



Designation: C1909 – 21

Standard Test Method for Moisture Analysis of Plutonium Dioxide (PuO₂) by Thermogravimetric Mass Spectrometry (TGA-MS)¹

This standard is issued under the fixed designation C1909; 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 reappraisal. A superscript epsilon (ε) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method provides necessary information to determine the total amount of moisture (physisorbed and chemisorbed water molecules) in a plutonium dioxide (PuO₂) sample using a combination of thermogravimetric and mass spectrometric analyses. This test method is useful when performing analysis in cases where a maximum amount of moisture content in PuO₂ samples has been agreed upon by interested parties. For example this method can be used to determine the moisture content of some types of PuO₂ packaged to meet the requirements of DOE-STD-3013 (1),² “Stabilization, Packaging, and Storage of Plutonium-Bearing Materials,” when such PuO₂ meets the specifications given in this test method (2).

1.2 This test method is applicable to PuO₂ samples having the following characteristics: Plutonium mass fraction ≥ 83 % (the plutonium in the sample should be close to stoichiometric PuO₂ which is approximately 88 wt% plutonium depending on the isotopic composition of the plutonium, but can have several weight percent impurities), moisture ≤ 1 %.

1.3 The temperature range of test is typically room temperature to greater than 1000 °C. Typically the PuO₂ is heated to 1100 °C.

1.4 This test method utilizes an inert gas environment (argon, nitrogen, or helium).

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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² The boldface numbers in parentheses refer to a list of references at the end of this standard.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*³

C859 Terminology Relating to Nuclear Materials

C1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within Nuclear Industry

E473 Terminology Relating to Thermal Analysis and Rheology

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E1142 Terminology Relating to Thermophysical Properties

E1582 Test Method for Temperature Calibration of Thermogravimetric Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 Except as otherwise defined herein, definitions of terms are as given in Terminology C859, E473, and E1142.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *rotary riffler, n*—a piece of laboratory equipment capable of subdividing large samples into smaller sub-samples by means of vibration of the large sample into a rotating set of sub-sample containers.

3.2.1.1 *Discussion*—This technique minimizes operator error and bias as compared with many other types of sample dividing.

4. Summary of Test Method

4.1 This test method is an empirical technique using thermogravimetry and mass spectrometry in which the mass of a

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

sample of PuO₂, heated at a controlled rate in a gaseous environment of known composition is recorded as a function of time and temperature while the evolved moisture is measured simultaneously on a mass spectrometer. Mass loss over specific temperature ranges and recorded signals corresponding to water are measured to provide a compositional analysis of the moisture in the PuO₂ sample.

5. Significance and Use

5.1 This test method is intended for use in quality control laboratories where a quantitative analysis of adsorbed moisture on a PuO₂ sample is desired.

5.2 The parameters described should be considered as guidelines. They may be altered to suit a particular analysis or type of analyzer, provided the changes are validated by the laboratory and noted in the report.

5.3 The quantity of an adsorbed gas on a given PuO₂ sample may indicate specific quality or end use performance characteristics. Specific limits on moisture content, for example, are required in cases where PuO₂ will be packaged and stored for extended periods of time.

6. Interferences

6.1 PuO₂ samples which contain impurities that could undergo chemical reactions (for example, redox reactions) or phase changes which would result in mass differences not related to devolatilization of sorbed or structural gases must have a specific temperature and/or time region identified for the measurement. An example of this is metallic gallium which can exist in some PuO₂ samples and may oxidize at high temperatures causing a mass gain. Although not part of this test method, heat flow / heat capacity can be measured in parallel with the thermogravimetric analyzer (TGA) measurement via differential scanning calorimetry (DSC) or differential thermal analysis (DTA) to verify that increases and decreases in mass correspond to attributable exothermic or endothermic chemical reactions and phase changes.

7. Apparatus and Other Equipment

7.1 The minimum essential equipment required for thermogravimetric and mass spectrometric analysis capability for this test method includes:

7.1.1 Thermobalance, composed of (1) a furnace to provide uniform controlled heating of a specimen to a constant temperature or at a constant rate within 25 °C to 1500 °C, (2) a temperature sensor (thermocouple) to provide an indication of the specimen/furnace temperature to ±10.0 °C, (3) an electronic balance to continuously measure the specimen mass with a sensitivity of ±2 µg, and (4) a means of sustaining the specimen/container under atmosphere control with a purge rate of 1 cm³/s to 2 cm³/s. This purge gas flow is directed to the mass (60 mL/min to 120 mL/min).

