



Standard Test Method for Determination of Oxygen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique¹

This standard is issued under the fixed designation E 1409; 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 covers the determination of oxygen in titanium and titanium alloys in concentrations from 0.04 and 0.3 %.

1.2 The values stated in both inch-pound and SI units are to be regarded separately as the standard. The values given in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Note 2.

2. Referenced Documents

2.1 ASTM Standards:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals²

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals²

3. Summary of Test Method

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

3.2 The test sample, plus flux, is fused in a graphite crucible under a flowing inert gas stream (Ar, He, or N₂) at a temperature sufficient to release oxygen. The released oxygen combines with carbon to form CO. Depending on instrument design, the CO is oxidized to CO₂ or left as CO and swept by the inert gas stream into either an infrared or thermal conductivity detector. The detector output is compared to that of calibration standards and the result is displayed as percent oxygen.

3.3 In a typical instrument whose detection is based upon thermal conductivity (see Fig. 1) the sample gases are swept with helium through heated rare earth/copper oxide that converts CO to CO₂. The water produced during fusion is absorbed by magnesium perchlorate and the remaining nitro-

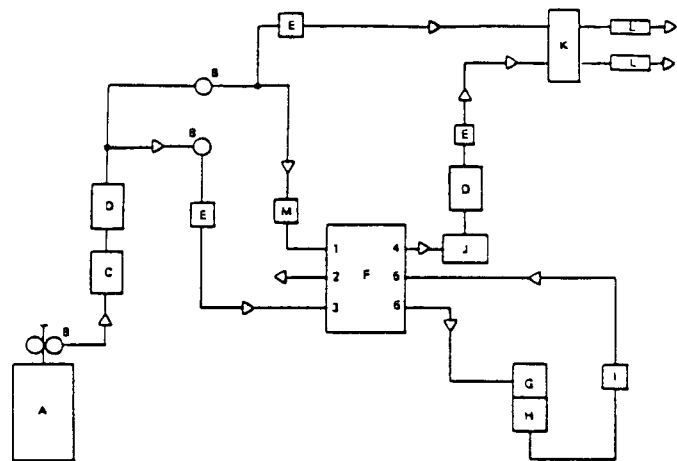


FIG. 1 Apparatus for Determination of Oxygen by the Inert Gas Fusion-Thermal Conductivity Method

gen and carbon dioxide are separated chromatographically. The oxygen, as CO₂, enters the measuring cell and the thermistor bridge output is integrated and processed to display percent oxygen.

3.4 In a typical instrument based on infrared detection (see Fig. 2) the test sample is fused in a stream of nitrogen or argon and the evolved gases are passed directly into an infrared cell through which infrared energy is transmitted. The CO in the sample gases absorbs some of the transmitted infrared energy and the decrease in energy reaching the detector is processed and displayed directly as percent oxygen. Some instruments utilize helium carrier gas and oxidize the CO to CO₂ before it is passed into the infrared cell.

4. Significance and Use

4.1 This test method is primarily intended as a referee 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.

5. Interferences

5.1 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.

¹ This test method is under the jurisdiction of ASTM Committee E-1 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.

Current edition approved April 10, 1997. Published June 1997. Originally published as E 1409 – 91. Last previous edition E 1409 – 96.

² *Annual Book of ASTM Standards*, Vol 03.05.

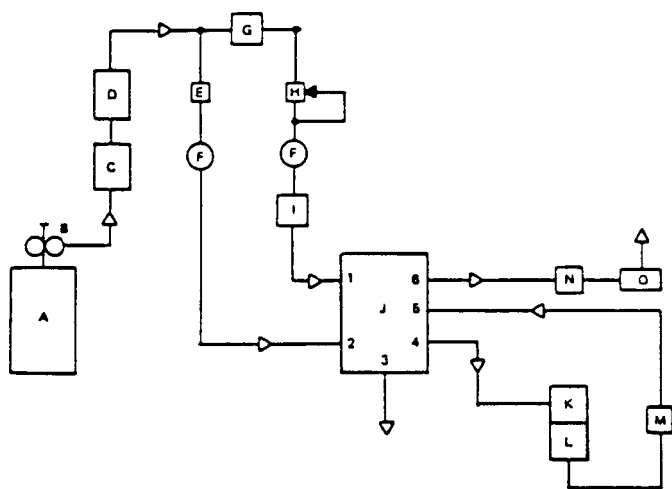


FIG. 2 Apparatus for Determination of Oxygen by the Inert Gas Fusion-Infrared Absorption Method

6. Apparatus

6.1 *Instrument*—The general features of the instruments are shown in Figs. 1 and 2.

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

6.3 *Flux*—Wire baskets must be made of high-purity nickel and the dimensions must meet the requirements of the automatic sample drop, if present, on the instrument. (See Note 1.)

NOTE 1—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.

6.4 *Tweezers*—Six inches (152 millimetres), solvent and acid-resistant plastic (used during the sample preparation process).

7. Reagents

7.1 *Acetone*—Residue after evaporation must be < 0.0005 %.

