Designation: C1817 − 16

Standard Test Method for The Determination of the Oxygen to Metal (O/M) Ratio in Sintered Mixed Oxide ((U, Pu)O_2) Pellets by Gravimetry[1]

1. Scope

1.1 This practice is an alternative method to Test Method C698 for the determination of the oxygen-to-metal atom ratio (O/M) in sintered mixed oxide fuel (MOX) pellets. The method presented in Test Method C698 is a one-step thermogravimetric method for determining O/M ratio in sintered MOX powders and pellets. As stated in Test Method C698, thermogravimetric methods using a two-step heating cycle are also satisfactory (**1, 2**).[2] The method presented in this test method is a two-step heating cycle method. This test method is applicable to sintered MOX pellets containing up to 10 weight percent PuO_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 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:*[3]

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, Sinterable
C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets
C859 Terminology Relating to Nuclear Materials
C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
C1672 Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer
D1193 Specification for Reagent Water
D1356 Terminology Relating to Sampling and Analysis of Atmospheres

2.2 *ISO Standards:*[4]

ISO 21484 Nuclear Fuel Technology – Determination of the O/M Ratio in MOX Pellets – Gravimetric Method – First Edition

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 *average of the relative atomic mass*—the weighted average of the relative atomic mass of an element calculated as a function of its isotopic composition.

3.2.2 *mole fraction*—the ratio of the number of molecules (or moles) of a compound or element to the total number of molecules (or moles) present (Terminology D1356).

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

3.2.4 *O/M*—ratio of the oxygen atoms divided by the metal atoms in the sample.

3.2.5 *relative atomic mass*—a dimensionless physical quantity, the ratio of the average mass of atoms of an element (from a single given sample or source) to 1⁄12 of the mass of an atom of carbon-12 (known as the unified atomic mass unit).

3.2.6 *scavenging*—the process of pushing a gas out by introducing a fresh flow in.

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

[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.

[4] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

3.2.7 *sintering*—to increase the bonding in a mass of powder or a compact by heating below the melting point of the main constituent.

4. Summary of Test Method

4.1 The purpose of the analysis is to test the stoichiometry of the MOX pellet by the determination of the O/M ratio. The principle of the method is that one or a number of MOX pellets are heated under a specific set of atmospheric conditions in order to add or subtract oxygen molecules to the MOX pellets. This process results in an O/M ratio of 2 in the MOX pellets after heating. The mass of the oxygen molecules added to or subtracted from the MOX pellets to achieve an O/M ratio of 2 is quantified by weighing the MOX pellets before and after the heating step. Once the difference in mass is known, the number of atoms of oxygen added to or subtracted from the MOX pellets can be determined. The resulting data are used to calculate the O/M ratio in the pellets prior to heating.

4.2 Three or four MOX pellets are weighed before and after an oxidation-reduction heat treatment at specified time and temperature intervals.

4.3 The heating and atmospheric conditions required to achieve an O/M ratio of 2 in the MOX pellets are as follows (**3-5**):

(1) Oxidation of the pellets in a current of air at 900 ± 20°C to increase the O/M ratio. There is no evidence that oxygen can be absorbed interstitially by plutonium dioxide to produce hyperstoichiometric oxide containing plutonium ions having a valency higher than four. On the contrary, uranium oxide can be hyperstoichiometric.

(2) Reduction of the pellets in a stream of argon/hydrogen gas at 900 ± 20°C to reduce the O/M ratio to 2. Under these conditions (temperature and reducing atmosphere), the O/M ratio is adjusted to 2. The choice of these parameters is based upon a compromise between selecting a temperature low enough to prevent reduction of plutonium oxide to a hypostoichiometric state but high enough to reduce hyperstoichiometric uranium oxide to UO_2.

NOTE 1—The O/M ratio increases during the cooling process after the heat cycles described above unless it is done under Ar or Ar/H_2 atmosphere. So, control of the cooling atmosphere is needed.