NOTE 1—This test method has been developed using a Netzsch Simultaneous Thermal Analyzer (STA)-409PC Luxx coupled to a Pfeiffer ThermoStar GSD301T3 mass spectrometer. As noted in 5.2, operating parameters may need to be adjusted for analyzers from different manufacturers. Follow manufacturer instructions for specific operating parameters. This does not apply for parameters that are method specific and not

analyzer specific. Examples include heat rate, type of carrier gas, mass of sample, etc.

7.1.2 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace between selected temperature limits and capable of a heating rate of less than 10 °C/min constant to within ±1 % for a minimum of 120 min.

7.1.3 *Data Collection Device*, to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for TGA-MS analyzers are mass, temperature, time and ion current.

NOTE 2—The capability to display the first derivative of the signal may be useful in the measurement of obscure thermostability ranges.

7.1.4 *Containers (Pans, Crucibles, Etc.)*, which are inert to the specimen and which will remain dimensionally stable within the temperature limits of this test method. Examples include alumina and platinum-rhodium alloy pans or crucibles.

7.1.5 *Gas Flow Control Device*, with the capability of controlling flow of carrier gas. Gas flow control device, with the capability of controlling flow of carrier gas.

7.1.6 *Mass Spectrometer*, capable of a resolution of ≤1 AMU in the mass range 17 AMU to 18 AMU.

7.1.7 *Heated Transfer Line*, capable of transferring evolved moisture from the TGA chamber to the mass spectrometer.

7.1.8 *Chiller*, used to provide chilled water for cooling the furnace between samples.

7.1.9 *Relative Humidity Detector*, for measuring the RH of the glovebox atmosphere (0 % to 100 % RH).

7.1.10 *Regulator*, for the compressed inert carrier gas.

7.1.11 *Laboratory Balance*, capable of measuring 3 g ± 0.1 mg readability, ±0.1 mg repeatability, for measuring items outside of the TGA-MS.

7.1.12 *Gas Bench*, for distribution of the inert carrier gas.

7.1.13 *Rotary Riffler*, for subdividing larger powder samples into smaller sub-samples.

8. Reagents and Materials

8.1 Ultra High Purity (UHP) compressed inert gas, 99.999 % purity, meeting the following additional specifications:

- 8.1.1 Maximum water content of 1.0 µg/g,
- 8.1.2 Maximum hydrocarbon content of 0.5 µg/g,
- 8.1.3 Maximum oxygen content of 1 µg/g, and
- 8.1.4 Maximum total impurities of 100 µg/g.

8.2 Certified pure metals used for temperature calibration (see Table 1).

8.3 Certified reference materials for mass spectrometer moisture calibration (see Table 2).

9. Test Samples

9.1 Test samples consist of PuO₂ powder. The amount of sample needed to evolve measurable amounts of adsorbed moisture will vary depending on the moisture content of the sample. Test samples are measured as received.

9.2 Ensure that the analyzed sample is representative of the parent material from which it is taken. It is suggested that after

TABLE 1 Selected Pure Metals and Their Associated Certified Melting Temperatures May Be Used for TGA Temperature Calibration

Element	Symbol	Melting Temperature (°C)	Purity
Indium	In	156.6	99.99+ %
Tin	Sn	231.9	99.99 %
Bismuth	Bi	271.4	99.9995 %
Zinc	Zn	419.5	99.999 %
Aluminum	Al	660.3	99.999 %
Silver	Ag	961.8 ^A 951.5 ^B	99.99+ %
Gold	Au	1064.2	99.999 %
Nickel	Ni	1455 ^A	99.99+ %

^A Air excluded.

^B In static air atmosphere

TABLE 2 Selected Moisture Standards

Chemical	Recommended Purity	Volatiles
Ca(SO ₄) • 2H ₂ O	>99.8 %	H ₂ O = 20.9 %
Mg ₃ Si ₄ O ₁₀ (OH) ₂	N/A	H ₂ O = 4.75 %

the parent material is homogenized in a rotary blender, several grab samples are taken from different areas of the parent material and combined for a single determination. Use of a rotary riffler to subdivide powder or particulate samples is mandatory.

NOTE 3—Care should be taken not to change the moisture content of the sample compared to the parent PuO₂ material. Moisture is added in discrete mono layers to the surface of PuO₂ at a relatively fast rate at room temperature. The rate and total absorbable moisture content depends on the physical properties of the PuO₂ (specific surface area, particle size) and the relative humidity (RH) and pressure of the atmosphere to which the sample is exposed. Researchers have proposed a complex multi-step model for the adsorption and desorption of H₂O on to PuO₂ involving a mix of chemical and physical phenomena (3-6). Desorption of moisture from the surface of PuO₂ may not progress as easily or rapidly but does occur with increases in temperature, decreases in pressure, RH, or combinations thereof (7).

