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Standard Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Combustion and Inert Gas 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

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	Mass Fraction 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 9.50
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	0.001 to 0.45
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:

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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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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Specific hazards statements are given in Section 6.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1997)³

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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

E2857 Guide for Validating Analytical Methods

2.2 *ASTM Manuals*:²

MNL7 Presentation of Data and Control Chart Analysis, 9th Edition

3. Terminology

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

4. Significance and Use

4.1 This test method is intended for the testing of iron, steel, cobalt, and nickel alloys to verify compliance with compositional specifications such as those issued by Committees A01 and B02. It is assumed that all who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory.

4.2 Laboratories using this method shall prepare work procedures documenting how the test method is to be implemented in their specific laboratory operation.

4.3 This test method contains numerous references to “manufacturer’s recommendations”. When this statement is used, the user of this method is expected to refer to the instrument operation manual for the specific instrument being used or consult directly with the manufacturer to determine recommendations.

5. Apparatus and Reagents

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

5.2 The methods for nitrogen and oxygen were originally developed for older technology, using manual instrumentation, with the flow schematics indicated. Current commercially available instruments are more automated and may have slightly different flow schematics and should be capable of producing data meeting or exceeding the precision and bias requirements.

5.3 The method for carbon and sulfur was developed using current commercially available instruments.

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 electrical equipment to avoid personal injury by either burn or electrical shock.

7. Sampling

7.1 Refer to Practices **E55**, **E88** or **E1806** for suggested sampling procedures.

8. Rounding Calculated Values

8.1 Rounding of test results obtained using these test methods shall be performed as directed in Practice **E29**, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

9. Interlaboratory Studies

9.1 The test methods for carbon and sulfur have been evaluated in accordance with Practice **E691**. The test methods for nitrogen and oxygen have been evaluated in accordance with Practice **E173**. The Reproducibility R_2 of Practice **E173** corresponds to the Reproducibility Index R of Practice **E691**. The Repeatability R_1 of Practice **E173** corresponds to the Repeatability Index r of Practice **E691**.

CARBON AND SULFUR BY COMBUSTION

10. Scope

10.1 This test method applies to the determination of carbon and sulfur in iron, steel, nickel, and cobalt alloys in mass fractions from 0.002 % to 9.50 % for carbon and 0.001 % to 0.45 % for sulfur.

10.2 This method has been interlaboratory tested for the quantification ranges specified in **10.1**. The ranges in **10.1** indicate intervals within which results have been demonstrated by interlaboratory study to be quantitative. It may be possible to extend this method to different ranges provided that a method validation study is performed and that the results of this study show that the method extension is meeting laboratory data quality objectives. Guide **E2857** provides information on how to perform method validation studies. The laboratory may use other documented validation methods.

10.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section **6**.

11. Interferences

11.1 The elements ordinarily present in iron, steel, nickel, and cobalt alloys do not interfere.

12. Apparatus

12.1 *Combustion and Measurement Apparatus*—Automatic elemental analyzer, capable of determining carbon only or carbon and sulfur, combined.

12.1.1 The analyzer will consist of an induction furnace, analytical gas stream impurity removal, and gas analysis systems.

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

auxiliary purification systems (if required by the manufacturer), and an infrared absorption detection system. Several models of commercial elemental analyzers are available and presently used in industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's instructions for operational details.

12.2 Ceramic Crucibles—Use the crucible design(s) recommended by the instrument manufacturer. Some crucible designs may have lids fitted to the crucible which help minimize or prevent spattering associated with vigorous combustion. The most commonly analyzed iron, steel, cobalt, or nickel-based materials will not require the use of lids. The lab should evaluate the necessity of lid use during the method development trials described in Section 14.

