

10. PRINCIPLES AND APPLICATIONS OF CALORIMETRIC ASSAY

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I. Introduction

Calorimetry is the quantitative measurement of heat. Applications of calorimetry include measurements of the specific heats of elements and compounds, phase-change enthalpies, and the rate of heat generation from radionuclides. The most successful radiometric calorimeter designs fit the general category of heat-flow calorimeters. Calorimetry is used as a nondestructive assay (NDA) technique for determining the power output of heat-producing nuclear materials. The heat is generated by the decay of radioactive isotopes within the item. Because the heat-measurement result is completely independent of material and matrix type, it can be used on any material form or item matrix. Heat-flow calorimeters have been used to measure thermal powers from 0.5 mW (0.2 g low-burnup plutonium equivalent) to 1,000 W for items ranging in size from less than 2.54 cm to 60 cm in diameter and up to 100 cm in length.

Calorimetric assay is the determination of the mass of radioactive material through the combined measurement of its thermal power by calorimetry and its isotopic composition by gamma-ray spectroscopy or mass spectroscopy. Calorimetric assay has been routinely used at U.S. and European facilities for plutonium process measurements and nuclear material accountability for the last 40 years [EI54, GU64, GU70, ANN15.22, AS1458, MA82, IAEA87]. Calorimetric assay is routinely used as a reliable NDA technique for the quantification of plutonium and tritium content. Calorimetric assay of tritium and plutonium-bearing items routinely obtains the highest precision and accuracy of all NDA techniques. Plutonium items usually contain varying amounts of ^{241}Am , which can be accounted for during the assay.

Uniqueness of Calorimetry NDA

Advantages

Calorimetric assay offers several distinct advantages over other NDA techniques and chemical analysis as follows:

- The calorimeter heat measurement is completely independent of material and matrix type; self attenuation cannot occur.
- No physical standards are required.
- The thermal power measurement is traceable to the U.S. or other National Measurement Systems through electrical standards used to directly calibrate the calorimeters or to calibrate secondary ^{238}Pu heat standards.
- Calorimetric assay can be used to prepare secondary standards for neutron and gamma-ray assay systems [IAEA87, AS1207, HY99, LE00].
- The heat from the entire item is measured, and the response of a well-designed calorimeter is independent of the source location inside the measurement chamber.
- P_{eff} remains the same (with correction for nuclear decay) as long as the isotopic composition is not changed; therefore, the same P_{eff} is applicable to a batch of material regardless of form.
- Calorimetry is very precise and nearly bias free. Biases can be quantitatively determined during instrument calibration.
- Only nuclear criticality safety considerations and the volume of the measurement chamber limit the quantity of material that can be measured in a calorimeter.
- Calorimetric assay is the most accurate method, NDA or otherwise, for the measurement of tritium and ^{241}Am .

- Calorimetry is the only practical measurement technique available for many physical forms of tritium compounds.

Limitations

Calorimetric assay is largely independent of the distribution of the nuclear materials in the matrix, but the accuracy can be degraded for materials with inhomogeneous isotopic composition because of uncertainty in determining the effective specific power. Calorimetry measurement times are typically longer than other NDA techniques. The packaging cannot change the heat output of the material but it is usually the determining factor for measurement time. Typical assay times are between one and eight hours. The calorimeter cannot distinguish between heat produced by radioactive decay and heat produced by other sources (e.g., phase changes and chemical reactions).

Heat from chemical reactions is generally not an issue because most items measured with calorimetric assay are hermetically sealed dry items. In addition, any large time dependence on the heat output would be an indication of heat from a chemical reaction.

Thermal Power Production from Radionuclides

The principal decay modes, specific heats, half-lives, and the associated uncertainties are listed in Table 1 for all plutonium isotopes, ^{241}Am , and tritium. Included in Table 1 are the specific power and half lives for uranium isotopes. The majority of the heat measured by calorimetry is due to spontaneous alpha-particle emission, except for ^{241}Pu and tritium, which predominately decay through beta decay. Each radionuclide has a disintegration energy associated with its particular decay scheme; for example, ^{240}Pu decays to ^{236}U with the emission of an alpha particle and the release of 5.15 MeV. The total reaction energy for alpha decay is the sum of the alpha-particle kinetic energy and the recoil energy of the daughter nucleus. The alpha particle and daughter nucleus have very short ranges in matter. Thus, virtually all of the energy released by alpha decay will remain within the item as heat. If the daughter product is not in the ground state after decay, an additional small amount of energy is released in the form of gamma-ray and internal conversion electron energy. The electron and low-energy gamma-ray energy is absorbed in the item. The rate of energy emission is equal to the product of the total decay energy and the activity. This product for a single radionuclide is called specific power, P , and is used to convert the power measurement into a mass of material. For multi-isotopic items, the analytical factor used to convert the heat measurement to mass of material is effective specific power, P_{eff} . The determination of P and P_{eff} will be discussed in later sections.

The determination of energy losses in matter is more complicated for beta emitters than with alpha emitters. With beta decay, the total reaction energy is in the form of a beta particle, neutrino, and the excitation and recoil energy of the daughter. The energy loss due to bremsstrahlung radiation, emitted as a result of deceleration of the beta particle, is negligible for ^{241}Pu and tritium; therefore, nearly all of the kinetic energy of the beta particle is absorbed by the item as heat. The neutrino is not absorbed in the item, therefore its energy is lost. The thermal power measured by a calorimeter from beta-decaying radionuclides is the product of the activity and the average beta-particle energy, which is on average one third of the maximum disintegration energy.

All of the uranium and plutonium isotopes listed in Table 1 have very small spontaneous fission branching ratios. When fission does occur, the fission daughter products will deposit all of their kinetic energy within the item. After fission, the daughter products can initially be in an excited energy state; this small amount of energy is released in the form of gamma rays and internal conversion electrons. The low-energy electromagnetic emissions will be highly attenuated in the item, container, and walls of the calorimeter depositing their energy with a resultant rise in the temperature of the calorimeter measurement well. The higher energy gamma-ray emissions can escape the calorimeter with minimal attenuation; thus, their energy is not measured. Another product of fission is neutrons. Because neutrons are very penetrating, a portion of the neutrons will escape the calorimeter without depositing their kinetic energy. The resultant total heat and heat loss because of fission is extremely small (<<1%) compared to the total heat release of the items measured. Quantitative details can be found in reference [BR02].

Isotope	Dominant Decay Mode ¹	Specific Power (mW/g)	% Std. Dev.	T ^{1/2} (y)	% Std. Dev.	References
²³⁸ Pu	α	567.57	0.05	87.74	0.05	WA77,ST78
²³⁹ Pu	α	1.9288	0.02	24119	0.11	ST78,SE78,GU78
²⁴⁰ Pu	α	7.0824	0.03	6564	0.17	RU84,LU84,BE84,ST84,JA78,ST84
²⁴¹ Pu	β	3.412	0.06	14.348	0.15	MA80,GA80,DE81,JO82,OE68
²⁴² Pu	α	0.1159	0.22	376300	0.24	OS76
²⁴¹ Am	α	114.2	0.37	433.6	0.32	JO82,OE67
Tritium	β	324	0.14	12.3232	0.017	RU77
²³³ U	α	2.81E-1	-	1.591E5	-	Calculation
²³⁴ U	α	1.80E-1	-	2.44E5	-	Calculation
²³⁵ U	α	6.00E-5	-	7.038E8	-	Calculation
²³⁶ U	α	1.75E-3	-	2.342E7	-	Calculation
²³⁸ U	α	8.51E-6	-	4.468E9	-	Calculation

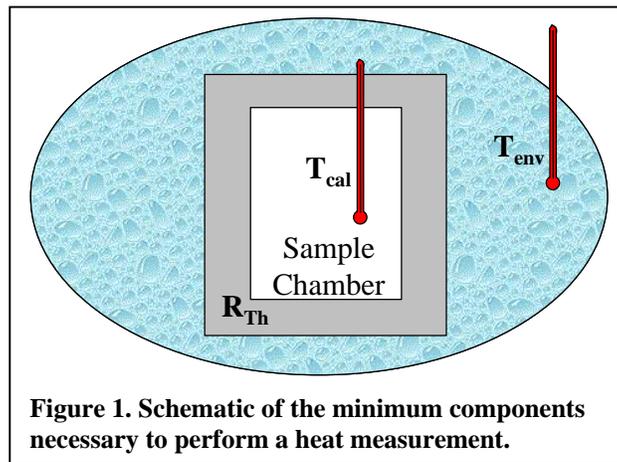
¹For all of the nuclides listed, the dominant decay mode has a branching ratio >99.99%.

A source of heat loss to consider is the loss of neutrons following (α, n) reactions. The lost neutron energy can be shown to be negligible, even for high-efficiency radioisotope neutron generators. For example, the neutron yield for ⁹Be(α, n) per 10⁶ ²⁴¹Am alpha particles is 70. Assuming that all the neutrons escape capture and using the fact that the average neutron energy is comparable to the Q-value of the original alpha decay, the fraction of lost heat would be 0.007%.

II. Heat-Flow Calorimeter Operation, Calibration, and Calculations

All calorimeters have four elements in common: (1) sample chamber, (2) well defined thermal resistance, (3) temperature sensor, and (4) an environment; these components are presented in a simple schematic in Figure 1. The interrelationship of these four components and the hardware that is used for each determine the type of calorimeter.

Radioactive material with a long half-life continuously produces heat at nearly a constant rate. There is some change due to decay and in growth of daughter products, but the time scale for a measurable change is generally weeks to months. Therefore, the most appropriate calorimeter design for radioactive material is an isothermally jacketed heat-flow calorimeter. The design of the calorimeter is determined by the size and heat output of the items to be measured and the required accuracy.



Heat-Flow Calorimeters

A heat-flow calorimeter consists of a sample chamber insulated from a constant temperature environment by thermal resistance and a means to measure the temperature difference across the thermal gradient produced by the thermal resistance and thus the heat generated by an item in the sample chamber. When an item is placed in the calorimeter, the temperature gradient across the thermal resistance is disturbed, and the gradient changes with time until it converges to a constant value and equilibrium is achieved. The heat produced in the sample chamber raises its temperature and causes heat to flow across the thermal resistance into the environment according to

$$\frac{dQ}{dt} = \frac{(T_{cal} - T_{env})}{R_{Th}} = \frac{\Delta T}{R_{Th}}, \quad (1)$$

where Q is the heat energy, R_{Th} is the thermal resistance, T_{cal} is the internal calorimeter temperature, and T_{env} is the external environment temperature. At equilibrium, dQ/dt is constant and ΔT , usually measured in volts, is proportional to the power of the item. The magnitude of the shift in the measured voltage (passive mode) or supplied power (servo mode) is used to determine the thermal power of the item in the calorimeter.

The curve describing the approach of the temperature difference to equilibrium is a function of several exponentials with different time constants. The time constants are related to the specific heats and thermal conductivities of the item matrix material, packaging, and, in some instances, the calorimeter. An example of a typical calorimeter approach to equilibrium is presented in Figure 2. Equilibrium may be detected by visual inspection of the measurement data vs time or through statistical tests [SM03, BU01] performed on a set of the latest data points in the time series. Statistical prediction algorithms [PE88, FE79, MA87, WE97, SM00, SM01] may be used earlier during transient temperature conditions to predict equilibrium and reduce measurement time. These typically consist of exponential functions that are used to fit the measurement data. The fitted parameters are then used to predict the final equilibrium power. The temperature of the item to be measured may be adjusted using preconditioning baths to shorten the time required to reach equilibrium.

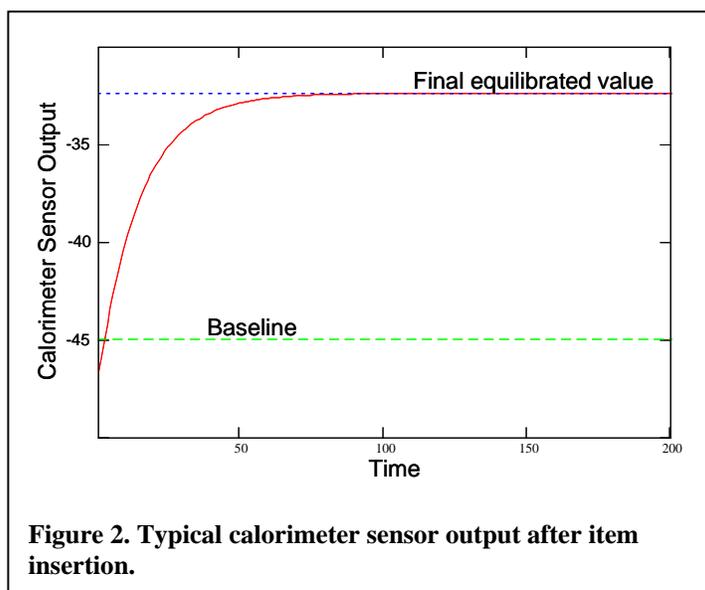


Figure 2. Typical calorimeter sensor output after item insertion.

The type and placement of the temperature sensors, the heat-flow path, and the type of heatsink are what differentiates between types of heat-flow calorimeters used for measuring radionuclides. The heat flow is directed to areas where the sensors are located by the use of conductive and insulating material or controlling temperatures.

The simplicity of a calorimeter measurement would allow a user to manually collect the necessary data to determine the item power by visually taking the sensor readings from the display of a digital multimeter. The results could be calculated by hand following the procedures described later in this Section. In practice it is much better to have a data-acquisition system display results and measurement diagnostics in real time. The data-acquisition system should also calculate results and store data. These software features ultimately increase facility productivity by automatically doing tasks that the operator would need to do manually. The calorimeter data acquisition, control, and analysis software package should be user-friendly, stable, and reliable. Software should store individual meter readings, provide graphical real-time display, reliably detect equilibrium, and provide a means of predicting equilibrium values. Ideally, the software should also be able to control multiple calorimeters with one computer, be easily configurable, and provide assay results in watts [SM00, SM01, BI00].

Calorimetric Assay Overview

The first step in a calorimeter measurement is to determine the zero power sensor output of the calorimeter. This measurement is designated a baseline, BP_0 , for passive calorimeters and basepower, W_0 , for servo-controlled calorimeters. Heat-flow calorimeters are typically operated in one of two modes, passive or servo controlled. Servo-controlled mode is also known as power-replacement mode or active mode. These two modes of operation will be discussed in detail later. The baseline/basepower measurement does not need to be done before every item measurement if the calorimeter is stable with time. The frequency of baseline/basepower measurements is normally determined by facility quality-control statisticians and is based on the observed sensor drift of the calorimeter. All baseline/basepower measurements are performed with no heat-producing material in the measurement chamber of the calorimeter. In some instances, the void space of the measurement well is filled with a low heat capacity thermal conductor to decrease measurement time. The operation of many radiometric calorimeters requires the item to be placed in a "calorimeter can" before being placed in the measurement well of the calorimeter. The "calorimeter can" is an inner liner with a high tolerance fit that prevents accidental contamination of the inside of the calorimeter and can reduce measurement time, if the item is loaded properly into the "calorimeter can," because of good thermal contact with the calorimeter.