10. Calibration

10.1 General Guidance:

10.1.1 Balance calibration, temperature signal calibration, mass spectrometer (evolved moisture) calibration should be performed on an annual basis (at minimum) and immediately following instrument transport or repair. Mass spectrometer calibration checks should be performed regularly (weekly/monthly) and following any change to the transfer line (for example, partial blockages, changes in temperature, cutting or replacement of the capillary column, etc.) or to the mass spectrometer operating parameters (for example, dwell times, ion source voltages, ion source focusing, ion detection parameters, etc.). Mass spectrometer calibration checks require measuring the release of H₂O vapor during the decomposition of compounds with structurally incorporated water molecules and comparing the analyzer response to the existing calibration data. It is important to note that no known certified reference materials exist for moisture calibration and verification. Therefore the use of pure compounds with structurally-incorporated

water molecules is the most appropriate way of calibrating the TGA-MS system for water content measurements.

10.1.2 More details related to measurement system quality control are found in Guide C1210. The frequency of calibration and calibration checks are highly dependent on the user's data quality objectives, frequency of analyzer use, and other factors specific to each user. Therefore, this standard does not prescribe a specific periodicity, but instead prescribes that the user assess and formalize a calibration and calibration check frequency based on the specific goals of the user.

10.2 Calibration Procedure:

10.2.1 Calibrate the TGA balance per the manufacturer's instructions. In most modern instruments this can be done by actuating an automatic sequence that uses a specially-designed internal weight.

NOTE 4—Calibrated check weight sets can be purchased separately and used to confirm calibrations made by the internal weight if required.

10.2.2 Calibrate the temperature signal from the apparatus according to the following steps (alternatively, Test Method E1582 may also be used as it is an acceptable method for TGA temperature calibration). The temperature axis (abscissa) of all apparent mass change curves must be calibrated accurately by adjusting the temperature measured at the sample to approximate the furnace temperature over the temperature range of interest. This is accomplished by the use of melting point standards. The data generated by steps 10.2.3 – 10.2.20 below are used to correct the temperature scale of the instrument by either a positive or negative amount using a multi-point temperature calibration with best fit line for the generated data.

NOTE 5—The following calibration procedure assumes that the indicated temperature of the instrument is linear over the range defined by the multi-point calibration and that this linearity has been verified.

NOTE 6—Selected pure metals and their associated certified melting temperatures are provided in Table 1. Metals should be obtained from, or

traceable to, a national standards body. Additional melting point standards are available and are listed in Test Methods E967 and E1582.

NOTE 7—Some of the pure metal standards such as zinc, aluminum and silver, are sensitive to air and humidity. In the case of zinc, oxidation begins above 225 °C, and therefore each piece of metal can only be used once for temperature calibration.

NOTE 8—Conditions during temperature calibration runs should closely match those of the subsequent sample measurements.

NOTE 9—High heating rates should be avoided close to the transition temperature of the pure metal standards. Heating rates below 20 °C/min are acceptable. Heating rates well below 20 °C/min may decrease the error in the temperature calibration further. A heating rate adapted to the required precision and bias of the method should be selected. Often times a rate of 10 °C/min is selected for PuO₂ samples. Heating rates during calibration should be the same as heating rates during sample measurement.

10.2.3 For temperature calibrations using pure metals, each calibration substance has to be cycled three times though each melting/crystallization point. In general, the end temperature of the heating phases should exceed the melting peaks by 50 °C to 75 °C. The cooling phases should reach a temperature that is approximately 75 °C to 100 °C below the melting point in order to guarantee complete pure metal crystallization.

10.2.4 Select a minimum of six (ideally eight) pure metal certified reference materials (CRM) with melting points that cover at a minimum the temperature range of interest for a particular analysis setup (0 °C to 1000 °C).

10.2.5 Using guidance in notes Notes 9-11, configure the heating profile and heating rate for each of the CRMs selected in the previous step. Ensure that the maximum and minimum temperatures selected for the CRM are sufficient to cause complete melting and complete crystallization.

NOTE 10—Most modern TGA analyzers have software that allows the user to program heating profiles and rates that can be stored and recalled at any time for future use.

10.2.6 Obtain a clean, empty TGA crucible or pan and weigh and record tare weight.

10.2.7 Using a spatula or tweezers as necessary, transfer 10 mg to 50 mg of the CRM into the pan or crucible.

10.2.8 Weigh the full crucible or pan (gross weight) and record the gross weight.

10.2.9 Move the crucible or pan over to the TGA and mount on to the carrier.

10.2.10 Close the balance and furnace assembly.

10.2.11 Purge the balance and furnace tube with inert carrier gas at the appropriate flow rate.

10.2.12 Check the inert carrier gas flow and adjust, if needed.

10.2.13 Select the appropriate heating profile sequence and heating rate configured in step for the CRM loaded in the furnace.

