**Designation: C 1458 – 00**

# Standard Test Method for
# Nondestructive Assay of Plutonium, Tritium and [241]Am by Calorimetric Assay[1]

This standard is issued under the fixed designation C 1458; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes the nondestructive assay (NDA) of plutonium, tritium, and [241]Am using heat flow calorimetry. For plutonium the range of applicability corresponds to < 1 g to > 2000 g quantities while for tritium the range extends from 0.001 g to > 10 g. This test method can be applied to materials in a wide range of container sizes up to 50 L. It has been used routinely to assay items whose thermal power ranges from 0.001 W to 135 W.

1.2 This test method requires knowledge of the relative abundances of the plutonium isotopes and the [241]Am/Pu mass ratio to determine the total plutonium mass.

1.3 This test method provides a direct measure of tritium content.

1.4 This test method provides a measure of [241]Am either as a single isotope or mixed with plutonium.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*
C 697 Test Methods for Chemical, Mass Spectrometry, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powder and Pellets[2]
C 859 Terminology Relating to Nuclear Materials[2]
C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry[2]
C 1030 Test Method for Determination of Plutonium Isotopic Composition by Gamma-Ray Spectrometry[2]
2.2 *ANSI Standards:*[3]

ANSI N15.22 Plutonium—Bearing Solids–Calibration Techniques for Calorimetric Assay
ANSI N15.54 Radiometric Calorimeters–Measurement Control Program

## 3. Terminology

3.1 *Definitions*—Terms shall be defined in accordance with Terminology C 859 except for the following:

3.1.1 *baseline*—the calorimeter output signal with no heat-generating item in the calorimeter sample chamber.

3.1.2 *basepower*—a constant thermal power applied in a calorimeter through an electrical resistance heater with no heat-generating item in the sample chamber.

3.1.3 *calorimeter*—a device to measure heat or rate-of-heat generation.

3.1.4 *calorimetric assay*—determination of the mass of radioactive material through the measurement of its thermal power by calorimetry and the use of nuclear decay constants and, if necessary, additional isotopic measurements.

3.1.5 *effective specific power*—the rate of energy emission per unit mass of plutonium at the time of measurement.

3.1.6 *equilibrium*—the point at which the temperature of the calorimeter measurement cell and the item being measured stops changing.

3.1.7 *heat distribution error*—the bias arising from the location of the heat source within the calorimeter chamber.

3.1.8 *heat-flow calorimeter*—a calorimeter so constructed that the heat generated in the calorimeter flows past a temperature sensing element, through a thermal resistance, to a constant temperature heat sink.

3.1.9 *passive mode*—a mode of calorimeter operation where no external power is applied to the calorimeter except the current needed to excite the Wheatstone Bridge circuit.

3.1.10 *sensitivity*—the change in calorimeter response per Watt of thermal power (usually in units of micro Volts per Watt) for a heat flow calorimeter.

3.1.11 *servo control*—a mode of calorimeter operation where a constant applied thermal power is maintained in a calorimeter measurement chamber through the use of an electric resistance heater in a closed loop control system.

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3.1.12 *specific power*—the rate of energy emission by ionizing radiation per unit mass of an isotope, such as [241]Am or tritium.

3.1.13 *thermal diffusivity*—the ratio of thermal conductivity to the heat capacity. It measures the ability of a material to conduct thermal energy relative to its ability to store thermal energy.

3.1.14 *thermal resistance*—ratio of the temperature difference at two different surfaces to the heat flux through the surfaces at equilibrium.

3.1.15 *thermal time constant*—an exponential decay constant describing the rate at which a temperature approaches a constant value.

3.1.16 *thermel*—the THERMal ELement of the calorimeter, including the sample chamber, and temperature sensor.

3.1.17 *traceability*—relating individual measurements through an unbroken chain of calibrations to U.S. or international primary reference materials or to accepted values of fundamental physical constants.

## 4. Summary of Test Method

4.1 The item is placed in the calorimeter measurement chamber and the total heat flow at equilibrium, that is, the thermal power, from the item is determined by temperature sensors and associated electronic equipment.

4.2 The thermal power emitted by a test item is directly related to the quantity of radioactive material in it. The total power generated by ionizing radiation absorbed in the item is captured by the calorimeter.

4.3 The mass of plutonium, tritium, or [241]Am (m) is calculated from the measured thermal power of an item ($W_i$) using the following relationship:

$$m = \frac{W_i}{P_{eff}} \qquad (1)$$

where:
$P_{eff}$ = the effective specific power calculated from the isotopic composition of the item (see Appendix X1 for details of the calculation of $P_{eff}$ for plutonium).