The calorimeter must be fully closed before any measurement is initiated. This may include the insertion of insulating plugs into the calorimeter or the movement of the body of the calorimeter into a closed position. No items, such as wires, should transverse the measurement well of the calorimeter to the outside room. A significant source of calorimeter noise is room temperature fluctuations influencing the sensors [SA04].

After the baseline/basepower measurement is completed, the calorimeter is opened and the item to be measured is placed in roughly the volumetric center of the calorimeter measurement well. The void space in the calorimeter or "calorimeter can" should be filled with a conductive material to prevent the possible loss of measurement precision, increasing bias, and/or increased measurement time. An item assay is initiated with the operating software. When thermal equilibrium has been established or predicted, the software should automatically terminate the calorimeter measurement. An additional baseline/basepower run may be taken after the item measurement if indicated by facility baseline/basepower requirements.

Calibration of a calorimeter is necessary to determine the power of an unknown item from the observed calorimeter output. Two types of heat standards are commonly used to calibrate calorimeters. The most reliable type of heat standard used in U.S. facilities is a radioactive source of known power whose calibration is traceable to the National Institute of Standards and Technology (NIST). These standards are normally made from ^{238}Pu oxide that is well characterized both chemically and physically. Plutonium-238 heat standards are used for calibrations more frequently than electrical-resistance heaters. Electrical heat standards contain an electrical circuit consisting of standard resistors and standard voltage cells. Such standards are traceable to the NIST or other national measurement systems. The resistor is used in place of a radioactive source, and the power dissipated in an electrical heater is measured using calibrated meters and calibrated resistors. The specifics of the calorimeter calibration depend on whether the calorimeter is operated in the servo or passive mode. During all calibration measurements, the calorimeter should be operated in the same manner used to make assay measurements.

The magnitude of heat-distribution error and convection noise should be quantified during initial calibration if the calorimeter will be operated under nonideal conditions.

Mass Calculation

The thermal power emitted by a test item is directly related to the quantity of radioactive material in it, and the total power generated by ionizing radiation absorbed in the item is measured by the calorimeter. The mass (m) of radionuclides present is calculated from the measured thermal power of an item (W) using the relationship

$$m = \frac{W}{P_{eff}} \quad , \quad (2)$$

where P_{eff} is the effective specific power calculated from the isotopic composition of the item. For all multinuclide items, the P_{eff} is not a constant and needs to be corrected for the decay and growth of the constituent radionuclides. See reference [RE91A] for details on decay correction of plutonium-bearing items. For monoisotopic items, the specific power, P , of the radioisotope is used in place of P_{eff} . The details of determining P_{eff} and P are discussed in the following two sections.

Specific Power

The specific power, P , is the rate of energy emission by ionizing radiation per unit mass of a single radionuclide. Nuclear decay parameters can be used to calculate the specific power, in watts per gram, of a single radionuclide according to the equation

$$P = \frac{2119.3}{T_{1/2} * A} * Q \quad , \quad (3)$$

where Q is the total disintegration energy (MeV) for alpha-particle emitters, or the average energy (MeV) of beta-particle emitters, $T_{1/2}$ is the half-life (years), and A is the gram atomic weight of the radionuclide. The specific power, P , can also be determined empirically, based on a total heat, W , measurement in watts of a single isotope, i , of known mass, m , of material in grams by rearrangement of Equation 2 to

$$P_i = \frac{W}{m} \quad . \quad (4)$$

The specific powers of a number of radionuclides are listed in Table 1. The values for the plutonium and americium isotopes were taken from reference [ANSI 15.22]. The uranium specific powers were calculated using Equation 3. Examination of Equation 4 shows that the specific power can be determined from direct measurement of an isotopically pure sample. The specific powers of ^{239}Pu , ^{240}Pu , ^{241}Pu , and ^{242}Pu were determined empirically on nearly pure isotopic samples. The ^{239}Pu and ^{240}Pu values were based on collaborative experiments [ST78, SE78, GU78, RU84, LU84, BE84, ST84, JA78, ST84A] while ^{241}Pu and ^{242}Pu specific powers were determined by individual experimenters [MA80, GA80, DE81, JO82, OE68, OS7620-25]. Equation 2 was used to calculate the specific power of ^{238}Pu and ^{241}Am [WA77, ST78, JO82, OE67].

The specific powers listed in Table 1 span a large range of values from a high value of over half a watt per gram of ^{238}Pu to a low value of less than 10 nW per gram of ^{238}U . The magnitude of P is inversely proportional to the half-life of the radionuclides regardless of the element. No isotopic determination is needed to determine total radioactive material mass for items containing a single isotope.

Effective Specific Power

Most items other than tritium do not contain a single radioactive isotope but rather multiple isotopes and/or multiple radioactive elements. An effective specific power, P_{eff} , in units of power per unit mass must be obtained for these items. The effective specific power of the material in the item is calculated by

$$P_{eff} = \sum_i R_i * P_i \quad , \quad (5)$$

where i includes all heat-producing radionuclides present, R_i is the abundance of the i -th radionuclide in the item, typically expressed as a mass fraction, and P_i is the specific power of the i -th radionuclide in the item in watts/gram.

Two methods exist for determining P_{eff} , a computational method and an empirical method. The computational method uses Equation 5 for determining P_{eff} and is appropriate when isotopic composition measurements can be made. The relative abundances of the radionuclides can be determined destructively using mass spectroscopy [ANN104, ANN572, AS697] or nondestructively using gamma-ray spectroscopy [RE91B, AS1030]. When measuring items in sealed containers, high-resolution gamma-ray spectroscopy using intrinsic germanium detectors is the only option for determining P_{eff} . The uncertainties on P_{eff} using gamma-ray measurements for plutonium-bearing items are generally less than 0.5%. If mass spectroscopy is used to determine P_{eff} of plutonium-bearing items, the ^{238}Pu contents should be determined using alpha spectrometry [AS697A] and ^{241}Am contents should be determined radiochemically. The effective specific power uncertainty is normally 0.1%, for isotopically homogeneous items. The computational method using gamma-ray spectroscopy for isotopic analysis is the dominant technique used in conjunction with calorimetry.

The empirical method of determining the effective specific power involves a calorimeter measurement to determine the total power produced by the sample and a chemical analysis to determine the total amount of nuclear material in the sample. Substituting these values into Equation 2 P_{eff} can be determined. The empirical method is potentially more accurate and precise than the computational method. The method can only realistically be implemented cost effectively on discrete batches of process materials or when it is difficult to determine the relative isotopic abundances of an item or batch of material. As with using mass spectroscopy in the computational method, the empirical method is a destructive technique that generates waste and requires long assay times to complete the analysis. These time and waste issues have increased the exclusive use of NDA techniques for the quantitative determination of special nuclear material (SNM) mass.

Passive Mode

In the passive mode, the most basic mode of heat-flow calorimeter operation, the only generated heat comes from the item being measured, and if a Wheatstone bridge sensor is used,

the small resistance heating of the sensors is due to the current required to excite the bridge inside the thermel.

The calibration of a passive mode calorimeter consists of determining the calorimeter sensitivity, S , the conversion factor between the differential voltage or resistance output of the sensor system and the thermal power of the item being measured. Whether radioactive heat standards or electrical calibration heaters are used, a series of calibration points within and bracketing the expected operating range should be measured. The number of points will depend on the magnitude of the calorimeter differential sensitivity and the calibration accuracy required. A minimum of three different standard powers should be used. The form of the calibration curve varies according to the calorimeter design but is usually well represented by a quadratic function.

A baseline measurement of the zero power calorimeter output is made. The equilibrium value of the calorimeter output is recorded as the baseline, $BP_{0(1)}$. A heat standard is then placed in the center of the calorimeter can. A measurement is started, and the equilibrium sensor output is recorded as BP_{std} . A baseline measurement is made after removing the heat source from the calorimeter can and recorded as $BP_{0(2)}$. Whether using radioactive or electrical heat standards, the calorimeter can must be removed from the calorimeter and opened between each measurement, baseline or standard. This removal is necessary even when using electrical standards to simulate as closely as possible real calorimeter operating conditions.

The average baseline, $BP_{0(av)}$ is calculated using

$$BP_{0(av)} = \frac{BP_{0(1)} + BP_{0(2)}}{2}. \quad (6)$$

Using the known power output of the heat standard, W_{std} , the calorimeter sensor value, BP_{std} , and the calculated average baseline, $BP_{0(av)}$, the sensitivity of the calorimeter can be calculated using

$$S = \frac{BP_{std} - BP_{0(av)}}{W_{std}}. \quad (7)$$

The sensitivity, S , is not usually a constant but varies slightly with the wattage of the standard, W_{std} , over the measurement range of the calorimeter. The change in sensitivity with power is described by

$$S = S_0 + k * W_{std}, \quad (8)$$

where S_0 is the mathematically determined sensitivity for zero power and k is the slope of the varying sensitivity. For most calorimeters, the magnitude of k is less than 1% of the zero power sensitivity over the operating power range. The sensitivity usually decreases with increasing power, which is qualitatively consistent with increased thermal conductivity of the material forming the primary thermal resistance. For example, the conductivity of dry air, a common thermal-gap material, increases at the rate of 0.3% per C° . The intrinsic high-order nonlinearity of thermopile sensors can lead to differential sensitivities that are negative or positive but still relatively small compared to the base sensitivity.

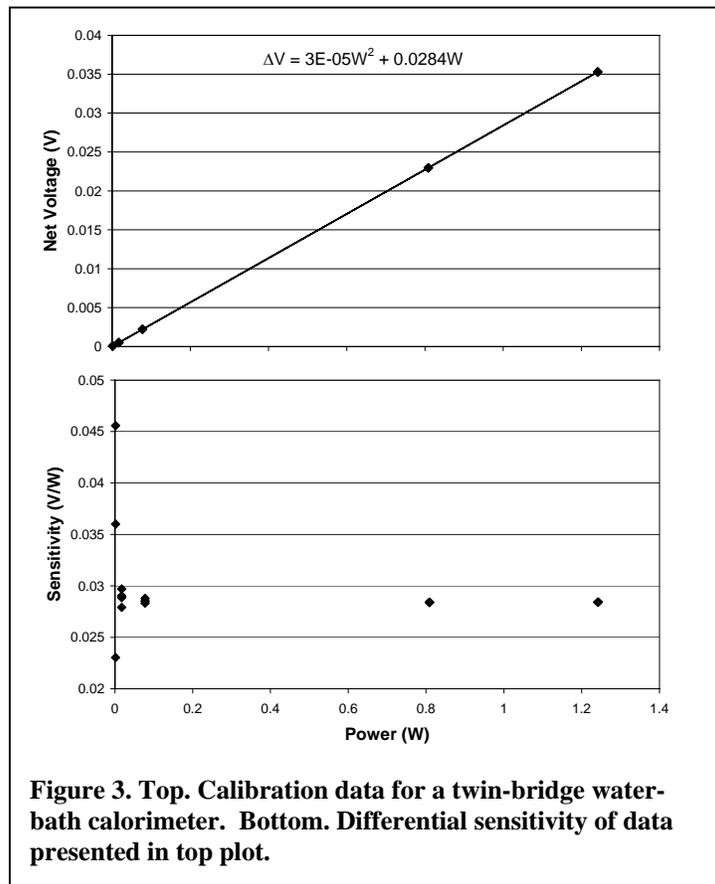
Three replicate measurements (minimum) are made at each power level, with each standard measurement bracketed by a baseline measurement as previously detailed. This detailed sensitivity determination at different power levels is typically done once after a calorimeter is fabricated. By combining Equations 7 and 8 and rearranging for net sensor output, $BP_{std} - BP_{0(av)}$, the equation to relate sensor output to watts is

$$(BP_{std} - BP_{0(av)}) = S_0 * W_{std} + k * W_{std}^2. \quad (9)$$

The fit parameters S_0 and k are determined by a least-squares fit to a plot of net sensor output as a function of standard watts. Because calorimeter noise is a function of the power of the item being measured, increasing variability with increasing power, the residuals of the least-squares fit will not be normally distributed. However, the parameter estimates are not affected by this abnormal distribution.

Actual calibration data used to determine the fit parameters in Equation 9 are presented in Figure 3. The data presented in Figure 3 were obtained using a twin-bridge water-bath calorimeter. Three to five heat standards measurements were made at each power. The linearity of the calorimeter response to power is typical of water-bath calorimeters.

A plot of the first derivative of calorimeter calibration data is normally designated a differential sensitivity plot. The data are presented as a differential plot in the bottom of Figure 3. It is easier to visually quantify the differential sensitivity of the calorimeter and the relative precision of the measurements at the different powers on a differential sensitivity plot than it would be from the top plot in Figure 3. It is apparent in the bottom plot in Figure 3 that multiple measurements were made using the three lowest-power heat standards; this observation is not possible in the top plot. The precision of this calorimeter is good enough so that the multiple measurements, three each, at the largest two powers are not resolved on this scale.



The passive-mode thermal power is determined by solving Equation 9 for an unknown power, W_i . The solution to the quadratic equation when $S_0 > 0$, [MA82A] is, for $k < 0$:

$$W_i = \frac{-S_0}{2 * k} - \left[\left(\frac{-S_0}{2 * k} \right)^2 - \left(\frac{BP_0 - BP_i}{k} \right) \right]^{1/2}, \quad (10)$$

and if $k > 0$, then W_i is

$$W_i = \frac{-S_0}{2 * k} + \left[\left(\frac{-S_0}{2 * k} \right)^2 - \left(\frac{BP_0 - BP_i}{k} \right) \right]^{1/2}. \quad (11)$$

Equations 10 and 11 are specialized rearrangements of the more familiar form of the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4 * a * c}}{2 * a}. \quad (12)$$

This solution is necessary due to the rounding errors that occur using equation 12 when the product of a and c is much smaller than b squared.

Servo Mode

In servo mode, the inside of the calorimeter is maintained at a constant temperature through the internal heater and a servo-controlled feedback signal. A schematic flow diagram for calorimeter digital servo-control is presented in Figure 4. The digital voltage meter (DVM) measures the signal from the Wheatstone bridge. The voltage reading is sent to the computer and compared to a control point voltage. The magnitude and sign of the difference between the reading and control point determine the adjustment made to the heater via the programmer and power supply. The temperature of the calorimeter measurement chamber is held several degrees above the temperature of the constant-temperature heatsink. The constant-temperature differential is proportional to the sensor signal (voltage or resistance).

