Designation: ~~C1458 – 09~~[ε1] C1458 – 16

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

This standard is issued under the fixed designation C1458; 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.

~~ε1 NOTE—Section 6.2 was corrected editorially in March 2009.~~

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 typical range of ~~applicability~~ applicability, depending on the isotopic composition, corresponds to ~~~1~~~0.1 g to ~~~2000~~~5 g quantities while for tritium the typical range extends from ~0.001 g to ~~~10~~~400 g. This test method can be applied to materials in a wide range of container sizes up to ~~50~~380 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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:*[2]
C697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets
C1009 Guide for Establishing and Maintaining a Quality Assurance Program for Analytical Laboratories Within the Nuclear Industry
C1030 Test Method for Determination of Plutonium Isotopic Composition by Gamma-Ray Spectrometry
C1592 Guide for Nondestructive Assay Measurements
C1673 Terminology of C26.10 Nondestructive Assay Methods
2.2 *ANSI ~~Standards:~~Standard:*[3]
ANSI ~~N15.22~~ N15.36 ~~Plutonium–Bearing Solids–Calibration Techniques for Calorimetric Assay~~Measurement Control Program – Nondestructive Assay Measurement Control and Assurance
~~ANSI N15.54 Radiometric Calorimeters–Measurement Control Program~~

3. Terminology

3.1 *Definitions:*
3.1.1 Terms shall be defined in accordance with C26.10 Terminology C1673 except for the following:

3.1.2 *active mode*—a mode of calorimeter operation where an external power, applied by means of a series of band heaters for instance, is used to maintain the calorimeter at constant temperature.

3.1.3 *baseline, n*—the calorimeter output signal with no heat-generating item in the calorimeter item chamber.

3.1.4 ~~*basepower,*~~ *base power, n*—a constant thermal power applied in a calorimeter through an electrical resistance heater with no heat-generating item in the item chamber.

3.1.5 *equilibrium, n*—the point at which the temperature of the calorimeter measurement cell and the item being measured ~~stops changing.~~ stabilizes.

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

3.1.7 *passive mode, n*—a mode of calorimeter operation where temperature change (caused by the heat to be quantified) is measured by means of temperature sensors with no external power ~~is applied to the calorimeter~~ applied except in the case of Wheatstone bridge temperature sensors where electrical current is needed to excite the bridge circuit.

~~3.1.7 *sensitivity, n*—the change in calorimeter response per Watt of thermal power (usually in units of micro Volts per Watt) for a heat flow calorimeter.~~

3.1.8 ~~*servo control*~~ *power compensation mode, n*—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. Historically, Mound Laboratory used to call this "Servo Control."

3.1.9 *sensitivity, n*—the change in calorimeter response per Watt of thermal power (usually in units of μV/W) for a heat flow calorimeter.

3.1.10 *specific power, n*—the rate of energy emission by ionizing radiation per unit mass of a radionuclide, such as ^{241}Am or tritium.

3.1.11 *thermal diffusivity, n*—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.

3.1.12 *thermal power, n*—the rate at which heat is generated in a radioactively decaying item.

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

3.1.14 *thermal time constant, n*—an exponential decay constant describing the rate at which a temperature approaches a constant value. ~~An item container combination~~ The combination of the item and its container will have numerous thermal time constants.

~~3.1.14 *thermel, n*—the THERMal ELement of the calorimeter, including the item chamber, and temperature sensor.~~

4. Summary of Test Method

4.1 The item is placed in the calorimeter measurement chamber and the 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 the radioactive material in it. The power generated by ionizing radiation absorbed in the item is measured by the calorimeter.

4.3 The total power W_{item} from a mixture of isotopes in the test item is the sum of the power from each heat-producing isotope:

$$W_{item} = \sum_i m_i \cdot P_i \tag{1}$$

where m_i is the mass of the ith isotope and P_i is the specific power (W/g isotope) with the sum taken over all heat-producing isotopes, most usually ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{241}Am for Pu-bearing items

4.4 The mass ~~(m)~~ of Pu, tritium, or ^{241}Am is calculated from the measured thermal power of an ~~item (item, refer~~W_i~~) using~~ to 11.3 ~~the following relationship:~~.

$$m = \frac{W_i}{P_{eff}} \tag{1}$$

~~where:~~

~~P_{eff} = the effective specific power calculated from the isotopic composition of the item (see 11.3.2 for details of the calculation of P_{eff} for plutonium).~~

4.4.1 When tritium is the only heat source the measured thermal power can be directly converted into the tritium mass using the specific power of tritium, P_{eff} = (0.3240 ± 0.00045) (SD) W/g (**1**).[4]

4.4.2 ~~For~~ When ^{241}Am ~~is the only heat source,~~ as a single isotope, the measured thermal power can be directly converted into mass using the specific power of ^{241}Am, P_{eff} = (0.1142 ± 0.00042) (SD) W/g (see ~~Table 1~~ Table 1).

