



Standard Test Methods for Determination of Mass Fraction of Carbon, Nitrogen, and Oxygen in Silicon Nitride Powder¹

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1. Scope

1.1 These test methods cover the determination of mass fraction % of carbon, nitrogen and oxygen in silicon nitride powder having chemical compositions within the following limits:

| Element | Mass Fraction % Range |
|----------|-----------------------|
| Carbon | 0.05 to 5.0 |
| Nitrogen | 30 to 45 |
| Oxygen | 0.1 to 1.5 |

1.2 Two test methods appear in this standard.

1.2.1 Total Carbon by the Direct Combustion-Infrared Measurement Method.

1.2.2 Nitrogen and oxygen by the Inert Gas Fusion-Thermal Conductivity Measurement Method.

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 hazard statements are given in Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

¹ These test methods are under the jurisdiction of ASTM Committee C28 on Advanced Ceramics and are the direct responsibility of Subcommittee C28.03 on Physical Properties and Performance.

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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.

E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys

E 1409 Test Method for Determination of Oxygen and Nitrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique

E 1569 Test Method for Determination of Oxygen in Tantalum Powder

E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

E 1941 Test Method for Determination of Carbon in Refractory and Reactive Metals and Their Alloys

3. Significance and Use

3.1 These test methods are for the chemical analysis of mass fraction of carbon, nitrogen and oxygen in silicon nitride powder. It is assumed that all who use these test methods will be trained analysts, capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

4. Apparatus and Reagents

4.1 The procedure was written with commercial carbon and nitrogen/oxygen analyzers in mind. For any other analyzer, the instrument manual specific to that analyzer shall be consulted for instrument set-up.

4.2 Specific apparatus and reagents required for each determination are listed in separate sections preceding the procedure.

5. Sampling

5.1 Procedures for sampling the materials refer to those parts of Practice **E 1806** pertaining to solid form samples of the type used for instrumental analysis.

6. Hazards

6.1 For hazards to be observed in the use of certain reagents in this test method, refer to Practice **E 50**.

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

7. Total Carbon in Silicon Nitride Powder by Direct Combustion—Infrared Detection Method

7.1 *Scope*—This test method covers the determination of carbon in concentrations from 0.05 to 5.0 % mass fraction.

7.2 *Summary of Test Method*³—The carbon is converted to carbon dioxide by combustion in a stream of oxygen. The amount of carbon dioxide is measured by infrared (IR) absorption.

7.3 *Apparatus*—This test method is written for use with commercial carbon analyzers, equipped to carry out the analyses operations automatically and calibrated using steel standards with known concentrations of carbon. The operating principles, specifications and descriptions of commercial carbon analyzers are given in the Practice of E 1019.

7.4 Reagents and Materials:

7.4.1 *Crucibles*—Expendable ceramic (alumina) or similar refractory crucibles as specified by commercial carbon analyzers' manufacturers. Both the crucible and cover, if used, must be prebaked for a sufficient time to produce constant blank values. Use the prebake schedule recommended by the instrument manufacturer.

7.4.2 *Crucible Tongs*—Capable of handling recommended crucibles with respect to their sizes, shape and temperature.

7.4.3 *Accelerators*—Carbon free (or containing a known amount of carbon) granular tungsten/tin and iron chip accelerators shall be used.

7.4.4 *Carbon Standard Material*—NIST SRM 8j (0.081 %C), SRM 11h (0.2 %C), SRM 12h (0.407 %C), and NIST RM 8983 (0.107 %C).

7.4.5 *Oxygen*—Ultra High Purity (99.95 % minimum purity) or Regular grade (99.5 %) purified by passing over heated CuO and through CO₂/H₂O absorbents. (When the instrument has a built in purifier, regular grade oxygen can be used.)

7.5 *Preparation of Apparatus*—Follow the operating instructions for the specific equipment used. After having properly set the operating controls of the instrument system, condition the apparatus by combustion of several blanks prepared with sample crucible and accelerator in the amounts to be used with the test specimen analyses. Successive blanks should achieve a steady state value.