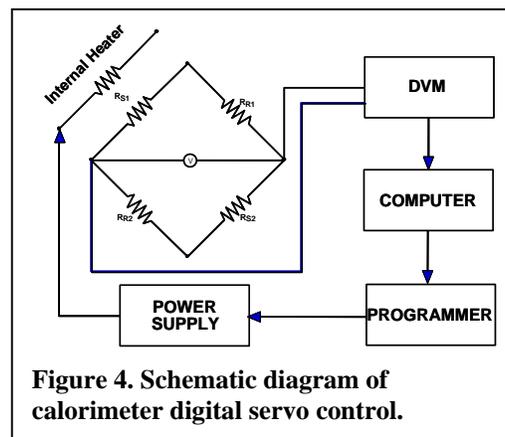


Figure 4. Schematic diagram of calorimeter digital servo control.

Calibration of a servo-mode calorimeter consists of setting the sensor output setpoint voltage corresponding to a specific base power and determining the stability of the heater power. A single sensitivity point, S , must be determined by making a single measurement of a heat standard. Any power within the operating range of the calorimeter is satisfactory. The bridge potential average, $BP_{0(av)}$, is determined as it was for the passive mode. The bridge potential setpoint (BP_{sp}) is calculated using

$$BP_{sp} = BP_{0(av)} + S * W \quad (13)$$

The heater power is servo controlled to maintain a constant sensor output equal to BP_{sp} . The actual supplied heater power (W_0) used to maintain BP_{sp} may be slightly different from the target value, W , because of the uncertainty in S used to calculate the setpoint. Measuring a standard power that is as close as possible to the value of W will minimize the difference between W and W_0 . The item power is the difference between the measured basepower, W_0 , with no item in the calorimeter and the measured heater power, W_H , at equilibrium with the item present. Therefore, carefully matching W and W_0 will not increase the performance of the calorimeter in any way; it will only minimize the difference between the requested basepower and the actual basepower.

The base power, W , of a calorimeter operated in servo mode should be set 10%–20% higher than the highest-power item expected to be measured. If the basepower is set less than the power of the item to be measured, the calorimeter will not be operating in servo control at equilibrium, and a power determination cannot be made. For some calorimeter designs a servo-controlled calorimeter can be used in passive mode if it has been calibrated as described above.

The basepower, W_0 , is determined the same way as a baseline is determined in passive mode. The calorimeter can be filled with a conductive material and no heat-generating items. The heater power measurement at equilibrium is the basepower, W_0 , corresponding to BP_{sp} . Replicate measurements should be made of the basepower to determine the standard deviation of the value. The calorimeter is opened and closed between repeat measurements of basepower.

When a heat-generating item is inserted into the measurement chamber, the external power applied by the closed-loop controller is decreased to precisely maintain the same signal differential. The controller power drops over time until the calorimeter and item come back to the original internal temperature of the calorimeter. The power of the item being measured is the difference between the two control power readings at equilibrium.

The calculation of item power, W_i , in servo mode is

$$W_i = W_0 - W_H \quad (14)$$

where W_0 is the basepower with no item in the calorimeter and W_H is the power supplied to the calorimeter with the item in the calorimeter. The measurement time for the servo mode of operation can be shorter than for the passive mode because the calorimeter components are at the equilibrium temperature and the servo-controlled internal heater can supply heat to actively bring the item to equilibrium.

Assay Error Determination

Mixed Radionuclides Example: Plutonium and ²⁴¹Am Mass

The mass, M , of plutonium in an item is the total power, W , divided by the effective specific power, P_{eff} , of the item. The measurement of these two quantities is independent so the relative uncertainty for the plutonium mass, M , can be written as

$$\frac{\sigma_M}{M} = \left[\frac{\sigma_W^2}{W^2} + \frac{\sigma_{P_{eff}}^2}{P_{eff}^2} \right]^{1/2}. \quad (15)$$

The uncertainty in the power measurement, σ_W , can be obtained from replicate power measurements of heat standards or from historical data. It should include both precision and bias components. The uncertainty in P_{eff} , $\sigma_{P_{eff}}$, comes from the uncertainty in the isotopic fractions, R_i , and isotopic specific powers, P_i . The uncertainties in the isotopic fractions are determined from uncertainties in the various techniques that might be used for the isotopic analysis, such as mass spectroscopy, alpha counting, or gamma-ray spectroscopy. There are sufficient gamma rays in plutonium to provide independent measured isotopic ratios of the major contributors to the item thermal power: ^{238}Pu , ^{240}Pu , and ^{241}Pu with respect to ^{239}Pu , and ^{241}Am with respect to total plutonium that allow R_i to be calculated. The mass fraction of ^{242}Pu , usually a minor contributor to the thermal power, is determined by isotopic correlation using the other plutonium isotopic data. The correlation technique is necessary because of the absence of gamma rays from ^{242}Pu . The uncertainties in the isotopic specific powers, P_i , as determined by different experiments, were previously given in Table 1. The test method for determining isotopic composition by gamma-ray spectroscopy is described in "C1030 Standard Test Method for Determination of Plutonium Isotopic Composition by Gamma-Ray Spectrometry" [AS1030]. Several commercially available gamma-ray analysis codes not only provide the isotopic composition but also the uncertainties of the isotopic fractions and the specific power of the item being measured. Error propagation of the isotopic fractions is discussed in Reference [SA83].

The uncertainty of the ^{241}Am mass mixed with plutonium is

$$\frac{\sigma_M}{M} = \left\{ \left(\frac{\sigma_W}{W} \right)^2 + \left(\frac{K}{P_{eff}} \right)^2 \left[\left(\frac{\sigma_K}{K} \right)^2 + \left(\frac{\sigma_{R_{Am}}}{R_{Am}} \right)^2 \right] + \left(\frac{R_{Am} \sigma_{P_{Am}}}{P_{eff}} \right)^2 \right\}^{1/2}, \quad (16)$$

where

$$K = P_{eff} - P_{Am} R_{Am}, \quad (17)$$

where P_{Am} is the specific power of ^{241}Am , R_{Am} is the mass ratio of ^{241}Am to plutonium, W is the thermal power, and σ_x are the respective uncertainties [AS1458].

Single Radionuclide Example Tritium Mass

The uncertainty of the effective specific power, P_{eff} , of tritium is the same as the isotopic specific power uncertainty; 0.00045 Watt [RU77]. Dividing by the specific power of tritium, 0.3240 W/g, results in

$$\frac{\sigma_{P_{eff}}}{P_{eff}} = 0.0014. \quad (18)$$

So for tritium, the relative uncertainty of the tritium mass is

$$\frac{\sigma_{tritium}}{M_{tritium}} = \left[\left(\frac{\sigma_W}{W} \right)^2 + (0.0014)^2 \right]^{1/2}. \quad (19)$$

For any item containing a single radionuclide, the contribution to the uncertainty caused by the isotopic composition determination is dependent only on the specific power uncertainty for that isotope and the uncertainty on W .

Details of measurement control can be found in [BR02, ANN15.54, AS1009, ANN15.20].

III. Measurement Performance

Calorimetric assay is considered the “gold standard” of NDA measurements for items containing more than 0.5 kg of plutonium of any form in a container less than 25.5 cm in diameter. Because calorimetry can measure entire items with very high precision and low bias, the results are often comparable to destructive analysis measurements. Calorimetry is frequently used as a standard measurement to determine uncertainties and/or biases in other NDA techniques such as neutron counters [AS1207] and tomographic gamma scanner systems [HY99, LE00].

The accuracy and reliability of calorimetric assay are primarily dependent on the thermal power generated by the item and on the methods used to determine P_{eff} . The total measurement uncertainty on P_{eff} determined for pure homogeneous items using gamma-ray spectroscopy is comparable to the power measurement uncertainty [SA99]. Major factors that can affect the precision of P_{eff} determined by gamma-ray isotopic assay can be found in [AS1030]. Major factors that can affect the bias of P_{eff} determined by mass spectrometric methods can be found in [AS697]. For materials containing reasonable concentrations of plutonium (>100 g Pu/liter), the precision and bias of calorimetric assay are comparable to good chemical assay techniques [WE95]. In this case, the largest source of calorimetry error is due to the uncertainty of the specific powers, P_i , of the individual radionuclides. For single radionuclide items, the uncertainties will be due only to the power measurement and the specific power of the radionuclide. The precision of a calorimeter measurement is dependent on the sensitivity of the calorimeter, baseline stability, and item power.

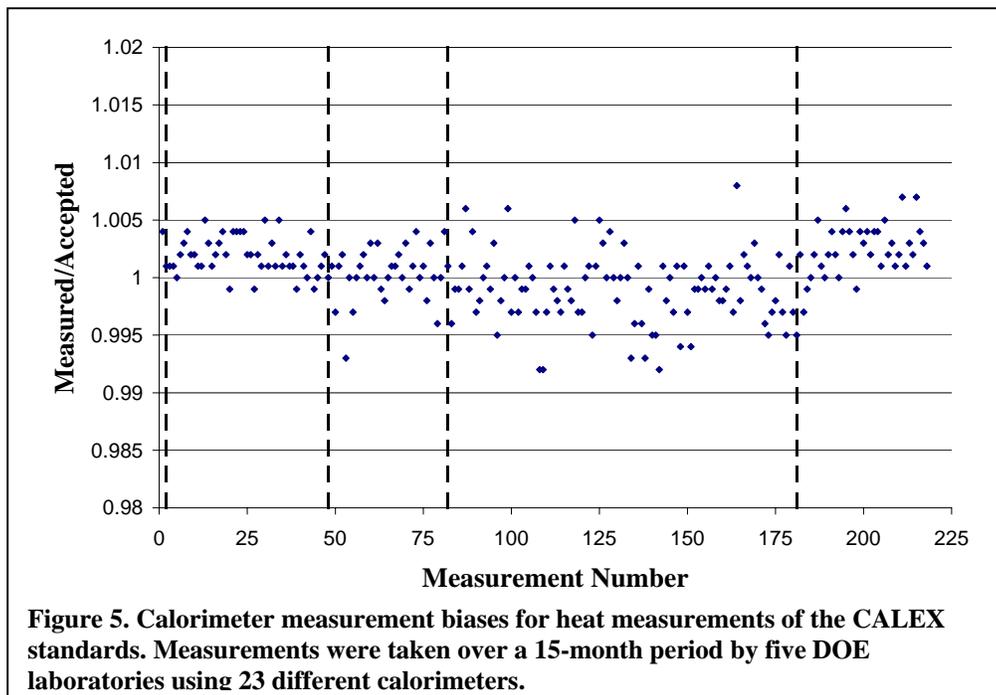
For impure or heterogeneous items, calorimetric assay can have lower uncertainties than destructive analysis techniques [WE95A] because of destructive analysis sampling error. The power measurement integrates all of the heat produced by the item regardless of inhomogeneity, and for heterogeneous items, the determination of P_{eff} by gamma-ray spectroscopy is a more representative average of the entire item than destructive analysis. In this case, in which the isotopic composition of the plutonium is determined by gamma-ray spectroscopy, the final uncertainty in the gram value determined by calorimetric assay is dominated by the uncertainty of the mass fractions, R_i , in P_{eff} . Quantitative examples of the measurement precision and bias obtainable using calorimetric assay are presented in the following subsection.

Calorimetric Assay Precision and Bias Data

Calorimetry Exchange

The DOE Calorimetry Exchange (CALEX) Program distributed identical PuO₂ items containing 400 g of plutonium with 5.86% ²⁴⁰Pu by weight. The program tabulates the results from the facility's measurements, yearly. Each facility collects data in a manner suitable for its own operations. The plutonium content and isotopic composition reference values of the mother lot of PuO₂ material used for these standards were measured by coulometry and mass spectrometry/alpha counting by four analytical laboratories. The power of the CALEX standard during the time periods of measurements described below was about 1 W.

Calorimeter biases for 23 calorimeters at five Department of Energy (DOE) facilities are presented in Figure 5. The dashed vertical lines separate the data submitted by each laboratory. These data were collected for the CALEX program over a 15-month period starting in October 1993. All measurements have a bias of less than ±0.8%. The average bias is 1.0004 with a standard deviation of the average of ±0.0002. The error expected on a single measurement would be 0.3% one relative standard deviation (1RSD).



The results of multiple calorimetric assay measurements by three facilities on the CALEX standards are shown in Table 2 [SP99]. The calorimetry and gamma-ray measurements used to determine plutonium mass variabilities and biases reported in Table 2 were taken over a one-year period. The within-facility variability and the bias of the calorimetric assay were calculated from results reported by each facility decayed to a common date. Each facility used different gamma-ray analysis codes for the isotopic measurements. For some, the reported values are the averages of measurements of the standard item with different calorimeters.

Table 2. Calorimetry/Gamma-Ray Assay Measurement of CALEX Standards¹				
Facility	Within-Facility Variability, g	Within-Facility Variability, % RSD	Bias, g	Bias, % RSD
A ²	1.5	0.38	0.03	0.01
B ²	1.5	0.38	-0.40	-0.10
C ³	1.4	0.36	0.04	0.01

¹All masses are in grams of plutonium decayed to a common date.

²Measurements made using multiple water-bath twin-bridge calorimeters.

³Measurements made using "air-bath" calorimeter.

CALEX data taken at five different DOE facilities are presented in Table 3. The data were collected over an eight-year period from 1990 to 1998. Not all facilities reported results each year. Therefore, the averages contained data from a maximum of eight years and a minimum of five years. Presented in Table 3 are the average percent measurement bias and percent relative standard deviation (RSD) from repeated measurements for P_{eff} and item power. The percent bias and percent RSD are comparable for power and P_{eff} measurements on this item.

Table 3. CALEX Precision and Bias Data for P_{eff} and Power				
Facility	Power		P_{eff}	
	% Bias ¹	% RSD ²	% Bias ¹	% RSD ²
A	0.11	0.61	-0.23	0.10
B	0.08	0.22	0.07	0.26
C	-0.01	0.17	0.13	0.21
D	-0.08	0.30	0.02	0.20
E	0.17	0.21	-0.18	0.48

¹% Measurement Bias = 100*[Measured – Accepted]/Accepted].

²% Relative Standard Deviation is based on repeated measurement of the same item.

Heat Standards

Data collected from a measurement control program can be used to calculate the precision and bias of the power measurement. A summary of the precision and bias of the power measurement obtained from replicate measurements of ²³⁸Pu heat standards in production facilities over a 0.5—1.0 year period is shown in Table 4. Generally, the greater the thermal power of an item in a calorimeter, the better the relative precision. Extensive calorimetric assay precision and bias data can be found in references [BI00A, SP99, LO90, FL86, WE95A, WE95, LI87]; all of these references are summarized in [BR02].

Heat standard Power, Watts	Calorimeter diameter, m	Calorimeter Type, operation mode	Number of Meas.	Precision, % RSD	Bias, %
98.0	0.06	rod, servo	29	0.065	0.02
3.5	0.15	rod, servo	55	0.09	0.00
4.0	0.25	twin, passive ¹	22	0.05	0.03
4.9	0.30	twin, passive ¹	34	0.06	0.05
0.0786	0.04	Solid state, passive ²	10	0.23	0.001

¹Pooled results from two calorimeters.

²Measurements made in laboratory.

