Designation: E2792 − 13

Standard Test Method for Determination of Hydrogen in Aluminum and Aluminum Alloys by Inert Gas Fusion[1]

This standard is issued under the fixed designation E2792; 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 aluminum and aluminum alloys in concentrations from 0.05 mg/kg to 1 mg/kg.

1.2 *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:*[2]

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
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1914 Practice for Use of Terms Relating to the Development and Evaluation of Methods for Chemical Analysis

3. Terminology

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

4. Summary of Test Method

4.1 The specimen, contained in a high-purity graphite crucible, is heated to just below the melting point to drive off the surface hydrogen. The sample is then heated to just beyond the melting point under a flowing carrier gas atmosphere. Hydrogen present in the sample is released as molecular hydrogen into the flowing gas stream. The released hydrogen is separated from other liberated gases such as carbon monoxide and subsequently measured in a thermal conductivity cell.

4.2 Calibration is made using gas dosing with either helium or hydrogen or reference materials of known hydrogen content.

4.3 This test method is written for use with commercial analyzers equipped to carry out the above operations automatically.

5. Significance and Use

5.1 This test method is intended for the routine testing of aluminum and aluminum alloys to qualitatively determine the concentration of hydrogen in aluminum and aluminum alloys. It is not intended to verify compliance with compositional specifications because of the lack of certified reference materials. It is assumed 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 aluminum and aluminum alloys do not interfere.

7. Apparatus

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

7.2 *Graphite Crucibles,* machined from high-purity graphite. Use the crucible design(s) recommended by the manufacturer of the instrument.

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[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 E01.04 on Aluminum and Magnesium.

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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.

7.3 *Quartz Crucibles,* for analysis of steel reference materials on some instrument types. Use the crucible design(s) recommended by the manufacturer of the instrument.

7.4 *Crucible Tongs,* capable of handling recommended crucibles.

8. Reagents and Materials

8.1 *Acetone*—Reagent Grade or ACS certified grade or higher purity.

8.2 *Ethyl Alcohol*—Reagent Grade or ACS certified grade or higher purity.

8.3 *Isopropyl Alcohol*—Reagent Grade or ACS certified grade or higher purity.

8.4 *Sodium Hydroxide on Clay* (Commonly known as Ascarite II).

8.5 *High-Purity Gas (99.99 %)*—Argon, nitrogen, and helium or hydrogen (Note 1).

NOTE 1—Carrier and dosing gases vary by instrument model and include high-purity argon, nitrogen, helium or hydrogen. Gas purity requirements shall be specified by the instrument manufacturer.

8.6 *Magnesium Perchlorate* (commonly known as Anhydrone).

8.7 *Molecular Sieve,* as specified by the instrument manufacturer.

8.8 *Schutze Reagent*—Iodine pentoxide on granular silica, purity as specified by the instrument manufacturer.

8.9 *Copper Wire,* to convert CO to CO_2 in thermal conductivity cell instruments. Characteristics should be specified by the instrument manufacturer.

8.10 *Glass wool,* used to pack reagents.

8.11 *OMI™ Purifier Tube*—Organolithium polymer used by some instruments to remove O_2, water vapor, CO, CO_2, most sulfur compounds, most halogen compounds, alcohols, and phenols to less than 10 ppb from the carrier gas.

9. Hazards

9.1 Refer to Practices E50 for potential hazards present when using this test method.

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

10. Preparation of Apparatus

10.1 Assemble the apparatus as recommended by the manufacturer.

10.2 Provide the manufacturer's recommended electrical power and gas requirements. Prepare the apparatus for operation in accordance with the instrument manufacturer's recommendations.

10.3 Set the instrument to the operational mode in accordance with the instrument manufacturer's recommendations.

10.4 Test the furnace and analyzer to ensure that the gas stream meets manufacturer's requirements for acceptable leak rate.

10.5 Optimize the crucible pretreatment power settings (commonly called outgas), the surface and analysis power settings, crucible pretreatment time and analysis integration time for aluminum alloys.

10.5.1 Most manufacturers offer application guidance on appropriate settings to achieve optimum performance for aluminum alloys. Refer to this application guidance literature for assistance in determining optimum settings.

10.5.2 If the instrument is capable; optimize the crucible pretreatment time and power settings to achieve a stable blank (see 12.2.2).

10.5.3 If the instrument is capable; optimize the analysis time and power settings to obtain the optimum signal to noise ratio for the analysis of aluminum alloys.

10.5.4 It will not be necessary to optimize the analysis set-up routinely. Store the settings into the instrument hardware or software for routine use.

11. Sampling and Sample Preparation

11.1 Samples can be taken either from molten aluminum during casting or from the appropriate areas of finished product.

11.1.1 Samples from molten aluminum should be taken using the procedure described by Ransley and Talbot.[3] Briefly, a ladle is used to pour molten metal into a copper sampler that is designed to minimize porosity, cracks, voids, pits, and other defects that may lead to erroneously high hydrogen results.

