



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

This standard is issued under the fixed designation E 1937; 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 provides a procedure for the determination of nitrogen in titanium and titanium alloys in concentrations from 0.007 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 hazards statements are given in 7.8 and Section 8.

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 in a flowing helium gas stream at a temperature sufficient to release nitrogen. The nitrogen is swept by the helium gas stream into a thermal conductivity detector. The detector response is compared to that of calibration standards and the result is displayed as percent nitrogen.

3.3 In a typical instrument (Fig. 1) the sample gases are swept with helium through heated rare earth/copper oxide which converts CO to CO₂ and H₂ to H₂O. The CO₂ is absorbed on sodium hydroxide impregnated on clay, and the H₂O is removed with magnesium perchlorate. The nitrogen, as N₂, enters the measuring cell and the thermistor bridge output is integrated and processed to display percent nitrogen.

4. Significance and Use

4.1 This test method is primarily intended as a referee method for compliance with compositional specifications. It is

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 Titanium, Zirconium, Tungsten, Molybdenum, Tantalum, Niobium, Hafnium, and Rhenium.

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

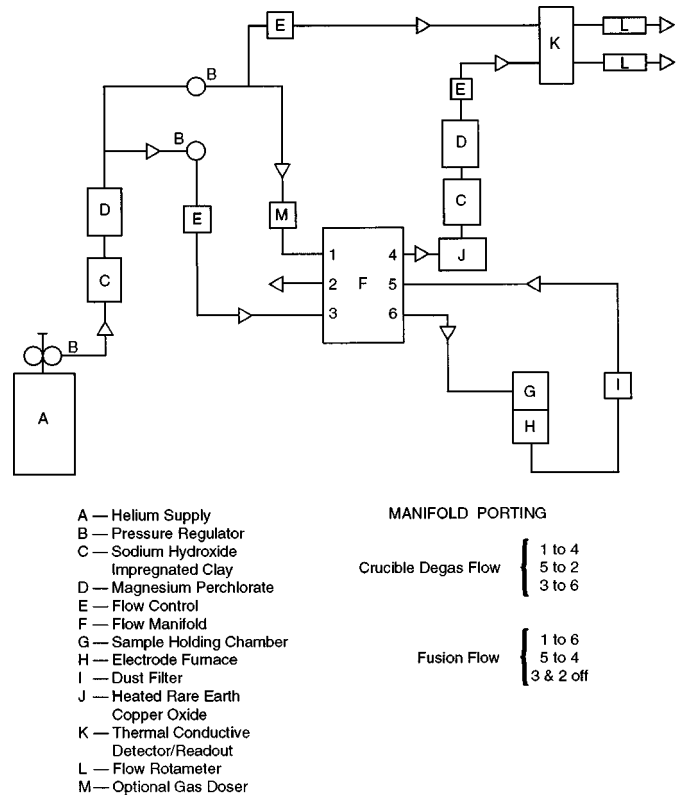


FIG. 1 Apparatus for Determination of Nitrogen by the Inert Gas Fusion-Thermal Conductivity Method

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.

6. Apparatus

6.1 *Instrument*—The general features of the typical instrument are shown in Fig. 1.

6.2 *Graphite Crucibles*, made of high-purity graphite of the dimensions recommended by the instrument manufacturer.

6.3 *Flux*—Wire baskets consisting of platinum or high-purity nickel of dimensions that meet the requirements of the

automatic sample drop, if present, on the instrument (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 weight ratio of flux to sample. When using platinum as a flux, graphite powder should not be added to the crucible.

6.4 *Tweezers*—Six inch solvent and acid-resistant plastic.

7. Reagents

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

7.2 *Graphite Powder*, of purity specified by the instrument manufacturer.

7.3 *Helium*, of purity and type specified by the instrument manufacturer.

7.4 *Magnesium Perchlorate, Anhydrous*—Used in the instrument to absorb water. Use the purity specified by the instrument manufacturer. (Known commercially as Anhydron.)

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 the instrument to oxidize CO to CO₂. Use the purity specified by the instrument manufacturer.

7.7 *Sodium Hydroxide on Clay*—Reagent used in some instruments to absorb CO₂. Use a purity specified by the instrument manufacturer. (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. (**WARNING:** HF causes serious burns which may not be immediately painful; refer to the paragraph about HF in the Safety Precautions section of Practices E 50.)