Tritium

Calorimetry was used to measure the quantity of tritium gas in containers. Because tritium was the only radioactive isotope, no isotopic measurements were required for the assays. After the calorimeter measurement, the gas was quantitatively transferred to tanks with calibrated volumes, and the quantity of tritium was determined using calibrated pressure and temperature transducers and mass spectrometric analyses. A comparison of measurement results between calorimetry and pressure/temperature measurements in a calibrated volume combined with mass spectrometric analysis (PVT/MS) was made for 50 containers [LI87]. The tritium content of the containers ranged from 15 to 16 g. The relative mean bias for the calorimetric assay compared to PVT/MS was -0.12%. One RSD of the mean was 0.05%. A twin-bridge water-bath calorimeter was used for the calorimeter measurements.

Automated Plutonium Assay System (APAS)

The precision observed from repetitive calorimeter measurements of six items containing 26 to 258 grams of Pu (17% ²⁴⁰Pu) in PuO₂-UO₂ (26% Pu) was calculated; the results are shown in Table 5 [BI00A]. These 1,872 measurements were made over a 56-day period using a robotic loader with 24-hour-a-day operation. The calorimeter was a water-bath over-under twin bridge. A common P_{eff} factor for all six items was determined using the plutonium isotopic composition and ²⁴¹Am content that was determined by mass spectrometry and alpha counting. The calorimeter can size was 6.4 cm in diameter × 16.5 cm high. The calorimeter measurement time was fixed at 1 hour. The calorimeter was run in the servo mode, and the items were preconditioned to reduce the measurement time. The high-precision results listed in Table 5 are direct evidence that automated loading and unloading of items into the calorimeter can improve measurement precision. The APAS was the first implementation of a robotics-operated calorimetry assay system and showed that continuous, fast calorimeter measurements could be performed over long periods of time with high accuracy. The results also confirm the relationship between calorimeter precision and item power.

ID	Mass ^{1,2} , g by Chem	Mass ² , g by Cal ³ /MS/ α ⁴	Precision ⁵ , g	Precision, % RSD	Bias, g	Bias, %
4	257.70	257.54	0.14	0.06	-0.16	-0.06
5	206.09	206.06	0.13	0.06	-0.03	-0.02
6	206.18	206.12	0.14	0.07	-0.06	-0.03
7	128.81	128.94	0.12	0.09	0.13	0.10
8	77.28	77.35	0.12	0.15	0.07	0.09
9	25.79	25.99	0.11	0.42	0.20	0.78

¹Mass of plutonium determined by coulometry using reference material NBS 949E. Plutonium percentage of mixed oxide, 0.25759, based on triplicate measurements of six samples.

²Plutonium masses reported here decayed to a common date.

³Final results based on 117 replicate calorimeter measurements per item.

⁴Isotopic composition determined by 12 replicate measurements by mass spectrometry (²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu, ²⁴²Pu) and six replicate alpha-counting (²³⁸Pu, ²⁴¹Am) measurements.

Average Pu isotopic and ²⁴¹Am results were used to calculate P_{eff}.

⁵Precision because of calorimetry power replicate measurements.

Possible Sources of Bias because of Calorimeter Design

The following sections will describe possible sources of bias during calorimetry measurements. For most calorimeter designs, these effects are negligible but their magnitude should be quantified for all calorimeters. If a measurable effect is observed, the bias should be corrected by creating a bias correction curve across the range of the parameter being characterized.

Weight Effects

A shift in the calorimeter signal proportional to the mass of the item in the sample chamber is known as the “weight effect.” The shift is caused by stressing the temperature-sensing element of the calorimeter and is typically linear with mass. To evaluate this effect, a series of paired baseline measurements is made. First, the baseline is measured with the sample chamber empty. Second, the baseline is measured with the sample chamber loaded with non-heat-producing material of approximately the same mass as the heaviest items to be assayed. If an effect is observed, further tests should be performed at other masses to verify the linearity of the effect. Bias corrections can be made for weight effects by weighing the item to be measured and making the correction to the calorimeter output. If a weight effect is observed, the bias correction factor should be confirmed periodically as a part of the measurement control program.

Well-designed modern calorimeters should not show a weight effect. Weight effect can be identified with a single measurement of significant mass after the calorimeter has been fabricated. If a weight effect is not observed for a calorimeter, it does not need to be reevaluated.

Heat Distribution Error (HDE)

Heat distribution error (HDE) is a variation in the calorimeter response because of the location of the heat source within the measurement chamber. For example, the same heat source may

produce a larger calorimeter output in the bottom of the sample chamber than in the top. The HDE could lead to a bias if the source location is unknown. HDE is quantified by measuring the same heat source placed at different vertical positions within the calorimeter measurement well. Multiple measurements are necessary to determine if the calorimeter output for the various positions is statistically different or the same. The power of the heat source should be the same or greater than the highest expected power of the items to be measured. The magnitude of an HDE will increase with increasing power. If an HDE is measured, the uncertainty associated with HDE must be included in the final uncertainty of the power determination. An HDE can be minimized or removed by fabricating thick-walled calorimeter cans if a reduction in sample chamber size can be accommodated. Another possible solution is placing additional insulation at the top and/or bottom of the measurement chamber. The magnitude, polarity (loss or gain), and position of the HDE dictates which solution is best suited for a particular HDE. Well-designed calorimeters should not show an HDE.

Heater-Lead Error

Heater-lead error is potentially present for any calorimeter designed with built-in heaters or using insertable heaters. Even though the heater may be removable, the electrical leads should always be part of the calorimeter even during sample runs, because the heat loss or gain through the electrical leads is present when the heater is in use [BI97, BR02A]. If they are not present during item measurements, the thermal resistance of the calorimeter is changed and the electrical calibration is no longer valid. The magnitude and outcome of the effect is dependent on the design of the calorimeter (i.e., twin or gradient) and heater (insertable or fixed), the powers being measured, and what the heaters are used for (i.e., calibration, servo mode, or calorimeter response check).

For electrical calibration purposes, a four-terminal heater should be employed with two current-carrying leads and two leads for making potential measurements. The same size, type, and length of wire should be used for these leads so that the lead errors can be measured and compensated for. The use of identical wire is also necessary for heater-lead heat generation and leakage compensation in twin calorimeters. The heater circuit used in twin calorimeters is shown in Figure 6. In the configuration shown in Figure 6, passing the same current through two leads on each side of the twin calorimeter compensates for the heat generated in the leads of the calibration heater. The heater leads are usually not brought directly out of the calorimeter. The leads usually exit the calorimeter along a path that maximizes the heater-lead contact with the controlled environment. This configuration is usually accomplished by winding around the circumference of the calorimeter, as physically close to the reference temperature as possible. The heater leads should be of low-electrical resistance compared to the heater to reduce heater-lead resistive heating. The use of low-resistance copper leads minimizes electrical resistance but also constitutes a heat-leakage path out of the calorimeter, potentially leading to an electrical calibration that is biased low.

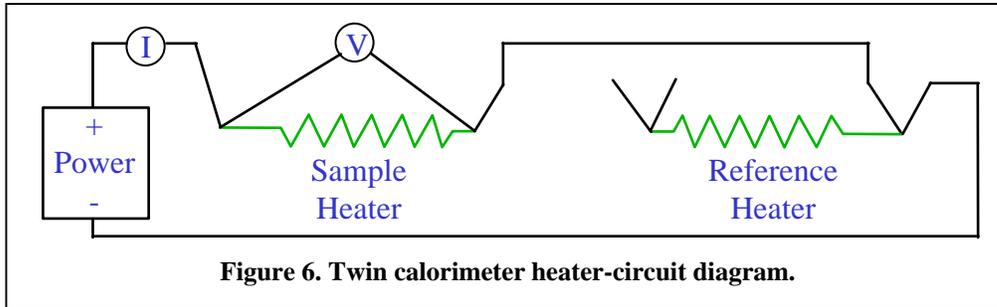


Figure 6. Twin calorimeter heater-circuit diagram.

Estimation of calorimeter heater-lead heat in gradient calorimeters is accomplished by passing a series of different currents through one current lead and out the corresponding potential lead in series. The calorimeter output at each current is compared to the calorimeter zero. The correction for the heater-lead errors should be calculated from

$$\frac{V_i - V_0}{S_i} = a (I_i^2 R_h) \quad , \quad (20)$$

where V_i is the calorimeter sensor signal with measured current, I_i , in the leads, V_0 is the sensor signal with no current in leads, S_i is the sensitivity, a is a proportionality constant relating the heat in leads to that from the heater resistance, and R_h is the heater resistance.

When the internal or insertable heater is used for calibration, the high-impedance digital voltmeters used for voltage and current measurements must be calibrated against certified electrical reference standards. If current is measured indirectly through a voltage drop across a calibrated resistor, the resistor must be a certified standard resistor. A stable high-precision power supply must be used to supply power to the heater. The calibrated voltmeter(s) and, if used, resistor must be recertified with a frequency consistent with facility-defined metrology practices.

If electrical heaters are used for calibration, a check of heater bias should be made against a certified heat standard. This check is most important for high powers, greater than a few watts, and very small powers, less than 200 mW. The cross measurement should be done if any portion of the heater circuit is changed or if a new calibration is made.

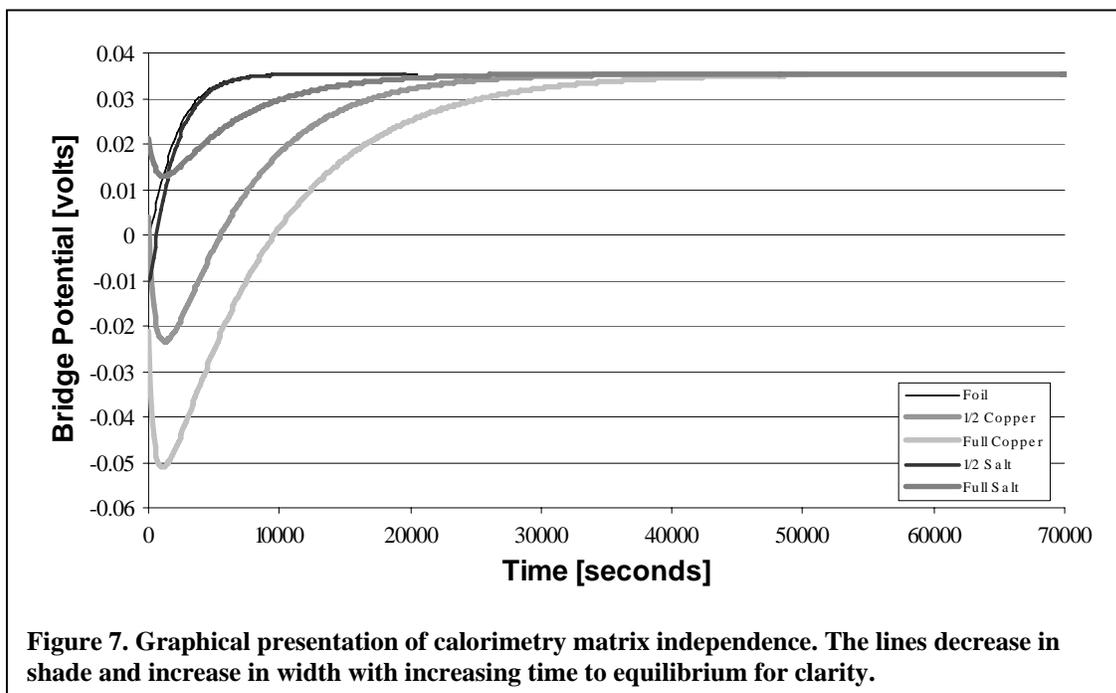
Possible Assay Interferences

- Interferences for calorimetry are those processes that would add or subtract thermal power from the power of the radionuclides being assayed.
- Interferences can be phase changes or endothermic or exothermic chemical reactions, such as oxidation.
- Radioactive decay energy can drive endothermic reactions in aqueous solutions.
- Undetected heat-generating radionuclides would add additional thermal power to the measurement.
- The accuracy of the method can be degraded for materials with inhomogeneous isotopic composition because of the increased uncertainty in the isotopic ratios.
- Room-temperature variation may affect the stability of the reference temperature and increase measurement uncertainty.

- Noise in the electronics AC supply power generated by machinery may increase the measurement uncertainty.
- Energy can be lost due to high-energy gamma rays with large branching ratios.

Parameters Affecting Assay Time

Calorimetry measurement times are typically longer than other NDA techniques. The packaging conditions and matrix of the item cannot change the heat output of the material, but they are usually the determining factor for measurement time. Time series data collected with a twin-bridge water-bath calorimeter operated in passive mode are presented in Figure 7 [SM01A]. The series of lines represent different matrix conditions. The effect of matrix on measurement time is apparent in Figure 7. It can also be seen that the matrix has no effect on the magnitude of the final answer (i.e., the bridge potential at equilibrium). For each measurement presented in Figure 7, the calorimeter can, including the matrix and source, was pre-equilibrated to the same temperature before insertion into the calorimeter. Pre-equilibration was done to minimize the time response due to starting temperature variability, therefore maximizing the time sensitivity to matrix. The different matrices containing the same 1.25 W heat standard reached equilibrium in a time range of 3 to 14 hours. The matrices in order of increasing time to equilibrium were 1/2 full salt, full foil, full salt, 1/2 full copper, and full copper.



Typical assay times are between one and eight hours. Small, well-packaged thermally conductive samples can be assayed in less than one hour, but large nonconductive items, such as salts, and poorly packaged items (i.e., multiple layers of air gaps and thermal insulators) can take as long as 24 hours. Pre-equilibrating the sample temperature to match the final internal calorimeter temperature can reduce the measurement time of any sample. Pre-equilibration is usually used with a calorimeter operating in servo-control mode. An inherent benefit of the Department of Energy (DOE)/(OSS)-developed heat-flow calorimeters is that equilibrium prediction can also be used to reduce measurement times by 40% or more, depending on measurement conditions. The thermal diffusivity of the matrix of the item and its packaging will determine the thermal time constant for heat transfer from the item and hence the measurement time. Increases in measurement time are expected for items with large masses and small power, items that make poor thermal contact with their containers, items that contain a large amount of insulating material or dead air spaces, and items with multiple layers of containment.

The measurement time for the servo mode of operation can be shorter than for the passive mode because the calorimeter components are such that the equilibrium temperature and the servo-controlled internal heater can supply heat actively to drive the item to equilibrium.

The time necessary for a calorimeter to reach thermal equilibrium during the assay of an item is dependent on a number of factors: initial temperature of item relative to final equilibrium temperature of the item/calorimeter (sample preconditioning can reduce measurement time by reducing this difference), type of heat-flow calorimeter used (passive or active), calorimeter size and thermal properties (thermal conductivity and total heat capacity) of the fabrication materials, thermal properties of the item and item packaging (usually more important than calorimeter properties), size and weight of the item and the calorimeter, use of an equilibrium prediction algorithm, and required assay accuracy.