4.4 The reactions involved are:

$$(U, Pu)O_{2\pm x} \pm x/2 O_2 \rightarrow (U, Pu)O_{2+x} \quad (1)$$

$$(U, Pu)O_{2+x} + xH_2 \rightarrow (U, Pu)O_{2.000} + xH_2O \quad (2)$$

4.5 The calculation of the stoichiometry is based on the weight difference of the pellets before and after heat treatment and the mean atomic mass of the heavy metals in the MOX pellets (see Section 11 for details of the calculation).

5. Significance and Use

5.1 MOX is used as a nuclear-reactor fuel. This test method is designed to determine whether the O/M ratio meets the requirements of the fuel specification. Examples for establishing a fuel specification 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.

6. Interferences

6.1 Impurities in the sample may lead to inaccuracies in the determination of O/M ratios either due to loss of volatiles or gain due to redox reactions. Even inert impurities present in sufficiently high amounts compromise the accuracy of O/M ratios because the true mass of the ((U, Pu)O_2) subjected to the oxidation-reduction process remains unknown. When purified PuO_2 and UO_2 powders with maximum total impurity contents specified in Specifications C753 and C757 are used, the change in mass due to the non-volatile and volatile impurities is insignificant to the method. This method assumes that the requirements of these two standards are met and therefore does not take into account the impact of impurities. If impurity contents are higher than those specified in Specifications C753 and C757, an evaluation should be performed to determine their impact on the method. This test method assumes that pellets are sintered. It does not correct for moisture or volatile additives as the content of these impurities is negligible after sintering.

6.2 The crucibles if not clean can be a potential interference. If necessary, the crucibles are cleaned and fired before use as described in 10.1. If crucible cleanliness is tracked and if crucibles are cleaned when necessary, the potential for the crucibles to be a source of interference is insignificant.

6.3 If crucibles are made from materials that oxidize under the test conditions, they may prevent proper equilibration of the stoichiometry of the sample by consuming available oxygen. In addition, they would change weight and would impact the difference in mass calculation. This method assumes that the crucible is made out of a material that is inert under the test conditions, such as platinum alloyed with 20 % rhodium.

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 Loss of weight due to pellet chipping would invalidate the analysis. Handle pellets with care.

6.6 The average of the relative atomic mass of the uranium and plutonium in the samples impacts the accuracy of the calculation. The average of the relative atomic mass of uranium and plutonium are measured by Thermal Ionization Mass Spectrometry (TIMS) in accordance with Test Method C1672 and this measured value is accounted for in the calculation.

7. Apparatus

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

7.2 *Tube Furnace,* capable of controlling temperatures 900 ± 20°C and fitted with a fused quartz tube chamber which allows for sweeping the chamber with various gasses.

7.3 *O/M Apparatus*—See Fig. 1. This apparatus is not typically commercially available and users of this test method must build a similar device.

NOTE 2—It is important that the thermocouple be located such that it can monitor the temperature in the zone in which the sample is placed, or can be calibrated to account for any physical offset. It is also important