10.2.14 Tare the TGA balance so that the mass reads zero.

10.2.15 Start the heating profile sequence.

10.2.16 When the standard melts, the heat flow signal will show an endothermic peak. A typical curve is shown in Fig. 1.

NOTE 11—Most modern TGA analyzers have subroutines that continuously measure the difference between the observed sample temperature and the linear change in the furnace temperature to calculate the melting point of the CRM.

10.2.17 Allow the analyzer to cool and return to a configuration that allows for opening the furnace and removal of the crucible or pan.

10.2.18 Remove the crucible or pan.

10.2.19 Repeat steps 10.2.3 – 10.2.15 for all 6-8 CRMs covering the temperature range specified in step 10.2.1.

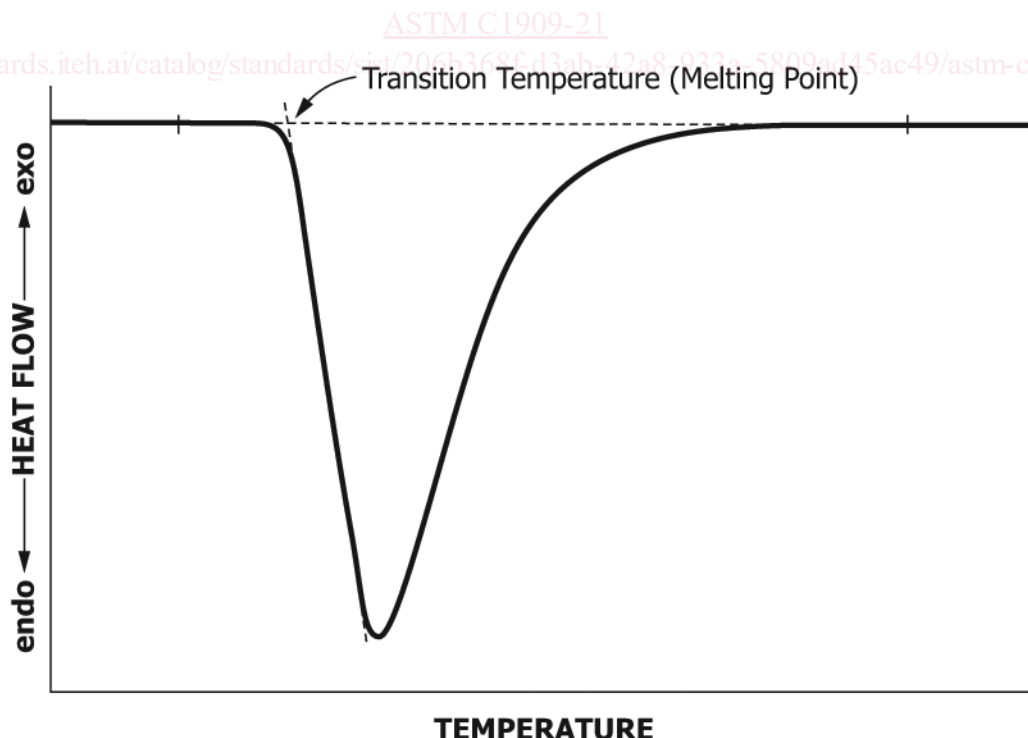


FIG. 1 Reference Material Melting Endotherm

10.2.20 Once all measurements of CRMs are complete, the temperature calibration curve is then obtained by a mathematical best-fit between the certified and measured transition temperatures obtained.

NOTE 12—Most modern TGA analyzers have subroutines that perform the calculations needed to determine the best-fit between the theoretical and measured transition temperatures. For those circumstances where a manual calibration must be performed using the data generated, refer to Test Method E1582.

10.3 Correct for buoyancy effects according to the following steps.

NOTE 13—As the crucible (or pan) is heated, there is a concomitant apparent mass gain caused by a combination of thermal effects. Heating decreases the density of the surrounding atmosphere and increases the convective movement of gas molecules within the furnace. Heating may also have subtle effects on the balance mechanism itself. Buoyancy corrections can be made by running an empty crucible through the analytical temperature profile exactly as one would run a corresponding sample. The buoyancy effect on the empty crucible can then be subtracted from the analytical results.

