Designation: C 1457 – 00

Standard Test Method for Determination of Total Hydrogen Content of Uranium Oxide Powders and Pellets by Carrier Gas Extraction[1]

This standard is issued under the fixed designation C 1457; 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 applies to the determination of hydrogen in nuclear-grade uranium oxide powders and pellets to determine compliance with specifications. Gadolinium oxide (Gd_2O_3) and gadolinium oxide-uranium oxide powders and pellets may also be analyzed using this test method.

1.2 This standard describes a procedure for measuring the total hydrogen content of uranium oxides. The total hydrogen content results from absorbed water, water of crystallization, hydro-carbides and other hydrogenated compounds which may exist as fuel's impurities.

1.3 This test method covers the determination of 0.05 to 200 µg of residual hydrogen.

1.4 This test method describes an electrode furnace carrier gas combustion system equipped with a thermal conductivity detector.

1.5 The preferred system of units is micrograms hydrogen per gram of sample (µg/g sample) or micrograms hydrogen per gram of uranium (µg/g U).

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

2. Referenced Documents

2.1 *ASTM Standards:*

C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder[2]

C 776 Specification for Sintered Uranium Dioxide Pellets[2]

C 888 Specification for Nuclear-Grade Gadolinium Oxide (Gd_2O_3) Powder[2]

C 922 Specification for Sintered Gadolinium Oxide-Uranium Dioxide Pellets[2]

3. Summary of Test Method

3.1 The total hydrogen content is determined using a hydrogen analyzer. The hydrogen analyzer is based on the carrier gas method using argon or nitrogen as carrier gas. The actual configuration of the system may vary with vendor and model.

3.2 The samples to be analyzed are dropped into a preheated graphite crucible, and then, heated up to a temperature of more than 1700°C in a graphite crucible. At that temperature hydrogen, oxygen, nitrogen, and carbon monoxide (oxygen is converted to CO when it reacts with the crucible) are released. The release gas is purified in the carrier gas stream by oxidation and absorption columns. The hydrogen is separated by chromatographic means and analyzed in a thermal conductivity detector.

4. Significance and Use

4.1 Uranium dioxide is used as a nuclear-reactor fuel. Gadolinium oxide is used as an additive to uranium dioxide. In order to be suitable for this purpose, these materials must meet certain criteria for impurity content. This test method is designed to determine whether the hydrogen content meets Specifications C 753, C 776, C 888, and C 922.

5. Interferences

5.1 Contamination of carrier gas, crucibles, or samples with extraneous sources of hydrogen may cause a positive bias. A blank correction will help to minimize the bias from carrier gas and crucibles. Interference from adsorbed hydrogen on samples may be eliminated by keeping the sample in an inert atmosphere or vacuum.

5.2 The purification system typically associated with the recommended combustion and detection equipment is designed to minimize other expected sources of interferences, such as sulfur, halogens, carbon monoxide, carbon dioxide, and water.

5.2.1 The nitrogen and hydrogen peaks are close together and must be well-separated to prevent falsely high result from the nitrogen. The molecular sieve must be sufficiently long to separate the peaks and must be changed when the column becomes loaded with contaminants that prevent proper peak separation.

5.3 The temperature of >1700–1800°C must be reached. If not, the decomposition of the released water to hydrogen and carbon monoxide may not be complete. The temperature will depend upon the instrument and type of graphite crucible used. Single wall crucibles will require a lower temperature (power) than double wall crucibles.

5.4 Incomplete fusion may result in partial or a late release

[1] This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] *Annual Book of ASTM Standards*, Vol 12.01.

of hydrogen resulting in low results.

5.5 At temperatures of more than 2200°C uranium metal may be formed, and carbon dioxide released because of reduction of UO_2 by the graphite crucible.

5.5.1 Carbon dioxide will interfere with the thermal conductivity measurement. This is normally covered by use of chemical absorption, or a molecular sieve column, or both.

5.5.2 Excess temperature, from too much power, or crucible hot spots, from misaligned electrodes may cause analysis errors. Uranium samples should be evenly fused and should fall out freely of the crucibles and contain very little uranium metal.

6. Apparatus

6.1 *Hydrogen Analyzer*, consisting of an electrode furnace capable of operation at least up to 2200 to 2500°C, a thermal conductivity detector for measuring, and auxiliary purification systems.

6.2 *Balance*, with precision of ± 1 mg.

7. Reagents and Materials

7.1 *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. 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.

7.2 *Carrier Gas*—Nitrogen ≥ 99.998 % or Argon ≥ 99.995 %.

7.3 *Carrier Gas Purifiers*:

7.3.1 *Copper Oxide*, or rare earth copper oxide (converts H to H_2O), or

7.3.2 *Copper Turnings*, or granules.

7.4 *Molecular Sieve-Sodium Hydroxide*, on a fiber support (sodium hydroxide[3] reacts with CO_2 to yield water; the molecular sieve separates N_2 and H_2).

7.5 *Schutze Reagent*, iodine pentoxide over silica gel (converts CO to CO_2).

7.6 *Magnesium Perchlorate*[4]—removes water.

7.7 *Silicone Vacuum Grease*.

7.8 *Tin Flux*, if Zr or Ti hydride standards are to be used.

7.9 *Graphite Crucibles*.

7.10 *Tin Capsules*.

7.11 *Aluminum Oxide (Al_2O_3)*, to check furnace temperature.

7.12 *Hydrogen Standard Materials*—Calibrate the instrument using either high purity (99.9999 %) certified hydrogen gas or NIST-traceable, or equivalent, metal standards. Steel standards[5] are the preferred metal standards because no flux is used, and this best matches the conditions used to analyze uranium oxide samples. Zr- or Ti-hydride standards may be used, but require the use of a flux metal.