7.2 *Graphite Powder*—High-purity graphite powder specified by the instrument manufacturer.

7.3 *Inert Gas*—Use the purity and type (Ar, N₂, or He) specified by the instrument manufacturer.

7.4 *Magnesium Perchlorate, Anhydrous*³—Used in the instrument to absorb water. Use the purity specified by the instrument manufacturer.

7.5 *Nickel Flux Cleaning Solution*—Prepare a fresh solution of nickel cleaning solution by combining 75 mL of acetic acid, 25 mL of HNO₃ and 2 mL of HCl.

7.6 *Rare Earth/Copper Oxide*—Reagent used in some instruments to oxidize CO to CO₂ for thermal conductivity detection. Use the purity specified by the instrument manufacturer.

7.7 *Sodium Hydroxide on Clay*⁴—Reagent used in some instruments to absorb CO₂. Use a purity specified by the instrument manufacturer.

³ Known commercially as Anhydron.

⁴ Known commercially as Ascarite II.

7.8 *Titanium Sample Pickle Solution*—Prepare a fresh solution of 3 parts 30 % H₂O₂ and 1 part 48 % HF. HNO₃ may be substituted for 30 % H₂O₂ (see Notes 2 and 3).

NOTE 2—**Warning:** HF causes serious burns that may not be immediately painful; refer to the paragraph about HF in the Safety Precautions Section of Practices E 50.

NOTE 3—In 1996, alternative sample preparation procedures were investigated by two laboratories, both active members of subcommittee E01.06, which has jurisdiction over E1409. The first alternative allows direct substitution of nitric acid for hydrogen peroxide when preparing titanium pickle solution and subsequent etching of the test specimen as specified in 10.2. The second entails removing surfaces of the sample specimen by filing with a file, thus eliminating the need to use any leaching procedure. The results of the interlaboratory study comparing these two preparation techniques is summarized in Table 1.

8. Preparation of Apparatus

8.1 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.

8.2 Change the chemical traps and filters as required. Test the furnace and analyzer to ensure the absence of leaks. Make a minimum of two test runs using a sample as directed in 12.3 and 12.4 to condition the newly changed filters before attempting to calibrate the system or to determine the value of the blank.

9. Flux Preparation

9.1 Immerse the flux in nickel flux cleaning solution (see 7.5) for 50 to 60 s, then rinse in running water for 2 to 3 min. Pour flux onto paper towels to remove excess water.

9.2 Place flux in sealable glass container, rinse with acetone and decant. Replace with fresh acetone and store flux under acetone until used. (See Notes 4 and 5.)

NOTE 4—Nickel is necessary to flux the titanium fusion reaction but significant oxidation can be present on the surface of nickel wire baskets that can cause interference with the analysis.

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

10. Sample Preparation

10.1 The optimum test sample is a pin approximately 1/8 in. (5 mm) in diameter and nominally weighing 0.12 to 0.15 g. Cut the sample to this approximate weight range.

10.2 Leach the test sample in the titanium sample pickle solution (see 7.8 and Notes 2 and 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.

10.3 Immediately remove the reacting test sample with tweezers and rinse it twice with water and once with acetone and allow to air dry. This test sample should now weigh between 0.100 and 0.140 g.

10.4 Alternatively, the test sample may be prepared for clean surfaces by filing or cutting off all outside edges, retaining only fresh surfaces, and finishing by rinsing with acetone and air drying. The test sample should now weigh between 0.100 and 0.140 g.

10.5 All subsequent operations on the test sample and flux must be done without introducing contamination to either. Use

only clean tweezers and never let the test sample or flux contact the analyst's skin. In the event this does happen, rinse the sample plus nickel basket with acetone and air dry before analysis.

11. Calibration

11.1 *Calibration Standards*—Select only titanium or titanium alloy standards. Select one containing approximately 0.2 % oxygen. The accuracy of the test method is largely dependent upon the accuracy of the oxygen values assigned to the reference materials and upon the homogeneity of these materials. Thus, wherever possible, specimens used to confirm instrument calibration should be National Institute of Standards and Technology (NIST) Standard Reference Materials or other certified reference materials.

11.2 *Gas Dosing*—Automatic and manual gas dosing, recommended by some manufacturers, can be used to set up the instrument, but instrument response must be verified by calibration with standards because of the fusion characteristics of the furnace/sample combination.

11.3 *Initial Adjustment of Measurement System*—Weigh a titanium standard to the nearest milligram, place it in a nickel basket and transfer it to an outgassed graphite crucible containing graphite powder (see Note 6); some instruments allow for the use of an automatic sample drop port. Proceed as directed in 12.3 and 12.4. Repeat until an absence of drift is indicated. Using the last three analyses, adjust the instrument signal to provide a reading within the range of the certified value of the standard. (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 addition of graphite powder (0.1 to 1.0 g depending on crucible size and style) is designed to optimize furnace performance and facilitate the release of oxygen from the test sample. Refer to the instrument manufacturer's instructions for recommended graphite powder additions.

