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ABSTRACT

Calorimetric assay provides a precise nondestructive analytic (NDA) method for determining sample plutonium content based on the heat emitted by decaying radionuclides. Calorimetry has a plutonium-detection sensitivity of 20 ppm, and power measurement precision better than 0.1% is obtainable. It is insensitive to the chemcial form of the plutonium and is independent of measurement-bias problems due to sample geometric configuration and sample matrix composition. Also, the ability of an operator to calibrate a calorimeter using electrical-heat standards eliminates the necessity of transporting plutonium calibration sources. These considerations make calorimetry an important assay tool which can be used by itself or for calibrating more rapid, but less accurate, NDA techniques. The total plutonium mass of the sample may be obtained nondestructively by combining the calorimetric power measurement with a gamma-spectrometer analysis of the sample isotopic content.

Conventional calorimetric design measures the temperature rise of a plutonium-containing sample chamber in contact with a large water-bath heat sink. This design lacks the mobility needed by inspection personnel. The Argonne National Laboratory (ANL) air-chamber isothermal calorimeters are low-thermal capacitance devices which eliminate the need for large, constant-temperature heat sinks.

A bulk calorimeter designed to measure sealed containers holding up to 3 kg Pu, and a small-sample calorimeter designed to measure mixed-oxide fuel pellets and powders will be discussed. The operational characteristics of these instruments will be described, and the results of sample assays will be presented.

I. INTRODUCTION

Increased emphasis on on-site verification of nuclear material inventories has magnified the need for techniques capable of in-field nondestructive analysis (NDA) of plutonium. Because of the large variations encountered in the chemical form of plutonium, the nonstandard measurement geometries, and the presence of radiation absorbers, there are often large uncertainties associated with on-site assays. Calorimetry has provided a precise NDA method for the determination of plutonium content in the laboratory.[1] It has also been applied routinely to help satisfy plant-shipper/receiver accountability requirements.[2] The lower limit of sensitivity of this technique is approximately 0.1 g Pu-239 in a one-liter container.[3] However, it is for the analysis of dense, heterogeneous mixtures of relatively high Pu content that the method is best suited. Linear sample power-mass relations have been obtained for items containing plutonium in the kilogram region. A measurement precision of better than 0.1% is readily attainable.[4,5] This is not true of gamma-ray and neutron techniques where photon absorption and neutron multiplication cause considerable nonlinearity in assaying high mass samples.[6,7] Among the advantages of calorimetric assay are its insensitivity to the chemical form of the plutonium and its independence from measurement-bias problems due to sample geometric configuration and sample matrix composition. Also, the ability of an operator to calibrate a calorimeter with electrical heat eliminates the necessity of transporting plutonium calibration sources. These considerations suggest calorimetry as an important in-field assay tool which could be used by itself or as a selective cross-calibration of more rapid, but less accurate, NDA techniques. Argonne isothermal calorimeters have been constructed as low-thermal-capacitance devices in which the water-bath heat sinks have been eliminated. This design has shown promise of reducing the assay time and of increasing the mobility of the system.[8] This report will discuss work in progress on a set of calorimeters designed to assay the types of materials normally encountered by IAEA personnel. A bulk (storage container) calorimeter, designed to measure sealed cans holding up to 3 kg Pu, and a small-sample calorimeter, designed to measure mixed-oxide fuel pellets and powders, will be reviewed.[5,9] The operational characteristics of the instruments will be described, and the results of sample assays will be presented.