---

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

TABLE 1 Nuclear Decay Parameters for Pu Calorimetric Assay[A]

Isotope	Half-Life, Years	~~Standard Deviation, Years~~	Specific Power, W/g	~~Standard Deviation, W~~	References		
[238]Pu	87.74	0.04 (0.05 %)	0.56757	0.00026	(0.05 %)		(2,3)
[239]Pu	24 119	16 (0.11 %)	1.9288 × 10⁻³	0.0003 × 10⁻³	(0.02 %)		(3-5)
[240]Pu	6564	11 (0.17 %)	7.0824 × 10⁻³	0.0020 × 10⁻³	(0.03 %)		(6-11)
[241]Pu	14.348	0.022 (0.15 %)	3.412 × 10⁻³	0.002 × 10⁻³	(0.06 %)		(12-16)
[242]Pu	376 300	900 (0.24 %)	0.1159 × 10⁻³	0.00026 × 10⁻³	(0.22 %)		(17)
[241]Am	433.6	1.4 (0.32 %)	0.1142	0.00042	(0.37 %)		(15,18)

TABLE 1 Nuclear Decay Parameters for Pu Calorimetric Assay[A]

Isotope	Half-Life, Years	RSD (%)	Specific Power (W/g)	RSD (%)	References
[238]Pu	87.74	0.05	0.56757	0.05	(25, 26)
[239]Pu	24 119	0.11	$\frac{1.9288 \times}{10^{-3}}$	0.02	(26-28)
[240]Pu	6564	0.17	$\frac{7.0824 \times}{10^{-3}}$	0.03	(29-34)
[241]Pu	14.348	0.15	$\frac{3.412 \times}{10^{-3}}$	0.06	(35-39)
[242]Pu	376 300	0.24	$\frac{0.1159 \times}{10^{-3}}$	0.22	(40)
[241]Am	433.6	0.32	0.1142	0.37	(38, 41)

[A] ~~Numbers in parentheses are % relative standard deviation (RSD).~~ANSI N15.22, the original compiled source for these parameters, is no longer an active ANSI standard. The References are those from ANSI N15.22 and are the appropriate references for the values in Table 1.

4.4.3 ~~For~~The [241]Am ~~mixed with plutonium, the~~ [241]Am mass, Mm_{Am}, in a plutonium-bearing item is determined by

$$M_{Am} = R_{Am} M_{Pu} \tag{2}$$

multiplying the Pu mass by the Am/Pu mass ratio. The Am/Pu mass ratio is typically determined by gamma-ray spectroscopy.

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

5. Significance and Use

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

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) (~~19~~2, ~~20~~3). This test method has been routinely used at U.S. and European facilities for Pu process measurements and nuclear material accountability ~~for the last 40 years~~ since the mid 1960's (~~19-2-26~~9).

5.1.2 Pu-bearing materials have been measured in calorimeter containers ranging in size from about 0.025 m to about ~~0.60~~0.63 m in diameter and from about 0.076 m to about ~~0.9~~1.38 m in height.

5.1.3 Gamma-ray spectroscopy typically is used to determine the ~~Pu-relative~~Pu isotopic composition and [241]Am to Pu ratio (see Test Method C1030). ~~Isotopic~~However, isotopic information from mass spectrometry and alpha counting measurements may be used instead (see Test Method C697).

5.2 This test method is considered to be the most accurate NDA method for the measurement of tritium. For many physical forms of tritium compounds calorimetry is currently the only practical measurement technique available.

5.3 Physical standards representative of the materials being assayed are not required for the test method.
5.3.1 This 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 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 (~~24-7-29~~12).

5.6 ~~Calorimetry measurement times are typically longer than other NDA techniques.~~ Four parameters of the item and the item packaging affect measurement time. These four parameters are density, mass, thermal conductivity, and change in temperature. The measurement well of passive calorimeters will also affect measurement time because it too will need to come to the new equilibrium temperature. Calorimeters operated in ~~servo~~ power compensation mode maintain a constant measurement well temperature and have no additional effect on measurement time.

5.6.1 Calorimeter measurement times range from 20 minutes (**3013**) for smaller, ~~temperature-conditioned,~~temperature-conditioned containers up to ~~24~~72 h (**14**) 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~~by operating the calorimeter using the ~~servo-control technique.~~power compensation technique, or by optimization of the item container (low thermal mass and high thermal conductivity) and packaging.

6. Interferences

6.1 For plutonium-bearing items alpha decay heating is usually the dominant heat source and any interferences are typically negligible. These minor effects included the points 6.2 and 6.3.

6.2 Interferences for calorimetry are those processes that would add or subtract thermal power from the power of the radionuclides being assayed. Some examples include phase changes, endothermic or exothermic chemical reactions, such as oxidation, ~~radiolisis~~radiolysis of liquids, and bacterial action.