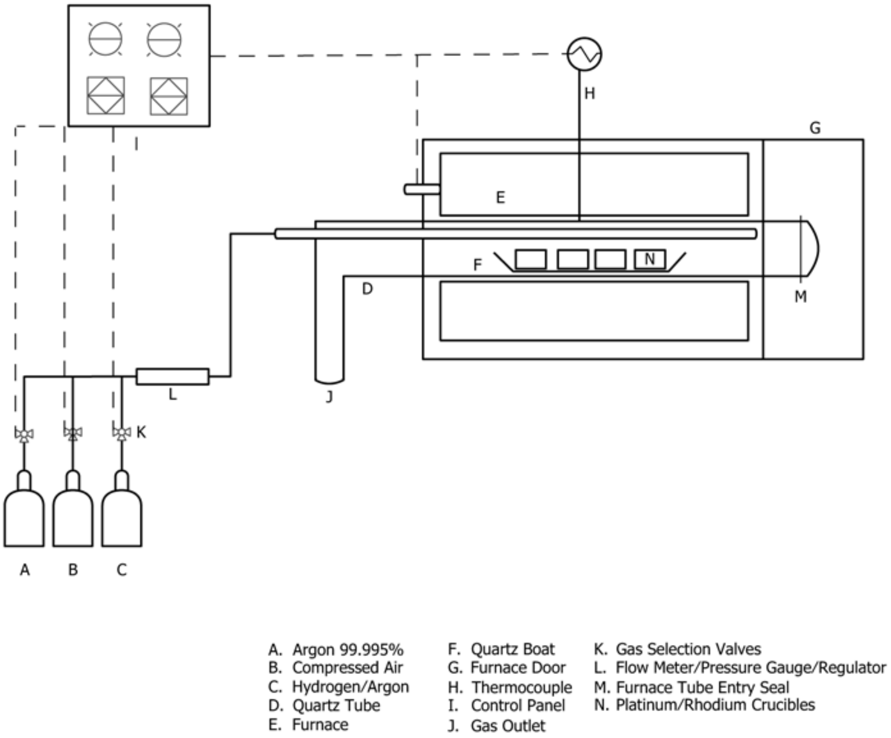

FIG. 1 O/M Apparatus

that the furnace is designed so that the temperature remains stable across the region in which the sample is placed. For safety reasons, it is important to ensure that the design of the furnace limits the possibility of mixing air with the hydrogen/argon gas mixture.

7.4 *Platinum sample crucibles*—alloyed with 20 % rhodium.

7.5 *Fused Quartz Boats (if needed),* designed to hold multiple platinum sample crucibles if more than one sample is measured at the same time.

7.6 *Pair of Stainless Steel Tweezers.*

7.7 *Pair of Tongs (if using cleaning method 2 described in 10.1).*

7.8 *Hot Plate (if using cleaning method 2 described in 10.1).*

7.9 *Beaker (if using cleaning method 2 described in 10.1).*

7.10 *Gas Flow Meter, Pressure Gauge, and Regulator.*

8. Reagents and Materials

8.1 *Purge Gases:*

8.1.1 *Argon*—Certified 99.995 % purity (O_2 <5 $mg.kg^{-1}$, H_2O <5 $mg.kg^{-1}$, N_2 <20 $mg.kg^{-1}$).

8.1.1.1 Flow rate: 16 litres/hour.

8.1.1.2 Pressure: 200 kPa.

8.1.2 *Air*—Filtered and dried (Suggested air treatment system features: filter efficiency ≥98 % of 0.01 µm, dew point ≤20°C, total hydrocarbons ≤5 $mg.m^{-3}$).

8.1.2.1 Flow rate: 12 litres/hour.

8.1.2.2 Pressure: 200 kPa.

8.1.3 *Argon/Hydrogen Mixture*—Certified 99.995 % purity with the total amount of impurities ($O_2 + H_2O + C_nH_m$) <10 $mg.kg^{-1}$. The gas mixture shall be (5 % <H_2 <7 %).

8.1.3.1 Flow rate: 16 litres/hour.

8.1.3.2 Pressure: 200 kPa.

8.2 *Liquid Reagents:*

8.2.1 *Water (if using cleaning method 2)*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water in conformance with Specification D1193, Type 1.

8.2.2 *Nitric Acid (if using cleaning method 2)*—(16 M HNO_3) concentrated, specific gravity 1.42.

8.2.3 *Nitric Acid 7M (if using cleaning method 2)*—Add 440 mL of concentrated HNO_3 to 900 mL of DI water, dilute to a final volume of 1 litre.

8.3 *Reference Materials:*

8.3.1 There are no certified reference materials (MOX pellets) for the O/M ratio determination by the thermogravimetric treatment method (**6**).

9. Precautions

9.1 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 (**7, 8**).

9.2 The furnace, sample tube, and sample crucibles are heated to 900 ± 20°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.

9.3 Exercise appropriate caution when working with compressed gases.

9.4 Hydrogen is explosive when mixed with oxygen in the presence of an ignition source. Using a mixture of argon and hydrogen instead of pure hydrogen, limiting the hydrogen content to a maximum of 7 % and ensuring that the design of the furnace does not allow for the hydrogen/argon mixture to react with air limits the safety risk of this method. Using a glove box with an inert atmosphere also reduces the risk and improves the method performance.