II. DISCUSSION OF CALORIMETRIC TECHNIQUE

Calorimetric analysis of plutonium relies on the ability of the assay device to measure thermal power with high precision and accuracy. Thermal energy is generated by the absorption and degradation of the radiation released in the decay of the Pu isotopes. The principal decay modes of the isotopes of interest produce alpha particles and low-energy beta and gamma rays, which are easily converted to heat energy within the measurement chamber. In unirradiated fuel, only the isotopes Pu-238-242 and Am-241 have high enough specific activities to contribute to the total heat. Thus we may relate thermal power to grams of plutonium by using the proper conversion factor, known as the effective specific power (P_{eff}). P_{eff} has been defined as the weighted-average isotopic power per gram of sample.[5]

$$P_{eff} = P_S/M_t = \sum^{n} M_i P_i/M_t = \Sigma\ (KRQ\lambda)_i$$

where

P_S = sample power

$M_t \triangleq$ sample plutonium mass = Σ mass of Pu isotopes

P_i = isotopic thermal power/gram

R_i = M_i/M_t

Q_i = isotopic total decay energy

λ_i = isotopic decay constant

K_i = isotopic normalized constant

The ANSI standard on calorimetry suggests two methods for determining P_{eff}.[3] The methods are distinguished by whether an isotopic analysis is conducted. The empirical method requires that a combined chemical and calorimetric analysis be performed on a set of representative samples to determine the total Pu content per watt of measured power. Samples must be reassayed at a later time to account for changes due to radioactive decay. The second method requires that an isotopic analysis be performed to determine the content of Pu-238-242 and Am-241. The P_{eff} may be calculated at any future time by applying the known decay laws.[3]

The determination of P_{eff} often accounts for the largest portion of the uncertainty associated with calorimetric assay. In certain circumstances this may be avoided by accepting the agreement between heat output as determined by the shipper and that determined by the receiver. While this method of operation may not be desirable for material in long term storage, the change in power output resulting during normal shipment between facilities would not be significant. During a one-month period, ZPPR-fuel power output will increase less than 0.15% (see Table 1).

III. INSTRUMENT DESIGN

In classical heat-flow calorimeters, the temperature difference developed across a thermal resistance linking the sample chamber and a heat sink is proportional to the power produced by the samples. ANL calorimeters are designed as servo-controlled devices in which electrical power is provided to maintain the unit at a constant temperature above ambient. No temperature gradients are developed during an analysis. When a heat-producing source (P_S) is assayed, the electrical power necessary to maintain the steady state condition (P_C) is reduced from the empty chamber baseline power (P_0). Thus the sample-produced power may be determined from the differences between the calorimeter-applied powers with and without a sample.

$$P_S = P_0 - P_C$$

In the Argonne design, the calorimeter is most simply viewed as a constant temperature oven composed of a series of concentric chambers (Fig. 1). Each of these chambers is constructed from an aluminum cylinder upon which resistive heating coils and heat sensors are mounted. The cylinders are separated from one another by high thermal-resistance material. The ends of the cylinders are similarly protected by nonconducting plugs and by pancake-type heater coils. Alternating zones of high and low thermal conductivity in this manner tends to minimize the effects of localized external temperature changes. A temperature profile is established within the calori-

meter to eliminate axial heat flow and to ensure that a negative radial temperature gradient is maintained. In the schematic drawing in Fig. 1, the electronic feedback control circuits will maintain the relation $T_3 > T_2 > T_1 > T_0 > T_{ambient}$. The inner two cylinders (T_3, T_2) act as the measurement chamber. The calorimeter-supplied electrical power is adjusted to maintain the temperature difference between these cylinders to ± 20 microdegrees. Noninductively wound Ni coils on these chambers act as both heaters and temperature sensors using the principles of resistance thermometry. The T_3 Ni coil may be visualized as being a temperature-sensitive element in a resistive bridge. The control circuits will supply sufficient electrical power (P_C) so that the total thermal source ($P_S + P_C$) will be adequate to maintain the temperature necessary to "null" the bridge.

Figure 2 gives a simplified description of the inner-chamber control circuit. The system works on a negative feedback principle. This causes the electrical power applied to R_3 to be increased or decreased in response to the chamber temperature. The outer shells act as protective buffers for the inner measurement chambers. These are adjusted by a series of YSI thermistors and copper heating coils so that the measurement chamber is unaffected by changes in the ambient temperature.