12.2.1 New crucibles may be contaminated with small amounts of carbon or sulfur or both and should be conditioned prior to use by heating in a suitable furnace for not less than 40 min at 1000 °C or not less than 15 min at 1250 °C and allowed to safely cool. Exact timing of the crucible heating cycle is not required. The conditioned crucibles shall only be handled with tongs and may be stored in a covered container for up to four hours prior to use. Crucibles not used within four hours may be re-conditioned and used for analysis. Exact timing of the crucible standing time is not required. Alternatively, the laboratory may use a different combination of time and temperature parameters for conditioning provided the precision and bias demonstrated meet the laboratory's quality objectives. If lids are used these should be conditioned using the same heating conditions used for crucibles.

12.2.2 Conditioning may not be necessary if the carbon and sulfur contents of the unconditioned crucibles are insignificant to the required measurement quality. It is incumbent upon laboratories choosing not to condition crucibles to assess the impact to laboratory measurement quality objectives. Comparing results obtained using unconditioned crucibles to the data presented in the Precision and Bias tables of this method may provide an objective evaluation of the impact to the measurement results. This method was tested using conditioned crucibles; therefore, laboratories that do not condition crucibles may not be able to demonstrate repeatability and bias similar to that presented in the Precision and Bias tables.

12.2.3 Crucibles should be stored in a dry environment.

12.3 Crucible Tongs—Capable of handling recommended crucibles.

13. Reagents and Materials

13.1 Accelerators—These will typically be copper, tungsten, iron, tin, or a mixture of these metals. Composition, form and purity are typically recommended by the instrument manufacturer. The exact composition to be used will be determined per Section 14.

13.2 Acetone—Used for sample drying and decontamination. The laboratory should determine the quality of acetone necessary to meet data quality objectives. A.C.S. reagent grade acetone has been found to produce acceptable results.

13.3 Calibration Reference Materials—Iron, steel, nickel or cobalt alloys with reference values and uncertainty estimates

for carbon or sulfur or both, containing analyte mass fractions adequate to calibrate for the expected range of carbon or sulfur or both in the laboratory's expected analytical range.

13.4 Gas Purification Reagents—Composition, form and purity are typically specified by the instrument manufacturer. The reagents used may vary somewhat from analyzer to analyzer.

13.4.1 Sulfur Trioxide Absorber—Cellulose has been used for this purpose.

13.4.2 Water Absorber—Magnesium perchlorate or phosphorous pentoxide have been used for this purpose.

13.4.3 CO₂ Absorber—Sodium hydroxide on clay has been used for this purpose.

13.5 Gas Conversion Reagents—Composition, form and purity are typically specified by the instrument manufacturer. The reagents used may vary somewhat from analyzer to analyzer.

13.5.1 CO to CO₂ Converter—Platinum or platinumized silica have been used for this purpose.

13.5.2 Hydrogen/Hydrocarbon Contaminant Converter—Rare earth copper oxide has been used for this purpose.

13.6 Combustion/Carrier Gas-Oxygen—Purity as specified by the instrument manufacturer.

14. Preparation of Apparatus

14.1 Analytical instrumentation shall be installed following the manufacturer's recommendations.

14.1.1 For implementation of this test method on existing equipment that is currently producing analyses which meet laboratory data quality objectives, the performance of steps 14.2 – 14.5 may be unnecessary and is, therefore, non-mandatory. For newly installed equipment, steps 14.2 – 14.5 shall be performed.

14.2 Using the instrument software, set up an analytical protocol with measurement parameters. Instrument manufacturers typically provide application notes with suggested parameters. Refer to these application notes as a starting point for method development. Parameters that are typically specified are as follows:

14.2.1 Instrument Measurement Parameters:

14.2.1.1 Gas Flow—This may be fixed by the design of the equipment.

14.2.1.2 Purge Time—Use of inadequate purge time may adversely affect the analysis precision of low mass fraction content specimens.

14.2.1.3 Measurement times (integration time(s), delay time(s)).

14.2.1.4 Furnace parameters (furnace power, power ramp protocol).

14.2.1.5 Calibration and specimen analysis may only be made on materials with analyte mass fractions falling into the instrument manufacturer defined linear range of the equipment. Therefore, only calibration protocols using first order line fits may be used with this test method. Select a calibration protocol from either (1) or (2) while giving consideration to (3) and (4).

