569687671D 01			1600
T = -0.100000000000000D 02	WS = 0.305679954267244D 01			
T = -0.900000000000000D 01	WS = 0.305706335207886D 01			
T = -0.800000000000000D 01	WS = 0.305732712510070D 01			
T = -0.700000000000000D 01	WS = 0.305759086174271D 01			
T = -0.600000000000000D 01	WS = 0.305785456200963D 01			1605
T = -0.500000000000000D 01	WS = 0.305811822590622D 01			
T = -0.400000000000000D 01	WS = 0.305838185343720D 01			
T = -0.300000000000000D 01	WS = 0.305864544460733D 01			
T = -0.200000000000000D 01	WS = 0.305890899942134D 01			
T = -0.99999999999999D 00	WS = 0.305917251788399D 01			1611
T = 0.0	WS = 0.305943600000000D 01			
T = 0.99999999999999D 00	WS = 0.305969944577412D 01			
T = 0.200000000000000D 01	WS = 0.305996285521109D 01			
T = 0.300000000000000D 01	WS = 0.306022622831564D 01			1615
T = 0.400000000000000D 01	WS = 0.306048956509252D 01			
T = 0.500000000000000D 01	WS = 0.306075286554646D 01			
T = 0.600000000000000D 01	WS = 0.306101612968226D 01			
T = 0.700000000000000D 01	WS = 0.306127935750448D 01			
T = 0.800000000000000D 01	WS = 0.306154254901802D 01			
T = 0.900000000000000D 01	WS = 0.306180570422758D 01			1620
T = 0.100000000000000D 02	WS = 0.306206882313788D 01			
T = 0.110000000000000D 02	WS = 0.306233190575365D 01			
T = 0.120000000000000D 02	WS = 0.306259495207963D 01			
T = 0.130000000000000D 02	WS = 0.306285796212055D 01			
T = 0.140000000000000D 02	WS = 0.306312094588115D 01			1625
T = 0.150000000000000D 02	WS = 0.306338387336615D 01			
T = 0.160000000000000D 02	WS = 0.306364677458028D 01			
T = 0.170000000000000D 02	WS = 0.306390963952329D 01			
T = 0.180000000000000D 02	WS = 0.306417246821489D 01			
T = 0.190000000000000D 02	WS = 0.306443526064431D 01			1630
T = 0.200000000000000D 02	WS = 0.306469801682279D 01			
T = 0.210000000000000D 02	WS = 0.306496073675354D 01			
T = 0.220000000000000D 02	WS = 0.306522342044181D 01			
T = 0.230000000000000D 02	WS = 0.306548606789231D 01			
T = 0.240000000000000D 02	WS = 0.306574867910977D 01			1635
T = 0.250000000000000D 02	WS = 0.306601125409892D 01			

Tables 6 and 7 are computer printouts for each sample giving watts and grams of each plutonium isotope as of the calorimetry date and total grams of plutonium (G) as of mass spectrometric analysis date. Also given is sample power versus day (day 1612 = June 1, 1970). This type of printout can be used to give a quick check for shipper-receiver comparisons.

Table 8 gives the comparison of these values with shipper values. The differences (+1.1% for the LWR sample and -0.5% for the FRF sample) are less than half of the error possible due to the uncertainty in the mass ratios.

Table 8

COMPARISON OF CALORIMETRY RESULTS WITH SHIPPER VALUES

Sample:	LWR	FRF
Shipper Value (grams plutonium):	896.24	990.3
Calorimetry value (grams plutonium):	905.98	985.3
Difference (grams) (Cal. value - shipper value):	+9.74	-5.0
Difference (%):	+1.1	-0.5

Table 9 gives an estimate of the possible errors for each sample. The error in the plutonium content is included as part of the error in americium concentration. The maximum possible calorimeter error, 0.05%, is considered insignificant and not included. The estimated uncertainties are intended to be representative of industrial facilities. In any case, it is quite clear that the major source of error is uncertainty in the ^{238}Pu isotopic ratio.³ As stated earlier, there are several reasons for this. First, its specific power is 250 times greater than ^{239}Pu . Second, the ^{238}Pu peak is affected by "toe-tailing" from the adjacent, large ^{239}Pu peak in the mass spectrometry analysis. There is a distinct possibility that the results might be improved by paying more attention to this region of the mass spectrum. The ^{238}Pu abundance can be determined more accurately by performing a separate α pulse height analysis for ^{238}Pu . The extent of these limitations is best visualized when one considers that if the uncertainty in the ^{238}Pu ratio were reduced to 2%, it would still be a larger source of error than all of the other uncertainties combined.