Measurement time data are presented in Table 6 and show the effects of matrix type on measurement time. The columns labeled “Eq. Time” list the times in hours it took the calorimeter to reach equilibrium. All of the items were pre-equilibrated to 24.0°C before insertion into the calorimeter. The initial internal calorimeter temperature was 25.0°C. Pre-equilibration was done so the matrix effects could be seen more easily. The calorimeter can had a volume of about three liters. The can was filled with the matrix type listed in Table 6. Measurements were made under two-power conditions: zero power and 0.8 watts of power. The size and weight of the heat standard were negligible compared to the volume of the calorimeter can, with the exception of air as the matrix. Times-to-equilibrium tracked well for both power conditions.

IV. Types of Heat-Flow Calorimeters

A variety of heat-flow calorimeter designs has been used to measure nuclear material. Four major designs that have been used for accountability measurements are (1) water-bath calorimeters, (2) solid-state calorimeters, (3) isothermal “air bath” calorimeters, and (4) fuel rod calorimeters. The air-bath and fuel-rod calorimeters described below have been operated exclusively in the servo mode, and the water-bath calorimeters have been operated in the passive or servo mode. Solid-state and water-bath calorimeters can be operated in passive or servo mode if internal heaters are built into the design.

Table 6. Item Measurement Time Dependence on Matrix Material.				
	No heat source		0.8 watt source	
Matrix Type	Mass (kg)	Eq. Time (h)	Mass (kg)	Eq. Time (h)
Air	0.668	4.8	0.766	5.0
Poly beads	1.722	25.0	1.723	18.7
Al foil (1)	0.094	6.8	0.094	5.0
Al foil (2)	0.286	6.0	0.287	5.8
Copper shot	15.820	25.3	15.824	21.5
Salt	3.102	15.0	3.358	15.0
Al bars/foil	3.636	17.0	3.636	15.0
Sand	4.580	15.0	4.580	13.8
Steel shot	13.782	27.0	13.782	30.0
Lead shot	20.738	12.5	20.739	12.5
Poly beads	1.728	20.0	-	-
Sand	4.670	16.5	-	-

Calorimeters are used to measure material in sealed storage containers (off-line) and to measure material in process (in-line). Calorimeters have been fabricated for use during material processing by mounting the calorimeter under gloveboxes. Off-line calorimeters are essential for routine facility accountability measurements, evaluation of shipper/receiver differences, and measurement of difficult material categories with unknown and/or heterogeneous matrices. Transportable calorimeters have also been built that can be moved from area to area within a facility or between facilities. Different calorimeter designs will be described in the following sub-sections.

Water-Bath Calorimeter

Heat-flow calorimeter designs developed under the OSS Technology Development Program are the most extensively used calorimeter designs throughout the DOE complex. These high-precision calorimeters are based on nickel-wire temperature sensors connected in a Wheatstone bridge configuration. A precision temperature-controlled water bath is commonly used to provide a constant reference temperature and infinite heatsink. Over two hundred heat-flow calorimeters have been built for use throughout the DOE complex and the world over the last 50 years. Currently a total of about 50 Wheatstone bridge calorimeters are being used for accountability measurements of plutonium and tritium at Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), Rocky Flats, Hanford, Savannah River, and other sites.

The elements common to all current Wheatstone bridge calorimeters are labeled in Figure 8. The components are described starting from the innermost elements in Figure 8. The measurement chamber (sample and reference) is occupied by a removable calorimeter can that holds the item being assayed and provides good thermal contact with the chamber wall while preventing any potential contamination of the inside of the calorimeter. If an internal heater is specified in the calorimeter design, the circumferences of both measurement chambers are wound with manganin wire, which is used as the internal calorimeter heater. Two lengths of nickel wire are wound concentrically about the internal heater windings and serve as two sensor arms of the Wheatstone bridge. The thermal resistance between the sample sensor windings and the water bath are identical to the thermal resistance between the reference sensor windings and the water bath. This thermal resistance matching is done to maximize cancellation of water-bath temperature fluctuations in the Wheatstone bridge. The sensitivity of the calorimeter is directly proportional to the thermal resistance of the thermal gap. The thermal gap material usually consists of up to 0.3 cm of air or up to 1.0 cm of epoxy, for either type of calorimeter. The wider the thermal gap, the larger the internal temperature rise of the sample chamber for a given thermal power. The insulating material at the top and bottom of the measurement cells is used to force all of the heat radially through the sensing element.

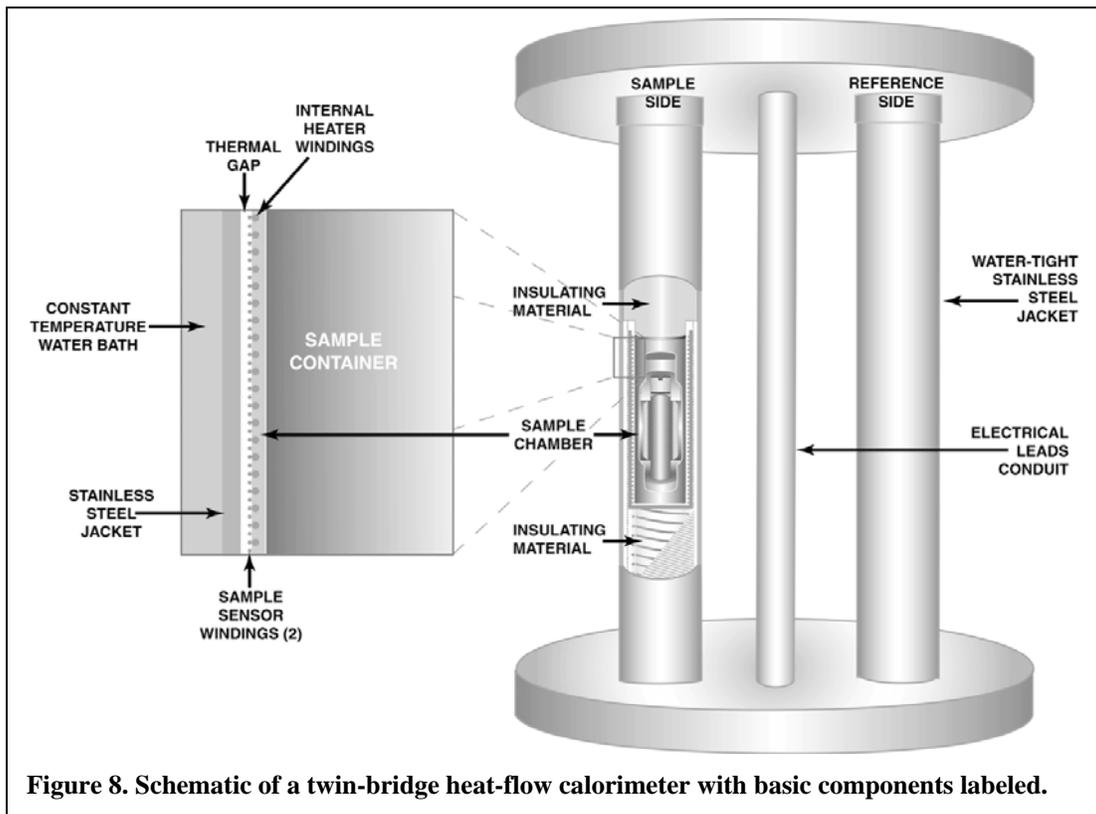


Figure 8. Schematic of a twin-bridge heat-flow calorimeter with basic components labeled.

The outermost surface of the calorimeter is a stainless-steel jacket. The stainless-steel jacket is used to keep the inside of the calorimeter dry when submerged in the water bath. A water bath with stirrer or circulating pump is used to maintain a constant reference temperature and serves as a heatsink. The water-bath reference temperature is maintained using feedback servo control. These units may use refrigeration compressors, resistance heaters, thermoelectric cooling units, evaporative cooling, or any combination of the above-listed for temperature control. The thermally stable reference bath is controlled to better than $\pm 0.001\text{ C}^\circ$, which is critical to high-precision, low-power measurements.

Twin- and gradient-bridge are the two broad classes of water-bath calorimeters commonly in use. For both types of calorimeters, the Wheatstone bridge circuit shown in Figure 9 is used to measure heat flow. The reference and sample arms of the bridge are wound with high-purity nickel wire. The change in resistance with temperature is linear with a sensitivity of about $+0.6\%$ per C° . The temperature rise in the sample side caused by the presence of radioactive material causes the resistance of the sample arms of the Wheatstone bridge to increase while the resistances of the reference arms remain constant. This resistance change causes an imbalance in the bridge and the voltage across the bridge (the bridge potential) changes in proportion to the size of the temperature change. The reference sensor wire arms and sample sensor wire arms of the Wheatstone Bridge are each helically wound interleaved (bifilar winding) and concentrically around a cylindrical chamber. The differentiation between twin- and gradient-bridge is made based on where the arms of the Wheatstone bridge are placed relative to each other. In the twin-bridge configuration, two windings are on one measurement chamber and two windings are on an identical measurement chamber as in Figure 8. A schematic of a gradient-bridge calorimeter is presented in Figure 10. In this case, the two windings are wound concentrically about the inner pair of windings with a thermal gap between the two pairs. Twin-bridge calorimeters have also been built with the reference thermel located under and coaxial to the sample thermel (“over-under” design) to save space. This configuration is also presented in Figure 10.

Twin-bridge calorimeters are usually placed in a large (550–1,000 liters) water bath to provide a stable reference temperature. These water baths are mixed using a propeller on a shaft rotated by a motor. Multiple calorimeters have been fitted into one water bath. For heat-flow calorimeters using a water-bath reference temperature, the identical windings on the reference chamber are used as a fixed reference resistance for two arms of a Wheatstone bridge while the sample sensor windings around the sample chamber change resistance as a result of heat flow from the sample. Small reference-bath temperature fluctuations are further corrected for by the twin-bridge design. Because both the reference and sample windings have identical thermal heat paths to the reference bath, any resistance changes in the windings caused by temperature fluctuations are canceled in the twin-bridge configuration.

Gradient-bridge calorimeters usually have circulating water through an outer jacket of the calorimeter connected to a separate temperature conditioning system through connecting hoses. Smaller volumes of water, less than 76 liters, are required for this type of water-bath system. The smaller water volumes and connecting hoses increase the reference temperature noise caused by ambient room-temperature fluctuations. Also, with the gradient design, cancellation of reference temperature fluctuations are not maximized because of the time lag between when the reference arms of the bridge change resistance from temperature change and the time the sample windings change resistance because of the same temperature change of the water bath. Although the gradient calorimeter is more sensitive to bath temperature fluctuations, for higher-power measurements, these fluctuations do not add significantly to the measurement uncertainty.

A block diagram of the instrumentation and communication typically used to operate a Wheatstone bridge calorimeter is presented in Figure 11. All of the electronics used are standard, commercially produced items. A 7.5-digit digital multimeter is used to read out bridge potential, and 6.5-digit multimeters are used to read out bath temperature, bridge current, and room temperature. A General Purpose Interface Bus (GPIB) bus is used as the communication link between the electronics and the computer.

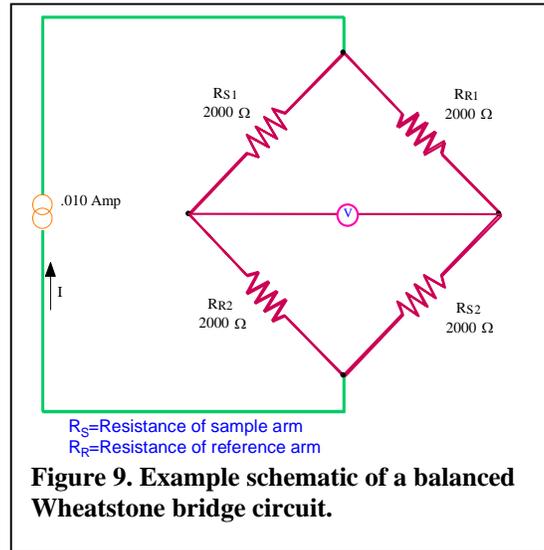
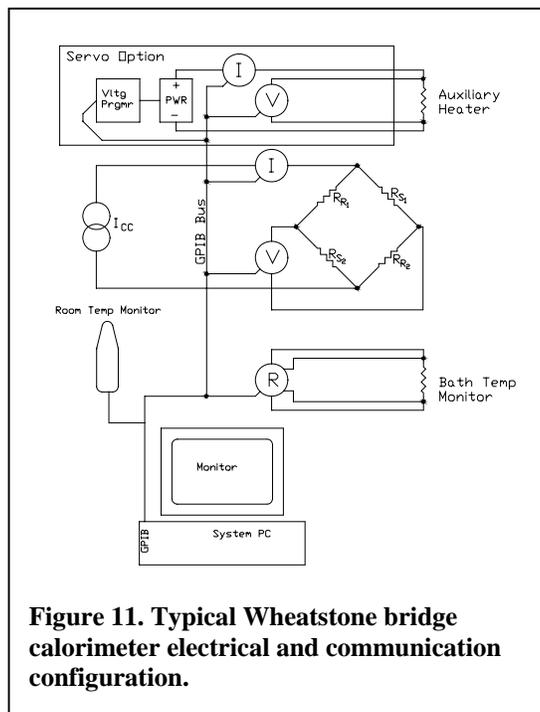
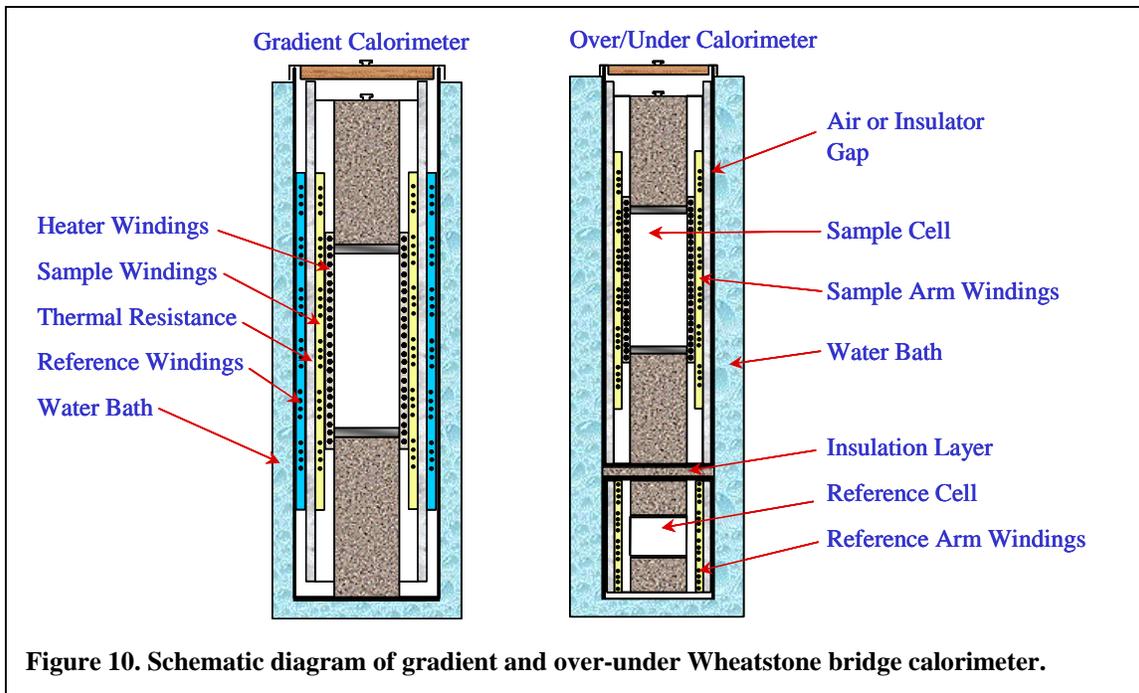


Figure 9. Example schematic of a balanced Wheatstone bridge circuit.



