



Designation: E1409 – 13

# Standard Test Method for Determination of Oxygen and Nitrogen in Titanium and Titanium Alloys by Inert Gas Fusion<sup>1</sup>

This standard is issued under the fixed designation E1409; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method covers the determination of oxygen in titanium and titanium alloys in mass fractions from 0.01 % to 0.5 % and the determination of nitrogen in titanium and titanium alloys in mass fractions from 0.003 % to 0.11 %.

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.* Specific warning statements are given in 8.8.

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

**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

**E173** Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)<sup>3</sup>

**E1601** Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

## 3. Terminology

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

## 4. Summary of Test Method

4.1 This test method is intended for use with automated, commercially available, inert gas fusion analyzers. These

<sup>1</sup> 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.

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

analyzers typically measure both oxygen and nitrogen simultaneously or sequentially utilizing parallel measurement systems.

4.2 The test sample, plus flux, is fused in a graphite crucible under a flowing inert gas stream at a temperature sufficient to release oxygen and nitrogen. Oxygen combines with carbon to form carbon monoxide (CO) and nitrogen is released as N<sub>2</sub>. Depending on instrument design, the CO may be oxidized to carbon dioxide (CO<sub>2</sub>). The CO or CO<sub>2</sub>, or both, are swept by the inert gas stream into either an infrared or thermal conductivity detector. The detector response generated by analysis of the test sample is compared to the response generated by analysis of reference materials and the result is displayed as percent oxygen. The nitrogen is swept by the inert gas stream into a thermal conductivity detector. The detector response generated by analysis of the test sample is compared to the response generated by analysis of reference materials and the result is displayed as percent nitrogen.

4.3 In a typical instrument for the determination of nitrogen, the sample gases are swept with inert gas through heated rare earth/copper oxide that converts CO to CO<sub>2</sub> and hydrogen (H<sub>2</sub>) to water (H<sub>2</sub>O). The CO<sub>2</sub> is absorbed on sodium hydroxide impregnated on clay, and the H<sub>2</sub>O is removed with magnesium perchlorate. The nitrogen, as N<sub>2</sub>, enters the measuring cell and the thermistor bridge output is integrated and processed to display percent nitrogen.

## 5. Significance and Use

5.1 This test method is primarily intended as a test for compliance with compositional specifications. 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 usually present in titanium and its alloys do not interfere but there is some evidence to suggest that low purity flux can cause some adsorption of the released oxygen.

## 7. Apparatus

7.1 *Instrument*—Fusion and measurement apparatus, automatic oxygen and nitrogen determinator consisting of an

electrode furnace, provision for scrubbing impurities from analytical gas stream; infrared or thermal conductivity measurement system(s), or both, and auxiliary gas purification systems (**Note 1**).

**NOTE 1**—Several models of commercial oxygen and nitrogen determinators are available and presently in use by industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's instruction manual for operational details.

**7.2 Graphite Crucibles**—The crucibles must be made of high-purity graphite and be of the dimensions recommended by the instrument manufacturer.

**7.3 Flux**—Flux must be made of high-purity nickel. If nickel baskets are used, the dimensions must meet the requirements of the automatic sample drop, if present, on the instrument. (See **Note 2**.) Ultra high-purity nickel flux is commercially available and may eliminate the need to clean the flux before using it.

**NOTE 2**—In some instruments, nitrogen and oxygen are run sequentially and platinum is the required flux for nitrogen. High-purity platinum can be substituted for nickel in the same ratio of flux to sample.

**7.4 Tweezers or Crucible Tongs**, made of solvent and acid resistant material.

## 8. Reagents

**8.1 Acetone**—Low residue reagent grade or higher purity.

**8.2 Graphite Powder (optional)**—High-purity as specified by the instrument manufacturer.

**8.3 Inert Gas**—Use the purity and type specified by the instrument manufacturer.

**8.4 Magnesium Perchlorate, Anhydrous<sup>4</sup>**—Used in the instrument to absorb water. Use the purity specified by the instrument manufacturer.

**8.5 Nickel Flux Cleaning Solution**—An acid solution capable of removing surface contamination from the nickel flux. A solution made by combining 75 mL of acetic acid, 25 mL of HNO<sub>3</sub>, and 2 mL of HCl has been found suitable for this purpose.

**8.6 Copper Oxide or Rare Earth/Copper Oxide**—Reagent used in some instruments to oxidize CO to CO<sub>2</sub> for detection. Use the purity specified by the instrument manufacturer.