4.3.1 For tritium the measured thermal power can be directly transformed into mass using the specific power of tritium, $P_{eff} = 0.3240 \pm 0.00045$ (SD) W/g **(1)**.[4]

4.3.2 For [241]Am as a single isotope the measured thermal power can be directly transformed into mass using the specific power of [241]Am, $P_{eff} = 0.1142 \pm 0.00042$ (SD) W/g (see Table X1.1).

4.3.3 For [241]Am mixed with plutonium, the [241]Am mass, $M_{Am}$, is determined by

$$M_{Am} = R_{Am}M_{Pu} \qquad (2)$$

where:
$R_{Am}$ = the mass ratio of [241]Am to Pu, and
$M_{Pu}$ = the mass of plutonium.

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[4] The boldface numbers in parentheses refer to the list of references at the end of this standard.

## 5. Significance and Use

5.1 This test method is presently the most accurate NDA technique for the assay of many physical forms of plutonium. Isotopic measurements by gamma-ray spectroscopy or destructive analysis techniques are part of the test method when it is applied to the assay of plutonium.

5.1.1 Calorimetry has been applied to a wide variety of Pu-bearing solids including metals, alloys, oxides, fluorides, mixed Pu-U oxides, mixed oxide fuel pins, waste, and scrap, for example, ash, ash heels, salts, crucibles, and graphite scarfings) **(2,3)**. The test method has been routinely used at U.S. and European facilities for plutonium process measurements and nuclear material accountability for the last 30 years **(2-6)**.

5.1.2 Plutonium-bearing materials have been measured in calorimeter containers ranging in size from 0.025 to 0.30 m in diameter and from 0.076 to 0.43 m in height.

5.1.3 Gamma-ray spectroscopy typically is used to determine the plutonium isotopic composition and [241]Am/Pu ratio (see Test Method C 1030). Isotopic information from mass spectrometry and alpha counting measurements may be used (see Test Method C 697).

5.2 The test method is the most accurate NDA method for the measurement of tritium. For many physical forms of tritium compounds calorimetry is the only practical measurement technique available.

5.3 Unlike other NDA techniques no physical standards representative of the materials being assayed are required for the test method.

5.3.1 The test method is largely independent of the elemental distribution of the nuclear materials in the matrix.

5.3.2 The accuracy of the method can be degraded for materials with inhomogeneous isotopic composition.

5.4 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.

5.5 Heat-flow calorimetry has been used to prepare secondary standards for neutron and gamma-ray assay systems **(7)**.

5.6 The calorimetry measurement times are typically longer than other NDA techniques. 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.

5.6.1 Calorimeter measurement times range from 20 minutes **(8)** for smaller, temperature-conditioned, containers up to 24 h for larger containers and items with long thermal-time constants.

5.6.2 Measurement times may be reduced by using equilibrium prediction techniques, by temperature preconditioning of the item to be measured, or operating the calorimeter using the servo-control technique.

## 6. Interferences

6.1 Interferences for calorimetry are those processes that would add or subtract thermal power from the power of the radionuclides being assayed.

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6.2 Interferences can be phase changes or endothermic or exothermic chemical reactions, such as oxidation.

6.3 Undetected heat-generating radionuclides would add additional thermal power to the measurement.

## 7. Apparatus

7.1 Calorimeters are designed to measure different sizes and quantities of nuclear material. Different types of heat-flow calorimeter systems share the common attributes listed below.

7.1.1 *Measurement Chamber*—Heat flow calorimeters have a cylindrical measurement chamber from which all of the heat flow generated by radioactive decay is directed through temperature sensors.

7.1.1.1 An electrical heater may be built into the walls or the base of the chamber to provide measured amounts of thermal power into the calorimeter well.

7.1.1.2 Insulation is used to shield the chamber from outside temperature variations that would influence the thermal power measurement. Typically, an insulated plug is inserted above the item container inside the calorimeter. For some calorimeter types an insulating plug is installed permanently below the measurement chamber.

7.1.2 *Calorimeter Can*—The item to be measured may be placed in a special can that is designed to be inserted and removed easily from the calorimeter. It will have only a small air gap to provide good thermal conductivity between the outer surface of the can and the inner surface of the measurement chamber.