8. Hazards

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

8.2 For precautions to be observed in the use of HF and other reagents in this test method, refer to Practices E 50.

9. Preparation of Apparatus

9.1 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.

9.2 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.

10. Nickel Flux Preparation

10.1 Nickel is necessary to flux the titanium fusion reaction but contamination can be present on the surface of the nickel wire baskets that must be removed before use.

10.2 Immerse the flux in Nickel Flux Cleaning Solution for

50 to 60 s, then rise in running water for 2 to 3 min. Pour flux onto paper towels to remove excess water. Place flux in sealable glass container, rinse with acetone and decant. Replace with fresh acetone and store flux under acetone until use.

11. Sample Preparation

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

11.2 Leach the test sample in the Titanium Sample Pickle Solution until the surface is clean. This will normally require approximately 5 s from the time of the initial vigorous reaction.

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

11.4 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.

12. Calibration

12.1 *Calibration Standards*—Select only titanium or titanium alloy standards. Select one containing approximately 0.02 % nitrogen. The accuracy of the test method is dependent upon the accuracy of the methods used to certify the nitrogen concentration of the certified reference materials, as well as upon their homogeneity. Thus, wherever possible, standards used to confirm instrument calibration should be NIST Standard Reference Materials or other certified reference materials.

12.2 *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 titanium standards because of the fusion characteristics of the furnace/sample combination.

12.3 *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 (Note 2). Proceed as directed in 13.3 and 13.4. Repeat until an absence of drift is indicated. Using the average of 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 2—In some instruments 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 nitrogen from the test sample. Refer to the instrument manufacturer's instructions for recommended graphite powder additions (Note 1).

12.4 *Determination of Blank*—Proceed as directed in 13.3 and 13.4 with a graphite crucible containing graphite powder (Note 1 and Note 2) and analyze the nickel basket but without a sample. Determine the average blank from 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.

12.5 *Calibration*—Follow the calibration procedure recommended by the manufacturer using titanium standard reference material. Confirm the calibration by analyzing a different standard after the calibration procedure is complete. The result should fall within the maximum allowable limit of the standard.

13. Procedure

13.1 Assemble the apparatus, calibrate it, and test the performance as directed in Sections 9 and 12.

13.2 Transfer a 0.100 to 0.140 g titanium test sample weighed to the nearest milligram to a nickel basket. (The weight of nickel must exceed the weight of sample by at least a factor of 10.)

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

13.4 Place the crucible containing graphite powder (Note 1 and Note 2) 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.

13.5 During the analysis of a series of test samples, a titanium standard reference material must be inserted at regular

intervals for monitoring drift and validating the initial calibration. Should the result fall outside the certified limits, repeat the calibration.

14. Calculation

14.1 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 nitrogen so that post-analysis calculations are normally not required.

15. Precision and Bias ³

15.1 *Precision*—Twelve laboratories cooperated in testing Samples 1 through 4. The data obtained are presented in Table 1. The testing and statistical analysis were performed according to the provisions of Practice E 173.

15.2 *Bias*—Information on the accuracy of this test method is incomplete at this time. The accuracy of this test method may be judged by comparing the results obtained from certified reference materials with their certified values for nitrogen.

16. Keywords

16.1 nitrogen content; titanium; titanium alloys

³ Supporting data are available from ASTM Headquarters. Request RR:E01-1024.

TABLE 1 Nitrogen in Titanium Metal Statistical Information

Standard	Weight Percent Certified Value	Weight Percent Certified Precision	Interlaboratory Testing Results (12 Laboratories) Weight Percent		
			Average	R ₁	R ₂ ^A
1. Leco ^B 501-653	0.002	0.001	0.0031	0.0024	0.0033
2. BCR ^C No. 24	0.0117	0.0013	0.0100	0.0039	0.0054
3. BCR ^C No. 59	0.0172	0.0027	0.0167	0.0056	0.0072
4. TIMET ^D B-10377	0.107	0.006	0.116	0.013	0.040

^A $m = 1$.

^B Calibration sample, Leco Corporation.

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

^D TIMET, Henderson Technical Laboratory, Nitrogen content determined by Kjeldahl distillation-titration method.

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