



Designation: C1865 – 18

Standard Test Method for The Determination of Carbon and Sulfur Content in Plutonium Oxide Powder by the Direct Combustion-Infrared Spectrophotometer¹

This standard is issued under the fixed designation C1865; 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 is for the determination of the carbon and sulfur contents in plutonium oxide (PuO_2) powder. The method utilizes an induction furnace purged with oxygen for combustion of the sample. Carbon dioxide and sulfur dioxide produced by the combustion are swept into absorption cells and quantified by infrared absorption spectrophotometers. This test method is an alternative to the methods for carbon and sulfur given in Test Method C697.

1.2 Determination of the carbon and sulfur contents in nuclear-grade sintered mixed oxide (MOX) fuel pellets requires the use of larger samples and is addressed in Test Method C1853.

1.3 The values stated in SI units are to be regarded as standard. Units of measurement in parentheses are included for information only.

1.4 *This standard may involve hazardous materials, operations, and equipment. 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.*

1.5 *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.*

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. 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
- C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
- C757 Specification for Nuclear-Grade Plutonium Dioxide Powder for Light Water Reactors
- C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets for Light Water Reactors
- C859 Terminology Relating to Nuclear Materials
- C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
- C1853 Test Method for The Determination of Carbon (Total) Content in Mixed Oxide ((U, Pu) O_2) Sintered Pellets by Direct Combustion-Infrared Detection Method

3. Terminology

3.1 For definitions of terms used in this test method but not defined herein, refer to Terminology C859.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *accelerant*—the material, like granular tungsten powder and iron, used for accelerating the combustion of the plutonium oxide powder.

3.2.2 *MOX*—nuclear fuel composed of a mixture of uranium and plutonium oxides ((U, Pu) O_2).

² 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.

3.2.3 *sintering*—the process of increasing the bonding in a mass of powder or a compact by heating below the melting point of the main constituent.

3.3 Acronyms:

3.3.1 *LANL*—Los Alamos National Laboratory

3.3.2 *LIMS*—Laboratory Information Management System

3.3.3 *NIST*—National Institute of Standards and Technology

3.3.4 *SRNL*—Savannah River National Laboratory

3.3.5 *WRM*—Working Reference Material

4. Summary of Test Method

4.1 The instrumentation used for carbon and sulfur content determinations typically includes a computer controlled induction furnace purged with oxygen. An analytical balance is used to weigh a known amount of the PuO_2 powder for analysis. The method consists of combusting a weighed sample of approximately 0.1 to 1 g of PuO_2 powder. The sample is covered with an accelerator material, usually granular tungsten and iron. Carbon dioxide and sulfur dioxide produced by the combustion are swept into absorption cells where each gas is quantified by infrared (IR) spectrophotometers. Blanks and quality control standards are analyzed following the same procedure as that used for the analysis of the samples. Drift corrections are performed, when necessary.

5. Significance and Use

5.1 Plutonium oxide powder is a component of MOX fuel. This test method can be used to determine whether the carbon and sulfur contents of the PuO_2 powder meets the requirements of Specifications [C757](#) and [C753](#) or other requirements as defined by agreement between the nuclear and fuel supplier and the customer.

5.2 MOX is used as a nuclear-reactor fuel. To be used as a fuel, MOX materials must meet specifications on the impurity element contents in them. Examples of these requirements are given in Specification [C833](#).

5.3 This method is suitable for pure plutonium oxide powder.

6. Interferences

6.1 Ideally, calibration should be performed with a standard having a matrix identical to that of the sample. Matrix matched calibration standards are not available for PuO_2 powder materials. Biased results can result if the calibration standards combust at different conditions than the samples or if the combustion behavior of the chosen standard is significantly different from that of the PuO_2 powder material analyzed.

6.2 Incomplete combustion can be caused by sample masses that are too large. When this occurs, results can be improved by reducing the sample mass to promote complete combustion. Combustion produces a mixture of CO , CO_2 , and SO_2 . The proportion of CO/CO_2 and SO_2 produced during the combustion depends on, among other factors: temperature, the accelerant properties, the coupling between the accelerant and the sample material, particle size of the oxide material, the

availability of sufficient quantities of O_2 , and the presence of impurity elements that can consume O_2 .