7.6 Blank Determination:

7.6.1 Prebake ceramic crucibles in a muffle or tube furnace at 1350° C for not less than 15 min or at 1000° C for not less than 40 minutes. The crucibles shall be removed from the furnace, allowed to cool for 1-2 min and placed in a desiccator for storage. If the crucibles are not used within four hours, they must be prebaked again. This prebaking procedure is to burn off any organic contaminants.

7.6.2 Prepare instrument as outlined in the operator's instruction manual.

7.6.3 Determine the instrument blank.

(a) Enter 1.000 g weight into weight stack.

(b) Add 1.000 g (± 0.005 g) of tungsten/tin accelerator and 1.000 g (± 0.005 g) of iron chip accelerator.

(c) Place crucible on furnace pedestal and analyze.

(d) Repeat steps 7.6.3a through 7.6.3c a minimum of three times.

(e) Enter blank value following routine outlined in operator's instruction manual.

7.7 Instrument Calibration Procedure:

7.7.1 This procedure was written specially for a carbon analyzer. The type and amounts of accelerator to be added shall be adjusted according to the manufacturers recommendations for the other instrumentation.

7.7.2 Weigh 0.1 to 0.5 g of calibration standard to the nearest mg into a prebaked ceramic or similar refractory crucible and enter appropriate weight into weight stack.

7.7.3 Add approx. 1.0 ± 0.005 g of tungsten/tin accelerator and approx. 1.0 ± 0.005 g of iron chips accelerator.

7.7.4 Place crucible on pedestal and analyze.

7.7.5 Repeat the above steps 7.7.2-7.7.4 a minimum of three times for each standard, and calibrate the instrument following the auto calibration procedure as outlined in the operator's instruction manual.

7.7.6 Check calibration by analyzing the calibration standard again if it is not within the reported range. If it is not, repeat steps 7.7.2-7.7.4.

7.8 Sample Analysis Procedure:

7.8.1 Weigh 0.1 to 0.5 g of sample to the nearest mg into a prebaked expendable ceramic or a similar refractory crucible and add appropriate weight to the weight stack.⁴

7.8.2 Repeat steps 7.7.3 and 7.7.4 in the calibration procedure.

7.8.3 Each sample shall be analyzed in triplicate and record the integral values of the sample.

7.9 *Calculation*—Most commercially available instruments calculate percent concentration directly. If the instrument does not give percent concentration, please follow the manufacturer's directions to ensure all the essential variables in the calculation of analysis results have been included.

Or perform the following calculation to determine percent concentration (% mass):

a. Calibration Constant:

$$K = \frac{G \times P/100}{A_c - A_b} \quad (1)$$

where:

K = calibration constant (g/integral value),

G = mass of calibration sample (g),

P = total carbon content of the calibration sample (% mass),

A_c = integral value of the calibration sample (7.7.6), and

A_b = integral value of the blank (7.6.3e).

b. Total Carbon Content:

³ The test method procedure was adapted from (a) ASTM E 1019-94, "Standard Test Methods for Determination of C, S, N, and O in Iron, Nickel and Cobalt Alloys" and (b) Application Bulletin: "Carbon and Sulfur in Ceramic and Similar Materials," LECO Corp., St. Joseph, MI.

⁴ The weight of sample is chosen based on the expected amount of carbon present and so the CO₂ produced will fall within the detection range of the IR detector.

$$C = \frac{(A_s - A_b) \times K \times 100}{m} \quad (2)$$

where:

- C = carbon content (mass %),
- A_s = integral value of the sample (7.8.3),
- A_b = integral value of the blank (7.6.3e),
- K = calibration constant (g/integral value), and
- m = mass of the sample (g).

7.10 *Report*—Report carbon concentration as mass fraction percentage to the desired decimal places as directed in Practice E 29, as well as times of replication of analysis and any deviations from the standard analysis procedure.

7.11 *Precision and Bias*:

7.11.1 *Precision*:

7.11.1.1 *Reproducibility*—Three laboratories cooperated in testing this method and obtained reproducibility data for SRM 8j, 1 lh, and 12h which are summarized in Table 1. Since the reference value with uncertainty of RM 8983 is determined during this round robin study, no reproducibility is reported.