(1) Single Point Calibration—A calibration line is determined using a blank or blank adjusted or blank adjusted

reference material containing carbon or sulfur or both mass fractions near or greater than that of the specimens. It may be necessary to secure separate reference materials for high carbon and high sulfur. For single point calibrations, the calibration bias check (16.5) will serve as a calibration linearity verification (see Section 16). See Section 18 for further information about calibration line calculations.

(2) *Multiple Point Calibrations*—A calibration line is developed using the measurement responses of two or more reference materials and simple linear regression. Depending upon system design the blank may be included in the calibration line. The group of reference materials must include a high analyte mass fraction reference material with carbon or sulfur or both mass fractions near or greater than that of the samples and a low analyte mass fraction reference material with carbon or sulfur or both mass fractions near the lowest mass fraction expected for the samples. Additional reference materials of varying mass fraction may be added to the calibration at the discretion of the laboratory. It may be necessary to secure separate reference materials for high carbon and high sulfur calibration. See Section 18 for further information about calibration line calculations.

(3) The calibration lines developed using the protocols of (1) or (2) may be designed to force the line intercept through zero or by calculating the intercept of the calibration line. See Section 18 for further information on calibration line calculations.

(4) Some instruments may have dual range measurement capability, and it may be necessary to develop a calibration protocol for both measurement ranges.

14.2.1.6 Due to differences in instrument design, there may be additional instrument parameters that must be considered. Refer to manufacturer specific recommendations when entering these parameters.

14.2.2 Ancillary Parameters:

14.2.2.1 Calibration material attributes (identification and analyte mass fraction information).

14.2.2.2 Associated reporting parameters such as replication, unit of measure, report destination, etc., if required.

14.2.2.3 Non-instrument analysis parameters that must be determined are as follows:

(1) *Specimen Mass*—Specimen masses are typically 0.5 g to 1 g. Use of specimen masses that are low may adversely affect result repeatability. Use of specimen masses that are too high may cause incomplete combustion or spattering of sample material from the crucible.

(2) *Accelerator Composition*—Accelerators used for the analysis of carbon and sulfur simultaneously are composed of tungsten, iron, tin or a mixture of these metals. For carbon determination only, copper metal may be used, which may minimize dust accumulation in the instrument. Copper must not be used for sulfur determination. Because some nickel and cobalt based alloys are more difficult to combust, accelerator composition and the mass ratio of accelerator to specimen may require optimization to yield adequate analytical performance.

(3) *Accelerator Mass*—The mass ratio of accelerator to specimen may require optimization to yield adequate analytical performance. When specimen mass significantly exceeds accelerator mass, the result may be incomplete combustion.

(4) *Crucible Lids*—These typically have a center hole to permit flow of gas into and out of the crucible. Use of a lid minimizes or prevents spattering if a material is prone to this.

(5) *Instrument Conditioning Requirements*—The equipment manufacturer may recommend that conditioning analyses be performed prior to using the instrument. Conditioning may also be required after reagents are changed or filters are cleaned/changed.

(a) Two conditioning analyses, following the manufacturer's recommendation, may adequately condition the instrument. However, if the conditioning material contains low sulfur content, additional analyses may be required to adequately condition the instrument. If possible, perform the conditioning analyses with specimens other than certified reference materials, to prevent premature depletion of certified reference material supplies. The optimal number of conditioning analyses should be established during method development.

14.3 Establish a test calibration to be used for method development using the parameters selected in 14.2.1 and 14.2.2 as a starting point for the method development study. Make test analyses on materials to assess the sensitivity and precision of analyses made using the selected conditions. Comparison of method development precision data to the data provided in the Precision and Bias tables of this method is useful for assessing acceptability of the selected parameters. This is done by comparing the standard deviation (s) of the development analyses to the calculated S_p in the Precision tables for materials with similar mass fractions. If $s \gg S_p$, the parameters selected may not be optimum. Further optimization of analysis parameters should be performed. If the results of this optimization are deemed acceptable for meeting the laboratory's measurement quality objectives then further study is not necessary.