6.3 Sample and standard masses (and particle sizes of the oxide materials) should be similar so that combustion conditions and behaviors are as similar as possible to prevent a systematic bias between the sample and standard data.

6.4 Daily, or before each use, the analyzer is checked with a blank and one or more quality control standards of known carbon or sulfur concentration. The instrument is calibrated daily with standards traceable to a national standards body such as the National Institute of Standards and Technology (NIST).

6.5 Weighing accuracy of the samples is critical to the method. If the balance meets the specification in [7.1](#), is calibrated in accordance with manufacturer's guidance, and is operated following facility guidelines for handling of the analytical balances, the potential for weighing uncertainties to be a major source of error is insignificant.

6.6 During normal operating conditions it is ensured that the furnace is operated at $<1700^\circ\text{C}$. Except when exothermic reactions are triggered inside the induction furnace, furnace temperatures do not exceed the normal operating temperatures.

6.7 CO and SO_2 are oxidized to CO_2 and SO_3 when exposed to the heated platinized silica reagent. CO_2 detection by IR is much more sensitive than the detection of CO . After detection, the odorous/toxic SO_2 in the exhaust system is converted to SO_3 .

6.8 Carbon is seen as a common environmental contaminant. A few of the more common sources of carbon interferences is CO and CO_2 from the air or carrier gas, crucibles, reagents, tools, and work area. To minimize blanks, the work areas are to be maintained clean.

6.9 Carrier gases may contain H_2O , CO , or CO_2 gases as a contaminant. This will cause a high background for carbon results. These contaminants may be scrubbed from the carrier gas prior to introduction of the gas to the sample chamber, or alternatively, minimized through the use of ultra-pure gas.

6.10 An additional known contaminant is methane (CH_4) or other organic gases, or both, which are part of the total hydrocarbon specification (THC) for oxygen supplies. A heated incoming gas scrubber is required to remove this contamination or higher purity grade of oxygen is required.

6.11 As received, crucibles typically have inherent carbon contamination levels at 20 ppm to 40 ppm relative to a 1 g steel sample, but it can be as much as several hundred ppm. This contamination from the handling, packaging, and storage conditions of the crucibles varies by lot and by manufacturer. For ultra-trace analysis (<100 ppm) and trace analysis (<1000 ppm), the crucibles must be cleaned prior to use by a high temperature bake out. Measured blanks takes into account the contributions from crucible blanks.

6.12 Accelerants can be a significant source of carbon contamination. Several manufacturers or lots may need to be screened prior to selecting an appropriate accelerant that has minimal C contamination. Measured blanks takes into account the contributions from accelerant blanks.

6.13 Opened reagents (sodium hydroxide and magnesium perchlorate) absorb water, CO, and CO₂ from the atmosphere after opening. This contamination will decrease the efficiency or capacity of reagents.

6.14 Environmental dust and skin residues often contain large amounts of carbon that will bias results. Good house-keeping of the workspace and use of clean tools and gloves are sufficient to keep this contamination source low.

6.15 Even with the use of air filters for the building air circulation system, wild fires in neighboring areas can temporarily increase the carbon blanks significantly.

7. Apparatus

7.1 *Analytical Balance*, with a combined standard uncertainty of ± 0.1 mg.

7.2 *Carbon/Sulfur Analyzer*, consisting of an induction furnace that is purged with oxygen. Carbon dioxide and sulfur dioxide produced during combustion are swept into absorption cells where each gas is quantified by an infrared detection system. The apparatus is usually computer controlled.

7.2.1 The analyzer typically uses the following chemicals: tungsten and iron (accelerants for combustion), magnesium perchlorate (oxidizer), sodium hydroxide (CO₂ trap), and cellulose (SO₃ trap). Alternate chemicals with equivalent properties may be used.

7.3 *Induction Furnace*, for heating samples.

7.4 *Crucible Tongs*, for handling crucibles.

7.5 *Low-Carbon Sample Crucibles*, for analyzing samples.