11.1.2 *Samples from Cast or Finished Product*—Samples from cast or finished product should be taken from an area that represents the nominal concentration of hydrogen in the piece being sampled. Hydrogen may segregate in product and may also accumulate around defects sometimes making it difficult to obtain a representative sample. It is incumbent on the user to insure that the area selected for sampling is satisfactory. A cubical piece should be cut from the product using a saw with a clean blade. Carbide tipped blades are recommended. The size of the cube needed depends on the final sample size required for the instrument.

11.2 Samples must be of an appropriate size to fit into the graphite crucible. In general, the sample should be as close to the maximum size for the crucible as possible. A sample size of at least 4 grams is recommended. Smaller samples may be analyzed, however, the amount of hydrogen generated will be smaller and the detection limit will be higher. Smaller samples also have a higher surface to bulk hydrogen ratio and the method parameters may not be ideal for separating the surface hydrogen from the bulk hydrogen.

11.3 The sample should be machined using a lathe or milling machine to the manufacturers recommended specifications. A fine surface is important for obtaining accurate results. Rough surfaces may lead to excessively high surface readings and may, in extreme cases, cause high bulk results. Diamond tipped tool bits and use of ethyl alcohol or isopropyl alcohol lubricant during machining may be used to improve the surface

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[3] C.E. Ransley and D.E.J. Talbot, "The Routine Determination of the Hydrogen Content of Aluminum and Aluminum Alloys by the Hot-Extraction Method". Journal of the Institute of Metals, Vol. 84, 1955-1956, 445.

finish. The average surface roughness for samples machined using a diamond tipped tool bit and alcohol lubricant is typically 40 micro inches to 50 micro inches. Surface area of the sample will increase as the surface roughness increases. Increased surface area will result in higher surface hydrogen readings and in extreme cases may affect the bulk hydrogen analysis.

11.4 Specimens must be handled with crucible tongs or in a manner that prevents surface contamination. Samples may be rinsed in acetone, ethyl alcohol, or isopropyl alcohol if surface contamination is suspected.

12. Calibration

12.1 Calibration can be done by two different methods; gas dosing or by the use of certified reference materials. Most instruments used for the analysis of hydrogen in aluminum alloys are calibrated by gas dosing due to the lack of certified reference materials for hydrogen in aluminum.

12.2 *Blank Determination Procedure:*

12.2.1 Both gas dose and reference material calibration require an accurate blank determination. The blank value may be included in the calibration curve or subtracted from all subsequent determinations.

12.2.2 Make at least three blank determinations using an empty graphite crucible following the manufacturer's guidelines.

12.2.3 If the average blank value exceeds 0.000 mg/kg ± 0.005 mg/kg then determine the cause, make necessary corrections, and repeat 12.2.2. Refer to the instrument manufacturer's instructions concerning the troubleshooting and correction of blank determinations not meeting the above criterion.

12.2.4 Enter the average blank value in into the instrument software following the manufacturers recommended practice. The software will automatically compensate for the blank value in subsequent calibration and sample analysis.

12.3 *Calibration by Gas Dosing*—Prepare at least four gas dose determinations as directed by the instrument manufacturer. Gas doses should have a mass fraction of hydrogen greater than or approximately equal to the unknown samples within the scope of this test method (0.05 mg/kg to 1.0 mg/kg).

12.3.1 Follow the gas dose calibration procedure recommended by the manufacturer. Some instruments have software capabilities that allow multi-point gas dose calibration which may improve the accuracy and precision of the calibration over the single-point calibration methodology. The gas dose procedure should be repeated before analysis of each group of samples or if the instrument has not been in use for four hours and/or the carrier gas has been changed.

12.4 *Calibration Using Reference Material*—Since there are no known reference materials for hydrogen in aluminum alloys the instrument may be calibrated with appropriate steel, nickel, titanium or other metal reference materials. Refer to the manufacturer's application specifications for the power and time settings for each base metal. It is not necessary to perform the reference material calibration procedure each time that the analysis procedure is performed. However, the calibration must be verified when a different lot of crucibles is used or the system has not been in use for 4 hours, and/or the carrier gas supply has been changed. Verification should consist of analyzing at least one aluminum control material or at least one steel, nickel, titanium or other reference material (12.5) and at least one linearity check reference material (12.6).

12.4.1 Prepare at least four approximately 1 g specimens of a steel, nickel, titanium or other metal reference materials for each concentration level to be included in the calibration. The specimens must be of an appropriate size to fit into the quartz or graphite crucible. The steel, nickel, titanium or other metal reference materials should have mass fraction of hydrogen greater than or approximately equal to the unknown samples within the scope of this test method (0.05 mg/kg to 1.0 mg/kg).

12.4.2 Follow the calibration procedure recommended by the manufacturer. If the instrument is capable of this functionality enter the mass fraction of the hydrogen content of the reference material into the instrument/software. Analyze at least three of the reference material specimens prepared in 12.4.1.

12.4.3 Use the average instrument response obtained for the reference materials to set the calibration slope in accordance with the manufacturer's recommendations.

12.4.4 Confirm the stability of the instrument/calibration by analyzing the fourth specimen of the hydrogen reference material (Note 2).

NOTE 2—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.