The advantages of twin-bridge calorimeters compared to gradient-bridge are best cancellation of thermal effects, lowest standard deviation of bridge potential, lowest detection limits, best precision and accuracy, and long-term stability.

The advantages of gradient-bridge calorimeters compared to twin-bridge are having the smallest footprint, using the fewest materials in construction, more suited to closed bath system, and making the smallest transportable calorimeter.

Solid-State Calorimeter

Solid-state calorimeters use thermopile components as heat-flow sensors [BR00, BR98, BR97]. A thermopile consists of numerous thermocouple pairs electrically connected in series. Thermocouples are formed by electrically joining one set of ends of two dissimilar conductors or semiconductors. A temperature difference between two thermocouple junctions causes the development of an electromotive force, known as the relative Seebeck effect that is proportional to the temperature difference. The greater the temperature difference, the larger the voltage measured from the sensor. The thermopile hot junctions are placed facing the sample chamber, but the cold junctions are held at the reference temperature.

A picture of a small-sample, solid-state calorimeter is presented in Figure 12. This calorimeter uses thermopile heat-flow sensors. It was designed and fabricated at Los Alamos National Laboratory and it is called the Solid-State Calorimeter System. It was fabricated from commercially available components and is capable of making high-precision measurements comparable to those made using much larger heat standards calorimeters. The data-collection electronics for the solid-state calorimeter system are commercially purchased digital voltmeters.



Figure 12. Picture of a high-precision solid-state calorimeter in a water bath. The IBM laptop in the foreground is used for data acquisition.

Another benefit of using high-sensitivity thermopile sensors in calorimetric NDA systems is that the calorimeters are more robust, with excellent portability and baseline stability.

A matched pair of thermopile heat-flow sensors is used as a replacement for the more commonly used Wheatstone bridge sensors. The sensors are used in a twin configuration where one cylinder is used as a reference chamber for the cylinder that contains the heat-producing item. The electrical difference between the sample thermopile output and the reference thermopile output is measured using a nanovoltmeter.

The availability of commercially produced high-sensitivity thermopile sensors has made them a viable alternative to the high-purity nickel wire used in a Wheatstone bridge sensor. With the passive thermopile sensor there is no self-heating of the calorimeter as there is with the constant current applied to a Wheatstone bridge. Without self-heating, more accurate

measurement of low-power items can be made. A water bath is used as a constant temperature heatsink, and when drained, the system is portable. After moving, the calorimeter is ready to make measurements within 24 hours.

With a source power of ~ 10 mW, equivalent to 4 grams of low-burnup plutonium, the relative standard deviation of six measurements using the solid-state calorimeter system was 0.11%. The extremely low noise of the heat-flow sensor has a standard deviation of 0.1 to 0.2 μV , allowing for high-precision measurements of items with powers in the submilliwatt range. The sensor response to heat is linear.

The advantages of thermopile heat-flow sensors compared to Wheatstone bridge sensors include the following: lower cost, wide commercial availability, scalability to any size or shape, passive signal, insensitivity to mechanical strains, intrinsically low noise, stable baseline (zero power output), increased portability, increased robustness, and no sensor self-heating.

The extremely stable baseline value makes it possible to reduce the frequency of or eliminate baseline measurements.



Figure 13. Photograph of the LVC with the calorimeter in up position after the 208-l drum has been loaded. The circular insulation below the drum is the LVC pedestal.

Large Volume Calorimeter (LVC)

The large-volume calorimeter (LVC) [BR04] is capable of measuring the power output from a standard 60-cm-diameter 208-l drum. With special positioning considerations, cylindrical items of up to 66 cm in diameter and up to 100 cm long can be measured in the LVC. The LVC uses thermopile heat-flow sensors that were developed for the solid-state calorimeter. The footprint of the calorimeter is 104 cm wide by 157 cm deep and 196 cm high in the closed position. The space for a standard electronics rack is also necessary.

The 208-l drums are lifted and placed onto the LVC pedestal using a drum handler. The pedestal is exposed by lifting the entire LVC shell and sensors. A photograph of the calorimeter in the open position is presented in Figure 13. The pedestal is a circular insulating plug of extruded polystyrene that prevents item heat leakage out the bottom of the calorimeter. The calorimeter consists of three concentric cylinders closed on the top and open on the bottom for the insertion of the 208-l drums and pedestal.

The LVC uses two conductive temperature zones heated by silicone rubber encapsulated wire surface heaters to provide a constant reference temperature to the cold side of the thermopile heat-flow sensors. Temperature control is achieved through servo controlled feedback loops for each heater. The temperature feedback signal is obtained from each heater through four-wire resistance readout of a thermistor. The LVC does not use any water or other significant neutron moderating or reflecting materials for temperature control. The LVC does not have the ability to actively cool.

In order to maintain a relatively small overall size, the LVC does not use any compensating chamber to reduce thermal noise in the reference temperature. Drift of the reference temperature is the largest source of noise in the system.

Isothermal “Air-Bath” Calorimeter

Isothermal air-bath calorimeters consist of three concentric cylinders separated by a heat-transfer medium. Each of the cylinders is equipped with temperature sensors. Nickel sensor wire and/or chains of thermistors may be used. The outermost cylinder is surrounded by a controlled temperature air bath rather than a water bath. The temperature sensors are measured using conventional Wheatstone bridge circuitry or by direct resistance measurement using a high-resolution multimeter. Power to control the temperature of each of the cylinders is supplied by power amplifiers. Heater coils are wound around each cylinder for this purpose.

The isothermal calorimeter operates so that each of the three concentric cylinders is at a successively lower temperature as one moves from the inner cylinder (measurement chamber) to the outer cylinder. This difference in temperature results in a temperature gradient and heat flow from the inner cylinder to the outer cylinder. The calorimeter operates in servo mode. The system controller works to maintain a constant total thermal power in the measurement chamber.

The total thermal power present in the measurement chamber is the power from the internal heaters and the power from the item being measured. Isolation from the thermal environment is achieved by circulating air through an exterior chamber either by forced air cooling using room temperature air or by a closed-loop air circuit employing a thermoelectric cooling unit to provide a sufficiently low heatsink temperature [AS1458].

Rod Calorimeter

The thermal unit of the rod calorimeter is made up of a sample chamber, item insertion/removal plug, thermal shielding, and a highly controlled heat-removal path. The calorimeter is operated in the servo mode. The heat removal path is through a highly conductive (typically copper) solid rod across which a constant temperature differential is maintained. The upper end of the rod, located at the base of the measurement chamber, is held at a constant temperature by supplying heat to the base (or side) of the measurement chamber. The lower end is held to a lower temperature, which creates a constant temperature differential. The thermal power supplied to the base of the measurement chamber is measured.

The thermal shield is made up of several components. The purpose of the thermal shield is to create a zero heat-transfer envelope around the measurement chamber with the exception of a highly controlled heat-removal path through the copper rod. Multiple constant-temperature thermal shields may be used. Depending on the ambient temperature variations, one or two shields may be incorporated. For lower power measurements, the outermost constant temperature shield is typically a controlled temperature enclosure. Temperature measurements are made using high-precision resistance measurements of a thermistor. The plug used to insulate the item being measured is a component of the zero heat-transfer envelope and mitigates thermal effects resulting from gaseous pressure differentials in the measurement chamber.

The thermal unit uses from 4–12 closed-loop control systems for control of the thermal shielding and heat removal. Control requires temperature measurement, computer control algorithms with digital-to-analog (D/A) conversion, and power supplies for driving the heaters and coolers of the thermal unit. The computer D/A outputs are connected to power supplies for driving the heaters/coolers. The power supplies are high grade, low noise, and configured in an operational amplifier mode. System stability analysis is automated and based on power variations and temperature indicators [AS1458].

V. Calorimetric Assay Applications

Table 7. Measurement Methods for LANL Pu Inventory Mass % for Each Material Form¹				
Material form	Calorimetry + gamma spec	Analytical chemistry	Neutron counter + gamma spec	Segmented gamma scanner
Metal	71%	29%	0.3%	0%
Compounds pure	64%	35%	0.9%	0.3%
Compounds impure	72%	23%	2.6%	2.6%

¹From LANL Material Accounting and Safeguards System (MASS) database April 1999.

At present, calorimetric assay is the most precise and accurate NDA technique for the assay of many physical forms of plutonium and tritium. Calorimetry has been applied to a wide variety of plutonium-bearing solids, including metals, alloys, oxides, fluorides, mixed plutonium-uranium oxides, mixed oxide fuel pins, waste, and scrap (e.g., ash, ash heels, salts, crucibles, and graphite scarfings) [RO81, RE91]. An example of the importance of calorimetric assay of plutonium-bearing items at LANL is presented in Table 7.

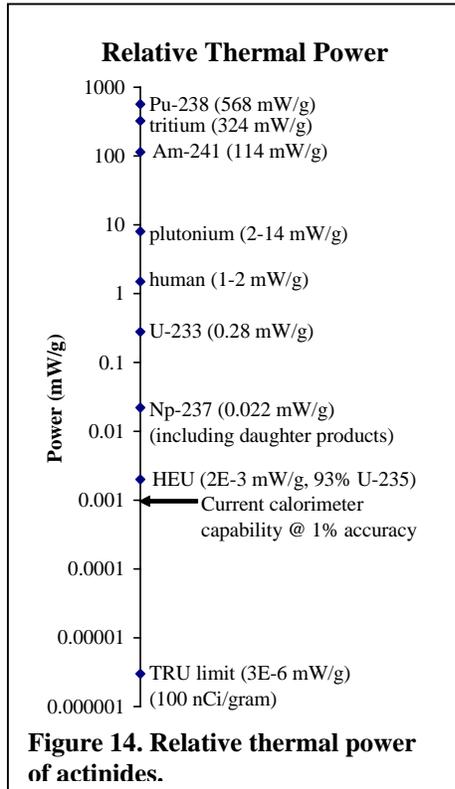


Figure 14. Relative thermal power of actinides.

Calorimetric assay has applications in a number of different areas: shipper/receiver measurements, accountability measurements, calibration of NDA standards, process control measurements, outlier resolution, and product acceptance measurements.

Of the items listed above, calibration of NDA standards and outlier resolution can only be done nondestructively using calorimetry.

Calorimetric assay can be applied to a number of different radionuclides: Plutonium, HEU, ^{233}U , ^{237}Np , $^{242,244,245}\text{Cm}$, $^{250,252}\text{Cf}$, $^{241,242\text{m},243}\text{Am}$, tritium, and fission products. It can be accurately used for any of the above items that fit in the instrument measurement well and are free from any chemical reactions. Figure 14 presents the range of specific powers for some of the radionuclides listed above. Items in the previous list will be discussed in the following subsections.

Plutonium

Calorimetric assay is most frequently used to measure plutonium-bearing items with varying amounts of ^{241}Am . The total amount of ^{241}Am is dependent on the time since separation and the fraction of plutonium that was originally ^{241}Pu . High-resolution gamma-ray spectroscopy measurements are usually made to determine the plutonium isotopic and ^{241}Am mass fractions; therefore, the effective specific power for plutonium-bearing items, using Equation 5. Sample calculations of typical effective specific powers for high- and low-burnup plutonium are shown in Table 8. The fraction of thermal power from each plutonium nuclide is also listed in Table 8. It should be noted that because of the inclusion of ^{241}Am , the sum of the relative fractions is greater than one by the amount of ^{241}Am contained in the sample. The mass fraction of ^{241}Am is in terms of grams per gram of plutonium. The final gram quantity of the item is determined by dividing the power by the effective specific power as shown in Equation 2.

Table 8: Plutonium Effective Specific Power Calculations.				
Radionuclide	Ri	Pi (mW/g)	Ri*Pi (mW/g)	Power (%)
High Burnup				
Pu-238	0.0120	567.57	6.8108	58.15
Pu-239	0.6253	1.9288	1.2061	10.32
Pu-240	0.2541	7.0824	1.7996	15.40
Pu-241	0.0668	3.412	0.2279	1.95
Pu-242	0.0419	0.1159	0.0049	0.04
Am-241	0.0145	114.4	1.6588	14.13
Sum	1.0146		11.6818	100.00
Low Burnup				
Pu-238	0.0001	567.57	0.0327	1.47
Pu-239	0.9636	1.9288	1.8586	83.43
Pu-240	0.0356	7.0824	0.2522	11.32
Pu-241	0.0006	3.412	0.0019	0.08
Pu-242	0.0002	0.1159	0.0000	0.00
Am-241	0.0007	114.4	0.0822	3.69
Sum	1.0007		2.2277	100.00

²³⁸Pu Heat Standards Calibration and Traceability

According to ISO Guide 30 [ISO30], a reference material is an item of one or more whose property values are sufficiently homogeneous, stable, and well-established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. Traceability is an unbroken chain or pathway of measurement comparisons to the nationally accepted reference base. In the case of heat standards, the power measurement is traceable to NIST electrical, resistance, and voltage standards and measured with certified voltage meters. The goal should be to ensure that the standards and the materials to be measured are consistent in all important characteristics that may affect the NDA measurements. Included in ISO Guide 30 are the criteria necessary for an entity to make certified reference material (CRM). A CRM is accompanied by a certificate stating that one or more of the values are certified by a procedure that establishes traceability and uncertainty at a stated level of confidence. For heat standards with a long pedigree, the power is usually certified to 0.05%–0.1%, 95% confidence limit. The power output of ²³⁸Pu heat standards used in the United States and certified by the Safeguards Science and Technology group at LANL are CRMs according to the International Standards Organization (ISO) Guide 30.

²³⁸Pu oxide heat standards are the heat standard of choice across DOE facilities. Many of the ²³⁸Pu heat standards used in the United States have been calibrated and in use for over 25 years. The calibration certification period is usually five years. Periodic recalibration by a heat standards calorimeter is necessary because of uncertainty in the isotopic composition, thus increasing the uncertainty in future decayed power outputs and regulations requiring recalibration. Details of heat standards recertification can be found in reference [BR02].

Plutonium-238 heat standards have a nominal isotopic composition of 80% ²³⁸Pu, 17% ²³⁹Pu, and minor amounts of ²⁴¹Pu and ²⁴⁰Pu. To minimize radiation dose, the oxygen used to make the oxide is usually enriched in ¹⁶O to reduce the neutron dose from ¹⁷O(α , n) reactions.