7.11.1.2 *Repeatability*—Three laboratories cooperated in testing this method and obtained repeatability data for SRM 8j, 1 lh and 12h which are summarized in Table 1. Since the reference value with uncertainty of RM 8983 is determined during this round robin study, no repeatability is reported.

7.11.2 *Bias*—No bias of this test method is established, since insufficient number of laboratories have participated this round robin study. The accuracy of a reading may be judged by comparing values obtained with NIST reference standards such as listed in Table 1 to their reference values and uncertainty.

8. Determination of Total Nitrogen and Oxygen in Silicon Nitride Powder by Direct Inert Gas Fusion-Thermal Conductivity Method

8.1 *Scope*—This test method covers the determination of nitrogen (N) in concentrations from 30 to 45 % mass fraction.

TABLE 1 Statistical Information for Carbon Analysis (Mass Fraction %)

| Test Specimen | Carbon Reference Value | Found | Repeatability Limit ^A | Reproducibility Limit ^B |
|----------------------------------|----------------------------|--------|----------------------------------|------------------------------------|
| Bessemer Steel (NIST SRM 8j) | 0.081 ± 0.001 ^C | 0.0796 | 0.0089 | 0.0066 |
| Open-Hearth Steel (NIST SRM 11h) | 0.200 ± 0.001 ^D | 0.2038 | 0.0022 | 0.0126 |
| Open-Hearth Steel (NIST SRM 12h) | 0.407 ± 0.003 ^E | 0.4211 | 0.0055 | 0.0383 |
| Silicon Nitride (NIST RM 8983) | 0.107 ± 0.015 ^F | ... | ... | ... |

^A The 95 % repeatability limit is defined as 1.96* U_{repeatability} which is the uncertainty of a difference of two averages, each based on 3 repeated measurements at one laboratory. This U_{repeatability} is also called repeatability standard deviation.

^B The 95 % reproducibility limit is defined as 1.96* U_{reproducibility} which is the uncertainty of a difference of two averages, each of which is based on 3 repeated measurements from two different laboratories. This U_{reproducibility} is also called reproducibility standard deviation.

^C The SRM 8j Certificate reports 4 determinations which have a standard deviation of 0.001.

^D The SRM 11h Certificate reports no deviation from the reference value by more than ±1 in the last significant figure.

^E The SRM 12h Certificate reports 5 determinations which have a standard deviation of 0.003.

^F The RM 8983 Certificate reports the uncertainty in the reference value which is expressed as expanded uncertainty U, at the 95 % level of confidence.

This test method also covers the determination of oxygen (O) in concentrations from 0.1 to 1.5 % mass fraction.

8.2 *Summary of Test Method*⁵—The specimen, contained in a small single-use graphite crucible, is fused under a flowing helium atmosphere at a minimum temperature of 1900° C which is sufficient to release oxygen, nitrogen and hydrogen from the sample. The oxygen combines with carbon from the crucible to form carbon monoxide (CO) which is carried by the helium inert gas stream to a thermal conductivity (TC) detector. Nitrogen present in the sample is released as molecular nitrogen into the flowing helium stream. The nitrogen is separated from other liberated gases such as hydrogen and carbon monoxide and is finally measured in a thermal conductivity cell.

8.3 *Apparatus*—This test method is written for use with commercial nitrogen/oxygen analyzers, equipped to carry out the analyses operation automatically and calibrated using standards with known mass fraction % of nitrogen/oxygen. The operating principles, specifications and descriptions of commercial nitrogen/oxygen analyzers are given in the Practice of E 1019.

8.4 *Reagents and Materials*:

8.4.1 *High Temperature Graphite Crucible* (resistance heated) as recommended by the manufacturer of the instrument.

8.4.2 *Graphite Crucible* (sacrificial heated) as recommended by the instrument manufacturer.

8.4.3 *Crucible Tongs* capable of handling recommended crucibles and capsules with respect to their sizes, shape and temperature.

8.4.4 *Tin Capsules* as recommended by the manufacturer of the instrument.

8.4.5 *Nickel Baskets (Flux)* as recommended by the instrument manufacturer.