Data manipulation for both the small-sample and the bulk calorimeters is performed by a microprocessor-based data acquisition system (DAS). The hardware for this module was designed to be common to all ANL calorimeters, thus facilitating operator training and use. The DAS hardware consists of a microprocessor, a 12-bit analog-to-digital converter (ADC), 8K bytes of nonvolatile memory, and 1K bytes of scratch-pad memory. A number of input-output (I/O) peripherals, including a printer and a keyboard, are also included. The entire unit is housed in an attache case and weighs approximately 5 kg. (Detailed circuit diagrams and program listings are supplied in the instrument design manual [9]).

The data-analysis program resides on the nonvolatile memory. While the code will differ slightly with each calorimeter, the basic data-acquisition and -handling routines have been structured to appear identical to the user. Among the routines included are a set of programs to calculate P_{eff} from the sample isotopic data. The code to correct the isotopic data for radioactive decay is also available. Standard assay operation proceeds as follows: The DAS monitors the electric power applied to the measurement chamber. The analog signal is digitized, and the average and the standard deviation of a predetermined number of power measurements is determined. The number of measurements needed to properly describe the behavior of the calorimeter at equilibrium depends upon the thermal time constant of the device and the sample being assayed. The power applied during an actual assay will be compared to either an electrical-heat calibration curve or to a zero-source power baseline reading. The sample power and its associated uncertainty are then calculated.

The small-sample calorimeter was designed as a portable, rapid assay device for analyzing small quantities of Pu, such as fuel pellets and mixed-oxide powders. The maximum sample power output which can be assayed is 32 mW (approximately 10 g of fast reactor Pu). The system is contained in two briefcase-sized packages and weighs a total of 18 kg. It consists of the calorimeter, the sample preheater, and a microprocessor-controlled data analysis system. The unit has been designed for in-field operation and is capable of operating under a sizable range of voltage and temperature conditions. It has a measurement cycle of 20 min with a measurement

precision of 0.1%.[5] (A detailed operating description for this device, including circuit diagrams, is available in the manual *ANL Small-Sample Calorimeter: System Design and Operation*, C. T. Roche, et al.[9])

The bulk calorimeter has been designed to assay large canisters of Pu-containing material normally found in fuel-processing facilities. The chemical form of this material may vary from Pu-metal alloys to mixed-oxide (MOX) powders. The material may be in any physical configuration from finished product to scrap. In addition, since it is often highly desirable that these canisters not be opened, it is possible that the exact constitutents and their geometric arrangement will be unknown. In developing a device which addresses these problems, we attempted to construct a system which would be capable of accurately assaying large concentrations of Pu, be relatively insensitive to ambient temperature fluctuations, and be transportable between facilities. The bulk calorimeter consists of 5 servo-controlled cylinders separated from each other by heat-conducting epoxy. The system power supplies and the control circuitry are located in a NIM standard power bin. The unit also includes a sample preheater and a microprocessor-controlled DAS. The calorimeter will assay cans up to 11.1 cm in diameter by 33 cm in length. The total sample power output may be as high as 26 W, which is equivalent to approximately 3 kg of high burn-up recycle Pu. Preliminary estimates of the sample-power measurement precision are less than 0.1%. The unit has been operated successfully in areas undergoing large temperature fluctuation. The temperature instability contribution to the total system uncertainty is less than 0.02%/°C. Unlike the small-sample calorimeter in which sample encapsulation is controlled by the analyst, the bulk calorimeter will often be assaying items with poor heat=transfer properties. This includes scrap containers in which the heat-emitting material is doubly wrapped in polyethylene within the storage canister. Under these conditions, the heat-transfer properties of the sample will provide the limiting time constant governing the equilibration period. An equilibration period of 5 hr was necessary for the material assayed in Table 1. Equilibration prediction techniques and more accurate sample preheating procedures are being examined as possible ways to reduce the assay time.