Tritium

Calorimetry can be used to measure the quantity of tritium in containers. In most cases tritium is the only radioactive isotope present; therefore, no isotopic measurements are required for the assays. A confirmatory gamma-ray assay may be necessary to confirm the lack of additional radionuclides for items with uncertain histories. High-precision and low-bias assays can be made on items containing more than approximately 0.01 g of tritium.

Highly Enriched Uranium (HEU)

Uranium with a natural abundance of 0.7% ²³⁵U generates too little thermal power to be accurately quantified by calorimetric assay. The major component of natural uranium, ²³⁸U, has too long a half-life, 4.5×10^9 years, to generate sufficient thermal power. As the 7.0×10^8 y ²³⁵U mass fraction increases during enrichment, the specific power of uranium increases. Although the specific power of ²³⁵U is higher than ²³⁸U, the major contributor to the increase of effective

Table 9. Calorimetric assay of HEU results.			
Material	Fraction U-235 (Wt %)	U Mass (chem.) g	U Mass (cal assay) g
U oxide	91.3	990	960 +/- 52
U oxide	66.0	990	860 +/- 31
U oxide	52.1	989	975 +/- 53
U metal	93.17	3954	4069 +/- 70

specific power is the ²³⁴U that is enriched along with the ²³⁵U. The specific power for ²³⁴U is

nearly 0.2 mW/g more than three orders of magnitude larger than for ²³⁵U; this is due to its relatively short half-life of 2.45×10^5 y. For an enrichment of 93% ²³⁵U, the ²³⁴U mass fraction is about 1%. With a mass fraction of 1%, the ²³⁴U component supplies about 96% of the total thermal power from the uranium, 1.85 mW/kg. This is a power density that can be measured to an accuracy of about 1% by some calorimeters.

The other necessary measurement for NDA HEU calorimetric assay is determination of the uranium isotopic composition by gamma-ray spectroscopy. This requires the measurement of the relative gamma-ray peak ratios of ²³⁴U, ²³⁵U, and ²³⁸U. An additional isotope, ²³⁶U, is difficult to measure because of the lack of a suitable gamma ray; however, the ²³⁶U mass fraction is typically less than 1%; therefore, not accounting for this isotope will lead to a small bias. The 121-keV gamma-ray from ²³⁴U decay is critical to relate the mass fraction of ²³⁴U to that of ²³⁵U. The closest intense ²³⁵U line above the K absorption edge of uranium is at 144 keV. Calorimetric assay measurement results on HEU metal and oxide are shown in Table 9. These measurements were made with a 12.5 cm diameter twin-bridge, water-bath calorimeter on well-characterized material [RU97].

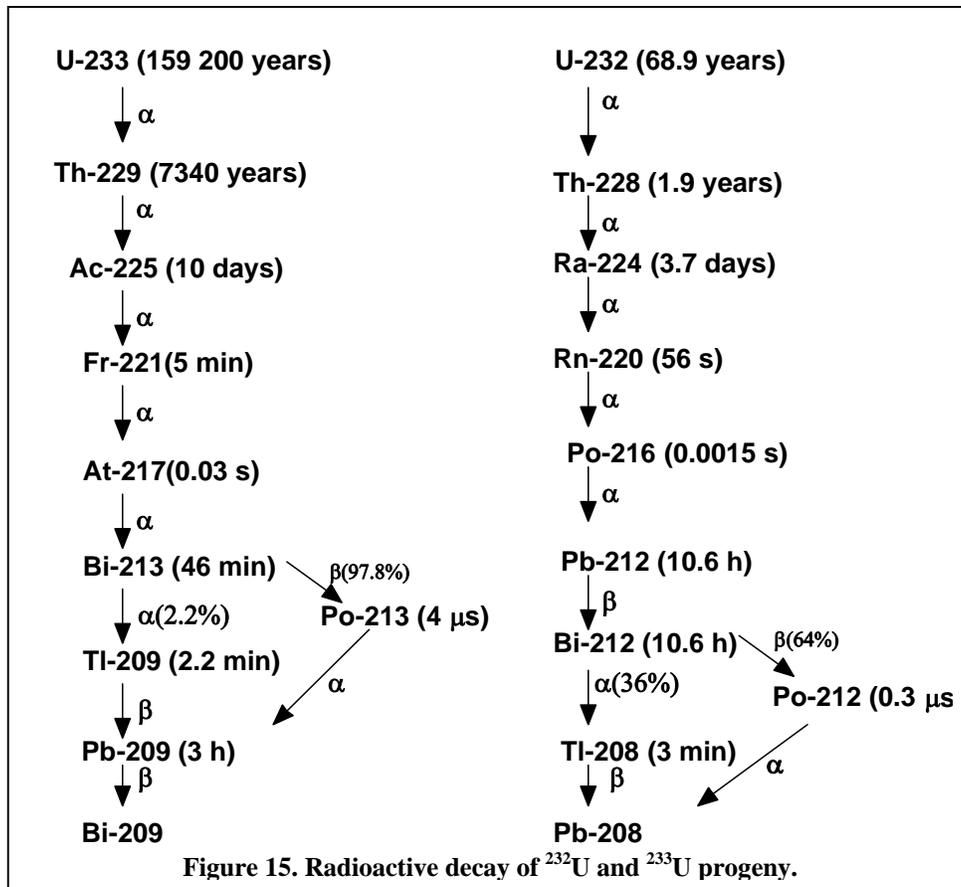
The precision for the 1-kg items ranged from 12 to 18 % RSD, while the thermal power for the 4 kg item, 7.8 mW, was measured with a precision of about 1% RSD. The low specific power of HEU limits calorimetric assay to matrices with high uranium content, such as metal, oxides, U alloys, and high-grade scrap.

²³³U

Another isotope of uranium, ²³³U, is produced in a reactor by irradiation of ²³²Th source material. An NDA technique to quantify ²³³U is in development [RU03]. The half-life of ²³³U, 1.59×10^5 y, is short enough so that measurable power is produced. Another power-generating isotope, ²³²U, is produced along with the ²³³U. Most of the gamma rays from ²³³U materials are due to the coproduced ²³²U. The decay schemes of ²³³U and ²³²U are shown in Figure 15. The short-lived 69.8 years ²³²U decays to 1.9 years ²²⁸Th that then serves as the parent of a series of subsequent decays terminating in ²⁰⁸Pb. Some of the ²³²U progeny are intense gamma-ray emitters, particularly ²⁰⁸Tl that emits a series of high-energy gamma rays, the highest energy transition yielding a 2.6 MeV line. The gamma-ray flux rate is high enough so that ²³³U must be handled behind radiation shielding. The decay rate, and the associated gamma dose rate, of the ²³²U progeny is within 1% of the ²³²U parent after 14 years. For ²³³U materials of this age and older, one can then equate the progeny decay rates with the ²³²U parent. The relatively short half-life of ²³²U and the subsequent alpha decays contribute a significant fraction of the total heat from a ²³³U item. For a ²³²U/²³³U mass fraction of 50 ppm, the decay heat from the ²³²U component equals the heat from the ²³³U component.

In parallel with the ²³²U decay chain, a series of decays result from the ²³³U decay chain. Uranium-233 decays into 7,340 years ²²⁹Th that also serves as the parent of a series of nuclides, some of which generate high-energy gamma rays. The long-lived ²²⁹Th produced by ²³³U decay grows in at the rate of 4.4 ppm/y. The decay chain of ²²⁹Th is also shown in Figure 15. Among the ²²⁹Th progeny, the isotopes ²¹³Bi and ²⁰⁹Tl have high enough gamma-ray branching ratios so that their gamma rays can be observed for aged ²³³U. The activities of these species reach effective secular equilibrium with the ²²⁹Th activity after several months. The decay of these ²³³U progeny contributes a small fraction of the total heat.

From Figure 14 one sees that the specific power of ²³³U is about an order of magnitude less than plutonium. This indicates that ²³³U can be measured with precisions somewhat less than Pu for similar masses of materials. The powers, however, are within the range of applicability for most calorimeters. Another consideration for calorimetric assay of this material is that a fraction of the decay energy is in the form of high-energy gamma rays that will escape the measurement chamber. The 2.6-MeV gamma ray from ²⁰⁸Tl represents about 2.5 % of the decay energy from ²³²U decay. This effect can be reduced by the use of shielding material in the calorimeter chamber. Only the decay energy and mass fractions of ²³³U and ²³²U and their progeny are used in the calculation of P_{eff} . However, ²³⁴U may also be produced in mass fractions up to several percent; exclusion of this nuclide from the calculation of P_{eff} can lead to biases.



A more difficult part of ^{233}U calorimetric assay is the determination of the mass ratio $^{232}\text{U}/^{233}\text{U}$ because of the intense gamma flux from ^{232}U progeny, particularly ^{208}Tl . The most intense high-energy gamma ray of ^{233}U , 317 keV, has a specific activity similar to the ^{239}Pu 414 keV line. The ^{232}U progeny gamma flux generates a high Compton background in the germanium detector that requires a long count time to observe and obtain good counting statistics for the 317-keV peak. A spectrum of ^{233}U in this energy region measured by a germanium detector is shown in Figure 16. The spectrum required a measurement time of 48 hours and was measured through the port of a hot cell.

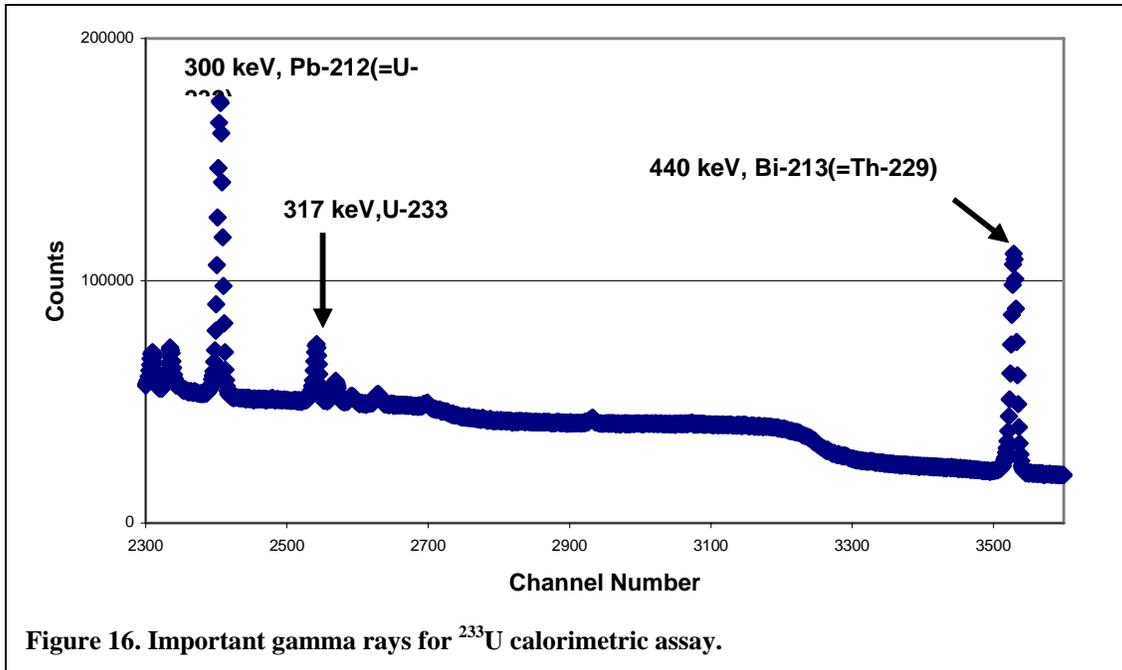


Figure 16. Important gamma rays for ^{233}U calorimetric assay.

Calorimetry and gamma-ray measurements were performed on 17 ^{233}U items with masses ranging from 41 grams to 343 grams. Gamma-ray measurements yielded $^{232}\text{U}/^{233}\text{U}$ ratios ranging from 4.3 to 27.9 ppm. The age of the ^{233}U , i.e., the time since chemical separation of ^{233}U from its progeny, was estimated from the ratio of $^{229}\text{Th}/^{233}\text{U}$ obtained from the ^{213}Bi to ^{233}U gamma ray ratio using the relationship

$$\frac{N_{\text{Th-229}}}{N_{\text{U-233}}} = \frac{\lambda_{\text{U-233}}}{\lambda_{\text{Th-229}} \lambda_{\text{U-233}}} \left(1 - e^{-(\lambda_{\text{Th-229}} - \lambda_{\text{U-233}})t} \right) \quad , \quad (21)$$

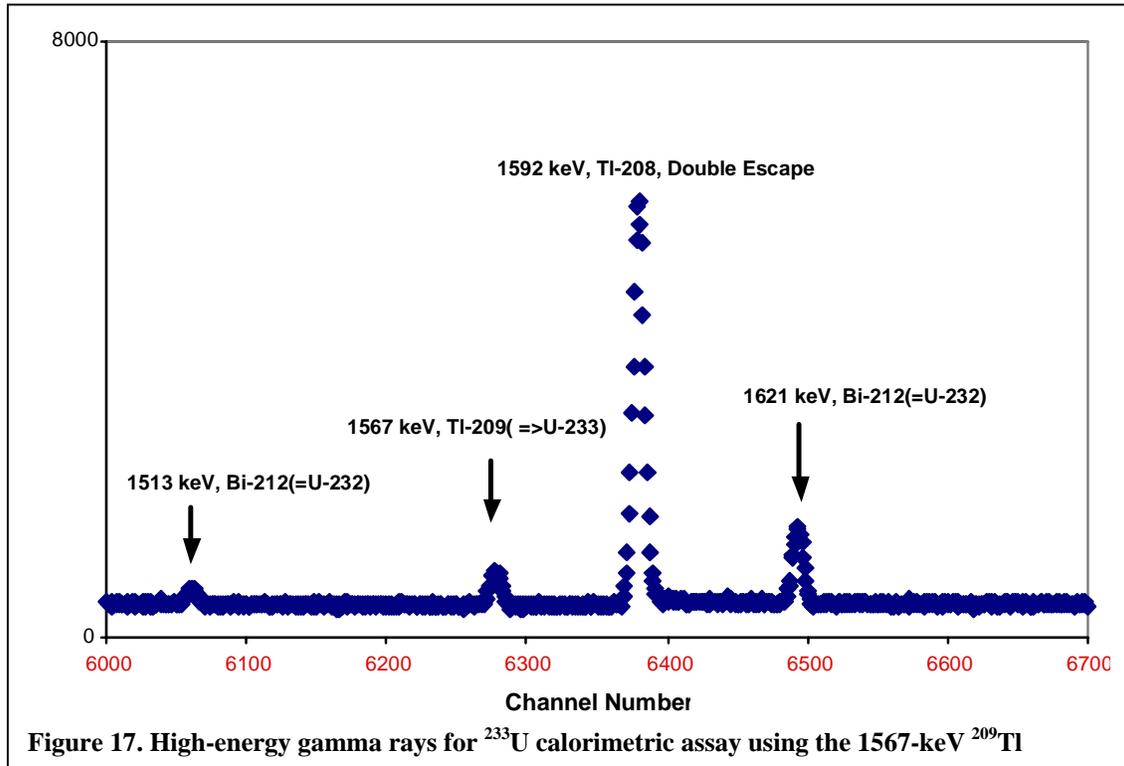
where $N_{\text{Th-229}}/N_{\text{U-233}}$ is the atom ratio, $\lambda_{\text{Th-229}}$, $\lambda_{\text{U-233}}$ are decay constants; and t is the time after separation. The total mass of the ^{233}U as determined by calorimetric assay was 2.17 kg as compared to the book value of 2.22 kg.