NOTE 14—Correcting for buoyancy effects is specific for a selected heating profile sequence (heat rate, max temperature, etc.) and the correction must match the heating profile sequence selected for a specific PuO_2 sample. Therefore, a new buoyancy correction must be performed if the sample heating profile or any other parameter in the analytical conditions is changed.

10.3.1 Obtain an empty previously run TGA crucible or pan and move the crucible or pan over to the TGA and mount on to the carrier.

10.3.2 Close the balance and furnace assembly.

10.3.3 Purge the balance and furnace tube with inert carrier gas at the appropriate flow rate.

10.3.4 Check the inert carrier gas flow and adjust, if needed.

10.3.5 Select the appropriate heating profile sequence and heating rate that corresponds to the selected sample.

10.3.6 Tare the balance so that the mass reads zero.

10.3.7 Start the heating profile sequence.

10.3.8 The TGA balance records the change in mass as a function of time and heating profile.

10.3.9 Allow the analyzer to cool and return to a configuration that allows for opening the furnace and removal of the crucible or pan

10.3.10 Remove the crucible or pan.

10.3.11 The TGA analyzer saves the buoyancy correction data and the user can select the appropriate buoyancy correction depending on the sample and corresponding heat sequence profile. See Fig. 2 for an example of a buoyancy correction graph.

10.4 Calibrate the moisture signal from the apparatus according to the following steps.

NOTE 15—The integrated TGA-MS can be used to quantify the amount of H_2O vapor released during the thermal decomposition of compounds via well-known stoichiometric reactions. Typically this is done by calibrating the mass spectrometer by measuring the release of H_2O vapor during the decomposition of compounds with structurally-incorporated water molecules such as talc (hydrous magnesium silicate) and gypsum (calcium sulfate dihydrate). The advantages to using both talc and gypsum are (1) the dehydration reaction for talc is kinetically slow and occurs at $\sim 850^\circ\text{C}$, while that of gypsum is relatively quick and occurs between 100°C and 150°C , (2) the compounds and their dehydration products do not react and can be run together in the same crucible, and (3) each compound contains very different amounts of structural H_2O which yield a good spread of data points on a calibration curve. The quantity of gypsum needed may vary from ~ 0.25 mg to 10 mg, while the quantity of talc needed may vary from ~ 1 mg to 100 mg. The goal is to obtain a set of calibration data that bracket the anticipated H_2O concentrations in the

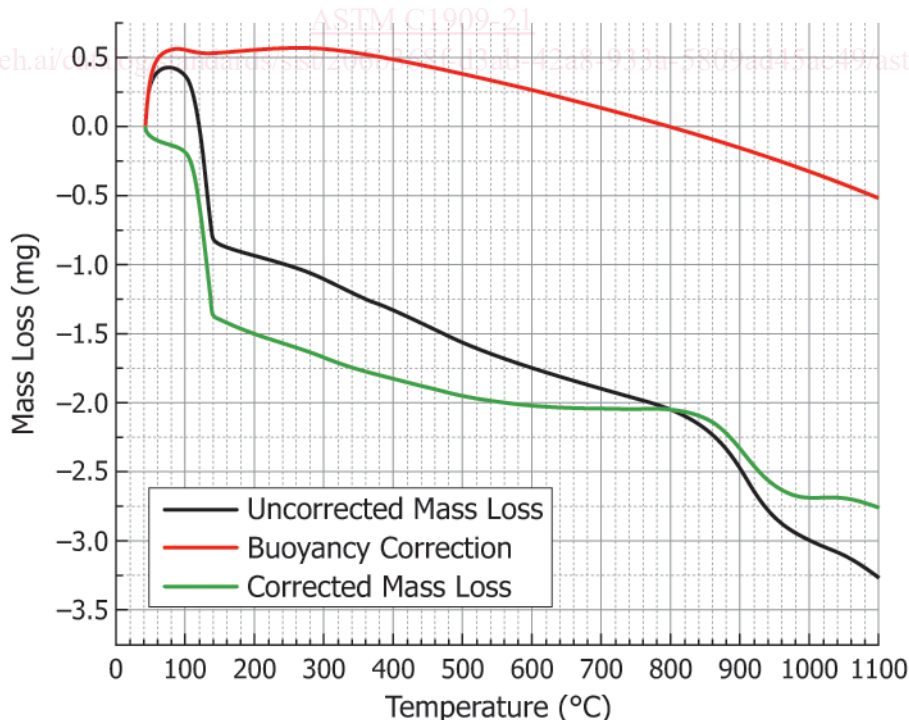


FIG. 2 Thermogram Showing Typical Buoyancy Correction (or Baseline, in Red) and Uncorrected Data (in Black) Versus Corrected Data (in Green)