



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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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 μ g, 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 $\pm$ 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 μ g/g,
- 8.1.2 Maximum hydrocarbon content of 0.5 μ g/g,
- 8.1.3 Maximum oxygen content of 1 μ g/g, and
- 8.1.4 Maximum total impurities of 100 μ g/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