If the age of a ^{233}U item is known and the ratio of $^{229}\text{Th}/^{232}\text{U}$ can be determined by gamma rays of their respective progeny, then the ratio $^{232}\text{U}/^{233}\text{U}$ can be determined by

$$\frac{N_{\text{U-232}}}{N_{\text{U-233}}} = \left(\frac{N_{\text{U-233}}}{N_{\text{Th-229}}} \right) \left(\frac{N_{\text{Th-229}}}{N_{\text{U-233}}} \right) \quad , \quad (22)$$

where N_i/N_j are the respective atom ratios. Using the result from this equation, P_{eff} for the ^{233}U material can be calculated. The advantage of using this more indirect way of determining the $^{232}\text{U}/^{233}\text{U}$ ratio is that one can use the high energy ^{212}Bi and ^{209}Tl gamma rays in the region 1.5–1.6 MeV, where the Compton background is lower than in the 0.3-MeV region, and the gamma rays are high enough in energy to penetrate significant thicknesses of shielding and intense enough to permit shorter counting times. Good agreement was observed between the direct determination of $^{232}\text{U}/^{233}\text{U}$ ratios that required 48-h counting times and the indirect known age technique that required 0.5-h counting times with the material in a lead-shielded drum. The high-energy ^{209}Tl 1567-keV gamma ray could be used directly with other gamma techniques

such as segmented gamma scanning to determine the ^{233}U content in heavily shielded items. Figure 17 presents a high-energy gamma ray spectrum of an aged ^{233}U item.



VI. Calorimetry Applied in Unconventional Ways

The calorimeter power measurement can be combined with other nondestructive assay information to determine previously untenable NDA measurement needs. Some of the potential applications of combining calorimetry with neutron and gamma-ray assay will be discussed in the following subsections. Calorimetry can also be applied independently to determine specific activities, total thermal power, and the specific activity of transuranic materials. Using calorimetry to determine transuranic-specific activity is discussed in the last subsection.

Combined Calorimetry/Neutron/Gamma-Ray Assay

Isotopic analysis is required for application of the calorimetric assay technique to items containing multiple types of power-generating isotopes. For most types of special nuclear material there is sufficient gamma-ray information to determine the relative abundance of these isotopes. Some nuclides, however, emit gamma rays with intensities too low to be detected. One example is ^{242}Pu . For most forms of plutonium, the mass fraction of ^{242}Pu is low and its mass fraction also can be estimated through the use of isotopic correlations, where the measured ratios of other plutonium isotopes are used to estimate the ^{242}Pu mass fraction. But in some cases the ^{242}Pu mass fraction is high, and/or there are less-accurate isotopic correlation relationships for the material type being assayed, such as for high-burnup plutonium or any previously processed plutonium. It has been found that by combining neutron counting and gamma-ray spectroscopy

with calorimetry, one can experimentally determine the ^{242}Pu mass fraction. The methodology is described below.

The measured ratio of spontaneous fission neutron emission rate to thermal power is defined by k in the following equation.

$$k = \frac{\sum_i n_i g_i}{\sum_i p_i g_i} \quad , \quad (23)$$

where n_i is the neutron emission rate of isotope i , n/s/g, caused by spontaneous fission, g_i is the mass of isotope in grams, and p_i is the isotopic specific power, W/g. The constants n_i and p_i are isotopic nuclear properties listed in reference [RE91]. The sum includes all the plutonium isotopes and ^{241}Am . The numerator of the equation is the item total neutron spontaneous fission rate that can be determined by neutron-coincidence or neutron-multiplicity counting or even singles counting techniques if there are no (α, n) or multiplication contributions. The denominator is the item power from a calorimeter measurement. We rearrange this equation so that the terms involving ^{242}Pu are on the right-hand side and divide the equation by the masses of all Pu isotopes except ^{242}Pu

$$\frac{\sum_{i'} (kp_{i'} - n_{i'}) g_{i'} + (kp_{Am} - n_{Am})^* g_{Am}}{\sum_{i'} g_{i'}} = \frac{n_{242} - kp_{242}}{g_{total} - g_{242}} \quad , \quad (24)$$

where the primes represent ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Pu , and g_{total} is the total mass of plutonium in the item. The following ratios are determined by gamma-ray spectroscopy of the plutonium isotopes and ^{241}Am with measurable gamma-ray intensities.

$$R_{i'} = \frac{g_{i'}}{\sum_{i'} g_{i'}} \quad , \quad R_{Am'} = \frac{g_{Am-241}}{\sum_{i'} g_{i'}} \quad . \quad (25)$$

With the above definitions of R_i , the previous equation can be rearranged to yield,

$$R_{242} = \frac{1}{1 + (n_{242} - kp_{242}) / \sum_j (kp_j - n_j)^* R_j} \quad , \quad (26)$$

where the summation is over the measured plutonium isotopes and ^{241}Am . All of the terms on the right hand side of the equation are physical constants and are the results of calorimetry, neutron counting, and gamma-ray measurements.

The mass fractions of the other components would be corrected by the following equation

$$R_i = R_{i'} (1 - R_{242}) \quad . \quad (27)$$

Once the mass fractions have been determined, then P_{eff} can be calculated and the calorimetry or neutron measurement result can be used to determine the plutonium mass.

Some results of using this technique on plutonium enriched in ^{242}Pu are shown in Table 10. The final masses in Table 10 were calculated using P_{eff} determined from the $cal/n/\alpha$ methodology. A similar approach has been investigated by Abousahl et al [AB03] with calorimeter, neutron, and gamma-ray measurements performed on medium-burnup PWR fuel pellets (6.5% ^{242}Pu). They found that better agreement with mass spectrometry results was

obtained with this technique than with isotopic correlations. The reported average relative difference between mass spectrometry and gamma-ray spectroscopy results for ^{242}Pu ranged from 0.45 +/- 1.59 % (RSD) to 4.14 +/- 2.59% depending on the gamma-ray peaks and versions of the gamma-ray code (MGA) used for the isotopic determination. Accurate ^{242}Pu mass fractions are important for plutonium assay using neutron coincidence count rates [AB03].

Table 10. Combined calorimetry/neutron/gamma-ray results on enriched plutonium.					
ID	Type	% ^{242}Pu (book)	% ^{242}Pu (cal/n/ γ)	Pu, g (book)	Pu, g (cal/n/ γ)
G17	Metal	88.8	90.6	363	358
G17A	Metal	88.8	90.9	391	372
G20A	Metal	88.8	90.9	53	55

The same methodology described above could be applied to uranium enriched in ^{236}U . Gamma rays from ^{236}U have a low emission rate so that it is difficult to assay. Gamma-ray information is available for the other uranium isotopes ^{234}U , ^{235}U , and ^{238}U so that partial mass fractions can be determined. This information in combination with passive neutron and calorimetry measurements could be used to determine the ^{236}U mass fraction. Other combinations of radionuclides could be measured with calorimetry and neutron counting such as ^{244}Cm and plutonium or enriched uranium mixed with low levels of plutonium.

Uranium Enrichment by Combined Calorimetry/Neutron Counting

Recent developments have been made in NDA to determine uranium enrichment without gamma-ray measurements by combining calorimetry and neutron counting [RU99, RU99A]. This new technique could be useful for large items and/or items heavily shielded with high atomic number material.

The thermal power and spontaneous fission neutron emission rate of uranium have different behaviors with increasing ^{235}U enrichment. The specific power of uranium increases with increasing ^{235}U mass fraction, primarily because of the simultaneous enrichment of ^{234}U . The neutron emission rate shows the opposite behavior with increasing enrichment. The major contributor to uranium neutron emission is ^{238}U , which has a neutron emission rate 45 times that of ^{235}U . As the ^{238}U mass fraction decreases with increasing ^{235}U mass fraction, the uranium neutron emission rate decreases. The ratio of uranium thermal power to neutron emission rate thus increases with ^{235}U enrichment. Figure 18 shows the calculated ratio of power to neutron emission rate for various ^{235}U enrichments. The power to neutron emission rate increases about four orders of magnitude from depleted uranium to a ^{235}U enrichment of 97% by mass. As a result, the ratio of a calorimeter measurement result to a measured spontaneous fission neutron counting result could be used to predict the enrichment of uranium. The advantage of this technique is that the enrichment of shielded uranium could be determined even though the usual ^{235}U gamma rays would be attenuated to an unusable level. The neutrons are more penetrating radiation, and the thermal flux cannot be shielded as effectively. The low specific power and low neutron emission rate would limit the applicability of this technique to multi-kilogram quantities of uranium.

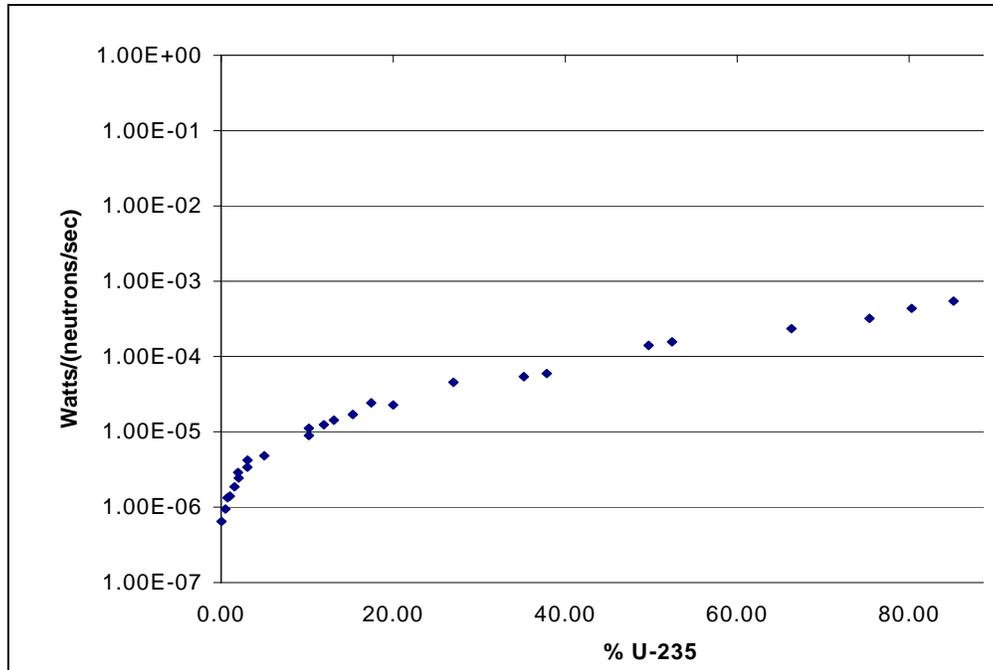


Figure 18. Uranium specific power (W)/neutron emission rate (n/s) dependence on ²³⁵U enrichment.

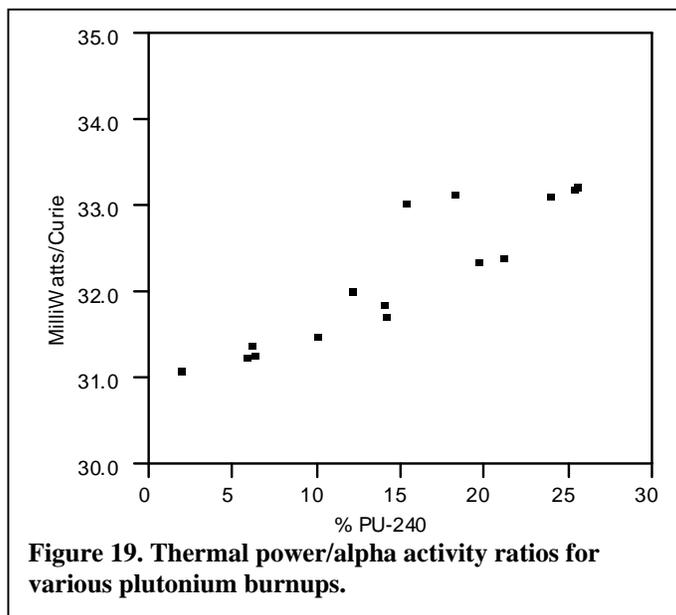
Calorimetric Specific Activity Determination

The total alpha activity of transuranic (TRU) materials can be determined by using calorimetry independently [RU00A, RU00]. This allows all of the benefits of the calorimeter heat measurement to be applied to the activity measurement of TRU waste. The most important benefit is the integrating nature of the measurement. All of the TRU waste activity will be measured by the calorimeter because the heat produced from decay cannot be created or destroyed, shielded or attenuated.

A calorimeter is similar in principle to an event-counting nuclear instrument operated in the rate-meter mode. The calorimeter is measuring the average decay rate of the radioactive material inside the measurement chamber. The efficiency of the calorimeter is nearly 100%; therefore, all of the detectable energy is captured. The thermal power (joules/s) measured by the calorimeter can be directly converted into the total decay rate (dis/s) of the material if the average decay energy of the nuclear species in the calorimeter can be calculated.

Nearly all of the radioactive decays of uranium and transuranic elements are alpha decays. One of the plutonium isotopes, ²⁴¹Pu, decays primarily by beta decay, but this represents typically less than 2% of the total power emitted by alpha decay from other associated plutonium isotopes. Americium-241 is always associated with plutonium; therefore, its power contribution should be included. The Q values for alpha decay are the energy released by plutonium isotopes and ²⁴¹Am and these range from 5.0 MeV for ²⁴²Pu to 5.6 MeV for ²⁴¹Am. The decay energy rate (MeV/s) can be transformed into thermal power (joules/s). The result is independent of the half-lives of the plutonium and ²⁴¹Am isotopes. For ²⁴²Pu the corresponding power-to-decay factor is 29.5 mW/Ci and ²⁴¹Am 33.4 mW/Ci. In Figure 19 a plot of these conversion factors is given for plutonium with different isotopic compositions. The overall range of this conversion factor is

less than 7%. A direct calorimeter thermal power measurement could be used to measure the total alpha activity of a sample within a few percent. The procedure would be to perform the calorimeter measurement and divide the result by the appropriate factor in Figure 19. For example, for plutonium with 6% ^{240}Pu the factor would be close to 31.2 mW/Ci. The result will be independent of the matrix and the isotopic or elemental inhomogeneity of the sample.



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