IV. EXPERIMENTAL EVALUATION

A series of experiments were performed as part of the program to evaluate the measurement reliability of these calorimeters. The samples assayed during these experiments were representative of the forms of plutonium encountered in the nuclear fuel cycle. The experimental procedure adopted required that the effective specific power and the thermal power output be determined for each sample. All P_{eff} were determined with the computational method (see Section II). With the exception of the ZPPR mixed-oxide fuel rods (Table 1), the isotopic composition of the samples was determined prior to calorimetric assay with a gamma-ray spectrometric technique.[10] The ZPPR rods had been well-characterized by previous chemical and mass-spectrometric analysis.[11] The gamma-spectrometric measurement used a low-energy photon spectrometer (LEPS) to analyze the 90-110 KeV region of the spectra. When the analysis is limited to this small energy range, the effects of gamma-ray absorption and sample nonuniformity can be ignored. Since gamma-assay of Pu samples does not determine Pu-242 content, the isotopic ratios are slightly biased. However, only low burn-up material is considered in these experiments, and the added uncertainty in P_{eff} is less than 0.2%. Typical precisions (1 σ) obtained in the determination of P_{eff}

for Pu are 0.5%, while precisions of 2.5% are obtained from analysis of mixed-oxide fuels (Pu, U). The increased uncertainty results from the presence of U X-rays in the 90-110 KeV region.

The calorimeter must be electrically calibrated before assaying samples. In this procedure, a precision voltage source supplies measured voltage increments to a Ni coil wound around the inner measurement chamber. The feedback control circuitry will correspondingly decrease the power to the heater-sensor coil to maintain the proper temperature balance. This simulates a series of radioactive heat standards being placed in the measurement chamber. The entire procedure is controlled automatically by the DAS. The microprocessor outputs the input calibration power and the calorimeter-supplied power. A linear least-squares fit to the data indicates a slope of -1.001 ± 0.003 with an intercept of 31.434 ± 0.003 mW for the small-sample calorimeter. A slope of -1.001 ± 0.001 and an intercept of 26.499 ± 0.008 W are found for the bulk calorimeter. Electrical calibration has the advantage of being traceable to high-precision electrical standards through organizations like the U. S. National Bureau of Standards. It also eliminates the necessity of transporting Pu heat standards.

Table 1 shows the results of assays performed by the bulk calorimeter. The samples in the first experiment consisted of stainless steel-encapsulated MOX fuel rods in a storage container 11 cm in diameter and 18 cm long. The fuel rods were placed in the canister, assayed, removed and replaced in a different arrangement, and then reassayed. Within the limit of measurement error, the assay was unaffected by the geometric arrangement of the rods. In addition, by changing the number of fuel rods assayed, we obtained a linear variation of measured sampled mass to reported mass, with a slope of 0.962 ± 0.001. This behavior differs from neutron and gamma-ray assay of large quantities of Pu where the geometric arrangement of the material may result in errors due to neutron multiplication or photon absorption.[6,7]

The second experiment was performed on a set of realistic scrap samples. The samples were constructed from a mixture of plutonium- and aluminum-oxide powders. The cans were agitated between measurements to test the system response to nonuniform changeable matrices. This rearrangement of the sample-matrix distribution had no effect on the assay. The calorimeter gives reasonable results for samples emitting as little as 60 mW, which is less than 0.25% of the full power of the system. The failure of the calorimeter to accurately assay the 5-g scrap sample sets a lower limit on the sensitivity of the device. This limit is a function of the calorimeter full-power setting and not an inherent limit of the design. A similar design with a full-scale power setting of 10 W was able to assay the sample accurately within the uncertainty of the system.

