Designation: C1853 – 17

Standard Test Method for
The Determination of Carbon (Total) Content in Mixed Oxide ((U, Pu)O_2) Sintered Pellets by Direct Combustion-Infrared Detection Method[1]

1. Scope

1.1 This test method is an alternative to Test Method C698 for the determination of carbon in nuclear grade sintered mixed oxide (MOX) fuel pellets. The method for the determination of carbon presented in Test Method C698 consists of combusting carbon contained in MOX pellets with oxygen in a high-frequency induction furnace and detecting the resulting carbon dioxide using a thermal conductivity cell. The method for the determination of carbon presented in this test method consists of combusting carbon contained in MOX pellets with oxygen in a high-frequency induction furnace and subsequent detection of the resulting carbon dioxide (CO_2) using a non-dispersive infrared detector (NDIR). Sulfur oxide is stripped from the carrier gas stream by a cellulose filter prior to the detection of CO_2.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard may involve hazardous material, 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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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:*[2]

C698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O_2)

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

C1408 Test Method for Carbon (Total) in Uranium Oxide Powders and Pellets By Direct Combustion-Infrared Detection Method

2.2 *ISO Standards:*[3]

ISO 21614 Nuclear Fuel Technology – Determination of Carbon Content of UO_2, (U,Gd)O_2 and (U, Pu)O_2 Powders and Sintered Pellets – Combustion in a High-Frequency Induction Furnace – Infrared Absorption Spectrometry

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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[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] 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] Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, http://www.iso.org.

3.2.2 *sintering*—the process of forming a solid mass of material by heat or pressure, or both, without melting it to the point of liquefaction.

3.2.3 *reference material*—non-matrix matched material traceable to a reference material from a national standards body such as the U.S. National Institute for Standards and Technology (NIST) or equivalent; matrix matched reference materials for MOX pellets are not available.

3.3 *Acronyms:*

3.3.1 *NDIR*—Non Dispersive Infrared Detector.

3.3.2 *THC*—Total Hydrocarbon

4. Summary of Test Method

4.1 The method consists of crushing a MOX pellet, weighing an approximately 1 g fragment of the pellet into a crucible with an accelerator and combustion of the carbon contained in the sample under a stream of high pressure oxygen in a high-frequency induction furnace followed by detection of the carbon dioxide by a non-dispersive infrared (NDIR) cell. During combustion of the sample, the carbon and sulfur components are oxidized to release carbon monoxide (CO), carbon dioxide (CO_2) and sulfur dioxide (SO_2). These sample impurities are swept by the oxygen (O_2) carrier gas through a series of filters to remove dust and water and then the gases flow through an oxidation furnace ($PtSiO_2$). All CO is oxidized to CO_2 and SO_2 is oxidized to SO_3. The SO_3 is trapped in a cellulose column and the CO_2 and carrier gas stream flow through a selective NDIR detector. Analyzers are often equipped with two NDIR cells, one for the detection of carbon and one for sulfur, but this practice describes only the detection of carbon. The simultaneous detection of carbon and sulfur can however be performed without impact to the performance of this test method, but in this case the cellulose column is not used.

4.2 The detector signal plotted against time is a function of the concentration of the CO_2 in the carrier gas. The area below the curve (integral) corresponds to the total amount of carbon in the sample. The peak is integrated by the software and the concentration is calculated taking into account the calibration factor, the blank analysis, and the sample weight. The calibration of the analyzer is made by means of a reference material. Blank values are obtained from analyzing the pre-ignited crucibles with no sample and an accelerator, which is added for optimum combustion. The blank results are stored. The final sample result is corrected by the blank value and the results are expressed in µg carbon/g MOX.

5. Significance and Use

5.1 MOX is used as a nuclear-reactor fuel. This test method is designed to determine whether the carbon content of the pellets meet the requirements of the fuel specification. Examples of these requirements are given in Specification C833.

