



Designation: **E1447–09 (Reapproved 2016) E1447 – 22**

# Standard Test Method for Determination of Hydrogen in Titanium and Titanium Reactive Metals and Reactive Metal Alloys by Inert Gas Fusion Thermal Conductivity/~~Infrared Detection Method with~~ ~~Detection by Thermal Conductivity or Infrared~~ Spectrometry<sup>1</sup>

This standard is issued under the fixed designation E1447; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method applies to the determination of hydrogen in ~~titanium and titanium alloys in concentrations from 0.0006 % reactive metals and reactive metal alloys, particularly titanium and zirconium, with mass fractions from 9 mg/kg to 0.0260 %.~~ 320 mg/kg.

1.2 ~~The values stated in SI units are~~ This method has been interlaboratory tested for titanium and zirconium and alloys of these metals and can provide quantitative results in the range specified in 1.1 to . It may be possible to extend the quantitative range of this method provided a method validation study, as described in Guide E2857 be regarded as standard. No other units of measurement are included in this, is performed and the results of the study show the method extension meets laboratory data quality objectives. This method may also be extended to alloys other than titanium and zirconium provided a method validation study, as described in Guide E2857 standard., is performed.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazards, see Section 9.~~

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:<sup>2</sup>

- ~~E696~~ E29 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets
- Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf, Re.

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<sup>2</sup> 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.

[E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method](#)

[E2857 Guide for Validating Analytical Methods](#)

[E1914E2972 Practice for Use of Terms Relating to the Development and Evaluation of Methods for Chemical Analysis Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials \(Withdrawn 2016\)](#)

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Terminology [E135](#) and [E1914](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *drift correction, n*—a procedure for normalizing the instrument response to account for drift of sensitivity or blank, or both.

3.2.1.1 *Discussion*—

A drift correction procedure is used to adjust the response of an instrument to maintain the viability of an existing calibration. A full correction of drift encompasses both the blank and the sensitivity. A full drift correction requires measurements of two points to establish correction factors, one for blank and one for sensitivity. A single correction for sensitivity may provide enough adjustment in instrument response to restore statistical control. Drift correction assumes the linearity of the instrument response has not changed.

### 4. Summary of Test Method

4.1 The specimen, contained in specimen is added to a small, single-use graphite crucible, is crucible with tin or nickel flux, or both, and fused under a flowing carrier gas atmosphere. Hydrogen present in the sample specimen is released as molecular hydrogen into the flowing gas stream. The hydrogen is separated from other liberated gases such as carbon monoxide and finally measured in a thermal conductivity cell.

4.1.1 The detection of hydrogen is different based on the instrument manufacturer. Either hydrogen is isolated from nitrogen in a helium or an argon stream with a molecular sieve and measured by a thermal conductivity (TC) cell, or hydrogen is measured directly by a thermal conductivity cell using nitrogen as the carrier gas

4.1.2 For infrared detection, hydrogen is converted to water by passing the gas stream over heated copper oxide or other appropriate oxidizing reagent and subsequently measured in an infrared (IR) cell.

4.2 Alternatively, hydrogen is converted to water by passing the gas stream over heated copper oxide and subsequently measuring in an appropriate infrared (IR) cell.

4.2 This test method is written for use with commercial analyzers/instruments equipped to perform the above operations automatically and is calibrated using reference materials (RMs) of known hydrogen content.

### 5. Significance and Use

5.1 This test method is intended to test for for the routine analysis of reactive metals and reactive metal alloys to verify compliance with compositional specifications. It is assumed specifications such as those specified by Committees B09 and B10. It is expected that all who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory.

### 6. Interferences

6.1 The elements ordinarily present in titanium and its zirconium and their alloys do not interfere.

### 7. Apparatus

7.1 *Fusion and Measurement Apparatus*—Automatic hydrogen determinator, determination system, consisting of an electrode furnace or induction furnace; furnace, analytical gas stream impurity removal systems; systems, auxiliary purification systems, and either a thermal conductivity cell hydrogen measurement system or an infrared hydrogen measurement system (or infrared cell hydrogen measurement system. **Note 1**).