7.1.3 *Temperature Sensors*—Temperature sensors consist of commercially available thermistors, thermocouples, temperature sensitive resistance wire, or thermopiles.

7.1.4 *Thermal Sink*—The temperature increases due to heat flows generated by items are measured against a reference temperature of a thermal sink. The thermal sink could be a water bath or air bath or a metal block maintained by a thermoelectric cooler/heater. In the case of servo-controlled calorimeters, the measurement chamber is maintained at an elevated temperature compared to the reference temperature.

7.1.5 *Electrical Components*—Sensitive, stable electronic components are required for accurate calorimeter measurements.

7.1.5.1 High precision voltmeters are required to measure the voltage changes generated from the temperature sensors. The resolution of the voltmeters should be better than one part per million of the voltage range.

7.1.5.2 Stable power supplies are necessary to provide constant current to resistance sensors and calorimeter heaters.

7.1.5.3 Precision resistors with certified resistances traceable to a national measurement system may be used with calibrated voltmeters to accurately determine electrical power delivered to heaters in the calorimeter chamber. If radioactive heat standards are used as part of the measurement control program the calorimeter voltmeters need not be calibrated, nor are precision resistors required.

7.1.5.4 For a calorimeter operated in the servo (power replacement) mode digital-to-analog controller units are used to supply power to an internal resistance heater to maintain a constant temperature differential across thermal resistances.

7.1.6 *Heat Standards*—Thermal power standards are required to calibrate the calorimeter and may be used as measurement control standards to check the stability of calorimeter performance **(9-12)**.

7.1.6.1 Radioactive heat standards, typically powered by $^{238}$Pu, also may be used to calibrate calorimeters over a range of thermal powers. These standards are calibrated against electrical standards traceable to the national measurement system.

7.1.6.2 Removable electrical heaters may be used to calibrate calorimeters. For this type of standard the power generated by the heater must be measured with electrical equipment regularly calibrated against standards or standard methods traceable to a national measurement system. The power supplied to the electrical calibration heater may be varied over the range of calibration.

7.1.7 *Wheatstone Bridge*—When temperature sensitive resistance wire is used as the sensor, it usually is arranged in a Wheatstone Bridge configuration shown in Fig. 1.

7.1.8 *Data Acquisition System*—Calorimeter data collection is performed using computer-based data acquisition systems. The system should be able to read signal voltages or resistances at a fixed time frequency and be able to calculate and report a power value from the item using software that detects equilibrium. Graphics and numerical data indicating system power and temperatures may be displayed to aid the operator.

7.1.9 *Adapters*—Cylindrical metal adapters may be fabricated to accept smaller calorimeter containers in the calorimeter well, and thus provide good thermal contact between the outer container surface and calorimeter inner wall. Heat-conducting metal foil or metal gauze fill material, typically Al or Cu, or metal shot can be used in place of machined metal adapters. Smaller items may be placed in the calorimeter container and the void space inside the container may be filled with metal fill material or shot to provide good thermal contact.

7.1.10 *Loading Apparatus*—A hoist or assist may be used to load and unload items. Robotic loading systems may be used to handle the items.

## 8. Heat-Flow Calorimeter Systems

8.1 *Equilibrium*—A heat flow calorimeter consists of a sample chamber thermally insulated from a constant temperature environment by a thermal resistance. When an item is placed in the calorimeter the temperature difference across the thermal resistance is disturbed and the difference changes with time until it converges to a constant value and equilibrium is achieved. 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.

8.1.1 The curve describing the approach to equilibrium of the temperature difference is a function of several exponentials with different time constants related to the specific heats and thermal conductivities of the item matrix material, packaging, and, in some instances, the calorimeter.

8.1.1.1 Equilibrium may be detected by visual inspection of the measurement data versus time or through statistical tests performed on a set of the latest data points in the time series.