**8.7 Sodium Hydroxide on Clay<sup>5</sup>**—Reagent used in some instruments to absorb CO<sub>2</sub>. Use a purity specified by the instrument manufacturer.

**8.8 Titanium Sample Pickle Solution**—Three parts 30 % hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and 1 part 48 % HF. Other pickle solutions may be substituted if there are data supporting the effectiveness of the solution on removing contaminants. For example, substituting concentrated HNO<sub>3</sub> for 30 % H<sub>2</sub>O<sub>2</sub> has been found effective (see **Note 3**). (**Warning**—HF causes serious burns that may not be immediately painful; refer to the paragraph about HF in the Hazards Section of Practices **E50**.)

**NOTE 3**—In 2004, alternative sample preparation procedures (Section **12**) were tested by seven laboratories. Three laboratories processed the sample materials by pickling their samples in HF-H<sub>2</sub>O<sub>2</sub> (**8.8**). Two laboratories utilized the HF-HNO<sub>3</sub> alternative pickle solution (**8.8**). Two laboratories utilized abrasion (in this case diamond saw and shear) in accordance with **12.2**. The prepared samples were distributed among the laboratories for analysis. Six laboratories analyzed these samples in random order under a single operator, single-day, single calibration sample run. The results of this testing are given in **Tables X1.1 and X2.1** for oxygen and nitrogen, respectively. In both cases, the analysis of variance (ANOVA) indicates that there is no significant difference at the 95 % level of confidence for either oxygen or nitrogen due to the preparation technique.

## 9. Hazards

**9.1** Use care when handling hot crucibles and operating furnaces to avoid personal injury by either burn or electrical shock.

**9.2** For precautions to be observed in the use of HF and other reagents in this test method, refer to Practices **E50**.

## 10. Preparation of Apparatus

**10.1** Assemble the apparatus as recommended by the manufacturer. Make the required power, gas, and water connections. Turn on the instrument and allow sufficient time to stabilize the equipment.

**10.2** Change the chemical reagents and filters as required. Test the furnace and analyzer to ensure the absence of leaks (**Note 4**). A minimum of two test runs using a sample as directed in **14.3** and **14.4** is recommended to condition the newly changed filters. This should be done before attempting to calibrate the system or to determine the value of the blank.

**NOTE 4**—Typical leak checks should be 0.0 mm Hg to 1.5 mm Hg. The maximum allowable leak check should follow the manufacturer's recommendation.

## 11. Nickel Flux Preparation

**11.1** Ultra high-purity nickel is commercially available that does not require the nickel cleaning procedure below. Its sufficiency must be verified by satisfactory blank determinations. If ultra high-purity nickel is not used, the nickel must be cleaned to remove contamination (**11.2**).

**11.2** Immerse the flux in freshly prepared nickel flux cleaning solution for 50 s to 60 s, then rinse in running water for 2 min to 3 min. Pour flux onto paper towels to remove excess water. Place flux in sealable glass container, rinse with acetone and decant. To prevent new oxidation from forming, the flux may be stored under fresh acetone until used. (See **Note 5**.)

**NOTE 5**—The fluxing agent must be of proper size to be introduced through the sample drop mechanism and into the graphite crucible.

## 12. Sample Preparation

**12.1** Remove the surface of the sample either mechanically (**12.2**) or chemically (**12.3**). Start with a sample of sufficient size that the final sample after surface removal will be between 0.100 g and 0.150 g.

**12.2** To mechanically remove the sample surface, abrade with a clean file or similar abrasive device to remove contamination. Other methods, such as shearing, saw cutting, or

<sup>4</sup> Known commercially as Anhydron.

<sup>5</sup> Known commercially as Ascarite II.

turning down on a lathe, may be employed for reducing sample size and removing the surface of the sample. 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. Rinse the sample in acetone and air dry. Weigh to  $\pm 0.001$  g. Proceed to 12.4.

12.3 To chemically remove surface contamination, follow 12.3.1 and 12.3.2.

12.3.1 Leach the test sample in the titanium sample pickle solution. (**Warning**—See 8.8.) (see Note 3) until the surface is clean. This will normally require approximately 5 s from the time of the initial vigorous reaction between the sample and the solution.

12.3.2 Immediately remove the reacting test sample and rinse it twice with water and once with acetone and allow to air dry. Weigh to  $\pm 0.001$  g.