**Note 1**—The apparatus and analysis system have been previously described in the Apparatus and Apparatus and Equipment sections of Test Methods

~~C696. Several models of commercial analyzers are available and presently in use in industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's instructions for operational details.~~

~~7.1.1 Several models of commercial instrument are available and presently in use in industry. Each has unique design characteristics and operational requirements. Consult the manufacturer's instructions for operational details.~~

~~7.2 Graphite Crucibles—The crucibles are machined/manufactured from high-purity graphite. Use the size crucibles recommended by the manufacturer of the instrument/crucibles specified for the model of instrument in use.~~

~~7.3 Crucible Tongs—Capable/Tongs or forceps capable of handling recommended/specified crucibles.~~

~~7.4 Tweezers—Tweezer, Scoops, or Forceps—For contamination-free sample handling.~~

## **8. Reagents and Materials**

~~8.1 Acetone, low-residue reagent grade or higher purity equivalent. Equivalency is defined as the required purity documented by the laboratory to not bias test results.~~

~~8.2 Sodium Hydroxide on Clay Base, commonly known as Ascarite II.~~

~~8.3 High-Purity Carrier Gas (99.99%)—Gas—Argon, nitrogen, or helium (Carrier gases vary by instrument model and include high-purity argon, helium, and nitrogen. Use a gas that meets or exceeds the Note 2). instrument manufacturer's specifications.~~

~~Note 2—Carrier gases vary by instrument model and include high-purity argon, nitrogen, and helium. Consult instrument manufacturer's instructions for proper gas recommendation.~~

~~8.4 High-Purity Tin Metal (Low Hydrogen)—Flux (Low Hydrogen) - Tin or Nickel Metal—Use the purity specified by the instrument manufacturer/metal that meets or exceeds the instrument manufacturer's specifications. Flux may come in various forms, including chips, pellets, baskets, or capsules. Tin and nickel may be used individually or together.~~

~~8.5 Magnesium Perchlorate, Anhydrous—Drying Agent - Magnesium Perchlorate or Phosphorus Pentoxide.~~

~~8.6 Molecular Sieve—Characteristics specified by the instrument manufacturer. Use material that meets or exceeds the instrument manufacturer's specifications. Not required for all measurement apparatus types - consult the manufacturer's literature for operational detail.~~

~~8.7 Schutze Reagent—Iodine Pentoxide Over Silica Gel, Iodine pentoxide over silica gel, commonly known as Schutze Reagent.~~

~~8.8 Copper Oxide Wire—Oxide—To convert hydrogen to water in IR-detection instruments. Characteristics specified by the instrument manufacturer. Use material that meets or exceeds the instrument manufacturer's specification.~~

~~8.9 Copper—Use material that meets or exceeds the manufacturer's specification. Not required for all measurement apparatus types.~~

## **9. Hazards**

~~9.1 For hazards to be observed in the use of that may be encountered using this test method, refer to Practices E50., to the safety data sheets for reagents, and to the instrument manufacturer's literature.~~

~~9.2 Use care when handling hot crucibles and operating electrical equipment/instrument to avoid personal injury by either burn or electrical shock.~~

## **10. Preparation of Apparatus and Measurement Conditions**

~~10.1 Instrumentation shall be installed in a manner consistent with the manufacturer's recommendations.~~

10.2 ~~Assemble the apparatus as recommended by~~ Using the instrument software, create an analytical method with measurement parameters. Instrument manufacturers typically provide application notes with suggested measurement parameters. Refer to application notes as a starting point for method development. Measurement parameters that must be specified are detailed in [10.2.1](#) and [10.2.2](#) ~~the manufacturer~~. For implementation of this test method on an existing instrument that is currently producing analyses that meet laboratory data quality objectives, the performance of steps [10.3 – 10.6](#) may be unnecessary and is therefore optional.

### 10.2.1 Instrument Measurement Parameters

10.2.1.1 Gas flow.

10.2.1.2 Purge time.

10.2.1.3 Measurement times (integration time(s), delay time(s), ramp time(s)).

10.2.1.4 Furnace parameters.

10.2.1.5 Calibration Protocol—Only first order calibration models may be used with this test method. See Section [12](#) for calibration requirements. See Section [14](#) for further instructions on calibration line calculation.