10. Procedure

10.1 *Crucible Cleaning*—The crucibles shall be clean and weighed before use. Cleaning prior to each use is not required, but an evaluation of the cleanliness of the crucible is required. Cleaning is required if dust is visible. If crucible cleaning is deemed required, the following are two examples of how the crucibles can be cleaned.

10.1.1 *Example Cleaning Method 1:*

10.1.1.1 Wipe out the empty crucible with disposable paper or cotton wipes.

10.1.1.2 Introduce the crucible (crucibles in the quartz boat if necessary) into the furnace using a pair of tweezers and seal the furnace door.

10.1.1.3 Place the furnace under argon/hydrogen by introducing the argon/hydrogen at a pressure of 200 kPa, and a flow rate of 16 L/h.

10.1.1.4 Turn on the furnace.

10.1.1.5 Heat the crucibles at 900 ± 20°C for 1 h.

10.1.1.6 Shut off the furnace and allow the crucible to cool to less than 150°C in the argon-hydrogen atmosphere within the furnace. If the glove box atmosphere is inert, the crucibles can be removed at a higher temperature.

10.1.1.7 Remove the crucibles (crucibles in the quartz boat if necessary) from the furnace using a pair of tweezers, shut off the argon-hydrogen and allow the crucibles to cool to less than 35°C.

10.1.1.8 Weigh each crucible to within ±0.1 mg. Record the value as m_0.

10.1.2 *Example Cleaning Method 2:*

10.1.2.1 Wipe out the empty crucible with disposable paper or cotton wipes.

10.1.2.2 Place the crucibles in a beaker with enough *7M* HNO_3 to completely cover the crucibles.

10.1.2.3 Place the beaker containing the crucibles onto a hot plate and boil the acid for approximately 30 min.

10.1.2.4 Allow the acid solution to cool and remove the crucibles using a pair of tongs.

10.1.2.5 Rinse the crucibles with deionized water in conformance with Specification D1193, Type 1.

10.1.2.6 Introduce the crucibles (crucibles in the quartz boat if necessary) into the furnace using a pair of tweezers and seal the furnace door.

10.1.2.7 Place the furnace under argon by introducing the argon at a pressure of 200 kPa, and a flow rate of 16 L/h.

10.1.2.8 Turn on the furnace.

10.1.2.9 Heat the crucibles at 150°C for approximately 30 min.

10.1.2.10 Shut off the furnace.

10.1.2.11 Remove the crucibles (crucibles in the quartz boat if necessary) from the furnace using a pair of tweezers, shut off the argon and allow the crucibles to cool to less than 35°C.

10.1.2.12 Weigh each crucible to within ±0.1 mg. Record the value as m_0.

10.2 *Weighing and Introduction of the Pellets:*

10.2.1 Using a pair of tweezers, place the pellets vertically into the empty crucible, and weigh to the nearest 0.1 mg. Record the value as m_1.

10.2.2 Using a pair of tweezers, introduce the sample crucibles containing the pellets (crucibles in the quartz boat if necessary) into the furnace and seal the furnace door.

10.2.3 Proceed with the oxidation.

10.3 *Oxidation:*

10.3.1 Place the furnace under argon by introducing the argon gas at a pressure of 200 kPa and a flow rate of 16 L/h.

10.3.2 Turn on the furnace.

10.3.3 Heat the pellets in the argon atmosphere at 900 ± 20°C for 5 min.

10.3.4 After 5 min turn off the argon gas and introduce the air at a pressure of 200 kPa and a flow rate of 12 L/h.

10.3.5 Heat the pellets in the furnace for 1 min under air scavenging.

10.3.6 After 1 min turn off the air and introduce argon under the conditions given in 10.3.1.

10.3.7 Heat the pellets in the argon atmosphere for 5 min.

10.3.8 This completes the oxidation cycle, turn off the argon and quickly initiate the reduction sequence.

10.4 *Reduction:*

10.4.1 Place the furnace under argon/hydrogen by introducing the argon/hydrogen at a pressure of 200 kPa and a flow rate of 16 L/h.