7.6 *Stainless Steel Scoop*, for transferring sample amounts to sample crucible.

8. Reagents and Materials

8.1 *Purity of Reagents*—Unless otherwise stated, reagent grade chemicals shall be used, where available. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without compromising the quality of the measurements.

8.2 *Anhydrous magnesium perchlorate (MgClO₄)*, also called *Anhydron*.

8.3 *Sodium hydroxide (NaOH) on an inert base (CO₂ trap)*.

8.4 *Cellulose (SO₃ trap)*.

8.5 *Iron chips (accelerator)*.

8.6 *Tungsten powder (accelerator)*.

8.7 *Glass wool (to trap particulates)*.

8.8 *Oxygen (>99.9 % purity)*.

8.9 *Platinized silica-gel (CO to CO₂ and SO₂ to SO₃ oxidizing catalyst)*.

8.10 *Silicone grease (used for O-rings)*.

9. Reference Materials

9.1 The calibration of the analyzer is made by means of a reference material standard from a national standards body such as the U.S. National Institute for Standards and Technology (NIST) or equivalent.

9.2 Standard materials in steel matrices (steel pins, steel rings, steel granules, and steel powder) are available and have been found to be satisfactory. Matrix matched standards for PuO₂ are rarely available.

9.3 As a best practice, analytical facilities are encouraged to develop well characterized, matrix matched working reference materials (WRMs) of similar carbon and sulfur contents as the samples analyzed routinely. During routine carbon and sulfur analysis following this method, these WRMs can then be used as quality control standards. See Guide C1128 for guidance on preparation of WRMs.

10. Precautions

10.1 Because of the toxicity of plutonium, all operations should be performed within approved glove boxes fitted with appropriate filters to protect personnel from uptake of small particles of plutonium. A detailed discussion of the necessary precautions is beyond the scope of this test method. Personnel involved in these analyses should be familiar with safe handling practices for radioactive materials and trained appropriately.

10.2 Containment devices shall be operational, with current inspections and glove change dates.

10.3 Specific hazards associated with the analyzer are the high-temperature components, high-voltage components, and corrosive/reactive/toxic reagents. High-pressure oxygen and nitrogen are regulated as recommended by the manufacturer, to provide an oxidant/carrier gas stream and to actuate the furnace pedestal. A pressure relief valve, set to relieve at appropriate pressure levels, is sometimes installed in the line. Exercise appropriate caution when working with compressed gases.

10.4 Ensure that the gas cylinder is fitted with facility approved regulator that has been inspected. Also ensure that the gas cylinder is securely fastened in place.

10.5 For handling of crucibles, use tongs or tweezers, not fingers.

10.6 Use appropriate precautions for handling corrosives, oxidizers, and gases.

10.7 Caution shall be used around the furnace surfaces, which may be hot during operation and for 10 minutes after use. Post appropriate warning signs (following facility procedures), when applicable.

10.8 The furnace pedestal is a pinch point hazard when operating the nitrogen supply valve and when testing for

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

lowering the furnace pedestal. Foreign objects (hands, glove-box gloves, cleaning tools, etc.) shall be kept out of the path of the furnace pedestal.

11. Preparation and Verification of Apparatus Prior to Sample Analysis

11.1 Perform initial instrument set up in accordance with manufacturer instructions. Ensure that all gas pressures are in the desired ranges based on manufacturer recommendations.

11.2 Perform the required daily checks on the balance to ensure that it performs at acceptable levels.

11.3 Prior to calibration or analysis, perform any required maintenance tasks based on manufacturer recommendations.

11.4 Prior to calibration or analysis, ensure that instrument parameters are within the range specified by the manufacturer.