(1) Single point calibrations employ one reference material, having a mass fraction greater than or approximately equal to the expected mass fractions of hydrogen in unknown samples. The line is constrained to pass through the origin. Some instrument manufacturers allow for the use of the blank in the calibration.

(2) Multi-point calibrations employ two or more reference materials with the highest mass fraction greater than or approximately equal to the expected highest sample mass fractions. Other reference materials will have mass fractions spanning the calibration range. The line may or may not be constrained to pass through the origin. Some instrument manufacturers allow for the use of the blank in the calibration.

10.2.1.6 Due to differences in instrument design, there may be additional measurement parameters that must be considered. Refer to manufacturer specific recommendations when entering these parameters.

### 10.2.2 Ancillary Parameters

10.2.2.1 Calibration material attributes (identification and analyte mass fraction information).

10.2.2.2 Associated reporting parameters such as replication, unit of measure, report destination, etc., if required.

10.2.2.3 Non-instrument analysis parameters that must be determined and documented are as follows.

(1) Specimen mass.

(2) Flux composition and mass. The flux mass to sample mass ratio is important. Laboratories should determine the minimum ratio required (Note 1).

NOTE 1—The limited ruggedness testing performed in the development of this test method showed a minimum ratio of flux mass to sample mass of 3.3 to be effective.

(3) Users of this method must consider the hydrogen content contained within the specimens and the reference materials when determining the requirements of unknown specimen mass and reference material mass. It is imperative that the milligram content of hydrogen contained within the unknown specimen does not exceed the milligram content of hydrogen contained within the reference material(s) used to develop the calibration.

(4) Maintenance intervals for changing reagents, filters, desiccants, electrodes, and cleaning intervals, if applicable.

10.3 Instrument Conditioning Requirements—The instrument manufacturer may recommend that conditioning analyses be performed prior to using the instrument. Examples of when these may be performed are after instrument start-up, prior to calibration, after changing reagents or carrier gas. Refer to manufacturers suggestions on performing conditioning analyses.

10.4 Establish a test calibration to assist method development using the parameters selected in [10.2](#) as a starting point for the study. Make test runs on materials to assess the precision and sensitivity of analyses made using the selected conditions. If the results of this study are deemed acceptable for meeting the laboratory's measurement quality objectives, further study is not necessary.

~~10.5 Test the furnace and analyzer to ensure the absence of gas leaks and make the required electrical power and water connections. Prepare the apparatus for operation in accordance with the manufacturer's instructions. Make a minimum of two determinations using a specimen as directed in 11.2. If the results of the preliminary study are not acceptable, continue to optimize the analysis parameters by adjusting them and making test runs on materials to assess the sensitivity and precision of analyses made using the selected conditions. It may be necessary to recalibrate the system or to determine the blank before attempting to calibrate the system or to determine the blank. be necessary to recalibrate the instrument after each parameter adjustment.~~

~~10.6 Once the optimal parameters have been established, the laboratory should perform some type of method validation study. Consult Guide E2857 for information.~~

~~10.7 It is not necessary to routinely perform method development or validation once the method is established.~~

## 11. ~~Sample~~Specimen Preparation

~~11.1 Use solid form specimens prepared as directed in 11.2. Weigh specimen with a mass not to exceed 0.3 g. Weigh to 0.001 g or better precision. Samples may be in the form of solids, chips, or powders. Specimens must be of an appropriate size to fit into the graphite crucible and should not exceed 0.30 g in weight. the instrument loading mechanism and graphite crucible. When a flux is used in the form of capsules, specimen size must fit the capsule. Follow the instrument manufacturer's guidance on use of capsules.~~

~~11.2 Cut the specimen to the approximate size of 0.15 g to 0.30 g (preferably by shearing). For specimens of unknown history or suspected surface contamination, abrade specimen surfaces with a clean file to remove contamination. Other methods, such as turning down on a lathe, may be employed for reducing sample size and removing the surface of the sample (Solid specimens should be cut to the appropriate mass, preferably by shearing, as specified by the laboratory while also adhering to Note 3). Rinse the sample in acetone, and air dry. Weigh to  $\pm 0.001$  g. Samples shall be handled only with tweezers or forceps after cleaning and weighing to prevent contamination.~~

~~NOTE 3—Regardless of the method used, the sample must not be allowed to overheat, as this will adversely affect the results of the analysis. Indications that the sample has overheated while being worked may include discoloration of the metal or the sample becoming too hot to handle without tools.~~