The results of the set of assays using the small-sample calorimeter are shown in Table 2. In these experiments, both mixed-oxide fuel and Pu-metal alloy fuel were analyzed.[5] The material was double-encapsulated in Al sample holders prior to assay. This encapsulation system was designed to maximize the rate of heat transfer, thus minimizing the sample assay time. (The capsules containing MOX pellets were sealed by W. Ulbricht of New Brunswick Laboratory.) The sample power was determined in a 4-min mea-

surement following a 15-min equilibration period. The 1 σ errors given in the power measurements include contributions from the system temperature stability, the sample heat distribution uncertainty, and the effect of multiple analyses of individual samples. The principal error contribution to the final conversion to grams of Pu is the uncertainty in the gamma-ray-determined value of P_{eff}. However, in all cases the calorimetrically determined Pu content came well within two standard deviations of the reported book value.

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Figure 1: Schematic Representation of ANL Isothermal Calorimeter Including Measurement and Control Components

Figure 2: Resistance Thermometry and Feedback Control Circuitry in ANL Isothermal Calorimeters

Table 1 Pu Analysis Performed by the ANL Bulk Calorimeter

A: Assay of ZPPR Mixed Oxide Fuel Rods

Sample Composition $(Pu,U)O_2$ Pu - 13.25%
Nominal Isotopic* $^{238}Pu = 0.05\%$ $^{239}Pu = 86.6\%$
$^{240}Pu = 11.5\%$ $^{241}Pu = 1.7\%$
$^{242}Pu = 0.02\%$ $^{241}Am = 0.2\%$
Effective Specific Power**: 3.54 mW/g

No. of Rods	Sample Power(mW)	Sample Mass(g)****	Reported Book value
6	233 ± 1	65.8 ± 0.3	70.9
13	528 ± 2	149.2 ± 0.6	154.0
25	1006 ± 1	284.2 ± 0.3	296.3
32***	1286 ± 1	363.3 ± 0.3	379.3
32	1286 ± 1	363.3 ± 0.3	379.3
45	1805 ± 2	509.9 ± 0.6	533.3

*Batch Isotopic analysis reported 8/11/70

**Effective Specific Power calculated from Batch Isotopic Data 7/1/78

***The first assay of 32 rods was performed with the rods in a close packed geometry, the second with maximum spatial separation.

****Uncertainties in the Isotopic Specific Power were not included in this analysis

Table 1 (Cont'd)

B: Assay of PuO_2 Scrap Samples

Sample Composition PuO_2, Al_2O_3, Pu - 1%

Nominal Isotopic* ^{238}Pu = 0.02% ^{239}Pu = 90.7%
^{240}Pu = 8.4% ^{241}Pu = 0.9%
^{242}Pu = 0.05%

Effective Specific Power** - 2.93 ± 0.02 mW/g

Sample Power(mW)	Sample Mass(g)	Reported Book Value
208 ± 1	71.0 ± 0.6	70.62
107 ± 1	36.5 ± 0.4	35.62
62 ± 2	21.2 ± 0.7	20.62
10 ± 3	3.4 ± 1.1	5.62

*Batch Isotopic Reported 10/30/67

**Effective Specific Power determined by Gamma-Spectrometry on 5/12/78

Table II Pu Analysis Performed by the ANL Small Sample Calorimeter

A: Assay of Mixed Oxide Fuel Pellets

Sample Composition - Pu = 11.5%, U = 76.5%, O = 12%
Nominal Isotopic - ^{238}Pu = 0.1%, ^{239}Pu = 86.5%, ^{240}Pu = 11.8%, ^{241}Pu = 1.5%, ^{242}Pu = 0.2%, ^{241}Am = 0.7%