5.2 This method is suitable for all sintered MOX pellets containing up to 12 weight % PuO_2 when the UO_2 and PuO_2 meet the requirements of Specifications C753 and C757. The method uncertainty is related to the concentration of the carbon in the sample. At lower concentrations, the relative uncertainty increases. At carbon contents close to the typical carbon content specification limit (100 µg carbon/g U + Pu metal) the method uncertainty is on the order of 5 %, but exact method performance is difficult to determine due to the lack of matrix matched certified reference material.

6. Interferences

6.1 The carbon detectors in the gas analyzer system are selective. The wavelength of detection is chosen to specifically detect only carbon dioxide. Furthermore, after the sample combustion the carrier gas containing the carbon dioxide and other potentially interfering impurities (sulfur, water, and small particulate matter) pass through a series of filters and purifying reagents that remove these impurities from the carrier gas stream leaving only CO_2 in the stream at the detector. If the MOX pellets are made from UO_2 and PuO_2 that meet the requirements of Specification C753 and C757, all interferences are eliminated by the purification system.

6.2 The crucibles and accelerator chemicals, if they contain carbon, will yield erroneously high results for the sample. The analytical method requires the use of pre-ignited crucibles and running blanks with accelerator chemical in pre-ignited crucible to reduce and correct for the blanks in the results for samples.

6.3 The O_2 carrier gas could contain water, hydrocarbons and CO_2 and is filtered prior to injection in the sample combustion chamber to remove these potentially interfering components.

6.4 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 checked by procedure, the potential for the balance to be a source of error is insignificant.

6.5 High levels of halides can damage the NDIR detector cells. Halides are not typically present in high concentrations in sintered MOX fuel pellets and therefore no specific filter is necessary for removal of halides.

7. Apparatus

7.1 *Analytical Balance,* with precision ±0.1 mg.

7.2 *Crucibles,* expendable alumina or similar refractory material. The crucible must be pre-ignited at a temperature of 900°C or higher for a time sufficient to produce constant blank values.

7.3 *Muffle Furnace or Tube Furnace,* capable of attaining temperature of 900°C, for pre-igniting crucibles.

7.4 *Desiccator,* used to store the pre-ignited crucibles.

7.5 *Pellet Crusher,* used to fragment the pellets.

7.6 *Carbon Analyzer,* consisting of an induction-heated furnace suitable for operation at 1600 to 1700°C, an NDIR for measuring carbon dioxide, and auxiliary purification systems.

7.6.1 Typical detector range (8 µg carbon/g U + Pu metal – 1000 µg carbon/g U + Pu metal).

7.7 *Aluminum Foil,* used to wrap the ceramic crucibles after pre-ignition to decrease impurity reabsorption.

7.8 *Tongs and Forceps,* for handling crucibles and lids.

7.9 *Stainless Steel Scoops and Spatulas,* for handling pellet fragments, accelerator, and reference materials.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Sodium Hydroxide (NaOH) on a Fibrous Support*—Captures CO_2.

8.3 *Magnesium Perchlorate ($Mg(ClO_4)_2$*—Removes H_2O.

8.4 *Platinized Silica ($PtSiO_2$)*—Oxidizes any generated CO and SO_2 to CO_2 and SO_3.

8.5 *Cellulose Trap Packing (Surgical Grade Cotton or Equivalent)*—Traps SO_3.

8.6 *Quartz Wool*—For dust traps and to plug the reagent tubes.

8.7 *Accelerators*—Use to achieve complete combustion of the samples. Copper metal, tungsten, tin-tungsten mixture, copper oxide, granular tin, and high purity iron chip accelerators for increased combustion temperature. These materials are available in appropriate purity and form from carbon analyzer vendors. The criterion for satisfactory results is the absence of significant additional carbon release upon recombustion of the specimen.

8.8 *Silica Gel*—Desiccant for the desiccator.

8.9 *Oxygen Carrier Gas*—≥99.999 % purity with inlet pressure 350 to 500 kPa (g) or as specified by the manufacturer.