8.1.1.2 Statistical prediction algorithms may be used earlier during transient temperature conditions to predict equilibrium
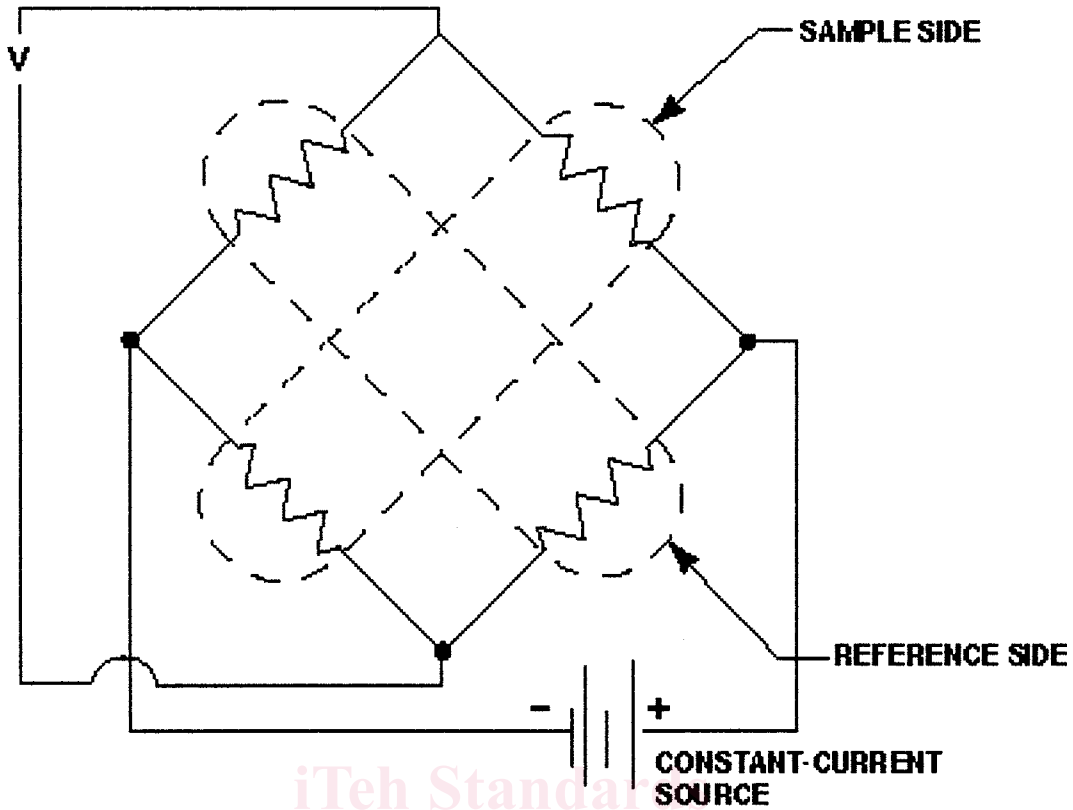
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**FIG. 1 Calorimeter Wheatstone Bridge Circuit**

and reduce measurement time. These typically consist of exponential functions that are used to fit the measurement data. The fitted parameters then are used to predict the final equilibrium power.

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8.1.1.3 The temperature of the item to be measured may be adjusted through the use of preconditioning baths in order to shorten the time required to reach equilibrium.

8.2 Heat-flow calorimeters are operated typically in one of two modes, passive or servo controlled (power-replacement).

8.2.1 *Passive Mode*—In this mode of calorimeter operation a Wheatstone Bridge is used as the sensor circuit. The only heat generated comes from the item being measured and the current required to excite the Bridge inside the thermel. A graph of the calorimeter response to a heat source is shown in Fig. 2. This plot shows that after a period of time the temperature transient caused by the insertion of the item into the calorimeter disappears and the calorimeter and item are in thermal equilibrium.

8.2.1.1 The item wattage, $W_i$, is calculated by the following:

$$W_i = (BP_s - BP_0)/S \qquad (3)$$

where:
$S$ = the calorimeter sensitivity (microvolts/Watt) determined by electrical or $^{238}$Pu standards,
$BP_s$ = the equilibrium bridge potential with the item in the calorimeter, and
$BP_0$ = the baseline bridge potential with no item in the calorimeter.

8.2.2 *Servo Mode (Power Replacement Mode)*—In this mode of operation, a constant amount of thermal power is applied to the sample chamber by electrical heaters. The temperature of the calorimeter chamber is held several degrees above the temperature of the environment by means of a servo-controller. The constant power causes a constant temperature differential to be maintained across the thermal

resistance separating the measurement chamber from a controlled reference temperature. The temperature differential is proportional to the signal, voltage or resistance, and is the temperature difference between a sensor (or sensors) located adjacent to the item being measured and the other(s) located at the reference temperature. A closed-loop controller monitors the output signal, and if a radioactive heat-generating item is inserted, the external power applied is decreased to precisely maintain the same signal differential. When the unknown item is placed in the calorimeter, the control power drops over time to a lower level. The power of the unknown is the difference between the two control power readings at equilibrium. A graph of the calorimeter response is shown in Fig. 3.