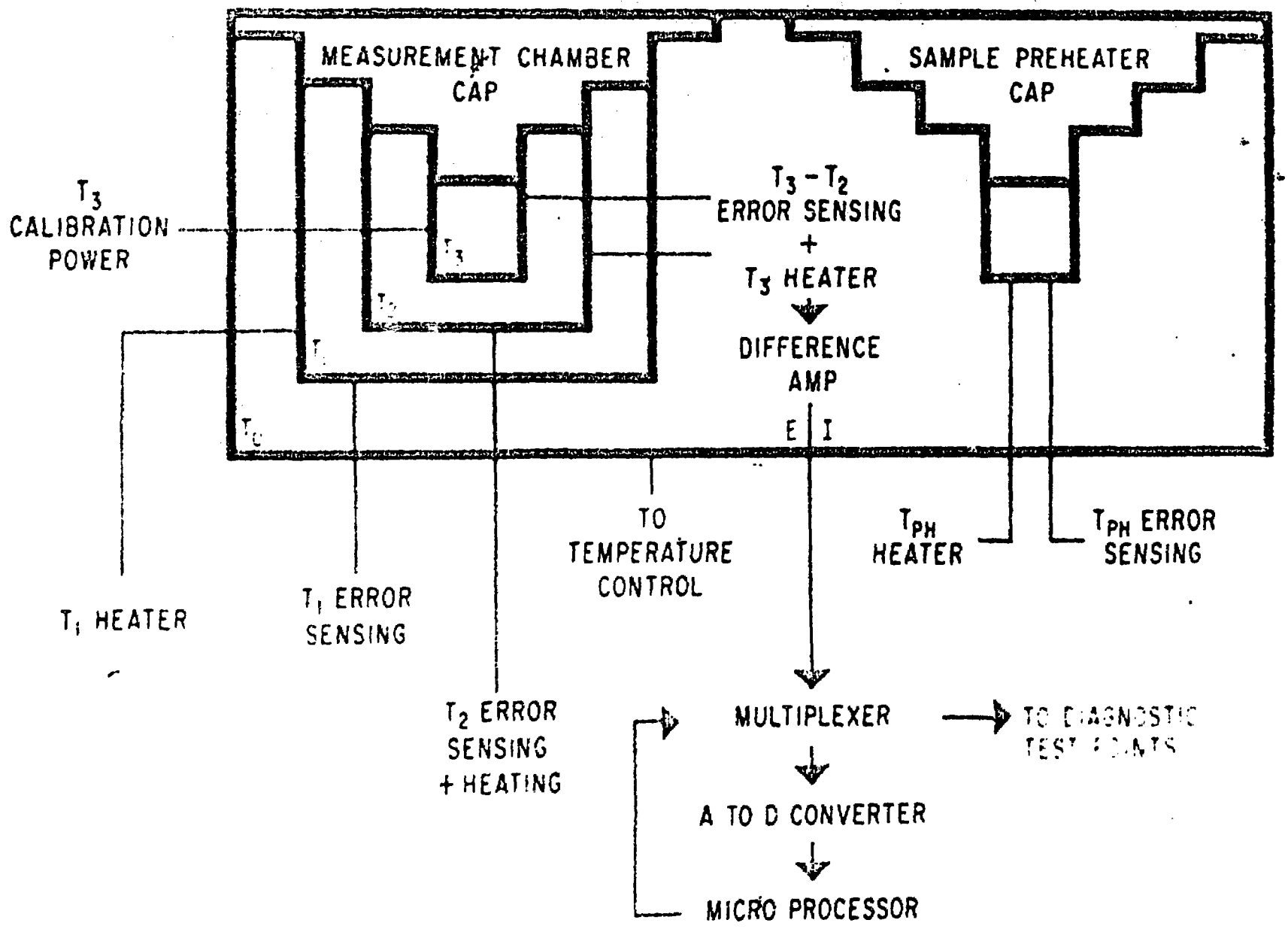
Peff (mw/g)	Sample Power (ms)	Sample Mass (g)	Reported Book Value
3.63 ± 0.08	11.13 ± 0.05	3.07 ± 0.07	2.91
8.87 ± 0.11	6.33 ± 0.02	1.64 ± 0.05	1.69