11.5 Perform an instrument leak test. If a leak is detected, follow manufacturer instructions for trouble shooting.

11.6 Pre-fire crucibles in a muffle or tube furnace at temperatures of at least 1000 °C for 2 h or at more than 1250 °C for at least 15 min. Pre-fired crucibles are removed from the heat, allowed to cool on a tray, and placed in a desiccator. The crucibles are then handled with clean tongs and removed individually from the desiccator for use. They must not be allowed to remain in an open-air environment too long as they can be contaminated with airborne particulate (dust). Although this procedure is typically reserved for low carbon (<0.1 %) and sulfur (<0.01 %) determination, the effects can be noticed on high carbon results when smaller sample weights are used. Prepare sufficient number of crucibles as a batch to complete all analyses necessary for a set of samples. Use of crucibles prepared in separate batches requires additional verification analyses. For <100 ppm carbon content measurements, the crucibles need to be pre-fired at 1350 °C (pre-firing at such high temperature will cause a few percent of the crucibles to crack).

11.7 Transfer the pre-fired (cleaned) crucibles into a desiccator for storage. Use the cleaned crucibles within 24 h of firing. Any crucibles not used within this time period shall be fired again or discarded.

12. Instrument Calibration

12.1 The calibration range and the number of standards will depend upon the instrument used and the expected range of carbon and sulfur in the samples being analyzed. The initial calibration curve for the instrument must be established using standards covering the entire range of samples that are expected to be analyzed at the facility. Once a firm calibration curve is established and linear behavior is assured, a one point calibration, preferably at or close to the origin of the curve and in the range of the concentrations routinely measured will be sufficient. The drift of the calibration curve depends on, among other factors, type of samples analyzed, laboratory environmental conditions, maintenance, analyst and the instrument capabilities. The user will have to establish a recalibration frequency by taking into consideration the above factors. At a minimum, recalibration is required when critical components

are changed, or when control chart data indicate that the instrument is failing to meet established performance criteria. For blank determinations, three or more measurements are recommended.

12.2 Calibration standards analyzed as quality control (QC) standards may require preparation prior to analysis. Follow the instructions provided by the manufacturer of the standard in their certificate of analysis to prepare the standards. For WRMs or other matrix matched standards prepared in-house the preparation steps can be drying in an oven at 105 to 110 °C for at least 1 h.

12.3 Transfer the dried standards immediately to a desiccator. Discard any dried standards not used within 24 h of drying.

NOTE 1—Steel pin certified reference materials may be used for instrument calibration or verification. When these are used, there is no requirement to clean, dry, or pre-weigh the pins prior to use.

12.4 Prepare blank standards by adding one scoop of each accelerator into prepared crucibles. The amount of accelerator material added must be sufficient to cover the sample and couple with the RF field. For the Los Alamos National Laboratory (LANL) data presented in [Annex A1](#), 1.5 g accelerator material was added. Follow manufacturer guidance on the mass of the accelerator material that needs to be added. Some manufacturers recommend that empty crucibles are analyzed until a stable area measurement is obtained. This is followed by blanks (crucibles plus accelerator).

12.5 Weigh target quantities of the calibration and QC standards using countertop balance and transfer to clean, tared crucibles. The actual weight of the calibration and QC standards shall fall within ± 15 % of the specified target values.

12.6 Weigh target quantities of the samples using countertop balance and transfer to clean, tared crucibles. The actual weight of the sample analyzed shall fall within ± 15 % of the specified target values.

12.7 Analyze sample blanks using new, empty ceramic crucibles (or as defined by the manufacturer). Analysis of three or more blanks is recommended.

12.8 Analyze aliquots of calibration material for each calibration point specified on the calibration sheet.

12.9 Ensure that the calibration curve is linear (regression coefficient >0.997). Recalibration will be necessary, if the calibration curve is non-linear.

12.10 Compare QC standard results to pre-established acceptance criteria. If acceptance criteria are not met, evaluate the cause and take appropriate corrective action.

NOTE 2—With regard to number of QC standards analyzed, analytical laboratories adopt specific criteria based on the quality assurance program requirements or on the data quality objectives of the specific project. The following is an example of criteria that could be adopted. Traceable QC standards shall be analyzed prior to analysis of samples, after analysis of every ten samples, and after analysis of a set of samples. WRMs, characterized to the desired levels of precision and accuracy (total uncertainty) by the analytical facility, may be used as QC standards.

13. Sample Analysis

13.1 A blank measurement is performed prior to analysis of the sample to ensure that carbon and sulfur levels are