Table 9

ERROR IN CALORIMETRY ANALYSIS DUE TO UNCERTAINTIES IN ANALYTICAL DATA

<u>Isotope</u>	<u>Weight Percent</u>	<u>Heat (%)</u>	<u>Estimated Uncertainty in Isotopic Ratio (%)</u>	<u>Potential Error^a (%)</u>
<u>LWR Sample</u>				
²³⁸ Pu	0.24	26.3	10	2.63
²³⁹ Pu	75.65	28.8	0.3	0.08
²⁴⁰ Pu	18.42	25.8	0.3	0.08
²⁴¹ Pu	4.59	3.0	1.0	0.03
²⁴² Pu	1.11	--	1.0	--
Am	0.74	16.1	1.0	0.16
TOTAL	100.74	100.0	$\left[\sum(x_i)^2\right]^{\frac{1}{2}} = 2.64$	
<u>FBR Sample</u>				
²³⁸ Pu	0.06	10.6	10.0	1.06
²³⁹ Pu	85.68	53.2	0.3	0.16
²⁴⁰ Pu	12.11	27.7	0.3	0.08
²⁴¹ Pu	1.94	2.1	1.0	0.02
²⁴² Pu	0.22	--	1.0	--
Am	0.16	6.4	1.0	0.06
TOTAL	100.16	100.0	$\left[\sum(x_i)^2\right]^{\frac{1}{2}} = 1.17$	

^aEstimated error = Heat (%) x Estimated Uncertainty in Isotopic Ratio (%).

CONCLUSIONS

In conclusion, calorimetry provides a well-established, precise, and nondestructive method for the assay of radioactive materials. Furthermore, high accuracies may be obtained if the radioactive constituents of the sample are well characterized. The sample geometry is such that the entire sample is measured simultaneously. Therefore, the need for taking aliquots is eliminated along with associated errors. Unlike other nuclear nondestructive methods, calorimetry is capable of bulk measurements unaffected by absorption or self-shielding so that sample homogeneity is not a problem. Calorimetry appears to be a very effective method of analysis in cases where the power density is sufficiently high as in PuO_2 . Current investigations indicate that calorimetry gives fairly good agreement with traditional chemical methods. Further, it might be possible to bypass the usual errors associated with the transfer of large quantities of material by accepting the agreement between the heat output determined by the receiver and that predicted by the shipper. It appears that this would give differences of 0.1% or less. Improved methods of measuring isotopic ratios, particularly one which would more precisely determine the amount of ^{238}Pu , would enable more accurate absolute determination of plutonium quantities. The excellent precision and accuracy shown here suggests that shipper-receiver exchanges be based on measured wattages. It would be extremely difficult for anyone to deliberately circumvent this system by the substitution of material having a different specific activity since this would require knowledge of the date on which the receiver would measure the heat output. Any undetected tampering of this sample would necessitate that the composite total specific powers of the substitute, as well as the rate of change of its specific power, exactly match that of the undisturbed sample. This would hardly be possible unless the constituent isotopes of the substitute were the same as that of the original and further that they were present in the same quantities so as to make the rate of change of the power output identical. One would hardly want to divert a quantity of fissile material if he had to replace it with the same quantity of identical material in order to prevent the detection of his diversion.

FUTURE PLANS

The applicability of calorimeters to the solution of Safeguards problems will continue to be investigated. The feasibility of using a calorimeter to determine the quantity of plutonium in lots of fuel pellets, platelets and high density scrap will be investigated. The possibility of using calorimeters to ascertain the actual abundances of various isotopes in standard samples will be pursued by analyzing the effect of various isotopic compositions on the rate of change of the sample power. This would permit an independent, absolute, and nondestructive calibration of these standards for use with other nuclear methods of analysis.

The potential use of calorimetry to determine amounts of uranium by inducing fission in a sample residing in the calorimeter will be considered. A preliminary analysis will be made of the quantity of power to be expected from a particular sample and source neutron flux. If this appears to be practical the work will expand to study geometry, packaging and other effects which may limit the accuracy.