B: Assay of ZPR-3 Alloy[5]

Sample Composition - Pu = 98.79%, Al = 1.17%
Nominal Isotopic - ^{238}Pu = 0.01%, ^{239}Pu = 95.2%, ^{240}Pu = 4.5%, ^{241}Pu = 0.2%, ^{242}Pu < 0.2%, ^{241}Am = 0.2%

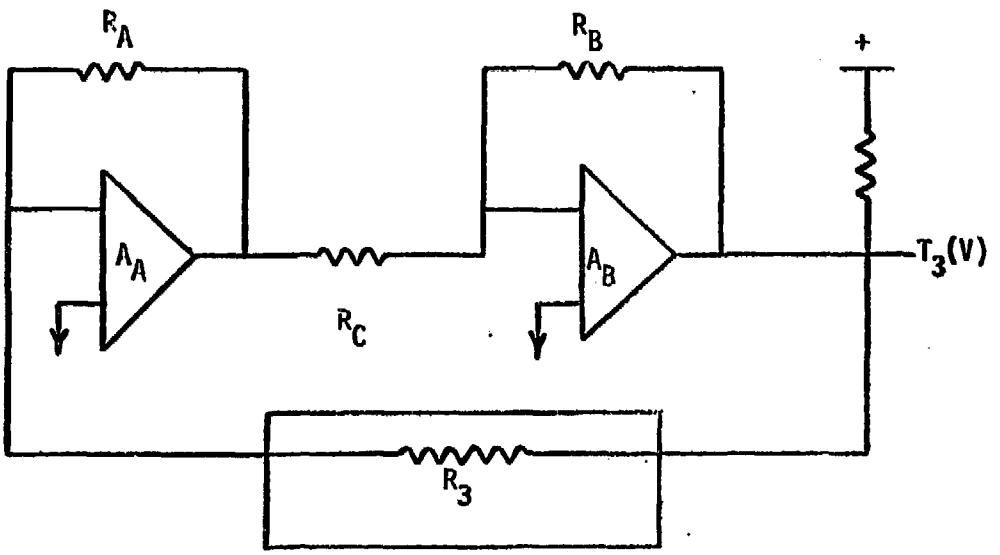
Peff (mw/g)	Sample Power (ms)	Sample Mass (g)	Reported Book Value
2.48 ± 0.01	4.261 ± 0.005	1.72 ± 0.02	1.72
2.49 ± 0.01	3.733 ± 0.004	1.50 ± 0.01	1.50
2.48 ± 0.01	4.409 ± 0.005	1.78 ± 0.01	1.76
2.51 ± 0.02	4.263 ± 0.005	1.70 ± 0.02	1.71

Figure 1: Schematic Representation of ANL Isothermal Calorimeter Including Measurement and Control Components



Block Diagram of the Main Control Components Used in ANL Colorimeters

Figure 2: Resistance Thermometry and Feedback Control Circuitry in ANL Isothermal Calorimeters



$$R_3 = R_0[1 + \alpha\Delta T]$$

$$\Delta T = T_3 - T_{equilib}$$

$$\alpha > 0$$

$$K_B = R_B/R_C \qquad dK_B/dT = 0$$

$$K_A = R_A/R_3 \qquad dK_A/dT < 0$$

$$K_A = R_A/R_0[1 + \alpha\Delta T]$$

System operating temperature set by condition

$$K_A K_B = 1.0 \quad T_{eq} = 20° + (1/\alpha)\left[\frac{R_B R_A}{R_C R_0} - 1\right]$$

SYSTEM OPERATING CHARACTERISTICS

ΔT	R_3	K_A	Feedback Loop Characteristics		
> 0	> R_A	< 1	Degenerative	$T_3(V)$	decreases
				P_S	decreases
				R_3	decreases
< 0	< R_A	> 1	Regenerative	$T_3(V)$	increases
				P_S	increases
				R_3	increases