8.2.2.1 The item wattage, $W_i$, is calculated by the following:

$$W_i = W_0 - W_H \qquad (4)$$

where:
$W_0$ = the basepower with no item in the calorimeter, and
$W_H$ = the power supplied to the calorimeter with the item in the calorimeter.

8.2.2.2 The measurement time for the servo mode of operation is shorter than for the passive mode because the calorimeter components are at the equilibrium temperature and the servo-controlled internal heater can supply heat actively to bring the item to equilibrium.

8.3 *Calorimeter Systems*—A variety of heat-flow calorimeter designs have been used to measure nuclear material. Three types of designs that have been used for accountability measurements are further described below. These are differentiated by the temperature control techniques and heat flow
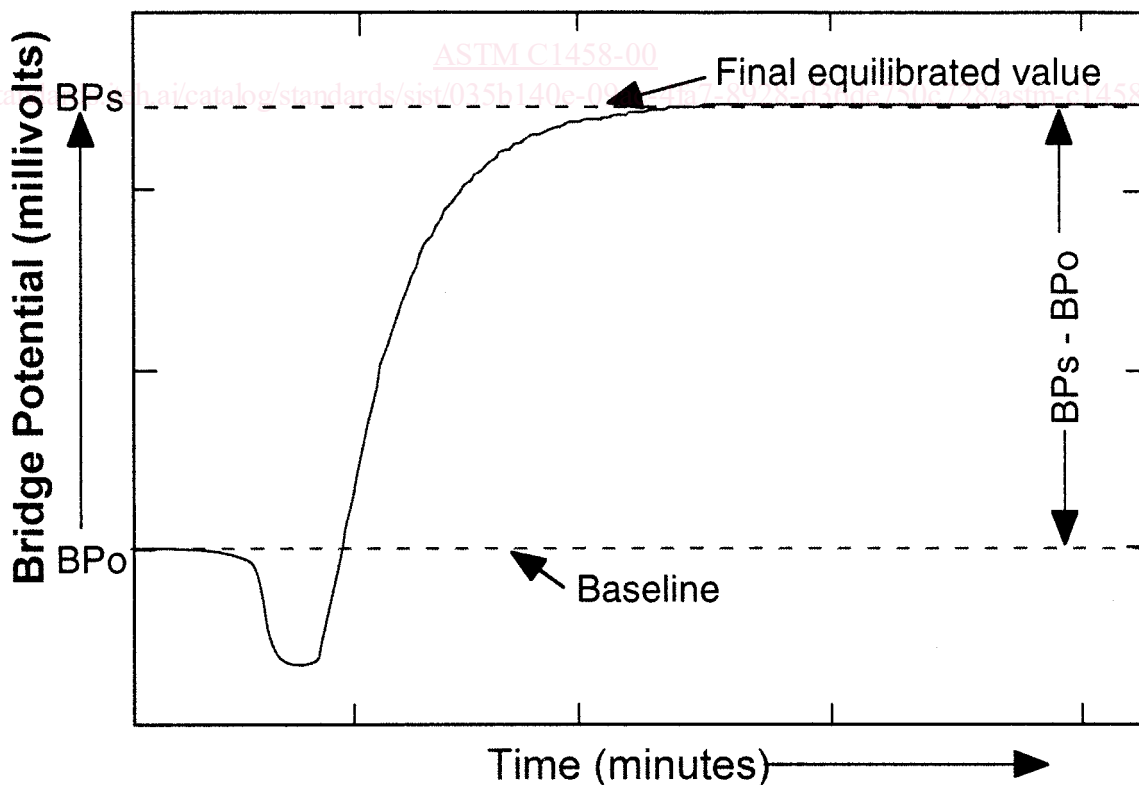