12.5 Confirm the calibration by analyzing a specimen of aluminum control material or with steel, nickel, titanium or other metal reference materials. If using aluminum control material, the results should fall within control limits based on the final product requirements. If using steel, nickel, titanium or other metal reference materials the results should fall within the uncertainty provided on the certification documentation. 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 or 12.4.1 and 12.4.2. See the instrument manufacturer's instructions concerning the troubleshooting and correcting of an errant calibration.

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

where:

p = one-half the prediction interval,
n = number of replicates used in 12.4.2,
t = student's t chosen for the 95 % confidence level for n replicate measurements (for example: $n = 3$ (degrees of freedom = 2) $t = 4.303$; $n = 4$ (degrees of freedom = 3) $t = 3.182$; $n = 5$ (degrees of freedom = 4) $t = 2.776$), and
s = standard deviation of n replicates in 12.4.2 (Note 3).

NOTE 3—s should be comparable to S_r, the repeatability standard deviation, given in Table 1. If $s \gg S_r$, there is evidence that the repeatability of the particular instrument is not acceptable for use with this test method. The user should determine and correct the cause, and repeat 12.4.1-12.4.3.

12.6 Confirm calibration linearity by analyzing at least three specimens of a mid-range aluminum control material or steel, nickel, titanium or other metal reference materials. Calculate the average and standard deviation(s) of these results. In the absence of bias among the reference materials, the average result for this reference material should agree with the certified value within a prediction interval defined by the repeatability of the measurement system at the mid-range of the calibration (Note 4). This prediction interval may be calculated using Eq 1 and the s and n values for the mid-range reference material. If the prediction interval does not encompass the certified value, determine and correct the cause and repeat 12.3.1 or 12.4.1 and 12.4.2 (Note 4).

NOTE 4—Typically, repeatability standard deviation is a function of the concentration of the analyte. Compare the values labeled *ILS Average* in Table 1 with the values for Repeatability Standard Deviation (s_r) to see a typical trend for laboratories using this test method. If your results are not comparable, investigate and correct the cause.

NOTE 5—The presence of bias between the gas doses used in 12.3.1 and the reference material used in 12.4.1 and 12.4.2 may cause the calibration to appear to be nonlinear. This cannot be corrected by making adjustments to the instrument.

13. Procedure

13.1 Prepare an approximate 4 g to 7 g specimen as directed in 11.3.

13.1.1 Place the specimen in the instrument loading device. Refer to the manufacturer's recommended procedure regarding sample introduction into the instrument.

13.1.2 Enter the sample weight into the instrument software to the nearest 0.001g following the manufacturer's recommended practice.

13.1.3 Place a crucible on the furnace electrode/pedestal assembly and close the furnace.

13.1.4 Place a crucible on the furnace electrode/pedestal assembly and close the furnace.

13.1.5 Start the analysis cycle, referring to the manufacturer's recommended procedure.

14. Calculation

14.1 Calibration can be based on a two or more point plot using a blank value and the response of the gas dose measurement(s) or the calibration reference material(s). The calibration function of the equipment will yield a linear plot described by Eq 2.

$$Y = mX \tag{2}$$

where:

Y = measurement response,
m = slope,
X = concentration.

14.2 Most modern commercially available instruments calculate mass fraction concentrations directly, including corrections for blank and sample mass.

15. Precision and Bias

15.1 *Precision*—The precision of this test method is based on an interlaboratory study conducted in 2010. Six laboratories tested two different aluminum alloys for hydrogen content. Every test result represents an individual determination. All laboratories were asked to submit ten replicate test results for each material tested. Practice E691 was followed for the overall design and analysis of the data. The details are given in RR:E01-1116.[4]

15.1.1 *Repeatability Limit, r*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the r value for that material; r is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

15.1.1.1 Repeatability limits are listed in Table 1.

15.1.2 *Reproducibility Limit, R*—Two test results shall be judged not equivalent if they differ by more than the R value for that material; R is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

15.1.2.1 Reproducibility limits are listed in Table 1.

15.1.3 The above terms (*repeatability limit* and *reproducibility limit*are used as specified in Practice E177.

15.1.4 Any judgment made in accordance with 15.1.1 and 15.1.2would have an approximate 95% probability of being correct.

15.2 The precision statement was determined through statistical examination of 118 test results, from six laboratories, on two aluminum alloys. These two materials were identified as the following:

Sample A	7075 alloy extruded rod
Sample B	5154 alloy continuous cast rod

To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

TABLE 1 Hydrogen Concentration (mg/kg)

Material	Average[A] , $\bar{x}$	Repeatability Standard Deviation, s_r	Reproducibility Standard Deviation, s_R	Repeatability Limit, r	Reproducibility Limit, R
Sample A	0.046	0.010	0.019	0.029	0.054
Sample B	0.105	0.015	0.030	0.043	0.084

[A] The average of the laboratories' calculated averages, which have been rounded to the nearest 0.5 rating.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1116.

15.3 *Bias*—No information on the accuracy is available for this method because there are no certified reference materials for hydrogen in aluminum and aluminum alloys.

16. Keywords

16.1 aluminum; aluminum alloys; hydrogen; inert gas fusion

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