~~11.2.1 For solid specimens of unknown history or suspected surface contamination, abrade specimen surfaces with a clean file to create a fresh, clean surface. Other methods, such as turning on a lathe or use of a wet abrasive may be employed for reducing sample size and removing the surface of the sample.~~

~~11.2.2 Regardless of the method used, the sample should not be allowed to overheat. If overheating occurs, this will adversely affect the results of the analysis. Indications that the sample has overheated while being worked may include discoloration of the metal or the sample becoming too hot to handle without tools.~~

~~11.2.3 Rinse the specimen in acetone and air dry. Specimen shall be handled only with tweezers, scoops, or forceps after cleaning to prevent contamination.~~

~~11.3 Chip specimens should be rinsed in acetone and allowed to air dry.~~

~~11.4 Powder specimens typically do not require preparation or acetone rinse due to the nature of the production process.~~

~~11.5 For a reference material, consult the producer's documentation on instructions for storage, handling, and use, which may include recommended minimum mass per sample and preparation instructions.~~

## 12. Calibration

~~12.1 It is not necessary to perform the calibration procedure each time the analysis procedure (Section 13) is performed. However, the laboratory must use a calibration control strategy such as described in 12.9.~~

~~12.2 The user must document the frequency of calibration, calibration confirmation, and linearity confirmation (12.8). The user shall document the conditions under which a new calibration or linearity confirmation, or both, beyond this frequency is required.~~

12.3 Perform calibration after initial method development.

12.4 Modern instruments permit a single or a multiple point calibration.

12.4.1 Single point calibrations employ one reference material, having a mass fraction greater than or approximately equal to the expected mass fractions of hydrogen in unknown samples. The line is constrained to pass through the origin. Some instrument manufacturers allow for the use of the blank in the calibration.

12.4.2 Multi-point calibrations employ two or more reference materials with the highest mass fraction greater than or approximately equal to the expected highest sample mass fractions. Other reference materials will have mass fractions spanning the calibration range. The line may or may not be constrained to pass through the origin. Some instrument manufacturers allow for the use of the blank in the calibration.

12.4.2.1 The reference material specimens may be two or more reference materials measured at the same sample mass, or they may be two or more reference materials measured at multiple sample masses.

12.5 Condition the instrument by performing a minimum of two determinations using a specimen as directed in 13.1 – 13.4.

~~12.6 Calibration Reference Materials—Determination of System Blank (Prior to Calibration): Select only titanium or titanium alloy reference materials (Note 4).~~

12.6.1 The system blank (reagent blank or blank) is an analysis of the entire measurement process less the sample. Prepare the instrument for analysis. Use a new crucible each time with the amount of flux required. Make at least three blank determinations for use as either a system blank or as a calibration point (Note 2).

NOTE 2—In some operating systems, all measured responses of calibration materials and specimens are corrected by subtracting the blank response. The process is called “blank calibration” and may require entry of the mean blank value into the software blank compensation function. In other operating systems, the blank can be included as a calibration point.

NOTE 4—Gas dosing: it is satisfactory to calibrate the unit by dosing known volume(s) of hydrogen gas into the detection system. If the instrument has this feature, refer to the manufacturer’s recommended procedure. In this case instrument response must always be verified by analyzing titanium or titanium alloy reference materials.

12.6.2 Perform a blank calibration or determine the average blank value and enter the value into the blank compensation function as required by the instrument. Include this blank value as part of the initial calibration as directed by manufacturer’s requirements (Note 2).

12.7 Determination of ~~Crucible/Fin~~Crucible/Flux Blank Reading:

12.7.1 If the instrument utilizes a system blank as determined in 12.6.1, the blank should be verified or recalculated, or both, on a routine basis beyond that of calibration, as defined by the laboratory. If the instrument is equipped with an electronic blank compensator, adjust to zero, and proceed with the determination of the blank value.

12.7.2 ~~Make at least~~Analyze a minimum of three blank determinations as directed in ~~13.2~~13.1 – 13.4 using the ~~weight~~mass of tin-flux as recommended by ~~determined in 10.2.2.3~~the instrument manufacturer ~~(2)~~. (Note 5). Use a fresh crucible each time.