Participation in the Plant Instrumentation Program sponsored by the AEC Office of Safeguards and Materials Management will be continued. Calorimeters are being furnished to industrial participants for use in the feed material and scrap phases. In addition, Mound Laboratory will function as consultants to those who are pursuing this type of analysis.

APPENDIX

MANUAL CALCULATION OF PLUTONIUM CONTENT IN LWR AND FBR FUEL SAMPLES

The exact calculation of plutonium content from calorimetry date requires the isotopic ratios first be decayed from the mass spectral analysis date to the calorimetry date. Then the mass ratios multiplied by the specific power are summed to give a weighted specific power of the sample in terms of watts per gram of plutonium. This value is then divided into the total power to give total grams at the date of isotopic analysis. The following involves a manual calculation of the plutonium content in an LWR sample

First, the americium concentration is normalized to plutonium content:

$$\frac{\text{Am Concentration}}{\text{Plutonium Content}} = \frac{0.006334}{0.8636} = 0.007334 \text{ g of Am/g of Pu.} \quad (1)$$

Next, each Pu isotopic ratio is decayed 63 days and the normalized Am concentration 78 days to the calorimetry date. To simplify this, Table A-1 shows $e^{-\lambda t}$ versus time for LWR and FBR samples. For four figure accuracy, it is not necessary to decay the isotopic ratios for ^{239}Pu , ^{240}Pu and ^{242}Pu . For ^{238}Pu and Am, first determine the number of days, months and years the sample is to be decayed. Next, find the decay factor ($e^{-\lambda t}$) on each table and multiply them together for the total decay. For example, to decay ^{241}Pu 65 days (2 months and 5 days):

$$e^{-\lambda t} = 0.992037 \times 0.999344 = 0.991386 \quad (2)$$

Also included in Table A-1 is a section giving the approximate amount of americium which grows in as a function of time due to the β -decay of ^{241}Pu . This should be calculated from the date of the americium analysis to include the amount which grows between the mass spectral analysis and americium analysis. To obtain the amount of ^{241}Pu which was present during americium analysis, it is necessary to back decay its isotopic ratio 15 days. This can be done by taking the decay factor for 15 days from the ^{241}Pu section in Table A-1 and dividing it into the isotopic ratio.

$$\begin{aligned} ^{241}\text{Pu at americium analysis} &= \frac{^{241}\text{Pu at mass spec}}{(e^{-\lambda t})} \\ &= \frac{0.04585}{0.998032} \\ &= 0.04594 \end{aligned} \quad (3)$$

The amount of americium which has grown in since americium analysis can be calculated from the following equation:

$$\frac{N_2}{N_1^0} = \frac{\lambda_1}{\lambda_2 - \lambda_1} [e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (4)$$

The ratio of ingrown ^{241}Am to ^{241}Pu present at day zero is N_2/N_1 and is computed in terms of days, months and years in Table A-1 at the end of this appendix. Here the factors are additive rather than multiplicative. For example, for 78 days after americium, add the factor for two months (60.9 days) to the factor for 17 days.

$$\frac{N_2}{N_1} = 0.00796 + 0.00223 = 0.01019$$

Table A-2 gives a summary of the Pu isotopic ratio calculation in the LWR sample. An additional example using the FBR sample is summarized in Table A-3.