8.4.6 *Inert Gases (Helium, Compressed Air, Nitrogen or Argon)*—Use type and purity specified by the instrument manufacturer.

8.4.7 *Calibration Standards*:

8.4.7.1 *Oxygen*—Select standards with appropriate concentrations.

8.4.7.2 *Nitrogen*—Select standards with appropriate concentrations.

8.4.7.3 *Oxygen and Nitrogen*—NIST RM 8983, Silicon Nitride Powder.

8.5 *Preparation of Apparatus and Samples*:

8.5.1 Follow the operating instructions for the specific equipment used. After having properly set the operating controls of the instrument system, condition the apparatus by analysis of several blanks prepared with sample crucibles and flux in the amount to be used with the test specimen analyses. Successive blanks should approach a constant value, allowing for normal statistical fluctuations.

8.5.2 The powder sample to be analyzed shall be dry and uniform with a particle size distribution of 100 mesh or finer.

⁵ Adapted from (a) ASTM E 1019-94, "Standard Test Methods for Determination of C, S, N, and O in Iron, Nickel and Cobalt Alloys" and (b) Application Bulletin, "Oxygen and Nitrogen in Nitride Powders," LECO Corp., St. Joseph, MI.

If the sample is in bulk form, the sample crushing shall be done without adding oxygen to the sample. Avoid using an Agate apparatus which will add oxygen in the form of Silicon Oxide. The sample and calibration standards shall be stored in desiccator.

8.6 Calibration—This procedure is written specifically for use with commercial Nitrogen/Oxygen Instruments, equipped to carry out the analyses operation automatically and calibrated with silicon nitride powder of known concentrations of nitrogen and oxygen. Therefore, please follow the instrument manufacturer's procedure closely. The types and amounts of flux to be added shall also be adjusted according to the instrumentation manufacturers' recommendations.

I. Determine the crucible, tin capsule and nickel baskets blank as follows:

8.6.1 Enter a 1.0 g mass into weight stack.

8.6.2 Place a Tin Capsule into a Nickel Basket as supplied by the manufacturer.

8.6.3 Use tweezers to pinch the nickel basket closed and then place the nickel basket into the loading head, tapered end down.

8.6.4 Position a High Temperature Graphite crucible on the lower electrode, close the furnace and analyze.

8.6.5 Repeat above steps 8.6.1-8.6.4 for a minimum of three times. If a steady state value is not obtained, check and correct any instrumental problems and then repeat the above steps 8.6.1-8.6.4.

8.6.6 Enter the average blank value into the analysis constants as described in the "Blanks Procedure" outlined in the operator's instrumental manual.

II. Calibrate the instrument as follows:

8.6.7 Weigh an appropriate amount of standard to the nearest 0.1 mg (refer to manufacturer's recommendations) into a Tin Capsule and enter the appropriate weight into the weight stack.

8.6.8 Seal the tin capsule and place it into a Nickel Basket.

8.6.9 Use tweezers to pinch the nickel basket closed and place the nickel basket into the loading head with the tapered end down.

8.6.10 Position a High Temperature Graphite crucible on the lower electrode, close the furnace and analyze.

8.6.11 Repeat the above steps 8.6.7-8.6.10 for a minimum of three times.

8.6.12 Enter the new Standard calibration value into the constants as outlined in the calibration Procedure in the operator's instruction manual.

8.7 Sample Procedure:

8.7.1 Weigh 0.02-0.06 g of sample to the nearest 0.1 mg into a Tin Capsule and enter the weight into the weight stack of the instrument.

8.7.2 Seal the tin capsule and place it in a Nickel Basket.

8.7.3 Use tweezers to pinch the nickel basket closed and place the nickel basket into the loading head with tapered head down.

8.7.4 Position a High Temperature Graphite Crucible on the lower electrode and close the furnace and analyze.

8.7.5 Each sample should be analyzed in triplicate and record the integral value of the sample.

8.8 Calculation—Most commercially available instruments calculate percent concentrations directly. If the instrument does not calculate percent concentration directly, please follow the manufacturer's directions to ensure that all essential variables in the calculation of analysis results have been accounted for, including the blank, weight of sample and calibration data.

