



Standard Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques¹

This standard is issued under the fixed designation E1019; 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 These test methods cover the determination of carbon, sulfur, nitrogen, and oxygen, in steel, iron, nickel, and cobalt alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.001 to 18.00
Antimony	0.002 to 0.03
Arsenic	0.0005 to 0.10
Beryllium	0.001 to 0.05
Bismuth	0.001 to 0.50
Boron	0.0005 to 1.00
Cadmium	0.001 to 0.005
Calcium	0.001 to 0.05
Carbon	0.001 to 4.50
Cerium	0.005 to 0.05
Chromium	0.005 to 35.00
Cobalt	0.01 to 75.0
Niobium	0.002 to 6.00
Copper	0.005 to 10.00
Hydrogen	0.0001 to 0.0030
Iron	0.01 to 100.0
Lead	0.001 to 0.50
Magnesium	0.001 to 0.05
Manganese	0.01 to 20.0
Molybdenum	0.002 to 30.00
Nickel	0.005 to 84.00
Nitrogen	0.0005 to 0.50
Oxygen	0.0005 to 0.03
Phosphorus	0.001 to 0.90
Selenium	0.001 to 0.50
Silicon	0.001 to 6.00
Sulfur (Metal Reference Materials)	0.002 to 0.35
Sulfur (Potassium Sulfate)	0.001 to 0.600
Tantalum	0.001 to 10.00
Tellurium	0.001 to 0.35
Tin	0.002 to 0.35
Titanium	0.002 to 5.00
Tungsten	0.005 to 21.00
Vanadium	0.005 to 5.50
Zinc	0.005 to 0.20
Zirconium	0.005 to 2.500

1.2 The test methods appear in the following order:

	Sections
Carbon, Total, by the Combustion-Instrumental Measurement Test Method	10-20
Nitrogen by the Inert Gas Fusion-Thermal Conductivity Test Method	32-42
Oxygen by the Inert Gas Fusion Test Method	43-54
Sulfur by the Combustion-Infrared Absorption Test Method (Calibration with Metal Reference Materials)	55-65
Sulfur by the Combustion-Infrared Absorption Test Method (Potassium Sulfate Calibration)	21-31

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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 Section 6.

2. Referenced Documents

2.1 ASTM Standards:²

- D1193 Specification for Reagent Water
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- 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 Metals³
- E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.

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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.

³ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

3. Terminology

3.1 For definition of terms used in this test method, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended to test such materials for compliance with compositional specifications. 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.

5. Apparatus and Reagents

5.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure.

6. Hazards

6.1 For hazards to be observed in the use of certain reagents in this test method, refer to Practices E50.

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

7. Sampling

7.1 For procedures for sampling the materials, refer to those parts of Practice E1806.

8. Rounding Calculated Values

8.1 Calculated values shall be rounded to the desired number of places as directed in Practice E29.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practice E173. The Reproducibility R_2 of Practice E173 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability R_1 of Practice E173 corresponds to the Repeatability Index r of Practice E1601.

TOTAL CARBON BY THE COMBUSTION INSTRUMENTAL MEASUREMENT TEST METHOD

10. Scope

10.1 This test method covers the determination of carbon in concentrations from 0.005 % to 4.5 %.

11. Summary of Test Method

11.1 The carbon is converted to carbon dioxide by combustion in a stream of oxygen.

11.1.1 *Thermal Conductivity Test Method*—The carbon dioxide is absorbed on a suitable grade of zeolite, released by heating the zeolite, and swept by helium or oxygen into a chromatographic column. Upon elution, the amount of carbon dioxide is measured in a thermistor-type conductivity cell. Refer to Fig. 1.

11.1.2 *Infrared (IR) Absorption, Test Method A*—The amount of carbon dioxide is measured by infrared (IR) absorption. Carbon dioxide (CO_2) absorbs IR energy at a precise wavelength within the IR spectrum. Energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed to only CO_2 and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measure chamber. Total carbon, as CO_2 , is monitored and measured over a period of time. Refer to Fig. 2.

11.1.3 *Infrared (IR) Absorption, Test Method B*—The detector consists of an IR energy source, a separate measure chamber and reference chamber, and a diaphragm acting as one plate of a parallel plate capacitor. During specimen combustion, the flow of CO_2 with its oxygen gas carrier is routed through the measure chamber while oxygen alone passes through the reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm (capacitor plate). Part of the IR energy is absorbed by the CO_2 present in the measure chamber while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm, thus distorting it. This distortion alters the fixed capacitance creating an electric signal change that is amplified for measurement as CO_2 . Total carbon, as CO_2 , is monitored and measured over a period of time. Refer to Fig. 3.

11.1.4 *Infrared (IR) Absorption, Test Method C, Closed Loop*—The combustion is performed in a closed loop, where CO and CO_2 are detected in the same infrared cell. Each gas is measured with a solid state energy detector. Filters are used to pass the appropriate IR wavelength to each detector. In the absence of CO and CO_2 , the energy received by each detector is at its maximum. During combustion, the IR absorption properties of CO and CO_2 gases in the chamber cause a loss of energy; therefore a loss in signal results which is proportional to concentrations of each gas in the closed loop. Total carbon, as CO_2 plus CO, is monitored and measured over a period of time. Refer to Fig. 4.

11.2 This test method is written for use with commercial analyzers, equipped to perform the above operations automatically and calibrated using steels of known carbon content.

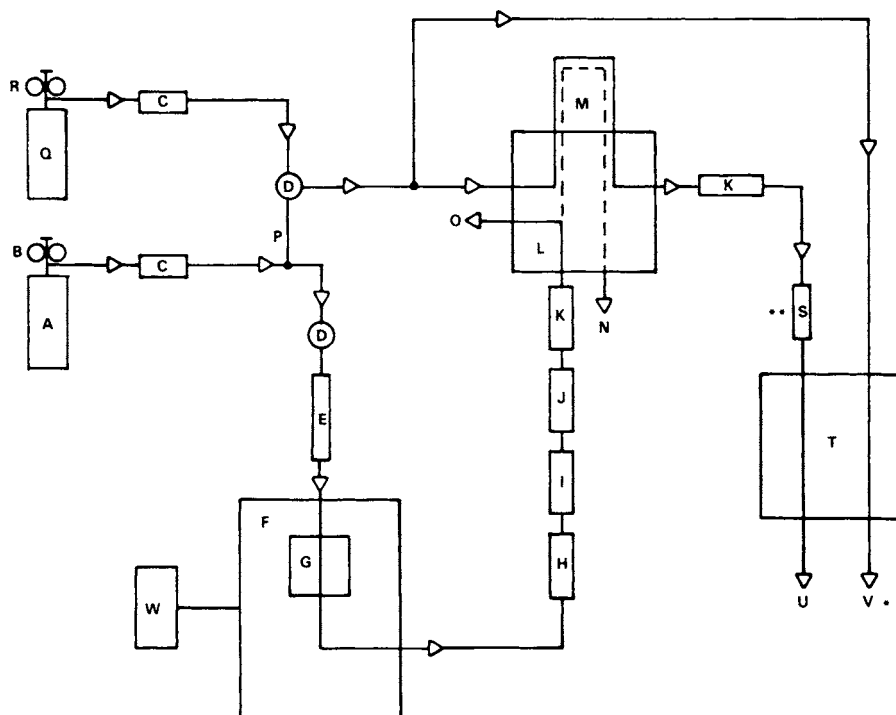
12. Interferences

12.1 For the scope of elements typically found in materials to be tested by this method refer to 1.1.

13. Apparatus

13.1 *Combustion and Measurement Apparatus*—See Figs. 1-4.

13.2 *Crucibles*—Use crucibles that meet or exceed the specifications of the instrument manufacturer and prepare the crucibles by heating in a suitable furnace for not less than 40 min at approximately 1000 °C. Remove from the furnace and cool before use. Crucibles may be stored in a desiccator prior to use. Heating of crucibles is particularly important when analyzing for low levels of carbon and may not be required if the material to be analyzed has higher levels of carbon such as



A—High Purity Oxygen
 B—Oxygen Regulator (2 Stage)
 C—Sodium Hydroxide Impregnated Clay/Magnesium Perchlorate
 D—Secondary Pressure Regulator
 E—Flowmeter
 F—Induction Furnace
 G—Combustion Tube
 H—Dust Trap
 I—Manganese Dioxide
 J—Heated CO to CO₂ Converter
 K—Magnesium Perchlorate
 L—Valve Manifold

M—CO₂ Collection Trap
 N—Furnace Combustion Exhaust
 O—Furnace Purge Exhaust
 P—Metal Connector To Use Oxygen As Carrier Gas
 Q—High Purity Helium
 R—Helium Regulator (2 Stage)
 S—Chromatographic Column
 T—TC Cell/Readout
 U—Measure Flowmeter
 V—Reference Flowmeter
 W—Furnace Power Stat

* May be sealed chamber if oxygen is carrier gas.

** Not required if oxygen is carrier gas.

FIG. 1 Apparatus for Determination of Carbon by the Combustion Thermal Conductivity Test Method

that found in pig iron. Above certain concentrations, as determined by the testing laboratory, the nontreatment of crucibles will have no adverse effect. The analytical ranges for the use of untreated crucibles shall be determined by the testing laboratory and supporting data shall be maintained on file to validate these ranges.

13.3 *Crucible Tongs*—Capable of handling recommended crucibles.

14. Reagents

14.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

14.2 *Acetone*—The residue after evaporation shall be < 0.0005 %.

14.3 *Copper (Low Carbon)*, granular (10 mesh to 30 mesh) (Note 1).

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K. (<http://uk.vwr.com>), and the *United States Pharmacopeia—National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD (<http://www.usp.org/USPNF>).

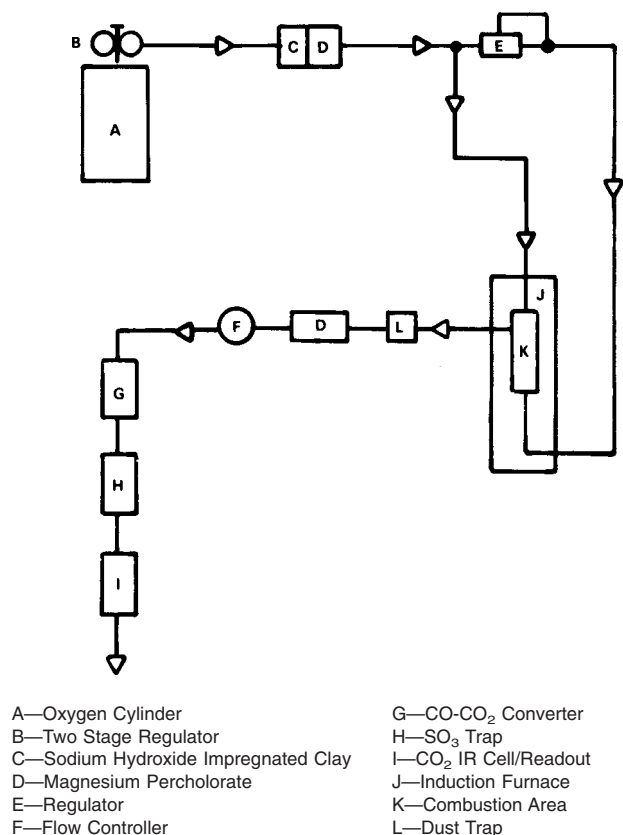


FIG. 2 Infrared Absorption Test Method A

14.4 *Magnesium Perchlorate*, (known commercially as *Anhydron*) — Use the purity specified by the instrument manufacturer.

14.5 *Oxygen*—Purity as specified by the instrument manufacturer.

14.6 *Platinum or Platinized Silica*, heated to 350 °C for the conversion of carbon monoxide to carbon dioxide. Use the form specified by the instrument manufacturer.

14.7 *Sodium Hydroxide*, on clay (known commercially as *Ascarite II*) — Use the purity specified by the instrument manufacturer.

14.8 *Tungsten (Low Carbon) Accelerator*, 12 mesh to 20 mesh (**Note 1**).

14.9 *Tungsten-Tin (Low Carbon) Accelerator*, 20 mesh to 40 mesh or 12 mesh to 20 mesh.

NOTE 1—The accelerator should contain no more than 0.001 % carbon. If necessary, wash three times with acetone by decantation to remove organic contaminants and dry at room temperature. The mesh size is critical to the inductive coupling which heats the sample. Some manufacturers of accelerators may not certify the mesh size on a lot to lot basis. These accelerators may be considered acceptable for use without verifying the mesh size.

15. Preparation of Apparatus

15.1 Assemble the apparatus as recommended by the manufacturer.

15.2 Test the furnace and analyzer to ensure the absence of leaks and make the required electrical power connections. Prepare the analyzer for operation in a manner consistent with

the manufacturer's instructions. Change the chemical reagents and filters at the intervals recommended by the instrument manufacturer. Make a minimum of two determinations using the specimen and accelerator as directed in **18.1.2** and **18.1.3** to condition the instrument before attempting to calibrate the system or determine the blank. Avoid the use of reference materials for instrument conditioning.

16. Sample Preparation

16.1 The specimens should be uniform in size, but not finer than 40 mesh. Specimens will typically be in the form of chips, drillings, slugs, or solids. Specimens shall be free of any residual lubricants and cutting fluids. It may be necessary to clean specimens to remove residual lubricants and cutting fluids. Any cleaned specimens shall be rinsed in acetone and dried completely before analysis.

16.2 If necessary, wash in acetone or another suitable solvent and dry.

17. Calibration

17.1 Calibration Reference Materials (**Note 2**):

17.1.1 For Range I, 0.005 % to 0.10 % carbon, select three certified reference materials containing approximately 0.005 %, 0.05 %, and 0.10 % carbon and designate them as Calibrants A, B, and C, respectively. Some labs may use accelerator with a certified carbon value as Calibrant A.

17.1.2 For Range II, 0.10 % to 1.25 % carbon, select two certified reference materials containing approximately 0.12 % and 1.00 % carbon and designate them as Calibrants BB and CC, respectively.

17.1.3 For Range III, 1.25 % to 4.50 % carbon, select two certified reference materials containing approximately 1.25 % and 4.00 % carbon and designate them as Calibrants BBB and CCC, respectively.

NOTE 2—The uncertainty of results obtained using this test method is dependent on the uncertainty of the values assigned to the calibration reference materials. The homogeneity of the reference materials shall be considered as well, if it was not included in the derivation of the published uncertainty values.

17.2 Adjustment of Response of Measurement System:

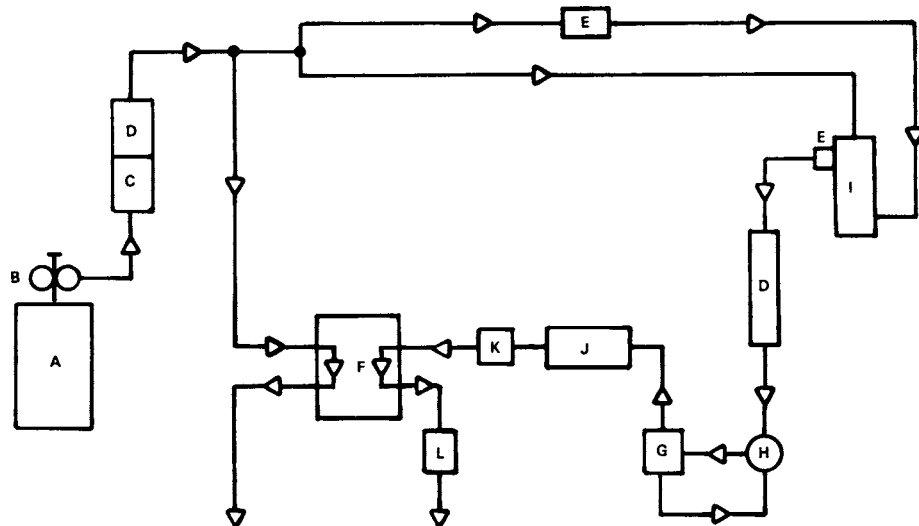
17.2.1 Modern instruments may not require adjustment of the measurement system response prior to calibration. For these instruments proceed directly to **17.3** after the conditioning runs described in **15.2**.

17.2.2 Transfer 1.0 g of Calibrant B, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator to a crucible. Some manufacturers provide scoops that dispense approximately 1.5 g of accelerator. Once it is verified that the scoop delivers this approximate mass, it is acceptable to use this device for routine dispensing of accelerator.

17.2.3 Proceed as directed in **18.1.2** and **18.1.3**.

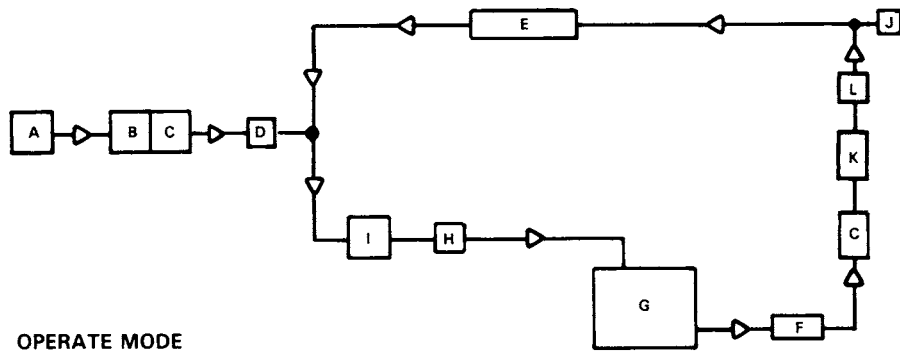
17.2.4 Repeat **17.2.2** and **17.2.3** until the absence of drift is indicated by stable carbon readings being obtained. Consistency is indicated by consecutive runs agreeing within 0.001 % carbon. If using an instrument which requires manual adjustment, adjust the signal to provide a reading within ± 0.003 of the certified percent carbon value for the certified reference material.

17.3 Determination of Blank Reading—Range I:

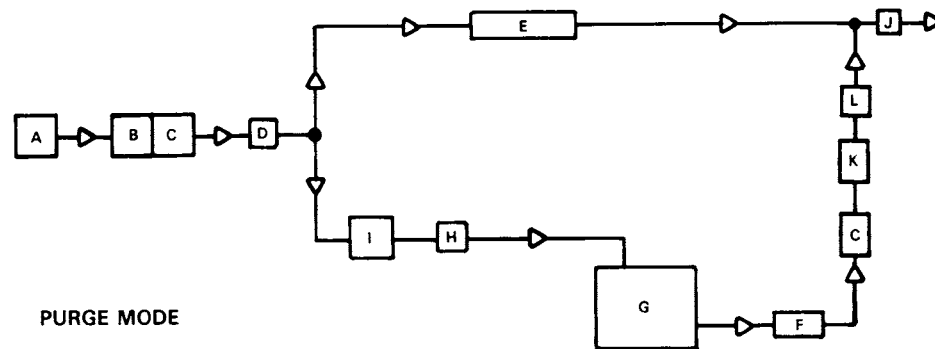


- | | |
|-------------------------------------|-----------------------------------|
| A—Oxygen Cylinder | G—Orifice |
| B—Two Stage Regulator | H—Pressure Regulator |
| C—Sodium Hydroxide Impregnated Clay | I—Combustion Chamber |
| D—Magnesium Perchlorate | J—CO to CO ₂ Converter |
| E—Dust Trap | K—SO ₃ Trap |
| F—IR Cell/Readout | L—Measure Flow Rotameter |

FIG. 3 Infrared Absorption Test Method B



OPERATE MODE



PURGE MODE

- | | |
|-------------------------------------|-----------------------------------|
| A—Oxygen Cylinder | G—Furnace |
| B—Sodium Hydroxide Impregnated Clay | H—Pump |
| C—Magnesium Perchlorate | I—Flow Meter |
| D—Press Regulator | J—Exhaust |
| E—IR Cell/Readout | K—CO to CO ₂ Converter |
| F—Dust Trap | L—SO ₃ Trap |

FIG. 4 Infrared Absorption Test Method C—Closed Loop

17.3.1 Add approximately 1.5 g of accelerator into a crucible. If required, 1.0 g of Calibrant A, weighed to the nearest 1 mg, may be added to the crucible.

17.3.2 Proceed as directed in 18.1.2 and 18.1.3.

17.3.3 Repeat 17.3.1 and 17.3.2 a sufficient number of times to establish that low (less than 0.002 % carbon) and stable (± 0.0002 % carbon) readings are obtained. Blank values are equal to the total result of the accelerator. If Calibrant A was used, blank values are equal to the total result of the accelerator and Calibrant A minus the certified value of Calibrant A.

17.3.4 Record the average value of the last three or more stable blank determinations.

17.3.5 If the blank readings are too high or unstable, determine the cause, correct it, and repeat the steps as directed in 17.3.1-17.3.4.

17.3.6 Enter the average blank value in the analyzer (Note 3). Refer to the manufacturer's instructions for specific instructions on performing this function. Typically the instrument will electronically compensate for the blank value.

NOTE 3—If the unit does not have this function, the blank value shall be subtracted from the total result prior to any calculation.

17.4 *Determination of Blank Reading—Range II*—Proceed as directed in 17.3.

17.5 *Determination of Blank Reading—Range III*:

17.5.1 Transfer 0.5 g of Calibrant A, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator to a crucible.

17.5.2 Proceed as directed in 17.3.2-17.3.6.

17.6 *Calibration—Range I (0.005 % to 0.10 % Carbon)*:

17.6.1 Weigh four 1.0 g specimens of Calibrant C, to the nearest 1 mg, then place in crucibles. To each, add approximately 1.5 g of accelerator (see Note 5).

17.6.2 Follow the calibration procedure recommended by the manufacturer. Use Calibrant C as the primary calibrant and analyze at least three specimens to determine the measurement response to be used in the calibration regression. Treat each specimen, as directed in 18.1.2 and 18.1.3, before proceeding to the next one.

17.6.3 Confirm the calibration by analyzing Calibrant C following the calibration procedure. The result should agree with the certified value within a suitable confidence interval (see Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 1, the calibration is acceptable.

$$\text{Test Result} - t \cdot s \leq \text{Certified Value} \leq \text{Test Result} + t \cdot s \quad (1)$$

where:

s = standard deviation of the analyses run in 17.6,

n = number of analyses (that is, 3 to 5), and

t = Student's t value, which is for $n = 3$, $t = 4.30$; for $n = 4$, $t = 3.18$; for $n = 5$, $t = 2.78$ at the 95 % confidence level.

NOTE 4—The procedure for verifying calibrants outlined in the original version of this test method required the test result to be compared to "the uncertainty limits of the certified value for the calibrant," typically interpreted as the range defined by the certified value plus or minus its associated uncertainty. The original version was utilized in the generation

of the data in this test method's precision and bias statements. The current method in 17.6.3 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 ($n > 30$), t may be set equal to 2 at the 95 % confidence level. At its discretion, the laboratory may choose to set a smaller range for the acceptable test result.

17.6.4 Weigh at least two 1.0 g specimens of Calibrant B, weighed to the nearest 1 mg, and transfer them to crucibles. To each, add approximately 1.5 g of accelerator.

17.6.5 Treat each specimen as directed in 18.1.2 and 18.1.3 before proceeding to the next one.

17.6.6 Record the results of 17.6.4 and 17.6.5 and compare them to the certified carbon value of Calibrant B. The result should agree with the certified value within a suitable confidence interval (see Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 1, the calibration is acceptable. If not, refer to the manufacturer's instructions for checking the linearity of the system.

NOTE 5—The use of 1.5 g of accelerator may not be sufficient for all determinations. The required amount is determined by the analyzer used, induction coil spacing, position of the crucible in the induction coil, age and strength of the oscillator tube, and type of crucible being used. Use the amount required to produce proper sample combustion using the same amount throughout the entire test method.

17.7 *Calibration—Range II (0.10 % to 1.25 % carbon)*:

17.7.1 Proceed as directed in 17.6.1-17.6.3, using Calibrant CC.

17.7.2 Proceed as directed in 17.6.4-17.6.6, using Calibrant BB.

17.8 *Calibration—Range III (1.25 % to 4.50 % carbon)*:

17.8.1 Weigh four 0.5 g specimens of Calibrant CCC, to the nearest 1 mg, and place in crucibles. To each, add approximately 1.5 g of accelerator. Follow the calibration procedure recommended by the manufacturer. Use Calibrant CCC as the primary calibrant and analyze at least three specimens to determine the calibration slope. Treat each specimen, as directed in 18.1.2 and 18.1.3, before proceeding to the next one.

17.8.2 Confirm the calibration by analyzing Calibrant CCC following the calibration procedure. The result should agree with the certified value within a suitable confidence interval (see Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 1, the calibration is acceptable.

17.8.3 If not, repeat 17.8.1 and 17.8.2.

17.8.4 Weigh at least two 0.5 g specimens of Calibrant BBB, weighed to the nearest 1 mg, and transfer to crucibles. To each, add approximately 1.5 g of accelerator.

17.8.5 Treat each specimen as described in 18.1.2 and 18.1.3 before proceeding to the next one.

17.8.6 Record the results of 17.8.4 and 17.8.5 and compare to the certified carbon value of Calibrant BBB. The result

should agree with the certified value within a suitable confidence interval (see [Note 4](#)). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 1, the calibration is acceptable. If not, refer to manufacturer's instructions for checking the linearity of the analyzer ([Note 6](#)).

NOTE 6—Verify the calibration when: (1) a different lot of crucibles is used, (2) a different lot of accelerator is used, (3) the system has been in use for 4 h, (4) the oxygen supply has been changed, and (5) the system has been idle for 1 h. Verification should consist of analyzing at least one specimen of each calibrant. Recalibrate as necessary.

18. Procedure

18.1 Procedure—Range I:

18.1.1 Stabilize the furnace and analyzer as directed in Section 15. Transfer approximately 1.0 g of specimen and approximately 1.5 g of accelerator to a crucible. (See [13.2](#).)

18.1.2 Place the crucible on the furnace pedestal and raise the pedestal into position. Use crucible tongs to handle the crucibles.

18.1.3 Refer to the manufacturer's recommended procedure regarding entry of specimen mass and blank value. Start the analysis cycle.

18.2 Procedure—Range II—Proceed as directed in [18.1](#).

18.3 Procedure—Range III—Proceed as directed in [18.1](#), using a 0.5 g specimen.

19. Calculation

19.1 The calibration function of the equipment shall yield a linear plot described by Eq 2.

$$Y = mX + b \quad (2)$$

where:

Y = measurement response,

M = slope,

X = calibrant concentration, and

b = Y intercept.

Calculation of the calibration function shall be done using a linear least squares regression. Some manufacturers recommend the use of a curve weighting factor where the calibrant concentration is derived as $1/X$. It is acceptable to use this type of curve weighting.

19.2 Since most modern commercially available instruments calculate mass fraction concentrations directly, including corrections for blank and sample mass, manual calculations by the analyst are not required.

NOTE 7—If the analyzer does not compensate for blank and sample mass values, then use the following formula:

$$\text{Carbon, \%} = [(A - B) \times C/D] \quad (3)$$

where:

A = DVM (Digital Volt Meter) reading for specimen,

B = DVM reading for blank,

C = mass compensator setting, and

D = specimen mass, g.

20. Precision and Bias ⁵

20.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in [Tables 1-3](#). Testing was performed in compliance with Practice [E173](#) (see [9.1](#)).

20.2 *Bias*—No information on the bias of this method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

SULFUR BY THE COMBUSTION-INFRARED ABSORPTION TEST METHOD (POTASSIUM SULFATE CALIBRATION)

21. Scope

21.1 This test method covers the determination of sulfur in the range of 0.001 % to 0.01 %. As written, this test method is not applicable to cast iron samples.

22. Summary of Test Method

22.1 The sample is combusted in a stream of oxygen that converts the sulfur in the sample to sulfur dioxide. The sulfur is measured using infrared absorption spectrometry

22.1.1 *Infrared Absorption Test Method A*—Sulfur dioxide (SO_2) absorbs IR energy at a precise wavelength within the IR spectrum. Energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Therefore, the absorption of IR energy can be attributed to only SO_2 and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measure chamber.

⁵ Supporting data are available from ASTM International Headquarters. Request RR:E01-1093.

TABLE 1 Statistical Information—Carbon, Range I

Test Specimen	Carbon Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
1. Electrolytic iron (NIST 365, 0.0068 C)	0.007	0.002	0.003
2. Bessemer carbon steel (NIST 8j, 0.081 C)	0.080	0.003	0.006
3. Type 304L stainless steel 18Cr-8Ni (NIST 101f, 0.014 C)	0.014	0.002	0.004
4. Type 446 stainless steel 26Cr (NIST 367, 0.093 C)	0.094	0.003	0.004
5. Nickel steel 36Ni (NIST 126b, 0.090 C)	0.092	0.003	0.004
6. Waspaloy 57Ni-20Cr-14Co-4Mo (NIST 349, 0.080 C)	0.078	0.003	0.004
7. Silicon steel (NIST 131a, 0.004 C)	0.004	0.002	0.002
8. High temperature alloy A286 26Ni-15Cr (NIST 348, 0.044 C)	0.046	0.003	0.004

TABLE 2 Statistical Information—Carbon, Range II

Test Specimen	Carbon Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
1. Basic open hearth steel (NIST 11h, 0.200 C)	0.201	0.006	0.010
2. Basic open hearth carbon steel (NIST 337, 1.07 C)	1.087	0.039	0.053
3. Low alloy electric furnace steel (NIST 51b, 1.21 C)	1.224	0.039	0.048
4. High temperature nickel alloy (LE 105, 0.130 C)	0.130	0.005	0.008
5. Tool steel 8Co-9Mo-2W-4Cr-2V (NIST 153a, 0.902 C)	0.905	0.023	0.027
6. Type 416 stainless steel (NIST 133b, 0.128 C)	0.126	0.005	0.013
7. Low alloy steel 1Cr (NIST 163, 0.933 C)	0.934	0.016	0.020

TABLE 3 Statistical Information—Carbon, Range III

Test Specimen	Carbon Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
1. Tool steel (CISRI 150, 1.56 C)	1.550	0.027	0.049
2. Low alloy electric furnace steel (NIST 51b, 1.21 C)	1.228	0.039	0.050
3. Cast iron (LECO 501-105, 2.20 C)	2.202	0.044	0.056
4. Ductile iron (LECO 501-083, 4.24 C)	4.244	0.083	0.091
5. White iron (LECO 501-024, 3.25 C)	3.274	0.064	0.074
6. Iron (BAM 035-1, 1.31 C)	1.314	0.034	0.048
7. Ferritic stainless steel (BAM 228-1, 2.05 C)	2.040	0.027	0.055

Total sulfur, as SO_2 , is monitored and measured over a period of time. Refer to Fig. 5.

22.1.2 *Infrared Absorption Test Method B*—The combustion is performed in a closed loop where SO_2 is detected in an infrared cell. The SO_2 is measured with a solid state energy detector, and filters are used to pass the appropriate IR wavelength to the detector. During combustion, the IR absorption properties of the SO_2 gas in the chamber causes a loss of energy, therefore a loss in signal results which is proportional to the concentration of the gas in the closed loop. Total sulfur, as SO_2 , is measured over a period of time. Refer to Fig. 6.

22.1.3 *Infrared Absorption Test Method C*—The detector consists of an IR energy source, a separate measure chamber and reference chamber, and a diaphragm acting as one plate of a parallel plate capacitor. During specimen combustion, the flow of SO_2 with its oxygen gas carrier is routed through the measure chamber while oxygen alone passes through the

reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm (capacitor plate). Part of the IR energy is absorbed by the SO_2 present in the measure chamber while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm, thus distorting it. This distortion alters the fixed capacitance creating an electric signal change that is amplified for measurement as SO_2 . Total SO_2 is measured over a period of time. Refer to Fig. 7.

23. Interferences

23.1 The elements ordinarily present do not interfere. For the scope of elements typically found in materials to be tested by this method refer to 1.1.

24. Apparatus

24.1 *Combustion and Measurement Apparatus*—See Figs. 5-7.

24.2 *Crucibles*—Use crucibles that meet or exceed the specifications of the instrument manufacturer and prepare the crucibles by heating in a suitable furnace for not less than 40 min at approximately 1000 °C. Remove from the furnace and cool before use. Crucibles may be stored in a desiccator prior to use. Above certain concentrations, as determined by the testing laboratory, the nontreatment of crucibles will have no adverse effect. The analytical ranges for the use of untreated crucibles shall be specified by the testing laboratory, and supporting data shall be maintained on file to validate these ranges.

24.3 *Micropipet*, (50 μL).

24.4 *Crucible Tongs*—Capable of handling recommended crucibles.

24.5 *Tin Capsules*—Approximate dimensions: diameter 6 mm, length 20 mm. Use the purity specified by the instrument manufacturer. Wash twice with acetone and dry at approximately 90 °C for not less than 4 h prior to use.

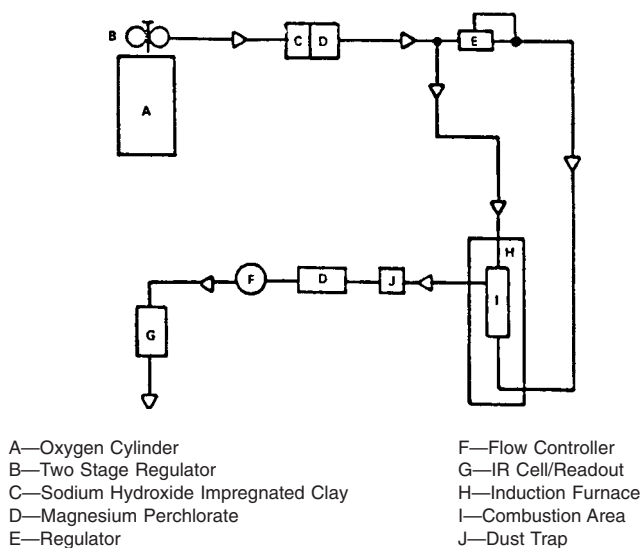
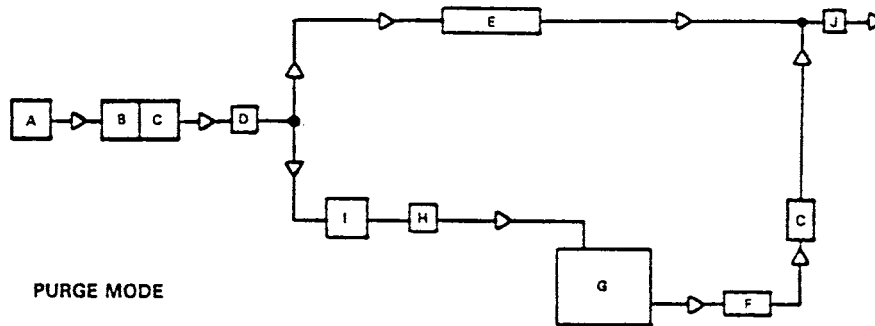
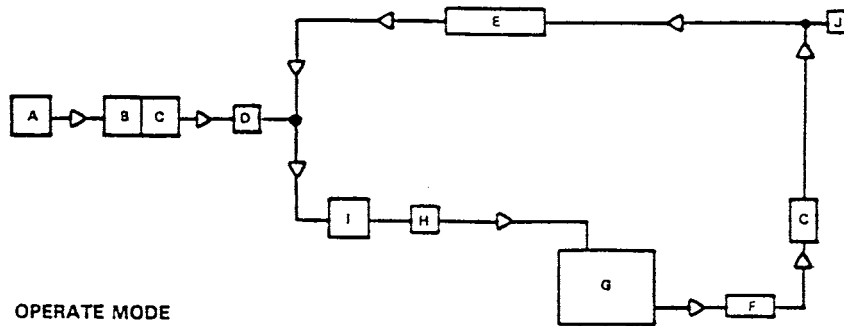


FIG. 5 Infrared Absorption Test Method A



A—Oxygen Cylinder	F—Dust Trap
B—Sodium Hydroxide Impregnated Clay	G—Furnace
C—Magnesium Perchlorate	H—Pump
D—Press Regulator	I—Flow Meter
E—IR Cell/Readout	J—Exhaust

FIG. 6 Infrared Absorption Test Method B

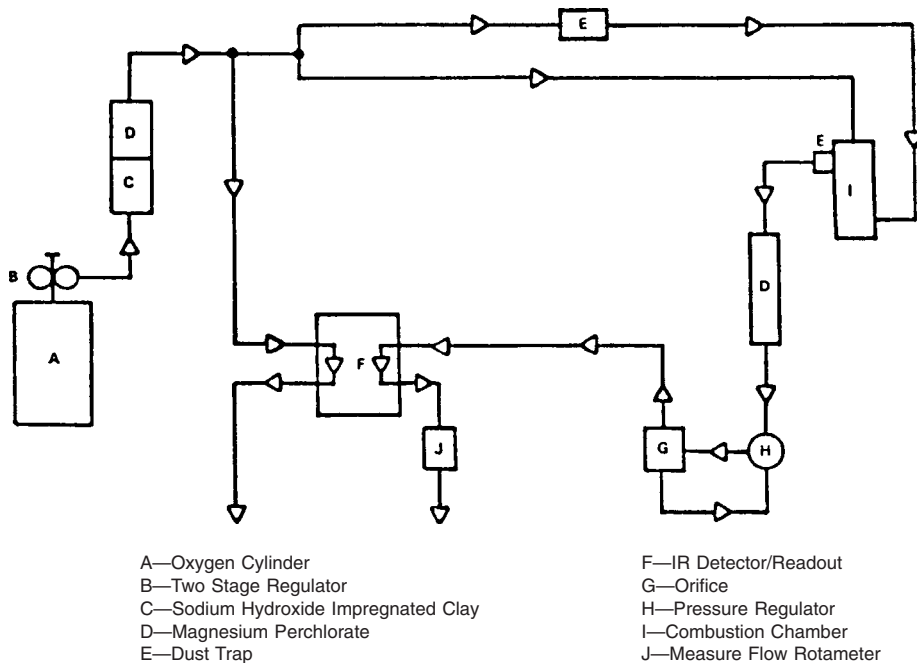


FIG. 7 Infrared Absorption Test Method C

25. Reagents

25.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

25.2 *Acetone*—The residue after evaporation shall be < 0.0005 %.

25.3 *Iron (purity, 99.8 % minimum)*—shall be free of sulfur or contain a low known sulfur content.

25.4 *Magnesium Perchlorate*, (known commercially as *Anhydron*). Use the purity specified by the instrument manufacturer.

25.5 *Oxygen*—Purity as specified by the instrument manufacturer.

25.6 *Potassium Sulfate (K₂SO₄)*—Dry 20 g of K₂SO₄ at 105 °C to 110 °C for not less than 1 h to a constant mass. Cool in a desiccator.

25.7 *Sodium Hydroxide*, on clay (known commercially as *Ascarite II*). Use the purity specified by the instrument manufacturer.

25.8 *Tungsten Accelerator (Low Sulfur)*:

Minus 20 mesh to +40 mesh.

25.9 *Tungsten-Tin Accelerator*, Minus 12 mesh to +40 mesh or -12 mesh to +20 mesh.

NOTE 8—The accelerator should contain no more than 0.001 % sulfur. If necessary, wash three times with acetone by decantation to remove organic contaminants and dry at room temperature. The mesh size is critical to the inductive coupling that heats the sample. Some manufacturers of accelerators may not certify the mesh size on a lot to lot basis. These accelerators may be considered acceptable for use without verifying the mesh size.

25.10 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

26. Preparation of Apparatus

26.1 Assemble the apparatus as recommended by the manufacturer.

26.2 Test the furnace and analyzer to ensure the absence of leaks, and make the required electrical power connections. Prepare the analyzer for operation in accordance with manufacturer's instructions. Change the chemical reagents and filters at the intervals recommended by the instrument manufacturer. Make a minimum of two determinations using the specimen and accelerator as directed in 29.2 and 29.3 to condition the instrument before attempting to calibrate the system or determine the blank. Avoid the use of reference materials for instrument conditioning.

27. Sample Preparation

27.1 The specimen should be uniform in size, but not finer than 40 mesh. Specimens will typically be in the form of chips, drillings, slugs, or solids. Specimens shall be free of any residual lubricants or cutting fluids, or both. It may be necessary to clean specimens to remove residual lubricants or

cutting fluids, or both. Any cleaned specimens shall be rinsed in acetone and dried completely before analysis.

28. Calibration

28.1 *Calibration Reference Materials*:

28.1.1 Weigh to the nearest 0.0001 g the following masses of K₂SO₄ to obtain the indicated solution concentrations:

Sulfur Solution	K ₂ SO ₄ (g)	Sulfur Concentration (mg/mL)
A	0.1087	0.2
B	0.2718	0.5
C	0.5435	1.0
D	1.0870	2.0
H	0.0000	0.0

28.1.2 Dissolve each quantity of K₂SO₄ in 50 mL of water in five 100-mL beakers.

28.1.3 Transfer quantitatively each solution to a 100-mL volumetric flask. Dilute to volume and mix.

28.1.4 Using a pipet, transfer 50 µL of the following sulfur solutions to individual tin capsules. Prepare the number of replicates indicated and then proceed as directed in 28.1.5.

Sulfur Solution	S (µg)	S, % in the Test Portion	Number of Replicates
H	0	0.0000	5
A	10	0.0010	2
B	25	0.0025	5
C	50	0.0050	2
D	100	0.0100	5

28.1.5 Dry the tin capsules slowly at about 90 °C to full dryness, and cool in a desiccator. Compress the top part of the tin capsule before placing in the instrument.

28.2 *Adjustment of Response of Measurement System*:

28.2.1 Modern instruments may not require adjustment of the measurement system response prior to calibration. For these instruments proceed directly to 28.3 after the conditioning runs described in 26.2.

28.2.2 Transfer one dried capsule of sulfur solution B to a crucible. Add approximately 1.0 g of pure iron, weighed to the nearest 5 mg, and approximately 1.5 g of tungsten accelerator to the crucible. Proceed as directed in 29.2 and 29.3.

28.2.3 Repeat 28.2.2 until the absence of drift is indicated by stable sulfur readings being obtained. Stability is indicated by consecutive runs agreeing within 0.0002 % sulfur. Prepare more capsules of sulfur solution B if necessary. If using an instrument that requires manual adjustment, adjust the signal to provide a reading of 0.0025 % ± 0.0003 % sulfur.

28.3 *Determination of Blank Reading*:

28.3.1 Transfer one dried capsule of sulfur solution H to a crucible. Add approximately 1.0 g of pure iron, weighed to the nearest 5 mg, and approximately 1.5 g of accelerator to the crucible. Some manufacturers provide scoops that dispense approximately 1.5 g of accelerator. Once it is verified that the scoop delivers this approximate mass, it is acceptable to use this device for routine dispensing of accelerator. Proceed as directed in 29.2 and 29.3.

28.3.2 Repeat 28.3.1 a sufficient number of times to establish that low (less than 0.0005 % of sulfur) and stable (± 0.0002 % of sulfur) readings are obtained. Blank values are equal to the total result of accelerator, iron, and tin capsule of solution H (purified water).

28.3.3 Record the average value of at least three consecutive blank determinations.

28.3.4 If the blank readings are too high or unstable, determine the cause, correct it, and repeat the steps as directed in 28.3.1-28.3.3. Prepare more capsules of sulfur solution H if necessary.

28.3.5 Enter the average blank value in the analyzer (Note 9). Refer to the manufacturer's instructions for specific protocol for performing this function. Typically the instrument will electronically compensate for the blank value.

NOTE 9—If the unit does not have this function, the blank value shall be subtracted from the total result prior to any calculation.

28.4 Calibration:

28.4.1 Transfer four dried capsules of sulfur solution D to crucibles. Add approximately 1.0 g of pure iron, weighed to the nearest 5 mg, and approximately 1.5 g of accelerator to each crucible.

28.4.2 Follow calibration procedure recommended by the manufacturer using dried capsules of sulfur solution D as the primary calibrant, analyzing at least three specimens to determine the measurement response to be used in the calibration regression. Treat each capsule as directed in 29.2 and 29.3 before proceeding to the next one.

28.4.3 Confirm the calibration by analyzing a capsule of sulfur solution D after the calibration procedure. The value should be 0.0100 % $\pm$ 0.0005 % sulfur. If not, repeat 28.4.1 and 28.4.2.

28.4.4 Transfer two dried capsules of sulfur solution A, B, and C to crucibles. Add approximately 1.0 g of pure iron, weighed to the nearest 5 mg, and approximately 1.5 g of accelerator to each crucible.

28.4.5 Treat each capsule as directed in 29.2 and 29.3 before proceeding to the next one.

28.4.6 Record the results of 28.4.5 and compare them to the theoretical sulfur values solutions A, B, and C. If they are not within 0.0003 % of the theoretical concentrations of sulfur in the test portions, refer to the manufacturer's instructions for checking the linearity of the system.

NOTE 10—Verify the calibration when: (1) a different lot of crucibles is used, (2) a different lot of accelerator is used, (3) the system been idle for 1 h, (4) the system has been in use for 4 h, and (5) the oxygen supply has been changed. Verification should consist of analyzing at least one specimen of each calibrant. Recalibrate as necessary.

29. Procedure

29.1 Stabilize the furnace and analyzer as directed in Section 26. Transfer approximately 1.0 g of specimen, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator to a crucible. (See 24.2.)

29.2 Place the crucible on the furnace pedestal and raise the pedestal into position. Use crucible tongs to handle the crucibles.

29.3 Refer to manufacturer's recommended procedure regarding entry of specimen mass and blank value. Start the analysis cycle.

NOTE 11—This procedure is for analysis of steel samples and a new blank shall be determined using approximately 1.5 g of accelerator only. Refer to 62.3.

30. Calculation

30.1 The calibration function of the equipment shall yield a linear plot described by Eq 4. Calculation of the calibration function shall be done using a linear least squares regression. Some manufacturers recommend the use of a curve weighting factor where the calibrant concentration is derived as 1/X. It is acceptable to use this type of curve weighting.

30.2 Since most modern commercially available instruments calculate mass fraction concentrations directly, including corrections for blank and sample mass, manual calculations by the analyst are not required.

NOTE 12—If the analyzer does not compensate for blank and sample mass values, then use the following formula:

$$\text{Sulfur, \%} = [(A - B) \times C/D] \quad (4)$$

where:

A = DVM (Digital Volt Meter) reading for specimen,

B = DVM reading for blank,

C = mass compensator setting, and

D = specimen mass, g.

31. Precision and Bias ⁶

31.1 *Precision*—Twenty-five laboratories participated in testing this method under the auspices of WG-3 of ISO Committee TC 17/SC 1 and obtained the data summarized in Table 4. Testing was performed in compliance with Practice E173 (refer to 9.1).

31.2 *Bias*—No information on the bias of this test method is known because suitable reference materials were not available at the time of the interlaboratory study. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

⁶ Supporting data are available from ASTM International Headquarters. Request RR:E01-1041.

TABLE 4 Statistical Information—Sulfur

Test Specimen	Sulfur Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
Low alloy steel (JK 24, 0.0010 S)	0.0010	0.00045	0.00051
Stainless steel (NIST 348, 0.0020 S)	0.00198	0.0005	0.00064
Silicon steel (IRSID 114-1, 0.0037 S)	0.00322	0.00051	0.0007
Plain carbon steel (JSS 240-8, 0.0060 S)	0.00549	0.00055	0.00099
Stainless steel (JSS 652-7, 0.0064 S)	0.00615	0.00084	0.00087

NITROGEN BY THE INERT GAS FUSION THERMAL CONDUCTIVITY TEST METHOD

32. Scope

32.1 This test method covers the determination of nitrogen (N) in concentrations from 0.0010 % to 0.2 % (Note 13).

NOTE 13—The upper limit of the scope has been set at 0.2 % because sufficient numbers of test materials containing higher nitrogen contents were unavailable for testing in accordance with Practice E173. However, recognizing that commercial nitrogen determinators are capable of handling higher concentrations, this test method provides a calibration procedure up to 0.5 %. Users of this test method are cautioned that use of it above 0.2 % is not supported by interlaboratory testing. In this case, laboratories should perform method validation using reference materials.

33. Summary of Test Method

33.1 The specimen, contained in a small, single-use graphite crucible, is fused under a flowing helium atmosphere at a minimum temperature of 1900 °C. 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. Refer to Figs. 8-11.

33.2 This test method is written for use with commercial analyzers equipped to perform the above operations automatically and calibrated using reference materials of known nitrogen content.

34. Interferences

34.1 The elements ordinarily present do not interfere. For the scope of elements typically found in materials to be tested by this method refer to 1.1.

35. Apparatus

35.1 *Fusion and Measurement Apparatus*—See Fig. 8.

35.2 *Graphite Crucibles*—Use the size crucibles recommended by the manufacturer of the instrument. Crucibles shall be composed of high purity graphite.

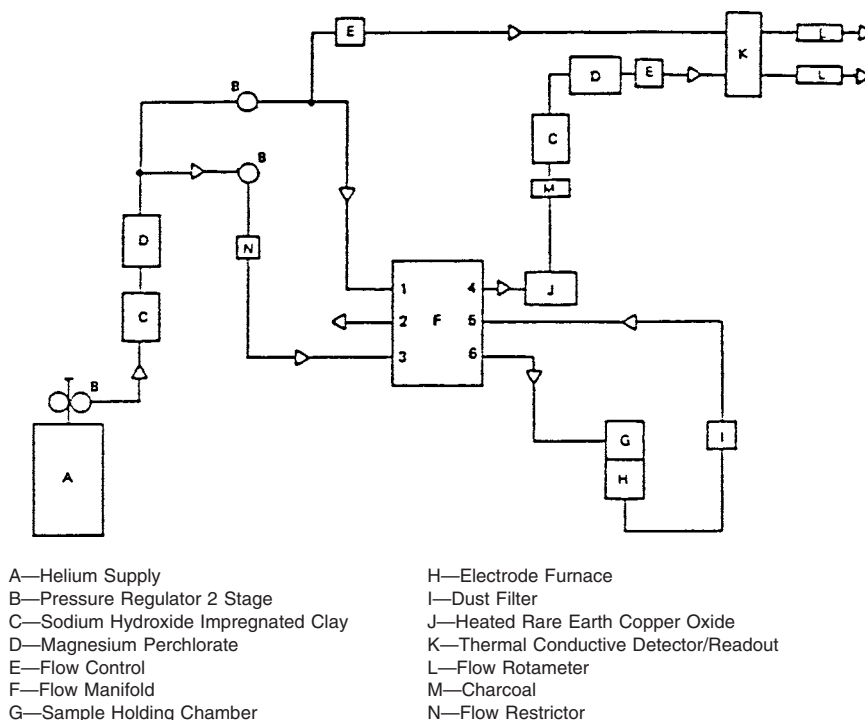
35.3 *Crucible Tongs*—Capable of handling recommended crucibles.

36. Reagents

36.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

36.2 *Acetone*—The residue after evaporation shall be <0.0005 %.

36.3 *Copper*—, use the purity and form specified by the instrument manufacturer.



Manifold Porting

Crucible Degas Flow { 1 to 4
5 to 2
3 to 6
Fusion Flow { 1 to 6
5 to 4
3 & 2

FIG. 8 Nitrogen Test Method A—Flow Diagram

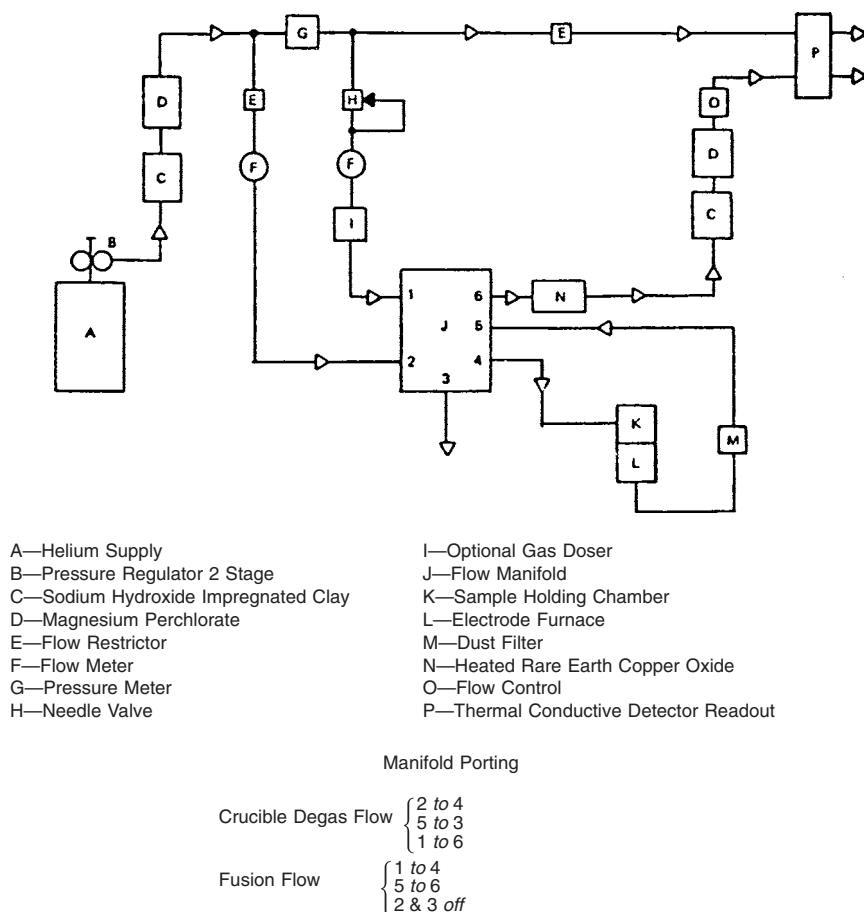


FIG. 9 Nitrogen Test Method B—Flow Diagram

36.4 Helium, high-purity (99.99 %).

36.5 Magnesium Perchlorate, (known commercially as *Anhydron*). Use the purity specified by the instrument manufacturer.

36.6 Rare Earth Copper Oxide—Use the purity as specified by the instrument manufacturer.

36.7 Silica, as specified by the instrument manufacturer.

36.8 Sodium Hydroxide, on clay, (known commercially as *Ascarite II*). Use the purity as specified by the instrument manufacturer.

37. Preparation of Apparatus

37.1 Assemble the apparatus as recommended by the manufacturer.

37.2 Test the furnace and analyzer to ensure the absence of leaks, and make the required electrical power and water connections. Prepare the apparatus for operation in a manner consistent with the manufacturer's instructions. Change the chemical reagents and filters at the intervals recommended by the instrument manufacturer. Make a minimum of two determinations using a specimen as directed in 40.2.1 or 40.2.2 to condition the instrument before attempting to calibrate the system or to determine the blank. Avoid the use of reference materials for instrument conditioning.

38. Sample Preparation

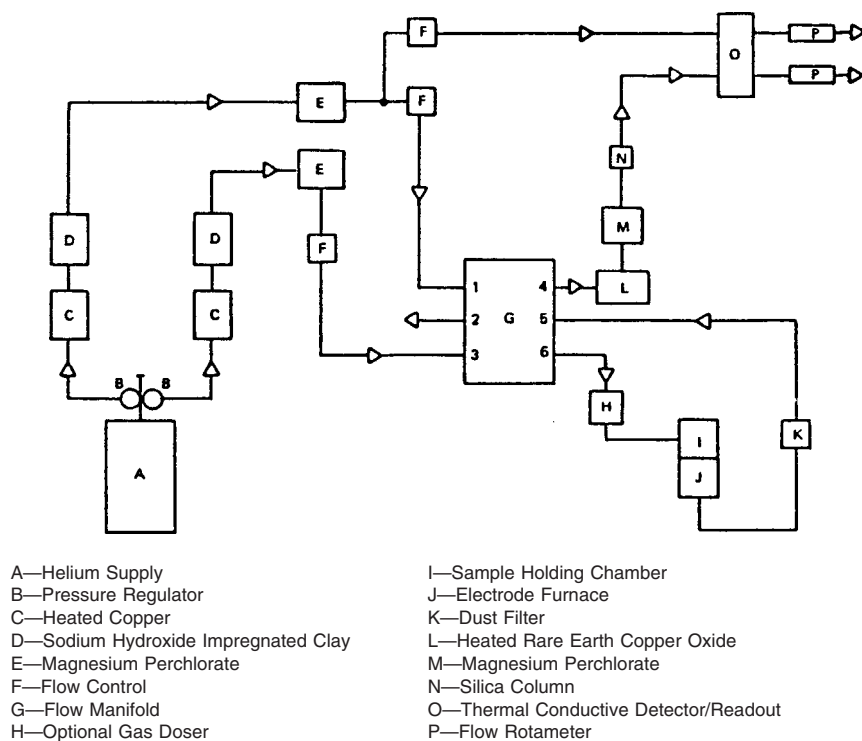
38.1 Practice E1806 provides some guidance for sampling and preparation of steel and iron alloys for gas analysis. Specimens will typically be in the form of chips, drillings, slugs, or solids. Final specimen preparation shall be performed as directed in 38.2 or 38.3 (Note 14).

NOTE 14—Size all specimens to permit free introduction through the loading device of the equipment or directly into the graphite crucible.

38.2 If a slug or solid-form specimens are used, cut them with a water-cooled abrasive cut-off wheel or by another means that will prevent overheating. Abrade the surface to remove surface oxidation. Using a clean file, die grinder, or silicon carbide grinding media. Again, care must be taken not to overheat the sample. If specimens are wet ground it will be necessary to rinse specimens in water followed by an acetone rinse. Samples shall be air dried well prior to analysis.

38.3 Clean, dry chips and millings may be analyzed without additional preparation; however, specimens shall be free of any lubricants and cutting fluids. It may be necessary to clean specimens to remove residual lubricants and cutting fluids. Any cleaned specimens shall be rinsed in acetone and dried completely before analysis.

38.4 Handle prepared specimens with tweezers; not with bare hands.



Manifold Porting

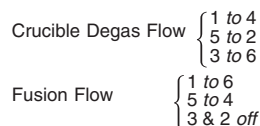


FIG. 10 Nitrogen/Oxygen Test Method A—Flow Diagram

39. Calibration

39.1 Reference Materials:

39.1.1 For Range I of 0.0005 % to 0.10 % nitrogen, select five certified reference materials containing approximately 0.002 %, 0.01 %, 0.03 %, 0.05 %, and 0.10 % nitrogen and designate them as Calibrants A, B, C, D, and E, respectively (Note 15).

39.1.2 For Range II of 0.10 % to 0.50 % nitrogen, select three certified reference materials containing approximately 0.10 %, 0.30 %, and 0.50 % nitrogen and designate them as Calibrants AA, BB, and CC, respectively (Note 15).

NOTE 15—The uncertainty of results obtained using this test method is dependent on the uncertainty of the values assigned to the calibration reference materials. The homogeneity of the reference materials shall be considered as well, if it was not included in the derivation of the published uncertainty values.

39.2 Adjustment of Response of Measurement System:

39.2.1 Modern instruments may not require adjustment of the measurement system response prior to calibration. For these instruments proceed directly to 39.3 after performing the conditioning runs described in 37.2.

39.2.2 Prepare an approximate 1.0 g specimen of Calibrant C weighed to the nearest 1 mg as directed in 38.2 or 38.3.

39.2.3 Proceed as directed in 40.2.1 or 40.2.2.

39.2.4 Repeat 39.2.2 and 39.2.3 and adjust as recommended by the manufacturer until the absence of drift is indicated by consecutive runs agreeing within 0.0004 %.

39.3 Determination of Blank Reading—Ranges I and II:

39.3.1 If the instrument is equipped with an electronic blank compensator, adjust to zero, and proceed with the determination of the blank value.

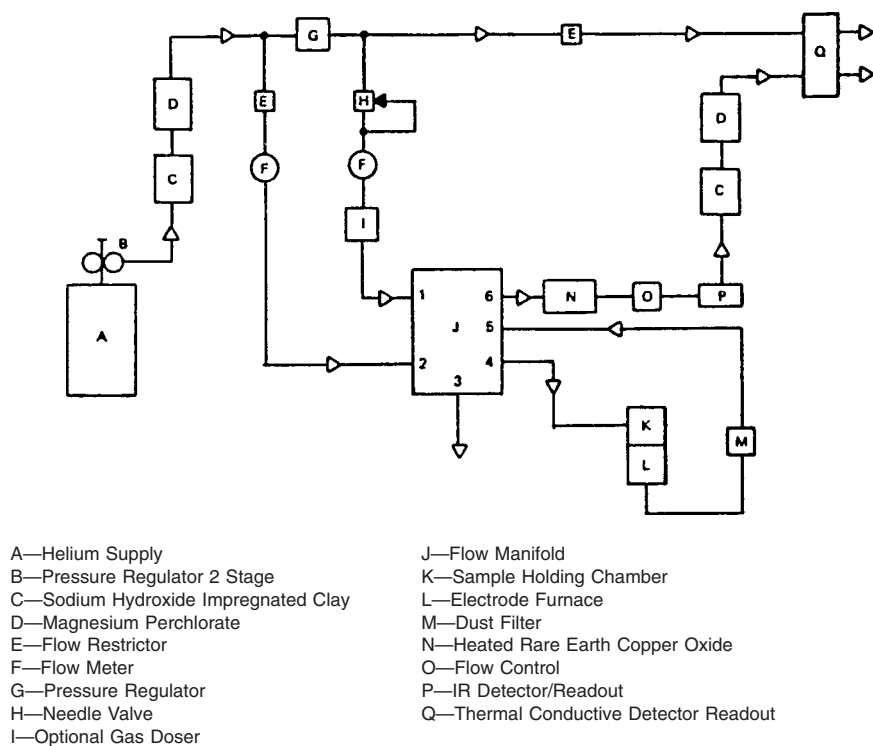
39.3.2 Make three blank determinations as directed in 40.2.1 or 40.2.2 with the sample omitted. Use a fresh crucible each time (Note 16).

NOTE 16—If the loading device is used to analyze the unknown or calibration sample, see Note 14.

39.3.3 If the blank values exceed 0.0003 % or a spread of three consecutive values exceeds 0.0003 %, then determine the cause, make necessary corrections, and repeat 39.3.1 and 39.3.2.

39.3.4 Record the average value of at least three blank readings.

39.3.5 Enter the average blank value in the appropriate mechanism of the analyzer (Note 17). Refer to the manufacturer's instructions for specific instructions on performing this function. This mechanism will electronically compensate for the blank value.



Manifold Porting

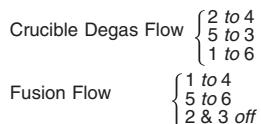


FIG. 11 Nitrogen/Oxygen Test Method B—Flow Diagram

NOTE 17—If the unit does not have this function, the average blank value shall be subtracted from the DVM readings for reference materials and specimens (Note 21).

39.4 Calibration Procedure—Range I:

39.4.1 Prepare four 1.0 g specimens of Calibrant D weighed to the nearest 1 mg, as directed in 38.2 or 38.3.

39.4.2 Follow the calibration procedure recommended by the manufacturer using Calibrant D as the primary calibrant. Analyze Calibrant D at least three times to determine the calibration slope. Treat each specimen as directed in 40.2.1 or 40.2.2 before proceeding to the next one.

39.4.3 Confirm the calibration by analyzing Calibrant D after calibration. The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 5, the calibration is acceptable. If not, repeat 39.4.1 and 39.4.2.

$$\text{test result} - t \cdot s \leq \text{certified value} \leq \text{test result} + t \cdot s \quad (5)$$

where:

s = standard deviation of the analyses run in 39.4.3,

n = number of analyses (that is, 3 to 5), and

t = student's t value which is for $n = 3$, $t = 4.30$; for $n = 4$, $t = 3.18$; for $n = 5$, $t = 2.78$ at the 95 % confidence level.

39.4.4 Prepare two 1.0 g specimens each of Calibrants A, B, C, and E weighed to the nearest 1 mg, as directed in 38.2 or 38.3.

39.4.5 Treat each specimen as directed in 40.2.1 or 40.2.2 before proceeding to the next one.

39.4.6 The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 5, the calibration is acceptable. If not, refer to the manufacturer's instructions for checking the linearity of the system.

NOTE 18—Verify the calibration when: (1) a different lot of crucibles is used, (2) the system has been idle for 1 h, (3) the system has been in use for 4 h, and (4) the helium supply has been changed. Verification should consist of analyzing at least one specimen of each calibrant. Recalibrate as necessary.

39.5 Calibration Procedure—Range II:

39.5.1 Proceed as directed in 39.4.1-39.4.3 using Calibrant CC.

39.5.2 Proceed as directed in 39.4.4-39.4.6 using Calibrants AA and BB (Note 18).

40. Procedure

40.1 Assemble the apparatus and condition it as directed in Section 37.

40.2 Procedure—Ranges I and II:

40.2.1 Manual Operation:

40.2.1.1 Set the analyzer to operate in the manual mode.

40.2.1.2 Place an empty crucible on the furnace lower electrode assembly and close the furnace.

40.2.1.3 Weigh a 1.0 g specimen to the nearest 1 mg and refer to the manufacturer's recommended procedure, including entry of sample mass.

40.2.1.4 Start the analysis cycle, referring to the manufacturer's recommended procedure (Note 19).

40.2.2 Automatic Operation:

40.2.2.1 Set the analyzer to operate in the automatic mode.

40.2.2.2 Place a 1.0 g specimen weighed to the nearest 1 mg in the loading device. Refer to the manufacturer's recommended procedure, including entry of sample mass.

40.2.2.3 Place an empty crucible on the furnace lower electrode assembly and close the furnace.

40.2.2.4 Start the analysis cycle, referring to the manufacturer's recommended procedure (Notes 19 and 20).

NOTE 19—If the samples are to be analyzed in the automatic mode, blank determination and calibration should also be performed in the automatic mode. If samples are to be analyzed in the manual mode, blank determination and calibration should be performed in the manual mode. Solid samples may be analyzed in either automatic or manual mode, but drillings or chips should be analyzed in the manual mode.

NOTE 20—The presence of nitrogen as refractory nitrides in the matrix may affect sample fusion and nitrogen evolution under standard operating conditions of the analyzer. It is therefore recommended that calibrants be of the same or similar composition as the samples to be analyzed when available.

41. Calculation

41.1 The calibration function of the equipment shall yield a linear plot described by Eq 6. Calculation of the calibration function shall be done using a linear least squares regression. Some manufacturers recommend the use of a curve weighting factor where the calibrant concentration is derived as $1/X$. It is acceptable to use this type of curve weighting.

41.2 Since most modern commercially available instruments calculate mass fraction concentrations directly, includ-

ing corrections for blank and sample mass, manual calculations by the analyst are not required. (Note 21).

NOTE 21—If the analyzer does not compensate for blank and sample mass values, then the equation is:

$$\text{Nitrogen, \%} = [(A - B) \times C/D] \quad (6)$$

where:

A = DVM (Digital Volt Meter) reading for specimen,

B = DVM reading for blank,

C = mass compensator setting, and

D = specimen mass, g.

42. Precision and Bias⁷

42.1 Precision—Nine laboratories cooperated in testing this test method and obtained the precision data summarized in Tables 5-7. Testing was performed in compliance with Practice E173 (refer to 9.1).

42.2 Bias—The accuracy of this test method can be inferred from the data in Tables 5-7 by comparing the certified values for nitrogen with the average values obtained (Note 22).

NOTE 22—Although this test method was tested to only 0.22 %, most commercial instruments are believed to be capable of analyzing samples containing nitrogen up to 0.5 %.

OXYGEN BY THE INERT GAS FUSION TEST METHOD

43. Scope

43.1 This test method covers the determination of oxygen in the concentrations from 0.001 % to 0.005 %.

NOTE 23—The upper limit of the scope has been set at 0.005 % because sufficient numbers of test materials containing higher oxygen contents were unavailable for testing in accordance with Practice E173. However, recognizing that commercial oxygen determinators are capable of handling higher concentrations, it may be that this test method can be used for oxygen concentrations outside the scope. In this case, laboratories should perform method validation using reference materials. Users of this test method are cautioned that use of it above 0.005 % is not supported by interlaboratory testing.

44. Summary of Test Method

44.1 This test method is written for use with automated, commercially available analyzers that are based on the inert

⁷ Supporting data are available from ASTM International Headquarters. Request RR:E01-1051.

TABLE 5 Statistical Information—Nitrogen, Range I (chip)

Test Specimen	Nitrogen Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
No. 1 High purity iron (Euro CRM 088.1, 0.0009 % N)	0.0010	0.0005	0.0008
No. 2 High purity iron (JSS-001, 0.0017 % N)	0.0016	0.0004	0.0010
No. 3 Carbon steel (BAM 028/1, 0.0029 % N)	0.0033	0.0007	0.0012
No. 4 Carbon steel (JK NR3B, 0.0054 % N)	0.0051	0.0005	0.0010
No. 5 Carbon steel (JK 2D, 0.0085 % N)	0.0099	0.0013	0.0015
No. 6 Tool steel (NIST 50 C, 0.012 % N)	0.012	0.0008	0.0010
No. 7 Tool steel (NIST 153a, 0.024 % N)	0.026	0.001	0.002
No. 8 Stainless steel (NIST 73c, 0.037 % N)	0.037	0.003	0.003
No. 9 Cast iron (NIST 890, 0.089 % N)	0.088	0.004	0.008

TABLE 6 Statistical Information—Nitrogen, Range II (chip)

Test Specimen	Nitrogen Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
No. 1 High-temperature alloy A661 (Car Tech, 0.1598 % N)	0.115	0.005	0.015
No. 2 Stainless steel (NIST 367, 0.168 % N)	0.158	0.005	0.017
No. 3 Valve steel (LECO 502-016, 0.218 % N)	0.203	0.009	0.020

TABLE 7 Statistical Information—Nitrogen, Range I (solid)

Test Specimen	Nitrogen Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
No. 1 Low alloy steel (NIST 1098, 0.0032 % N)	0.0041	0.0006	0.0014
No. 2 Low alloy steel (NIST 1096, 0.0040 % N)	0.0043	0.0006	0.0011
No. 3 Cast iron (ACIPCO; 0.01 % N)	0.0076	0.0011	0.0014
No. 4 Low alloy steel 4320 (TC, 0.0080 % N)	0.0083	0.0011	0.0015
No. 5 Tool steel (LSC, 0.064 % N)	0.067	0.004	0.006
No. 6 High temperature alloy Inco 600 (LTV, 0.1 % N)	0.088	0.008	0.015
No. 7 Stainless steel, Type 316 (LTV, 0.09 % N)	0.096	0.004	0.007

gas fusion principle and use a variety of gas conditioning and measuring techniques. Certified reference materials should be used for all calibrations.

44.2 The sample, contained in a small, single-use graphite crucible, is fused under a flowing inert gas stream at a temperature sufficient to release oxygen, nitrogen, and hydrogen. The oxygen combines with carbon from the crucible to form carbon monoxide (CO) and is carried by the flowing inert gas stream to either a thermal conductivity or an infrared detector. In some instruments the CO is converted to carbon dioxide (CO₂) and detected in an infrared cell as CO₂. The detector output is compared to that obtained from similar certified reference materials and is displayed as oxygen content of the sample.

44.3 In a typical instrument based on thermal conductivity detection (Fig. 12), the sample is fused in a stream of helium which carries the released gases over copper oxide which oxidizes CO to CO₂ and hydrogen to water. The water is then absorbed by magnesium perchlorate and the remaining nitrogen and carbon dioxide are separated chromatographically. The nitrogen is eluted from the chromatographic column within seconds and is either measured or disregarded. The oxygen (as CO₂) then elutes from the column and enters the measuring cell of the thermistor bridge. Bridge output is integrated and the data are processed and displayed directly as percent oxygen.

44.4 In a typical instrument based on infrared detection (Fig. 13), the sample is fused in a stream of inert gas and the evolved gases are passed directly into a cell through which infrared energy is transmitted. The absorption of infrared energy by the CO in the gas stream causes a reduction in the energy received at an infrared detector. The detector response data are processed and displayed directly as percent oxygen.

45. Interferences

45.1 The elements ordinarily present do not interfere. For the scope of elements typically found in materials to be tested by this method refer to 1.1.

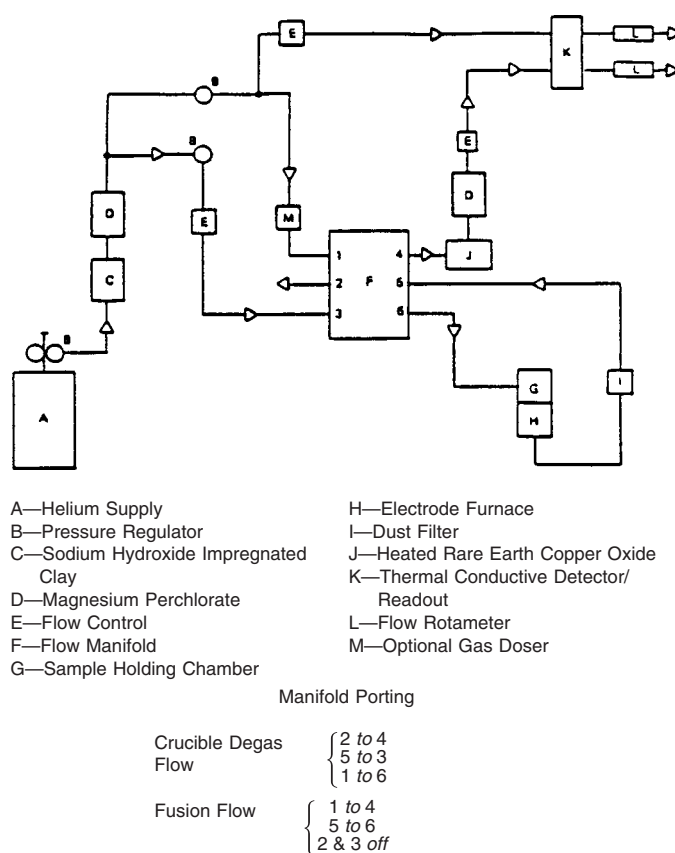
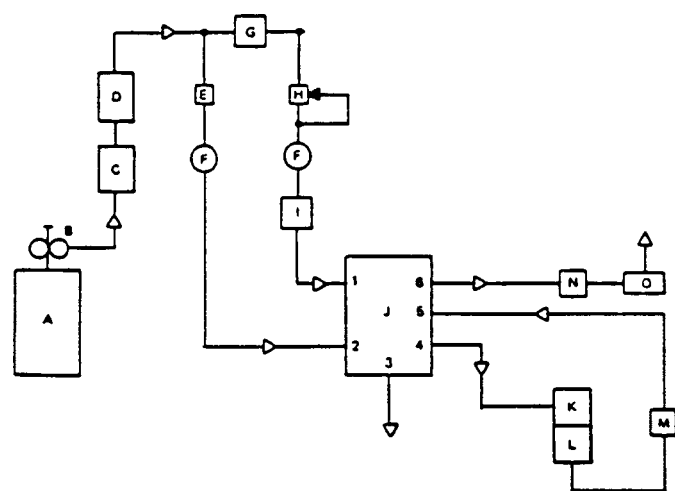


FIG. 12 Apparatus for Determination of Oxygen by the Inert Gas Fusion-Thermal Conductivity Test Method

46. Safety Precautions

46.1 For precautions to be observed in the use of certain reagents in this test method, refer to Practices E50.

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



- | | |
|-------------------------------------|--------------------------|
| A—Inert Gas | I—Optional Gas Doser |
| B—Pressure Regulator 2 Stage | J—Flow Manifold |
| C—Sodium Hydroxide Impregnated Clay | K—Sample Holding Chamber |
| D—Magnesium Perchlorate | L—Electrode Furnace |
| E—Flow Restrictor | M—Dust Filter |
| F—Flow Meter | N—Flow Control |
| G—Pressure Regulator | O—IR Detector/Readout |
| H—Needle Valve | |

Manifold Porting

- | | |
|---------------------|--|
| Crucible Degas Flow | $\begin{cases} 1 \text{ to } 4 \\ 5 \text{ to } 2 \\ 3 \text{ to } 6 \end{cases}$ |
| Fusion Flow | $\begin{cases} 1 \text{ to } 6 \\ 5 \text{ to } 4 \\ 3 \text{ \& 2 off} \end{cases}$ |

FIG. 13 Apparatus for Determination of Oxygen by the Inert Gas Fusion-Infrared Absorption Test Method

47. Apparatus

47.1 *Instrument*—The general features of the instruments used in developing the test data accompanying this test method are shown schematically in Figs. 12 and 13. These units are commercially available.

47.2 *Graphite Crucibles*—The crucibles shall be made of high-purity graphite and should be those recommended by the manufacturer or their equivalent.

48. Reagents

48.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

48.2 *Acetone*—Residue after evaporation shall be <0.0005 %

48.3 *Ascarite II (Sodium Hydroxide on Clay)*—Used in some instruments to absorb residual CO₂ in the inert gas stream. Use the purity specified by the instrument manufacturer.

48.4 *Inert Gas (Helium, Argon, or Nitrogen as Specified for the Instrument being Used)*—99.99 % purity minimum. Ultra high purity is recommended

48.5 *Magnesium Perchlorate (Mg(ClO₄)₂) (known commercially as Anhydron)*—Used in most instruments as a moisture trap. Use the purity specified by the instrument manufacturer.

48.6 *Rare Earth Copper Oxide*, as recommended by the instrument manufacturer.

49. Preparation of Apparatus

49.1 Assemble the apparatus as recommended by the manufacturer. Make the required power, gas, and water connections. Turn on the instrument and allow sufficient warm up time to stabilize the system.

49.2 Change the chemical reagents and filters at the intervals recommended by the instrument manufacturer. Test the furnace and the analyzer to ensure the absence of leaks. Make a minimum of two determinations using a sample as directed in Section 52 to condition the instrument before attempting to calibrate the system or to determine the value of the blank. Avoid the use of reference materials for instrument conditioning.

50. Sample Preparation

50.1 Use only solid specimens to minimize the potential for errors due to surface oxidation. Specimens shall be of the proper size to permit free introduction into the sample loading device, if required, and to fit in the graphite crucible.

50.2 Cut the specimens to an appropriate size using a silicon carbide, water-cooled cut-off wheel or by other means that will avoid overheating. Avoid oxide cutting or oxide abrading materials. Thin, flat specimens may be stamped using a punch and die. Abrade all surfaces of the specimen to remove all traces of surface oxidation or other impurities using a clean file, die grinder, or silicon carbide grinding media (wet or dry). Again care must be taken not to overheat the specimen. If wet grinding is done, it will be necessary to rinse specimens in acetone and air dry well. If dry grinding is used, care must be taken to avoid overheating of the specimen. For some material, such as plain carbon sheet steel, a rimmed or semi-killed deoxidation practice is used and the oxygen may not be uniformly distributed throughout the thickness of the sample. In these cases, the removal of too much surface material may cause erroneous results.

50.3 Ensure that all pores in the surface of the sample are free of acetone.

50.4 Do not touch the specimen with fingers during and following the final stages of cleaning. Some steel alloys may be prone to oxidation and it may be necessary to store these prepared specimens in a desiccator. If oxidation prone alloys are not analyzed within four hours of preparation, it may be necessary to repeat the filing step or grinding step prior to analysis.

NOTE 24—Careful adherence to the sample preparation procedures described above is critical to obtaining accurate and precise results. The use of small and irregular shaped samples requires a diligent effort to ensure that all surface contamination has been removed.

51. Calibration

51.1 Calibration Reference Materials—Select three reference materials containing approximately 0.0005 %, 0.002 %, and 0.005 % oxygen and designate them as Calibrants A, B, and C, respectively.

NOTE 25—The uncertainty of results obtained using this test method is dependent on the uncertainty of the values assigned to the calibration reference materials. The homogeneity of the reference materials shall be considered as well, if it was not included in the derivation of the published uncertainty values.

51.2 Gas Dosing—Automated and manual gas dosing (recommended by some instrument manufacturers) can be used to calibrate the instrument, but instrument response shall be confirmed as described below using the reference materials described in 51.1.

51.3 Adjustment of Response of Measurement System:

51.3.1 Modern instruments may not require adjustment of the measurement system response prior to calibration. For these instruments proceed directly to 51.4 after the conditioning runs described in 49.2.

51.3.2 Using Calibrant B as the sample, proceed as directed in 52.2. Repeat 52.2 until the absence of drift is indicated. Absence of drift is indicated when the last four results have a maximum variation range of 0.0005 % oxygen. Make appropriate adjustments to the calibration potentiometer, if applicable. Record potentiometer settings. Adjust the instrument calibration to provide a reading within ± 0.0003 % absolute of the certified value for the calibrant using the average of the last four results. Refer to the manufacturer's instructions for the specific protocol for performing this operation.

51.4 Determination of Blank Reading—Using Calibrant A or a blank crucible as the sample, proceed as directed in 52.2. Repeat a sufficient number of times to establish that a low average blank value (0.0002 % oxygen or less) and stable individual blank values (± 0.0001 % oxygen) are obtained. Blank values are equal to the total result from the crucible and Calibrant A minus the certified oxygen content of Calibrant A. Record the average value of four successive blank determinations that meet the above requirements for maximum and stable values. If the blank readings are too high or unstable, determine the cause, correct it, and repeat the steps as directed in 52.2. Enter the average blank value in the appropriate mechanism of the analyzer; refer to manufacturer's instructions for the specific protocol for performing this operation. This mechanism will electronically compensate for the blank value (Note 26).

NOTE 26—If the unit does not have this function, the blank value shall be subtracted from the total result prior to any calculation.

51.5 Calibration:

51.5.1 Weigh an appropriate sample size of Calibrant C (refer to manufacturer's instructions) to the nearest 1 mg and place it in the instrument sample loading device or directly in the outgassed crucible, following the manufacturer's direction.

51.5.2 Follow the calibration procedure recommended by the manufacturer using Calibrant C to determine the calibration slope. Run samples until the maximum range from four

successive samples does not exceed 0.0005 % oxygen. Treat each sample as directed in 52.2 before proceeding to the next one.

51.5.3 Confirm the calibration by analyzing an additional sample of Calibrant C after the calibration procedure is completed. The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 7, the calibration is acceptable. If the result is not acceptable, repeat the calibration procedure.

$$\text{test result} - t \cdot s \leq \text{certified value} \leq \text{test result} + t \cdot s \quad (7)$$

where:

s = standard deviation of the analyses run in 51.5.3,
 n = number of analyses (that is, 3 to 5), and
 t = student's t value which is for $n = 3$, $t = 4.30$; for $n = 4$, $t = 3.18$; for $n = 5$, $t = 2.78$ at the 95 % confidence level.

51.5.4 Next, weigh at least two samples of appropriate size of Calibrant B to the nearest 1 mg and transfer to the instrument sample loading device. Treat each sample as directed in 52.2 before proceeding to the next one.

51.5.5 Record the results and compare them to the actual certified oxygen value for Calibrant B. The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 7, the calibration is acceptable.

51.5.6 If the result is not acceptable, refer to the manufacturer's instructions for checking the linearity of the analyzer.

NOTE 27—Verify the calibration when: (1) a different lot of crucibles is used, (2) the system has been in use for 4 h, (3) the inert gas supply has been changed, and (4) the system has been idle for 1 h. Verification should consist of analyzing at least one specimen of each calibrant. Recalibrate as necessary.

52. Procedure

52.1 Assemble the apparatus and condition it as directed in Section 37.

52.2 Procedure—Ranges I and II:

52.2.1 Manual Operation:

52.2.1.1 Set the analyzer to operate in the manual mode.

52.2.1.2 Place an empty crucible on the furnace lower electrode assembly and close the furnace.

52.2.1.3 Weigh a 1.0 g specimen to the nearest 1 mg and refer to the manufacturer's recommended procedure, including entry of sample mass.

52.2.1.4 Start the analysis cycle, referring to the manufacturer's recommended procedure (Note 19).

52.2.2 Automatic Operation:

52.2.2.1 Set the analyzer to operate in the automatic mode.

52.2.2.2 Place a 1.0 g specimen weighed to the nearest 1 mg in the loading device. Refer to the manufacturer's recommended procedure, including entry of sample mass.

52.2.2.3 Place an empty crucible on the furnace lower electrode assembly and close the furnace.

52.2.2.4 Start the analysis cycle, referring to the manufacturer's recommended procedure (Note 19).

NOTE 28—If the samples are to be analyzed in the automatic mode, blank determination and calibration should also be performed in the automatic mode. If samples are to be analyzed in the manual mode, blank determination and calibration should be performed in the manual mode. Solid samples may be analyzed in either automatic or manual mode, but drillings, slugs, or chips should be analyzed in the manual mode.

53. Calculation

53.1 The calibration function of the equipment shall yield a linear plot described by the following function given in Eq 7. Calculation of the calibration function shall be done using a linear least squares regression. Some manufacturers recommend the use of a curve weighting factor where the calibrant concentration is derived as $1/X$. It is acceptable to use this type of curve weighting.

53.2 Since most modern commercially available instruments calculate mass fraction concentrations directly, including corrections for blank and sample mass, manual calculations by the analyst are not required.

54. Precision and Bias

54.1 *Precision*—Sixteen laboratories cooperated in testing this test method and obtained the data summarized in Table 8. Testing was performed in compliance with Practice E173 (refer to 9.1). Note that the values for R_1 and R_2 are based on $M = 3$ (see Practice E173). This means that similar values for R_1 and R_2 may be expected from the averages of triplicate determinations.

54.2 *Bias*—No information on the bias of this method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

SULFUR BY THE COMBUSTION-INFRARED ABSORPTION TEST METHOD (CALIBRATION WITH METAL REFERENCE MATERIALS)

55. Scope

55.1 These test methods cover the determination of sulfur in the range of 0.002 % to 0.35 %.

56. Summary of Test Method

56.1 The sample is combusted in a stream of oxygen that converts the sulfur in the sample to sulfur dioxide. The sulfur is then determined by infrared absorption.

56.1.1 *Infrared Absorption: Test Method A*—Sulfur dioxide (SO_2) absorbs IR energy at a precise wavelength within the IR spectrum. The energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. The absorption of IR energy can be therefore attributed to only SO_2 , and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measure chamber. Total sulfur, as SO_2 , is measured over a period of time. Refer to Fig. 5.

56.1.2 *Infrared Absorption: Test Method B*—The combustion is performed in a closed loop in which SO_2 is detected in an infrared cell. The SO_2 is measured with a solid state energy detector, and filters are used to pass the appropriate IR wavelength to the detector. The IR absorption properties of SO_2 gas cause a loss of signal at the detector that is proportional to the concentration of SO_2 in the closed loop. Total sulfur, as SO_2 , is measured over a period of time. Refer to Fig. 6.

56.1.3 *Infrared Absorption: Test Method C*—The detector consists of an IR energy source, a separate measure chamber and reference chamber, and a diaphragm acting as one plate of a parallel plate capacitor. During specimen combustion, the flow of SO_2 with its oxygen gas carrier is routed through the measure chamber while oxygen alone passes through the reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm

TABLE 8 Statistical Information—Oxygen (wt., %)

Test Specimen	Oxygen Found	Repeatability ^A (R_1 , Practice E173)	Reproducibility ^A (R_2 , Practice E173)
Ni-Cr-Mo Alloy (AISI 4330)	0.00048	0.00018	0.00040
Tool Steel (M-50)	0.00056	0.00015	0.00061
Cr-Alloy Steel (52100)	0.00080	0.00022	0.00088
Carbon Steel (1070)	0.00118	0.00026	0.00065
Carbon Steel (1570)	0.00126	0.00024	0.00071
Alloy Steel (33100)	0.00139	0.00023	0.00048
Cr-Alloy Steel (52100)	0.00218	0.00034	0.00091
Ni-Cr-Mo Alloy (8622)	0.00237	0.00034	0.00076
Carbon Steel (1026)	0.00357	0.00023	0.00092
Cr-Stainless (440C)	0.00437	0.00032	0.00108
Ingot Iron (NIST-466, 0.0050 wt. % oxygen)	0.00538	0.00031	0.00081

^A $M = 3$, see Practice E173, 4.11 and 4.12 and Note 1.

(capacitor plate). Part of the IR energy is absorbed by the SO₂ present in the measure chamber, while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm and thus distorting it. This distortion alters the fixed capacitance, creating an electric signal change that is amplified for measurement as SO₂. Total SO₂ is monitored and measured over a period of time. Refer to Fig. 7.

57. Interferences

57.1 The elements normally present do not interfere. . For the scope of elements typically found in materials to be tested by this method refer to 1.1.

58. Apparatus

58.1 *Combustion and Measurement Apparatus*—See Figs. 5-7.

58.2 *Crucibles*—Use crucibles recommended by the manufacturer of the instrument or equivalent, and prepare the crucibles by heating them in a suitable furnace for not less than 40 min at approximately 1000 °C. Remove them from the furnace and cool before use. Preheated crucibles may also be stored in a desiccator prior to use. Above certain concentrations, as determined by the testing laboratory, the nontreatment of crucibles will have no adverse effect The analytical ranges for the use of untreated crucibles shall be specified by the testing laboratory, and supporting data shall be maintained on file to validate these ranges.

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

59. Reagents

59.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

59.2 *Acetone*—The residue after evaporation shall be < 0.0005 %.

59.3 *Magnesium Perchlorate*, (known commercially as *Anhydron*). Use the purity specified by the instrument manufacturer.

59.4 *Oxygen*—Purity as specified by the instrument manufacturer.

59.5 *Sodium Hydroxide*, on clay, (known commercially as *Ascarite II*). Use the purity specified by the instrument manufacturer.

59.6 *Tungsten Accelerator (Low Sulfur)*, 12 mesh to 20 mesh (Note 29).

59.7 *Tungsten-Tin Accelerator*, 20 mesh to 40 mesh or 12 mesh to 20 mesh.

NOTE 29—The accelerator should contain no more than 0.001 % sulfur. If necessary, wash three times with acetone by decantation to remove organic contaminants and dry at room temperature. The mesh size is critical to the inductive coupling which heats the sample. Some manufac-

turers of accelerators may not certify the mesh size on a lot to lot basis. These accelerators may be considered acceptable for use without verifying the mesh size.

60. Sample Preparation

60.1 60.1 The specimen should be uniform in size, but not finer than 40 mesh. Specimens will typically be in the form of chips, drillings, slugs, or solids. Specimens shall be free of any residual lubricants, cutting fluids, or both. It may be necessary to clean specimens to remove residual lubricants or cutting fluids, or both. Any cleaned specimens shall be rinsed in acetone and dried completely before analysis.

61. Preparation of Apparatus

61.1 Assemble the apparatus as recommended by the manufacturer.

61.2 Test the furnace and analyzer to ensure the absence of leaks, and make the required electrical power connections. Prepare the analyzer for operation in accordance with the manufacturer's instructions. Make a minimum of two determinations using a specimen and accelerator, as directed in 63.2 and 63.3 to condition the instrument before attempting to calibrate the system or determine the blank. Avoid the use of reference materials for instrument conditioning.

62. Calibration

62.1 *Calibrants* (Note 30):

62.1.1 For Range I, 0.002 % to 0.010 % sulfur, select three certified reference materials containing approximately 0.001 %, 0.005 %, and 0.010 % sulfur and designate them as Calibrants A, B, and C, respectively.

62.1.2 For Range II, 0.010 % to 0.10 % sulfur, select two certified reference materials containing approximately 0.02 % and 0.08 % sulfur and designate them as Calibrants BB and CC, respectively.

62.1.3 For Range III, 0.10 % to 0.35 % sulfur, select two certified reference materials containing approximately 0.10 % and 0.40 % sulfur and designate them as Calibrants BBB and CCC, respectively.

NOTE 30—The uncertainty of results obtained using this test method is dependent on the uncertainty of the values assigned to the calibration reference materials. The homogeneity of the reference materials shall be considered as well, if it was not included in the derivation of the published uncertainty values.

62.2 *Adjustment of Response of Measurement System*:

62.2.1 Modern instruments may not require adjustment of the measurement system response prior to calibration. For these instruments proceed directly to 62.3 after performing the conditioning runs described in 61.2.

62.2.2 Transfer 1.0 g of Calibrant B, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator to a crucible (Note 31). Some manufacturers provide scoops that dispense approximately 1.5 g of accelerator. Once it is verified that the scoop delivers this approximate mass, it is acceptable to use this device for routine dispensing of accelerator.

62.2.3 Proceed as directed in 63.1.2 and 63.1.3.

62.2.4 Repeat the steps given in 62.2.2 and 62.2.3 until the absence of drift is indicated by stable sulfur readings. Consistency is indicated when consecutive runs of Calibrant B repeat

to within 0.0002%. . Adjust the signal to provide a reading within ± 0.0003 of the certified percent sulfur value for Calibrant B.

62.3 Determination of Blank Readings—Range I:

62.3.1 Transfer 1.0 g of Calibrant A, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator into a crucible (Note 31). Some labs may use accelerator with a certified sulfur value as Calibrant A.

NOTE 31—The use of 1.5 g of accelerator may not be sufficient for all determinators. The required amount is determined by the analyzer used, induction coil spacing, position of the crucible in the induction coil, age and strength of the oscillator tube, and type of crucible being used. Use the amount required to produce proper sample combustion using the same amount throughout the entire test method.

62.3.2 Proceed as directed in 63.1.2 and 63.1.3.

62.3.3 Repeat the steps given in 62.3.1 and 62.3.2 a sufficient number of times to establish that low (less than 0.00005 % of sulfur) and stable (± 0.00001 % of sulfur) readings are obtained. Blank values are equal to the total result of the accelerator and Calibrant A minus the certified value for the calibrant.

62.3.4 Record the average value of at least three blank determinations.

62.3.5 If the blank readings are too high or unstable, determine the cause, correct it, and repeat the steps as directed in 62.3.1-62.3.4.

62.3.6 Enter the average blank value in the analyzer (Note 32). Refer to the manufacturer's instructions for specific instructions on performing this function. This mechanism will compensate electronically for the blank value.

NOTE 32—If the unit does not have this function, the blank value shall be subtracted from the total result prior to any calculation.

62.4 Determination of Blank Reading—Range II—Proceed as directed in section 62.3.

62.5 Determination of Blank Reading—Range III:

62.5.1 Transfer 0.5 g of Calibrant A, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator to a preheated crucible (Note 31).

62.5.2 Proceed as directed in 62.3.2-62.3.6.

62.6 Calibration—Range I (0.002 % to 0.010 % Sulfur):

62.6.1 Weigh four 1.0-g test samples of Calibrant C, weighed to the nearest 1 mg, and then place them in crucibles. Add approximately 1.5 g of accelerator (Note 31) to each.

62.6.2 Follow the calibration procedure recommended by the manufacturer. Use Calibrant C as the calibrant and analyze at least three test samples to determine the calibration slope. Treat each test sample as directed in 63.1.2 and 63.1.3 before proceeding to the next one.

62.6.3 . The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 8, the calibration is acceptable. If not, repeat the steps given in 62.6.1 and 62.6.2.

$$\text{test result} - t \cdot s \leq \text{certified value} \leq \text{test result} + t \cdot s \quad (8)$$

where:

s = standard deviation of the analyses run in 62.6.3,
 n = number of analyses (that is, 3 to 5), and
 t = student's t value which is for $n = 3$, $t = 4.30$; for $n = 4$, $t = 3.18$; for $n = 5$, $t = 2.78$ at the 95 % confidence level.

(See Note 2.)

62.6.4 Weigh at least two 1.0-g test samples of Calibrant B, weighed to the nearest 1 mg, and transfer them to crucibles. Add approximately 1.5 g of accelerator (Note 31) to each.

62.6.5 Treat each test sample as directed in 63.1.2 and 63.1.3 before proceeding to the next one.

62.6.6 Record the results of 62.6.4 and 62.6.5 and compare them to the certified sulfur value of Calibrant B. The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 8, the calibration is acceptable. If not, refer to the manufacturer's instructions for determining the linearity of the system (Note 33).

NOTE 33—Verify the calibration when: (1) a different lot of crucibles is used, (2) a different lot of accelerator is used, (3) the system has been idle for 1 h, (4) the system has been in use for 4 h, and (5) the oxygen supply has been changed. Verification should consist of analyzing at least one specimen of each calibrant. Recalibrate as necessary.

62.7 Calibration—Range II (0.010 % to 0.10 % Sulfur):

62.7.1 Proceed as directed in 62.6.1-62.6.3, using Calibrant CC.

62.7.2 Proceed as directed in 62.6.4-62.6.6, using Calibrant BB.

62.8 Calibration—Range III (0.10 % to 0.35 % Sulfur):

62.8.1 Weigh four 0.5-g test samples of Calibrant CCC, to the nearest 1 mg, and place them in crucibles. Add approximately 1.5 g of accelerator (Note 31) to each.

62.8.2 Follow the calibration procedure recommended by the manufacturer. Use Calibrant CCC as the primary calibrant and analyze at least three test samples to determine the calibration slope. Treat each test sample as directed in 63.1.2 and 63.1.3 before proceeding to the next one.

62.8.3 Confirm the calibration by analyzing Calibrant CCC following the calibration procedure. The result should agree with the certified value within a suitable confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 8, the calibration is acceptable. If not, repeat the steps given in 62.8.1 and 62.8.2.

62.8.4 Weigh at least two 0.5-g test samples of Calibrant BBB, weighed to the nearest 1 mg, and transfer them to crucibles. Add approximately 1.5 g of accelerator (Note 31) to each.

62.8.5 Treat each test sample as described in 63.1.2 and 63.1.3 before proceeding to the next one.

62.8.6 Record the results of 62.8.4 and 62.8.5 and compare them to the certified sulfur value of the Calibrant BBB. The result should agree with the certified value within a suitable

confidence interval (Note 4). If the result agrees with the certified value within the uncertainty provided on the certificate of analysis, the calibration is acceptable. Also, if the certified value falls within an interval calculated as described in Eq 8, the calibration is acceptable. If not, refer to the manufacturer's instructions for determining the linearity of the analyzer (Note 33).

63. Procedure

63.1 Procedure—Range I:

63.1.1 Stabilize the furnace and analyzer as directed in Section 59. Transfer 1.0 g of test sample, weighed to the nearest 1 mg, and approximately 1.5 g of accelerator to a crucible (see 58.2) (Note 31).

63.1.2 Place the crucible on the furnace pedestal and raise the pedestal into position. Use crucible tongs to handle the crucibles.

63.1.3 Refer to the manufacturer's recommended procedure regarding the entry of test sample mass and blank value. Start the analysis cycle.

63.2 Procedure—Range II—Proceed as directed in 63.1.

63.3 Procedure—Range III—Proceed as directed in 63.1, using a 0.5-g test sample.

64. Calculation

64.1 The calibration function of the equipment shall yield a linear plot described by Eq 2. Calculation of the calibration function shall be done using a linear least squares regression. Some manufacturers recommend the use of a curve weighting factor where the calibrant concentration is derived as $1/X$. It is acceptable to use this type of curve weighting.

64.2 Since most modern commercially available instruments calculate mass fraction concentrations directly, including corrections for blank and sample mass, manual calculations by the analyst are not required (Note 34).

**TABLE 9 Statistical Information, Sulfur, Range I
(0.002 % to 0.010 % S)**

Test Material	Certified Value, % Sulfur	Sulfur Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
JK NR24	0.0010	0.00103	0.00025	0.00078
NIST 132b	0.0030	0.0027	0.00033	0.00094
High Temperature Alloy	...	0.0043	0.00051	0.00118
NIST 50c	0.0064	0.0065	0.0005	0.0024

**TABLE 10 Statistical Information, Sulfur, Range II
(0.010 % to 0.10 % S)**

Test Material	Certified Value, % Sulfur	Sulfur Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
NIST 890	0.015	0.0149	0.0015	0.0039
NIST 163	0.027	0.0264	0.0015	0.0092
NIST 73c	0.036	0.0356	0.0032	0.0078

**TABLE 11 Statistical Information, Sulfur, Range III
(0.10 % to 0.35 % S)**

Test Material	Certified Value, % Sulfur	Sulfur Found, %	Repeatability (R_1 , Practice E173)	Reproducibility (R_2 , Practice E173)
NIST 6g	0.124	0.1200	0.0076	0.0239
NIST 129c	0.245	0.2451	0.0074	0.0243
NIST 133	0.356	0.3683	0.0174	0.0373

NOTE 34—Use the following formula if the analyzer does not compensate for blank and sample mass values:

$$\text{sulfur, \%} = [(A - B) \times C/D] \quad (9)$$

where:

- A = DVM (Digital Volt Meter) reading for test sample,
- B = DVM reading for blank,
- C = mass compensator setting, and
- D = test sample mass in grams.

65. Precision and Bias

65.1 Precision—Nine laboratories cooperated in testing these test methods and obtained the precision data summarized in Tables 9-11 (see Note 35). Testing was performed in compliance with Practice E173 (refer to 9.1).

NOTE 35—In Tables 9-11, all results in Ranges I and II are from nine laboratories. The results in Range III are from eight laboratories.

65.2 Bias—The accuracy of these test methods can be inferred from the data given in Tables 9-11 by comparing the certified values for sulfur with the average values obtained (see Note 36).

NOTE 36—Although these test methods were tested to only 0.35 %, most commercial analyzers are believed to be capable of analyzing samples containing sulfur up to 0.5 %.

66. Keywords

66.1 carbon content; cobalt alloys; combustion; determination; fusion; gas dosing; inert gas fusion; infrared absorption; iron alloys; nickel alloys; nitrogen content; oxygen content; steel alloys; sulfur content; thermal conductivity

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