NOTE 5—Flux weight is dependent upon the model of the instrument and the manufacturer’s instruction. Refer to the manufacturer’s instructions and recommendations.

12.7.3 If the average blank value exceeds 0.0000 % ± 0.0001 %, or a standard deviation for the three consecutive values exceeds ± 0.0001 %, then Laboratories must document acceptable blank levels or precision, or both, based on laboratory quality objectives. If excessive blank values or poor precision are observed, determine the cause, make necessary corrections, and repeat ~~12.2.1 and 12.2.2~~12.7.1 (and ~~Note 6~~ 12.7.2). Refer to the instrument instructions concerning troubleshooting and correction of issues relating to blank determinations.

~~NOTE 6—Refer to the instrument manufacturer’s instructions concerning the troubleshooting and correction of blank determinations not meeting the above criterion.~~

~~12.7.4 Enter the average blank value in the appropriate mechanism of the analyzer operating system instrument (NOTE 7) according). Refer to the 12.9.3 manufacturer’s instruction. This mechanism will electronically compensate for the blank value for guidance on establishing blank control protocols.~~

~~NOTE 7—If the unit does not have this function, the average blank must be subtracted from the total result.~~

~~12.8 Calibration Procedure—Reference Material Measurement:~~

~~12.8.1 Determine the type of calibration to be performed: single or multiple point.~~

~~12.8.2 Obtain specimens of each reference material to be used in the calibration.~~

~~12.8.3 Weigh specimens, with mass not to exceed 0.3 g, of each reference material being used in the calibration. Refer to 10.2.2.3(2) for information pertaining to the proper minimum flux mass to specimen mass ratio.~~

~~12.8.4 Prepare at least four 0.15 g to 0.30 g specimens (at least one specimen if calibrating by gas dosing) of a titanium hydrogen reference material as directed in 11.2. For single point calibration, this reference material must have a hydrogen content greater than or approximately equal to the unknown samples within the scope of this test method (0.0006 % to 0.0260 %).~~

~~12.8.5 For multiple-point calibrations select a number of reference materials that will encompass the range of hydrogen content expected in the unknown samples. The highest calibration point should be near to or above the greatest unknown hydrogen content.~~

~~12.8.6 Measure a minimum of two specimens of each calibration reference material. Follow the calibration procedure protocol recommended by the manufacturer. Analyze at least three reference material specimens to determine the calibration slope (NOTE 8). Treat each specimen as directed in 13.2 before proceeding to the next one (NOTE 9).~~

~~NOTE 8—For calibration by gas dosing, perform at least three gas dose analyses to determine the calibration slope. Refer to instrument manufacturer’s instructions.~~

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~~12.8.6.1 For multiple point calibrations, the quality of the calibration must be verified. Instrument software may calculate a correlation coefficient for the calibration. It is acceptable to rely upon the correlation coefficient as a demonstration of calibration fit. The method for calibration acceptance must be documented.~~

~~NOTE 9—Some instruments have expanded computer capabilities that allow multi-point calibration which may improve the accuracy and precision of the calibration over the single-point calibration methodology as tested in the current interlaboratory study (ILS).~~

~~12.3.3 Confirm the calibration by analyzing a specimen of titanium hydrogen reference material (NOTE 10). The ILS used an acceptance criterion where the value fell within the allowable limits of the certified value. An alternate procedure can be implemented where this value should agree with the certified value within the limits of a prediction interval calculated using Eq 1. The prediction interval is defined as the range of values bounded by the analysis value  $-p$  and the analysis value  $+p$ . If the prediction interval does not encompass the certified value, determine and correct the cause, and repeat 12.3.1 and 12.3.2 (NOTE 11). Either acceptance limit criterion is acceptable for routine operation.~~

~~NOTE 10—Confirmation of the calibration does not ensure accuracy. The accuracy of this test method is largely dependent upon the absence of bias in the hydrogen values assigned to the reference materials and upon the homogeneity of these materials.~~

~~NOTE 11—See the instrument manufacturer’s instructions concerning the troubleshooting and correcting of errant calibration.~~

$$p = t \cdot \left( 1 + \frac{1}{\sqrt{n}} \right) \cdot s \quad (1)$$

where: