



Designation: E1447 – 22

Standard Test Method for Determination of Hydrogen in Reactive Metals and Reactive Metal Alloys by Inert Gas Fusion with Detection by Thermal Conductivity or Infrared Spectrometry¹

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 (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 reactive metals and reactive metal alloys, particularly titanium and zirconium, with mass fractions from 9 mg/kg to 320 mg/kg.

1.2 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. It may be possible to extend the quantitative range of this method provided a method validation study, as described in Guide E2857, 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, 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:²

¹ 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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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.

- [E29 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](#)
- [E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method](#)
- [E2857 Guide for Validating Analytical Methods](#)
- [E2972 Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials](#)

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Terminology E135.

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 is added to a small, single-use graphite crucible with tin or nickel flux, or both, and fused under a flowing carrier gas atmosphere. Hydrogen present in the specimen is released as molecular hydrogen into the flowing gas stream.

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

5. Significance and Use

5.1 This test method is intended for the routine analysis of reactive metals and reactive metal alloys to verify compliance with compositional 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 zirconium and their alloys do not interfere.

7. Apparatus

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

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 manufactured from high-purity graphite. Use crucibles specified for the model of instrument in use.

7.3 *Crucible Tongs*—Tongs or forceps capable of handling specified crucibles.

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

8. Reagents and Materials

8.1 *Acetone*, reagent grade or 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*—Carrier gases vary by instrument model and include high-purity argon, helium, and nitrogen. Use a gas that meets or exceeds the instrument manufacturer's specifications.

8.4 *Flux (Low Hydrogen) - Tin or Nickel Metal*—Use 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 *Drying Agent - Magnesium Perchlorate or Phosphorus Pentoxide*.

8.6 *Molecular Sieve*—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 *Iodine Pentoxide Over Silica Gel*, commonly known as Schutze Reagent.

8.8 *Copper Oxide*—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 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 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 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. 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 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 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. Specimen Preparation

11.1 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 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 Solid specimens should be cut to the appropriate mass, preferably by shearing, as specified by the laboratory while also adhering to the parameters developed in 10.2.2.

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 *Determination of System Blank (Prior to Calibration):*

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.

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/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 Analyze a minimum of three blank determinations as directed in 13.1 – 13.4 using the mass of flux as determined in 10.2.2.3(2). Use a fresh crucible each time.

12.7.3 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 12.7.1 and 12.7.2. Refer to the instrument instructions concerning troubleshooting and correction of issues relating to blank determinations.

12.7.4 Enter the average blank value in the operating system instrument (Note 2). Refer to 12.9.3 for guidance on establishing blank control protocols.

12.8 *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 For single point calibration, this reference material must have a hydrogen content greater than or approximately equal to the unknown samples.

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 protocol recommended by the manufacturer to determine the calibration slope.

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.

12.8.7 Confirm the calibration (single or multiple point) by analyzing one or more specimens of the reference materials. It is the responsibility of the laboratory to determine the allowable limits for the results of the confirming reference materials. Use one of the methods described in 12.8.7.2 – 12.8.7.4 to do this.

12.8.7.1 For single point calibrations, confirm calibration linearity by analyzing a mid-range reference material. It is the responsibility of the laboratory to determine the allowable limits for the results of the reference materials.

(1) Reference materials are not always available at the mass fraction required to have a true mid-point check. The mid-range material must have a hydrogen mass fraction that is greater than this method’s lower scope value but less than that of the highest calibration point, preferably as close to the mid-point of the calibration line as possible.

12.8.7.2 *Confirmation Method #1*—The laboratory may compare the result(s) of a run or runs of the confirming reference material(s) to the mean and uncertainty of the reference material.

(1) Analyze at least one run of the confirming reference material or reference materials.

(2) If multiple runs are made to the confirming reference material(s), determine the mean of the results. If a single run is made of the confirming reference material, use the result obtained.

(3) Compare the confirming reference material’s mean or single result to the interval of the stated uncertainty for reference material’s reference value. If the result is within this interval, the calibration is considered adequately confirmed.