6.3 ~~Heat-generating radionuclides~~For the ~~that~~P_{eff} ~~are not included in the P~~calculation, charged particles are assumed to be totally absorbed in the matrix.~~eff~~ ~~determination will~~ The contribution of high energy gamma-rays (for example, 1.173 MeV and 1.333 MeV of the ^{60}Co) needs to be calculated to not underestimate their contribution which could bias the measurement ~~results high.~~ results. These assessments requiring subject matter expertise are usually based on high-resolution gamma spectroscopy (HRGS) and need to be considered in a case by case basis. These effects are usually considered negligible (**15, 16**).

6.4 The loss of energy by escaping neutrons following spontaneous and induced fissions is about 1 %. The loss of energy by escaping neutrons following (α, η) reactions is around 0.007 % per alpha particle. These effects are also usually considered negligible (**15, 16**).

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 ~~typically~~ have a ~~cylindrical~~ cylindrical, cuboid, or hexagonal measurement chamber from which all of the heat flow generated by radioactive decay is directed through temperature sensors. It may also have a reference chamber in which a dummy can is placed (so-called twin cell calorimeter) (**15, 17, 18**).

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 or active heaters (or both) ~~are used~~ should surround the cavity to shield the chamber from outside temperature variations that would influence the thermal power measurement. Typically, an insulated plug or a temperature-controlled plug with an independent electrical heater 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 typically 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 thermistors, thermocouples, temperature sensitive resistance ~~wire, or thermopiles.~~wires, thermopiles, or Peltier modules working in Seebeck mode. Temperature sensors should be placed as close as possible in a geometrical homogeneous network all around the can.

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, air bath, ~~or a~~ ~~solid, usually metal,~~ solid block, usually metallic block, maintained at a constant ~~temperature.~~temperature or a combination of a solid block and water bath or air bath.

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

7.1.5.1 High precision voltmeters or voltage measurement devices are required to ~~measure~~quantify 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 Wheatstone bridge 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,~~calibrated nor are precision resistors required.

7.1.5.4 For a calorimeter operated in the ~~servo (power replacement)~~ power compensation 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 (~~31-19-34~~22).

7.1.6.1 Radioactive heat standards, typically ^{238}~~powered by~~ Pu heat~~^{238}Pu,~~ sources, also may be used to calibrate calorimeters over a range of thermal powers. These standards are calibrated against electrical standards traceable to a national measurement system. The certified power is typically decay corrected to the nearest day using certified decay tables.

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 calibration range.

7.1.7 *Wheatstone Bridge*—When temperature sensitive resistance wire is used as the sensor, it 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*—Low mass 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. Lack of fill material does not preclude measurement of the ~~item.~~item but it will increase the time to reach the calorimetric equilibrium and thus increase the total measurement time.

7.1.10 *Loading Apparatus*—A hoist or other 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 system consists of an item chamber thermally insulated from a constant temperature environment by a thermal resistance. It may also include a reference chamber (twin calorimeter) also insulated from a constant temperature environment by a thermal resistance (15, 17, 18). 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~~ (power compensation 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~~ of the temperature difference displaying the approach to the calorimetric equilibrium 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 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.
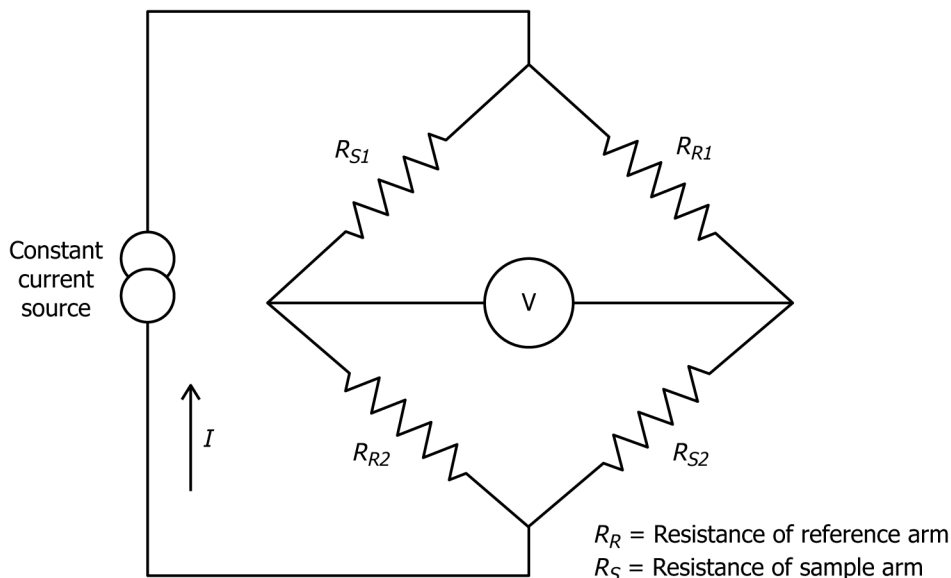

FIG. 1 Calorimeter Wheatstone Bridge Circuit

R_R = Resistance of reference arm
R_S = Resistance of sample arm

8.1.1.2 Statistical prediction algorithms 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 then are used to predict the final equilibrium power.

8.1.1.3 The temperature of the item to be measured may be adjusted through the use of preconditioning heaters or baths in order to decrease 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).~~mode or power compensation mode.

8.2.1 *Passive ~~Mode—~~Mode Operation—*~~In this mode of calorimeter operation a Wheatstone bridge is frequently used as the heat sensor. 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~~ A plot with an example of a passive mode 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.~~equilibrium after approximately 7 h in this example.

8.2.1.1 The item ~~wattage,~~power, $W_{\cancel{i}item}$, is calculated by the following:

$$W_i = (BP_s - BP_0)/S \tag{2}$$

$$W_{item} = (BP_s - BP_0)/S \tag{2}$$

where:

~~S = the calorimeter sensitivity (microvolts/Watt) at the power level, determined by electrical or ^{238}Pu standards,~~
$\underline{S}$ = the calorimeter sensitivity (μV/W) at the power level, determined by electrical or ^{238}Pu standards,
BP_s = the equilibrium sensor response with the item in the calorimeter, and
BP_0 = the baseline sensor response with no item in the calorimeter.

8.2.2 *Servo Mode (Power Replacement Mode)—Power Compensation Mode—*In this mode of operation, a constant amount of thermal power is applied to the item chamber by electrical heaters. The temperature of the calorimeter item chamber is held at a constant temperature difference above the temperature of the thermal sink by means of a ~~servo-controller.~~ controlled power unit. 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~~ plot with an example of the calorimeter response is shown in Fig. 3.
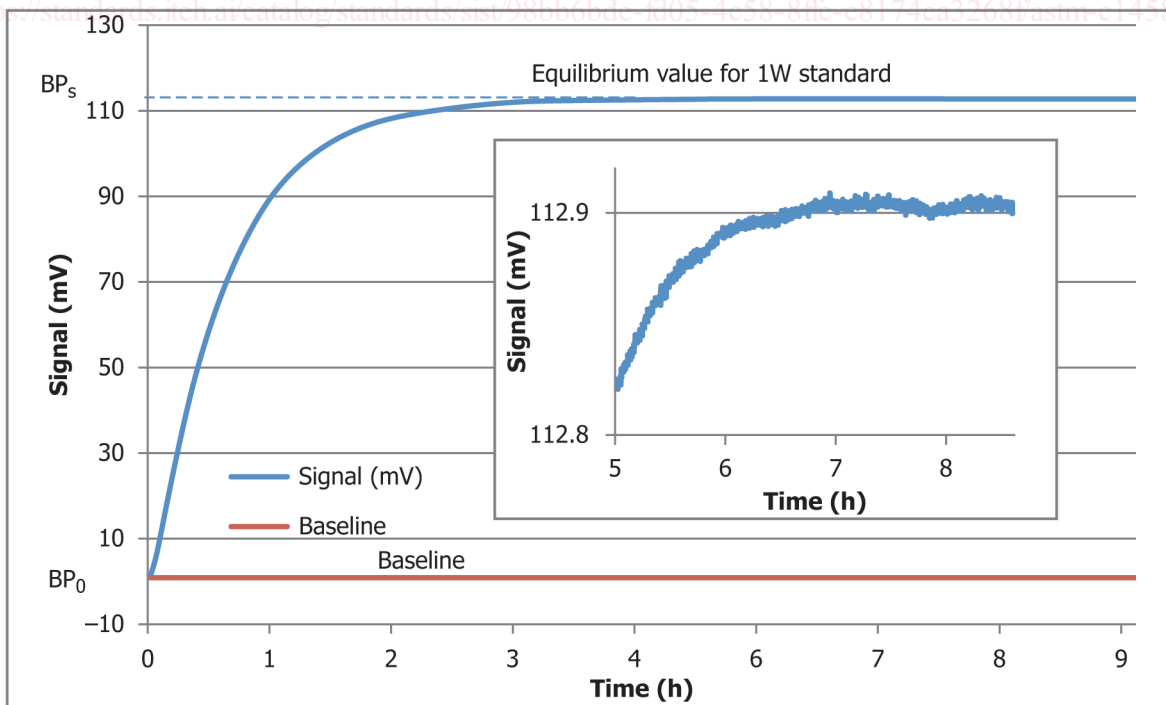

FIG. 2 Approach to Equilibrium for a Calorimeter ~~Operated~~ in the Passive Mode