Or follow the following equations to calculate percent concentration:

8.8.1 Calibration Constant (K):

$$K = \frac{G \times P/100}{A_c - A_b} \quad (3)$$

where:

K = calibration constant of nitrogen or oxygen (g/integral value),

G = mass of calibration sample (g),

P = nitrogen or oxygen content of the calibration sample (mass %),

A_c = integral value of the calibration sample (8.6.12), and

A_b = integral value of the blank (8.6.6).

8.8.2 Total Nitrogen or oxygen in the Sample:

$$C = \frac{(A_s - A_b) \times K \times 100}{m_s} \quad (4)$$

where:

C = total nitrogen or oxygen content (mass %),

A_s = integral value of the sample (8.7.5),

A_b = integral value of the blank (8.6.6),

K = calibration constant of nitrogen or oxygen (g/integral value), and

m_s = mass of the sample (g).

8.9 Report—Report nitrogen/oxygen concentration as mass fraction percentage to the desired number of places as directed in Practice E 29 as well as times of replication of analysis and any deviations from the standard analysis method.

8.10 Precision and Bias:

8.10.1 Precision:

8.10.1.1 Reproducibility—Three Laboratories cooperated in testing this method and obtained the reproducibility data summarized in Tables 2 and 3. No reproducibility value for RM 8983 is reported, since the reference values with uncertainty listed in the Table is derived from this round robin study.

8.10.1.2 Repeatability—Three laboratories cooperated in testing this method and obtained repeatability data summarized

TABLE 2 Statistical Information for Oxygen Analysis (Mass Fraction %)

| Test Specimen | Oxygen Reference Value | Found | Repeatability Limit ^A | Reproducibility Limit ^B |
|---------------------------------|--------------------------|--------|----------------------------------|------------------------------------|
| Titanium Sample (LECO 501-320) | 0.191 ± 0.004 | 0.1934 | 0.0035 | 0.0050 |
| Silicon Nitride (NIST, RM 8983) | 1.20 ± 0.14 ^C | ... | ... | ... |

^A The 95 % repeatability limit is defined as 1.96* U_{repeatability} which is the uncertainty of a difference of two averages, each based on 2 repeated measurements at one laboratory. This U_{repeatability} is also called repeatability standard deviation.

^B The 95 % reproducibility limit is defined as 1.96* U_{reproducibility} where U_{reproducibility} is the uncertainty of a difference of two averages, each based on 2 repeated measurements from two different laboratories.

^C The uncertainty in reference value given is expressed as an expanded uncertainty U, at the 95 % level of confidence.

TABLE 3 Statistical Information for Nitrogen Analysis (Mass Fraction %)

| Test Specimen | Nitrogen | Found | Repeatability Limit ^A | Reproducibility Limit ^B |
|---------------------------------|---------------------------|-------|----------------------------------|------------------------------------|
| Silicon Nitride (NIST, RM 8983) | 39.23 ± 1.06 | ... | ... | ... |
| β-Silicon Nitride | 38.99 ± 0.08 ^C | 38.77 | 0.284 | 3.268 |

^A The 95 % repeatability limit is defined as $1.96 \cdot U_{\text{repeatability}}$ where $U_{\text{repeatability}}$ is the uncertainty of a difference of two averages, each based on 2 repeated measurements at one laboratory.

^B The 95 % reproducibility limit is defined as $1.96 \cdot U_{\text{reproducibility}}$ where $U_{\text{reproducibility}}$ is the uncertainty of a difference of two averages, each based on 2 repeated measurements from two different laboratories.

^C Determined by Kjeldahl Method.

in Tables 2 and 3. No repeatability Value for RM 8983 is reported, since the reference values with uncertainty listed in Table is derived from this round robin study.

8.10.2 *Bias*—No bias of this test method is established, since insufficient number of participants have participated this round robin study. The accuracy of a reading may be judged by comparing values obtained with standards such as titanium sample (LECO 501-3200 and NIST RM 8983) listed in Table 2 to their reference values and uncertainty.

9. Keywords

9.1 advanced ceramics; mass fraction of carbon; nitrogen; oxygen; silicon nitride powder

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