9. Reference Materials

9.1 The calibration of the analyzer is made by measuring materials with carbon content in the range of concentration expected in the MOX pellet traceable to a reference material from a national standards body such as the U.S. National Institute for Standards and Technology (NIST) or equivalent. Suitable non-matrix matched materials traceable to a reference material in steel matrices (steel pins, steel rings, steel granules, and steel powder) ranging from 5 to 1500 µg carbon/g sample are available and have been found satisfactory. Matrix matched reference materials for MOX pellets are not available.

10. Precautions

10.1 Because of the toxicity of plutonium, all operations should be performed within an approved glove box fitted with appropriate filters to contain any small particle 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.

10.2 The furnace, sample tube, and sample crucibles are heated to >1600°C. Extreme care must be exercised to avoid burns or injury by quartz in a glove box and to avoid breaching the primary confinement boundary. Care should be taken to avoid contacting gloves with hot surfaces. Typically these hot surfaces are guarded and inaccessible during the heating process and therefore do not pose a risk to the operator.

10.3 Exercise appropriate caution when working with compressed gases.

10.4 This procedure uses hazardous chemicals. Use appropriate precautions for handling corrosives, oxidizers, and gases.

11. Preparation and Verification of Apparatus Prior to Sample Analysis

11.1 Turn on the analyzer and set the operating controls of the instrument system according to the operating instructions for the specific equipment used.

11.2 *Verification of the Gases*—Carrier gas flow and system pressure are two essential parameters that must be controlled to ensure satisfactory performance of the instrument. Most analyzers are equipped with pressure regulation and electronic flow control.

11.2.1 Ensure that the regulator valve is set to the correct value for the oxygen line per manufacturers' recommendations.

11.2.2 The following gas pressure parameters should be checked during the analysis and are often automatically monitored by the gas analyzer software: gas pressure when the furnace is opening, gas pressure during leak test and gas flow during analysis.

11.3 *Verification of the Reagents*—Change instrument column packing and reagents as recommended by manufacturer.

11.3.1 The sodium hydroxide changes color from dark to light gray due to the reaction with CO_2. It should be replaced when approximately half of the reagent tube has turned to a light gray color.

11.3.2 The cellulose should be replaced when approximately ⅓ of it has turned to a brown or black color.

11.3.3 Replace the magnesium perchlorate when approximately half of the contents of the reagent tube have been consumed due to absorbed water.

11.3.4 The platinized silica in the oxidation furnace regenerates itself in the oxygen carrier gas. However, due to possible contamination it should be replaced approximately semiannually, or based on use.

11.3.5 At regular intervals and at each replace of the reagents, the O-rings at the reagent tube holders must be inspected for wear and tear and replaced when appropriate.

11.4 *Cleaning the Analyzer*—Buildup of deposits on the oxygen injection nozzle and other orifices can impact the performance of the analyzer; therefore it is recommended that furnace cleaning should be performed after approximately ten

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[4] *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.

samples have been analyzed or as often as necessary depending on deposit buildup. Clean the furnace according to the operating instructions for the specific equipment used.

11.5 *Performing a Leak Test*—A leak test should be performed after the analyzer has been cleaned and after replacement of any reagent tubes.

11.6 *Pre-ignition of the Crucibles*—This is typically done in a muffle or tube furnace at temperatures of at least 900°C for 8 hours, or 1000°C for 2 hours or at more than 1250°C for at least 15 minutes. Then 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. 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.

11.7 *General Verifications*—Depending on the type of analyzer, other parameters that could require verification prior to sample analysis include the voltage supply of the NDIR detector and the temperature of the oxidation furnace.

12. Calibration

12.1 The calibration range and number of reference materials run will depend upon the instrument used and the expected range of carbon in the samples being analyzed. Two to four blank measurements and two to four reference materials are recommended for performing a calibration.

12.2 Weigh approximately 1.5 g of accelerator in a pre-fired crucible (the amount of accelerator will depend upon the instrument used and operating conditions).

12.3 Using a pair of tongs, load the crucible into the induction furnace and combust the accelerator according to the manufacturers' recommended operating conditions (combustion time will vary with the instrument used, but it is typically in the 30 to 120-s range). The result is typically recorded automatically in the analyzer software.

12.4 Repeat steps 12.2 and 12.3 two to four times.

12.5 Weigh approximately 1 g of non-matrix matched reference material to the nearest 0.1 mg in a pre-fired crucible and transfer the weight of the reference material to the analyzer.

12.6 Weigh approximately 1.5 g of accelerator and add it to the pre-fired crucible containing the non-matrix matched reference material (the amount of accelerator will depend upon the instrument used and operating conditions).

12.7 Using a pair of tongs load the crucible into the induction furnace and combust the non-matrix matched reference material according to the manufacturer's recommended operating conditions (combustion time will vary with the instrument used, but it is typically in the 30 to 120-s range). The result is recorded automatically in the analyzer software.

12.8 Repeat steps 12.5 to 12.7 two to four times.

12.9 Using the data collected during steps 12.2 to 12.8 and stored in the analyzer, calibrate the instrument according to the manufacturers' operating instructions. Calibration coefficients are normally stored in the analyzer software.

NOTE 1—Recalibration frequency will depend upon the type of instrument used. As a minimum, recalibration is required when critical instrument components are changed, or when control chart data indicates that the instrument is failing to meet performance criteria.

13. Procedure

13.1 *Pre-Sample Analysis Blank Measurement*—A blank measurement (crucible plus accelerator) is performed prior to sample analysis in order to check that the background carbon signal is not above an acceptable limit. The signal from the blank is saved and automatically subtracted from the sample (MOX) signal to take into account carbon in the crucible, accelerator, and carrier gas.

13.1.1 Weigh approximately 1.5 g of accelerator in a pre-fired crucible (the amount of accelerator will depend upon the instrument used and operating conditions).

13.1.2 Using a pair of tongs, load the crucible into the induction furnace and combust the accelerator according to the manufacturers' recommended operating conditions (combustion time will vary with the instrument used, but it is typically in the 30 to 120-s range). The result is typically recorded automatically in the analyzer software.

13.1.3 The blank result should not be higher than the limit of detection established for the analyzer (approximately 5 to 10 µg carbon/g U + Pu metal). If the limit is exceeded, the furnace should be cleaned and another blank should be run. If the blank is still not low enough, the reagents may need to be changed.

13.2 *Pre-Sample Calibration Verification*—An analysis of a reference material is performed prior to sample analysis in order to check that the stored calibration coefficient in the analyzer software is valid. The calibration coefficient is valid if the measured value of the reference material agrees with the reference value within the tolerance limits set for the analyzer based on the analyzer performance criteria.

13.2.1 Weigh approximately 1 g of reference material to the nearest 0.1 mg in a pre-fired crucible and transfer the weight of the reference material to the analyzer.

13.2.2 Weigh approximately 1.5 g of accelerator and add it to the pre-fired crucible containing the reference material (the amount of accelerator will depend upon the instrument used and operating conditions).

13.2.3 Using a pair of tongs, load the crucible into the induction furnace and combust the reference material according to the manufacturer's recommended operating conditions (combustion time will vary with the instrument used, but it is typically in the 30 to 120-s range). The result is typically recorded automatically in the analyzer software.

13.2.4 The reference material result should not fall outside of tolerance limits set for the analyzer based on the analyzer performance criteria. If the limit is exceeded, the furnace should be cleaned and another reference material should be run. If the reference material is still not within tolerance limits, perform a calibration.

13.3 *Sample (MOX) Measurement*—Crush pellet samples to obtain smaller pellet fragments of approximately 1 g each. (The fragment size and number of fragments required may vary according to the instrument used and operating conditions.)

13.3.1 Weigh approximately 1 g of sample to the nearest 0.1 mg in a pre-fired crucible and transfer the weight to the analyzer. The sample size should be chosen to provide adequate sensitivity and accuracy at low carbon concentrations.