Table A-1

DECAY FACTORS ($e^{-\lambda t}$) FOR VARIOUS ISOTOPES IN LWR AND FBR FUEL SAMPLES

Years	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{241}Am	^{241}Am Ingrowth ^a	Years
1	.99213378	.99997128	.99989398	.95316365	.99839937	.04679855	1
2	.98432945	.99994257	.99973798	.90852095	.99680130	.09133032	2
3	.97658651	.99991386	.99968199	.86596915	.99520579	.13370159	3
4	.96890447	.99988515	.99957601	.82541032	.99361283	.17401369	4
5	.96128286	.99985644	.99947004	.78675112	.99202243	.21236316	5
6	.95372121	.99982773	.99936409	.74990257	.99043457	.24884206	6
7	.94621904	.99979902	.99925814	.71477988	.98884925	.28353811	7
8	.93877588	.99977031	.99915221	.68130220	.98726647	.31653493	8
9	.93139127	.99974161	.99904629	.64939250	.98568622	.34791224	9
10	.92406475	.99971290	.99894037	.61897733	.98410850	.37774598	10
Months							Months
1	.99934210			.99601059	.99986651	.00398914	1
2	.99868464			.99203709	.99973305	.00796183	2
3	.99802761			.98807945	.99959960	.01191815	3
4	.99737102			.98413759	.99946617	.01585815	4
5	.99671486			.98021147	.99933275	.01978190	5
6	.99605912			.97630100	.99919936	.02368946	6
7	.99540382			.97240614	.99906598	.02758090	7
8	.99474895			.96852681	.99893262	.03145629	8
9	.99409452			.96466296	.99879928	.03531568	9
10	.99344051			.96081452	.99866596	.03915915	10
11	.99278693			.95698144	.99853265	.04298675	11
12	.99213378			.95316365	.99839937	.04679855	12
Days							Days
1	.99997837			.99986867		.00013132	1
2	.99995675			.99973736		.00026263	2
3	.99993513			.99960607		.00039392	3
4	.99991351			.99947480		.00052519	4
5	.99989189			.99934354		.00065644	5
6	.99987027			.99921230		.00078768	6
7	.99984865			.99908108		.00091890	7
8	.99982703			.99894988		.00105010	8
9	.99980542			.99881869		.00118128	9
10	.99978380			.99868752		.00131244	10
11	.99976218			.99855637		.00144359	11
12	.99974056			.99842523		.00157472	12
13	.99971895			.99829411		.00170583	13
14	.99969733			.99816301		.00183692	14
15	.99967572			.99803193		.00196800	15
16	.99965410			.99790086		.00209906	16
17	.99963249			.99776981		.00223010	17
18	.99961087			.99763878		.00236112	18
19	.99958926			.99750776		.00249212	19
20	.99956765			.99737676		.00262311	20
21	.99954603			.99724578		.00275408	21
22	.99952442			.99711482		.00288503	22
23	.99950281			.99698387		.00301596	23
24	.99948120			.99685294		.00314688	24
25	.99945959			.99672203		.00327778	25
26	.99943798			.99659114		.00340866	26
27	.99941637			.99646026		.00353952	27
28	.99939476			.99632940		.00367037	28
29	.99937315			.99619856		.00380119	29
30	.99935154			.99606773		.00393200	30

$$^a \frac{N_2}{N_1, 0} = \frac{\lambda_1}{\lambda_2 - \lambda_1} [e^{-\lambda_1 t} - e^{-\lambda_2 t}]$$

Table A-2

LWR PLUTONIUM HAND CALCULATION

Isotope	Mass Ratio (R_i)	Specific Power (F_i)	Decay Factor ($e^{-\lambda_i t}$)	$R_i F_i e^{-\lambda_i t}$
^{238}Pu	0.00236	0.56642	0.998598	0.0013349
^{239}Pu	0.75647	0.001924	1.0000	0.0014554
^{240}Pu	0.18424	0.007089	1.0000	0.0013061
^{241}Pu	0.04585	0.003389	0.991516	0.0001541
^{242}Pu	0.01108	0.0001146	1.0000	0.0000013
^{241}Am	0.007334	0.1145	0.999734	0.0008395
Ingrowth Am	0.04594	0.1145	0.01045	0.0000550
Total				0.0051463

$$\text{Pu Content} = \frac{\text{Av. Calorimeter Value (watts)}}{\text{Specific Power of Sample}} = \frac{4.6613}{0.0051463} = 905.8\text{g}$$

Calorimetry date = 63 days after mass spectral analysis and 78 days after americium analysis.

Table A-3

FBR PLUTONIUM HAND CALCULATION

Isotope	Mass Ratio (R_i)	F_i	$e^{-\lambda t}$	$R_i F_i e^{-\lambda_i t}$
^{238}Pu	0.00058	0.56642	0.9987	0.0003281
^{239}Pu	0.85676	0.001924	1.0000	0.0016484
^{240}Pu	0.12111	0.007089	1.0000	0.0008585
^{241}Pu	0.01940	0.003389	0.9915	0.0000652
^{242}Pu	0.00215	0.000115	1.0000	0.0000002
Am	0.001579	0.1145	0.9996	0.0001807
Am Ingrowth	0.01944	0.1145	0.01045	0.0000233
Total				0.0031044

$$\text{Pu Content} = \frac{\text{Av. Calorimeter Value (watts)}}{\text{Specific Power of Sample}} = \frac{3.0594}{0.0031044} = 985.5\text{g}$$

Calorimetry date = 65 days after mass spectral analyses and 80 days after americium analyses.

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