FIG. 2 Approach to Equilibrium for a Calorimeter Operated in the Passive Mode
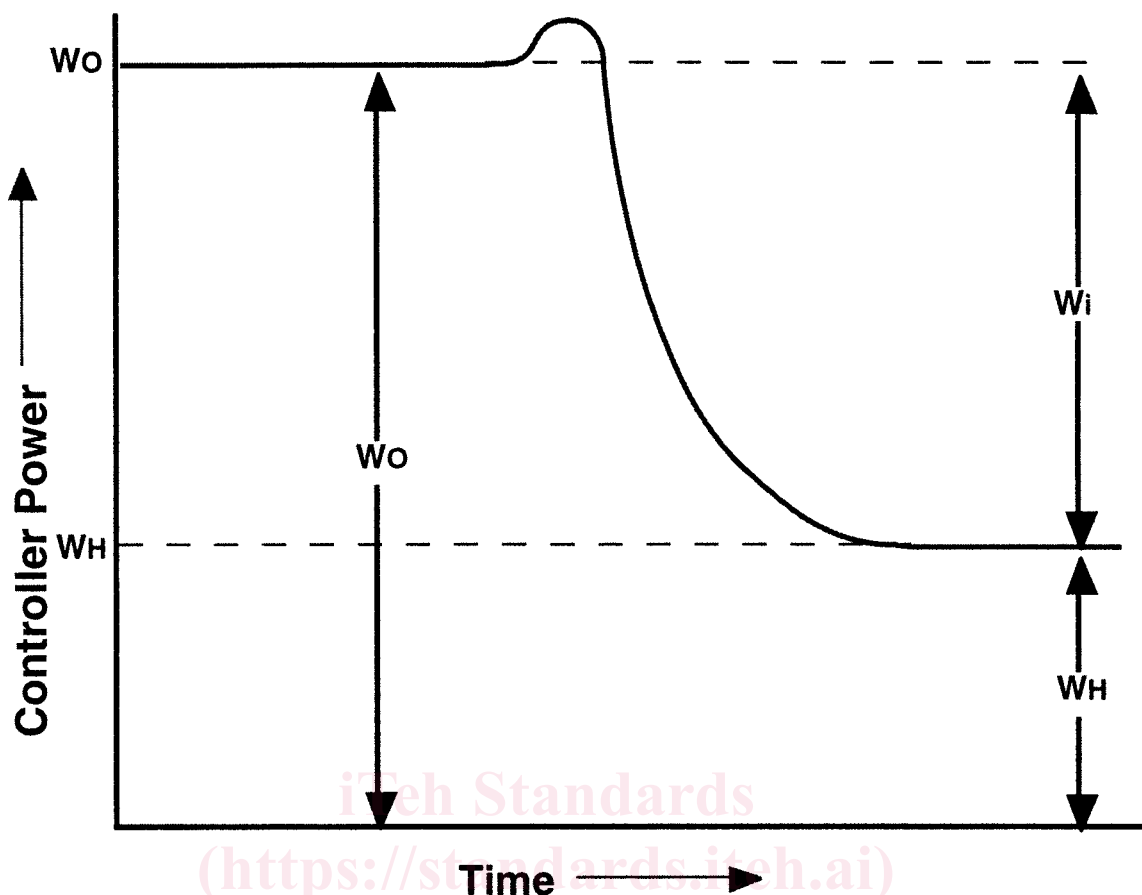
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FIG. 3 Approach to Equilibrium for a Calorimeter Operated in the Servo (Power Replacement) Mode

paths. They are an isothermal "air bath" calorimeter, water bath calorimeter, and rod calorimeter. The air bath and 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.

8.3.1 *Isothermal "Air Bath" Calorimeter (12)*:

8.3.1.1 A schematic diagram of an isothermal (constant temperature) air bath calorimeter is shown in Fig. 4. The calorimeter consists of three concentric cylinders separated by a heat-transfer medium. Each of the cylinders is equipped with temperature sensors. In general, both nickel sense wire and chains of thermistors are used. The outer cylinder is surrounded by a controlled temperature air bath.

8.3.1.2 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.

8.3.1.3 The isothermal calorimeter operates such 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.

8.3.1.4 The calorimeter operates in the power replacement mode described in section 8.2.2. The system controller works

to maintain the thermal power generated in the measurement chamber at a constant level.

8.3.1.5 The inner cylinder or measurement chamber of the calorimeter is operated at a fixed power known as the basepower. This basepower must be confirmed periodically as the measurement is based on the difference between the basepower and the final equilibrium or predicted power of the measurement chamber.

8.3.1.6 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 cold heat sink temperature.

8.3.1.7 Isothermal calorimeter measurement times may be reduced by item preheating. In this method items are placed in a temperature-controlled chamber that raises their temperature to the operating temperature of the inner cylinder of the calorimeter.

8.3.2 *Water Bath Calorimeter (3)*—Schematics of two different types of water bath calorimeters, the gradient bridge and twin bridge, are shown in Figs. 5 and 6. For both types of calorimeters the Wheatstone Bridge circuit shown in Fig. 1 is used to measure heat flow. The temperature rise in the sample side due to 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 causes an imbalance in the bridge and the