13.3.2 Weigh approximately 1.5 g of accelerator and add it to the pre-fired crucible containing the sample (the amount of accelerator will depend upon the instrument used and operating conditions).

13.3.3 Using a pair of tongs load the crucible into the induction furnace and combust the sample according to the manufacturers' recommended operating conditions (combustion time will vary with the instrument used, but it is typically in the 30 to 120-s range). The result is recorded automatically in the analyzer software.

NOTE 2—The number of replicates required per sample or lot will depend on the instrument used, the operating conditions, and the required quality of the result. Typically two samples are measured so that an average of the two analyses can be calculated and reported for a sample or lot result. Repeat 13.3 as many times as required in order to gather sufficient replicate data.

NOTE 3—The number of samples or lots that can be performed prior to steps 13.4 and 13.5 depend on the instrument used and the operating conditions. Typically 5 to 10 samples or lots for a total of 10 to 20 replicates can be analyzed before checking analyzer calibration.

13.4 *Post Sample Analysis Blank Measurement*—A blank measurement (crucible plus accelerator) is performed after sample analysis in order to check that the background carbon signal is not above an acceptable limit. To perform the blank analysis, repeat steps 13.1.1 to 13.1.3.

13.5 *Post Sample Calibration Verification*—An analysis of a reference material is performed after sample analysis in order to check that the stored calibration coefficient in the analyzer software is valid. The calibration coefficient is valid as long as the measured value of the reference material falls within the tolerance limits set for the analyzer based on the analyzer performance criteria. To perform the reference material analysis, repeat steps 13.2.1 to 13.2.4.

NOTE 4—Results from 13.2, 13.4, and 13.5 are not directly used for sample result calculation, but are often used to track analyzer performance (that is, control charts).

14. Calculation

14.1 Calculate the carbon content as follows (this calculation is typically performed by the analyzer software):

$$[C] = \frac{(C_s - C_b)}{W} \tag{1}$$

where:

$[C]$ = micrograms of carbon per gram sample (MOX),
C_s = micrograms of carbon in sample (MOX),
C_b = micrograms of carbon in a black run, and
W = grams of sample (MOX).

If multiple replicates are measured, the average content of carbon $[C]_a$ is calculated,

$$[C]_a = \frac{C_{s(n)} + C_{s(n-1)} + C_{s(n-2)} + \dots}{n} \tag{2}$$

14.2 For samples requiring carbon results expressed as µg carbon per g U + Pu, convert results to uranium plus plutonium metal basis as follows:

$$[C_m] = \frac{[C]}{f} \tag{3}$$

where:

$[C_m]$ = micrograms of carbon per gram of U + Pu in sample (MOX), and
f = mass fraction of U + Pu metal to UO_2 + PuO_2 in sample (MOX).

15. Precision and Bias

15.1 Within the different stages of the nuclear fuel cycle many challenges lead to the inability to perform interlaboratory studies for precision and bias. These challenges may include variability of matrices of material tested, lack of suitable reference materials, limited laboratories performing testing, shipment of materials to be tested, and regulatory constraints. Because of this each individual laboratory utilizing these test methods should develop their own precision and bias as part of their quality assurance program. Guidance can be found in Guide C1068.

15.2 *Precision*—The repeatability of the method as a relative standard deviation (1σ) as determined by a single laboratory using non-matrix matched reference materials has been determined to be 11 % at 18 ppm, 6 % at 48 ppm C, and 4 % at 109 ppm C. The reproducibility of this test method is not provided at this time because very few laboratories perform this analysis and because of the issues stated at the beginning of this section. As a result, it is not likely that reproducibility data will be available in the future.

15.3 *Bias*—The bias of the test method cannot be tested reliably because of the lack of suitable matrix matched reference materials. The bias observed using non-matrix matched reference materials is +12.2 % at 18 ppm, +1.2 % at 48 ppm, and –1.6 % at 109 ppm.

16. Keywords

16.1 carbon content; impurity content; mixed oxide; MOX; plutonium oxide; uranium oxide

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