11.4 *Determination of Blank*—Proceed as directed in 12.3 and 12.4 with a graphite crucible containing graphite powder (see Note 5) and analyze the nickel basket but without a sample. Determine the average blank of three to five individual runs (establishing that the blank is low and consistent) and enter this value into the appropriate mechanism of the analyzer. 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.

11.5 *Calibration*—Follow the calibration procedure recommended by the manufacturer using the titanium standard. Confirm the calibration by analyzing an additional sample after

the calibration procedure is complete. The result should fall within the maximum allowable limit of the standard.

12. Procedure

12.1 Assemble the apparatus, calibrate it, and test the performance as directed in Sections 8 and 11.

12.2 Transfer a 0.100 to 0.140-g titanium test sample to a nickel basket. (The weight of nickel must exceed the weight of sample by at least a factor of ten.) The weight tolerance of the titanium test sample must be ± 1 mg.

12.3 Place the test sample and nickel basket into the sample drop port.

12.4 Place the crucible containing graphite powder (see Note 6) on the furnace pedestal, raise the mechanism and start the analysis cycle. Refer to the instrument manufacturer's specific instructions for the specific instrument model regarding operation, entry of sample weight, and blank value. (See Note 7.)

NOTE 7—During the sample analysis run, the analysis of a titanium standard at regular intervals is recommended for monitoring drift and validating the initial calibration.

13. Calculation

13.1 Refer to the manufacturer's instructions to ensure that all essential variables in the analysis have been accounted for. The output of most modern fusion equipment is given directly in percent oxygen so that post-analysis calculations are normally not required.

14. Precision and Bias⁵

14.1 *Precision*—Eleven laboratories cooperated in testing Samples 1 through 7. The data obtained are presented in Table 2. The testing and statistical analysis were performed according to the provisions of Practice E 173.

14.2 Bias

14.2.1 Bias was evaluated according to the provisions of 10.4 of Practice E 173 by the regression analysis of the analyzed samples versus the sample's certified value.

$$\begin{aligned}
 y &= 1.0018x - 0.000023 & (1) \\
 a \pm 1.668 S_a &= -0.000023 \pm 1.668 (0.00125) \\
 &= -0.000023 \pm 0.0021 \\
 b \pm 1.668 S_b &= 1.0018 \pm 1.668 (0.00727) \\
 &= 1.0018 \pm 0.012
 \end{aligned}$$

14.2.2 Since the 95 % confidence limits for a include 0 and the 95 % confidence limits for b include 1, there is no evidence of overall bias in this test method over the range of values used.

15. Keywords

15.1 inert gas fusion; oxygen; titanium; titanium alloys

⁵ Supporting data have been filed at ASTM Headquarters and may be obtained by requesting RR: E01-1002.

TABLE 1 Results of Interlaboratory Study

Lab	Sample ID	Sample Desc.	Filed, % Oxygen	HF-HNO ₃ Etched, % Oxygen
Comparison of Filed versus HF-HNO ₃ Etched Sample Prep Procedures				
Lab 1	030	Ti-5A1-2.5Sn	0.160	0.164
Lab 2			0.161 ± 0.002, n = 3	0.165 ± 0.003, n = 3
Lab 1	035	CP-Ti	0.163	0.163
Lab 2			0.154 ± 0.001, n = 3	0.156 ± 0.001, n = 3
Lab 1	040	Ti-6A1-4V	0.164	0.160
Lab 2			0.156 ± 0.003, n = 3	0.155 ± 0.002, n = 3
Comparison of HF-H ₂ O ₂ Etched versus HF-HNO ₃ Etched Sample Prep Procedures				
			HF-H ₂ O ₂ Etched, % Oxygen	HF-HNO ₃ Etched, % Oxygen
Lab 2		CP-Ti	0.1412 ± 0.0025, n = 10	0.1422 ± 0.0016, n = 10
		Ti-6A1-4V	0.1425 ± 0.0026, n = 10	0.1418 ± 0.0021, n = 10

TABLE 2 Statistical Information—Oxygen in Titanium

Test Sample	Weight Percent O ₂ Certified	Weight Percent O ₂ Found	Repeatability, R1 ^A , Practice E 173	Reproducibility, R2 ^A , Practice E 173
1 GBW ^B 02603	0.119	0.115	0.008	0.012
2 GBW ^B 02604	0.273	0.275	0.011	0.015
3 BCR ^C No. 24	0.0608	0.063	0.008	0.013
4 BCR ^C No. 59	0.175	0.179	0.021	0.021
5 Leco ^D 501-653	0.044	0.044	0.008	0.009
6 TIMET ^E B	0.239	0.238	0.012	0.024
7 Leco ^D 501-664	0.154	0.153	0.010	0.014

^A $m = 1$.

^B Certified Reference Material, People's Republic of China.

^C Certified Reference Material, Community Bureau of Reference, Commission of the European Communities.

^D Calibration samples, Leco Corporation.

^E Interlaboratory tested material, TIMET, Henderson Technical Laboratory (four laboratories, vacuum fusion technique).

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