10.4.2 Heat the pellets under argon/hydrogen scavenging at 900 ± 20°C for 8 hours.

10.4.3 After the eight hour time period, shut down the furnace and allow the pellet samples to cool to 50°C or less under argon/hydrogen scavenging. This completes the reduction cycle.

10.4.4 Remove the crucibles (or crucibles in the quartz boat) from the furnace tube using a pair of tweezers and allow them to cool to 35°C or less. Turn off the argon-hydrogen.

10.4.5 Initiate the weighing sequence as quickly as practical after the crucibles have cooled down.

10.5 *Weighing:*

10.5.1 Weigh each platinum sample crucible containing the MOX pellets as quickly as practical to the nearest 0.1 mg. Record the final mass of the crucible as m_2.

11. Calculation

11.1 *Calculation of the Average Atomic Mass:*

11.1.1 Calculate the average atomic mass of the heavy metal oxide after heat treatment, assuming that the O/M ratio equals exactly 2, using the formula:

$$A_t = \frac{[A_t\,(P\,u)] \times Pu\% + [A_t\,(U)] \times U\% + [A_t\,(A\,m)] \times Am\%}{Pu\% + U\% + Am\%} + 2 \times At(0) \qquad (3)$$

where:

A_t = the average of the relative atomic mass of the heavy metal oxide,

$A_t(Pu)$ = the average of the relative atomic mass of plutonium in the oxide from a TIMS analysis,

$A_t(U)$ = the average of the relative atomic mass of uranium in the oxide from a TIMS analysis,

$A_t(Am)$ = the average of the relative atomic mass of americium in the oxide (^{241}Am),

$Pu\ \%$ = the mole fraction, in percentage, of plutonium in the oxide,

$U\ \%$ = the mole fraction, in percentage, of uranium in the oxide,

$Am\ \%$ = the mole fraction, in percentage, of americium in the oxide, and

$At(O)$ = the atomic mass of oxygen (15.9994).

NOTE 3—The measurement method for determining the mole fraction of americium in the oxide is not described in this standard. It can be measured using a suitable method, standardized or qualified internally by the laboratory using guidance in Guide C1068.

11.2 *Calculation of the O/M Ratio:*

11.2.1 Calculate the O/M ratio as follows:

$$O/M = 2.000 - \frac{A_t \times (m_2 - m_1)}{A_t(O) \times (m_2 - m_0)} \tag{4}$$

where:

m_0 = the mass, in grams, of the empty crucible,

m_1 = the mass, in grams, of the crucible with test sample before oxidation-reduction,

m_2 = the mass, in grams, of the crucible with test sample after oxidation-reduction heat treatment,

$A_t(O)$ = the relative atomic mass of oxygen (15.9994), and

A_t = the average of the relative atomic mass of heavy metal oxide calculated from Eq 3.

NOTE 4—This calculation does not take into account metallic or volatile impurities as they are considered negligible to the analysis, as discussed in 6.1.

12. Precision and Bias

12.1 *Precision*—The repeatability standard deviation (1σ) of the method as determined by a single laboratory has been determined to be between 0.001 and 0.002 O/M units. Typically, a repeatability of ±0.004 O/M units (2 times the standard deviation) is sufficient to measure the O/M ratio and verify that it meets the specification for MOX fuel. This thermogravimetric method, if performed as specified, meets this requirement. The reproducibility of this test method is not provided at this time because very few laboratories perform this analysis. In addition, the cost and complexity of the logistics associated with the transfer of MOX pellets between laboratories is considered to be prohibitive. As a result, it is not likely that reproducibility data will be available in the future. If any user is aware of repeatability data from other laboratories, please contact the technical committee having jurisdiction over this standard, and those data will be considered for future versions of the standard.

12.2 *Bias*—The bias of the test method cannot be tested reliably because of the lack of suitable reference or calibration materials. The absence of bias depends upon quantitative conversion of the sample to the stoichiometric dioxide. The conditions of analysis were selected on the basis of thermodynamic data to ensure complete conversion to the stoichiometric dioxide and therefore the bias does not have a significant impact on the uncertainty of the method.

13. Keywords

13.1 gravimetry; MOX; oxygen to metal (O/M) ratio; plutonium; thermal analysis; uranium

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