12.4 All subsequent operations on the test sample and flux must be done without introducing contamination to either. Use only clean tweezers or crucible tongs and never let the test sample or flux contact the analyst's skin. In the event this does happen, rinse the sample and nickel with acetone and air dry before analysis.

### 13. Calibration

13.1 *Reference Materials*—Select only titanium or titanium alloy reference materials such that the high point on the calibration curves will represent an amount of oxygen and nitrogen that is approximately equal to or greater than the amount expected in the samples. The accuracy of the test method is dependent upon the accuracy of the methods used to certify the oxygen and nitrogen values of the reference materials, as well as upon their homogeneity. Thus, wherever possible, reference materials used to confirm instrument calibration should be traceable to certified reference materials from a national or international metrological institute.

13.2 *Gas Dosing*—Automatic and manual gas dosing, recommended by some manufacturers, can be used to calibrate the instrument, but instrument response must be verified by calibration with titanium reference materials because of the fusion characteristics of the furnace/sample combination.

13.3 *Initial Adjustment of Measurement System (that is, "warm-up")*—Place a titanium material (not necessarily a titanium reference material) with nickel flux into an outgassed graphite crucible containing graphite powder (optional, see Note 6). Proceed as directed in 14.3 and 14.4. Repeat in duplicate. (Outgassing is accomplished automatically either as part of the continuous analysis cycle used with the automatic sample drop, or as the first step in a two-stage cycle associated with the manual addition of the sample to the crucible.)

NOTE 6—The use of graphite powder is optional. In some instruments the addition of graphite powder (0.01 g to 1.0 g depending on crucible size and style) is designed to optimize furnace performance and facilitate the release of nitrogen from the test sample. Refer to the instrument manufacturer's instructions for recommended graphite powder additions (Note 1). If graphite powder is used, it must be employed consistently for blanks, samples, and reference materials.

13.4 *Determination of Blank*—Proceed as directed in 14.2 and 14.3 with a graphite crucible containing graphite powder (Note 1 and Note 6) and analyze the nickel flux without a sample. Determine the average blank of three to five individual runs and enter this value into the appropriate mechanism of the analyzer. If each individual result is within 5  $\mu\text{g}$  of the average, the blank is acceptable. Alternatively, a maximum value may be used. Values of 0.0005 % for oxygen and 0.00007 % for nitrogen have been found adequate. Higher limits may be appropriate, particularly for reporting results that are not near the lower end of the scope. If other values are used, data showing that they are acceptable must be on file. Problems with inconsistent or high blank values must be corrected before the analysis can be continued. If the unit does not have provision for automatic blank compensation, then the blank value must be manually subtracted from the total result prior to any other calculation. Refer to the manufacturer's instructions for proper blanking procedures (Note 6).

13.5 *Calibration*—Follow the calibration procedure recommended by the manufacturer using titanium reference materials.

13.5.1 For each non-zero calibration point, weigh a titanium reference material to the nearest milligram, place it with nickel flux into an outgassed graphite crucible containing graphite powder if appropriate (Note 6).

13.5.2 Proceed as directed in 14.3 and 14.4.

13.5.3 Repeat 13.5.1 and 13.5.2. Analyze three to five specimens of each titanium reference material. For each reference material used to calibrate, calculate the average of these results, and compare the average to the certified value for the reference material. Adjust the instrument output to match the certified value unless the average already agrees with the certified value within the range of the uncertainty given on the certificate. (Note 7.)

NOTE 7—Some instruments have expanded computer capabilities that allow multi-point calibration which may improve the accuracy of the calibration over the single point calibration as tested in the current interlaboratory study (ILS). Either calibration type may be used.

13.5.4 Confirm the calibration by analyzing another specimen of the reference material after the calibration procedure is complete. The result should agree with the certified value within a suitable confidence interval (Note 8). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Alternatively, if the certified value falls within an interval calculated as described in Eq 1, the calibration is acceptable.

NOTE 8—The procedure outlined in the original version of 13.5.4 required the test result to "fall within the maximum allowable limit of the standard" typically interpreted as the range defined by the certified value  $\pm$  its associated uncertainty. The original version was utilized in the generation of the data in this method's Precision and Bias statements (Section 16). The current method for confirming the standardization is statistically rigorous and should be used in general practice. As an option, the laboratory may obtain an estimate of  $s$  from a control chart maintained as part of their quality control program. If the control chart contains a large number of measurements,  $t$  may be set equal to 2% at the 95% confidence interval. At its discretion, the laboratory may choose to set a smaller range for the acceptable test result.