7.13 *Sodium Tartrate or Sodium Tungstate* may be used as check standards for uranium powder analyses.

8. Hazards and Precautions

8.1 Take proper safety precautions to prevent inhalation or ingestion of uranium dioxide powders or dust during grinding or handling operations.

8.2 Operation of equipment presents electrical and thermal hazards. Follow the manufacturer's recommendations for safe operation.

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

9. Preparation of Apparatus

9.1 Inspect and change instrument column packing and reagents as recommended by manufacturer.

9.2 Check to ensure that the furnace heats properly on a periodic basis. A quarterly check is recommended. A properly functioning furnace, set at normal operating parameters should fuse Al_2O_3 (approximately 2050°C melting point, depending upon form).

9.3 Set the operating controls of the instrument system according to the operating instructions for the specific equipment used.

9.4 Condition the apparatus by combustion of several blanks prepared with sample crucible and accelerator, if any, in the amount to be used with the samples. Successive blanks should approach a constant value, allowing for normal statistical fluctuations.

9.5 The blank measurements prove the integrity of the purifying units and the tightness of the equipment. Blank values of more than ± 0.03 µg H_2 require adequate measures of correction.

10. Calibration Using Metal Standards

10.1 The calibration range and number of standards will depend upon the instrument used. Three to five standards, containing 3 to 6 µg hydrogen are recommended. The number of standards and calibration range will depend upon the availability, assay accuracy, and homogeneity of available standards.

10.2 Load and combust the standards according to the manufacturer's recommended operating conditions.

10.3 Calibrate the instrument according to operating instructions. Calibration coefficients normally are stored in the microprocessor memory.

10.4 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 standards data indicate that the instrument is failing to meet performance criteria.

10.5 *Calibration of the Analyzer Using Gas Dosing*:

10.5.1 *Instrument Calibration*—A well-defined volume of hydrogen calibration gas, which is corrected on standard conditions, is inserted and analyzed. This calibration is performed three times. A deviation of the calibration values of more than 2 % from the normal requires as readjustment.

10.5.2 *Check of the Calibration*—A titanium, zirconium, or

[3] Ascarite marketed by J.T. Baker has been found to perform satisfactorily.

[4] Anhydrone marketed by J.T. Baker has been found to perform satisfactorily.

[5] NIST-traceable steel standards marketed by LECO have been found to perform satisfactorily.

steel hydride standard is weighed to 1-mg accuracy and melted with the aid of tin granules. The released hydrogen is determined. The measured values may differ from the certified values by not more than 10 %. If not, the calibration is repeated. Alternately, for better safety, helium gas may be used, if the correlation between the response of the helium and hydrogen gas is established.

11. Sample Preparation

11.1 *Powder Samples*—The sample shall be exposed to ambient conditions for not longer than five minutes because alterations of the powder sample due to moisture adsorption or desorption or oxidation have to be avoided. The sample has to be stored in tight containers. The gas volume in the container should be as low as possible.

11.2 *Powder Samples*—Powder samples are filled into tin capsules, which subsequently are closed. Alternatively, the powder samples may be inserted as pressed bodies. Sampling is done with a tube shaped powder sampler having a inner diameter of more than 2.5 times of the maximum powder particle size.

11.3 *Pellets*—During pellet sampling the pellets have to be handled with forceps. The sample should be representative of the manufacturing process, for example, storage of the pellets.

11.4 *Pellets*—Pellets may be analyzed whole or may be crushed to particles as small as 1 mm (18 mesh). Crushing pellets will increase sample surface area and must be performed with great care. The possibility of increasing moisture adsorption and obtaining falsely elevated hydrogen results is very high.

12. Procedure

12.1 Weigh a portion of sample, to the nearest 1 mg, into the crucible. The sample size should be chosen to provide adequate sensitivity and accuracy at low hydrogen concentrations.

12.2 Load the crucible into the furnace and combust the sample according to the manufacturer's recommended operating conditions: Purify the empty graphite crucible in the carrier gas stream by heating at a temperature above 1700–1800°C. Drop the sample into the crucible, heat to > 1700–1800°C, and measure the hydrogen content (combustion time will vary with the instrument used).

12.3 Remove the sample crucible and examine it for proper fusion. See 5.4 and 5.5.

13. Calculation

13.1 Calculate the hydrogen content as follows:

$$\mu g\ H \text{ per g of sample} = (H_s - H_b)/W \quad (1)$$

where:

H_s = micrograms of hydrogen in test specimen,
H_b = micrograms of hydrogen in a blank run, entered if a blank correction is desired, and
W = grams of test specimen.

13.2 For samples requiring hydrogen results expressed as µg hydrogen per g U, convert results to uranium basis as follows:

$$H, \mu g/g\ U \text{ basis} = \frac{H\ \mu g/g \times 100}{\%\ U \text{ content of sample}} \quad (2)$$

14. Precision and Bias

14.1 The precision and bias for this method will depend upon the instrument used and the operating conditions. The following data[6] are provided as an example of method capability.

14.2 The relative standard deviation for a 5 µg/g steel standard was 5.8 % (1 s.d.). The bias, as measured by percent recovery of the standard's value, was + 0.1 %. These data represent 102 standards measured by seven operators using one instrument, over a one-year period.

14.3 The relative standard deviation for a 12 000 µg/g working sodium tungstate powder standard was 4.2 % (1 s.d.). The bias, as measured by percent recovery of the standard's value, was –5.7 %. These data represent 102 standards measured by seven operators using one instrument, over a one-year period.

15. Keywords

15.1 gadolinium oxide; gadolinium oxide-uranium oxide; hydrogen content; impurity content; uranium oxide

[6] Data were obtained from a LECO model 404.