14.4 If the results of the preliminary study are not acceptable, continue to optimize the instrument measurement and ancillary parameters by adjusting them and making test analyses on materials to assess the sensitivity and precision of analyses. It may be necessary to recalibrate the instrument after each parameter adjustment.

14.5 Once the optimal parameters have been established, it is recommended that the lab perform a method validation study. Guide E2857 provides guidance on approaches to method validation. The laboratory may use other documented validation methods.

14.6 It is not necessary to regularly perform method development or method validation after the analytical protocol is established.

14.7 After the calibration protocol is determined, establish a calibration drift control strategy; see 16.6. This should include provisions for the frequency at which the blank value is verified or reset.

14.8 After the analysis conditions and procedures have been established and validated, write a laboratory operating procedure for execution of the method. This operating procedure shall include the following:

14.8.1 Document the analytical program. It is not necessary to document the measurement parameters, however, an appropriate electronic backup of the measurement parameters should be made.

14.8.2 Document the ancillary parameters including:

14.8.2.1 The allowed specimen mass range;

14.8.2.2 The accelerator composition and quantity to be used. It is not necessary to state the accelerator quantity as a mass. However, the mass should be verified when scoops or other tools used to deliver accelerator are changed; and

14.8.2.3 The instrument conditioning requirements.

14.8.3 Frequency of calibration control verifier analysis (see 16.6).

14.8.4 Frequency of recalibration (see 16.1.2).

14.8.5 The specimen preparation requirements (see Section 15).

14.8.6 The maintenance intervals required for proper instrument operation. Use the manufacturer's recommendations as a resource for developing laboratory specific intervals.

15. Sample/Specimen Preparation

15.1 Specimens will typically be in the form of chips, drillings, powders, slugs or solids.

15.1.1 Solid or slug specimens can be cut and abraded with aluminum oxide, aluminum zirconium oxide or silicon carbide media, and subsequently, drilled, milled, turned or filed.

Warning—Do not use silicon carbide media if determining carbon content because this may contaminate the samples with carbon. Ensure that the surface is not burned (oxidized) during abrasion (see Note 1).

15.1.2 Ensure that drilling or chipping of a solid specimen does not overheat the material. Evidence of overheating is a dark blue color imparted to the drillings or chips (see Note 1).

NOTE 1—Overheating specimens during abrasion, drilling or chipping may cause localized decarburization of the drillings or chips, thereby, affecting the precision and bias of carbon test results.

15.1.3 For samples that have surface decarburization which cannot be removed by abrasion, this test method may not produce valid results.

15.2 Ensure the specimens are free of residual lubricants, cutting fluids, or other contamination. Certain testing operations may require that contaminants are removed chemically.

15.2.1 If contamination is suspected, clean the specimens with fresh acetone and dry thoroughly. It is important to maintain reagent and labware cleanliness during this operation to prevent cross contamination.

15.2.2 Acetone has been found to be a suitable cleaning solvent, but the user may determine that other solvents provide equivalent cleaning performance.

15.2.3 Excessively “dirty samples” may be cleaned in an ultrasonic cleaner or soaked with a solvent if necessary to remove contamination.

15.2.4 If required, optimize the sample preparation protocols for the materials being tested during method development. Optimization may involve assessing the cleaning protocol for effectiveness.

15.3 The final specimen mass obtained by preparation shall be consistent with that established during method development.

15.4 Typically, reference materials are purchased in a form that is ready for use without further preparation. Additional cleaning of these reference materials is not necessary. Refer to the reference material certificate for recommended handling and preparation instructions.

16. Calibration

16.1 Apply the calibration protocol developed per Section 14 using the following guidelines:

16.1.1 It is not necessary to perform the calibration procedure each time the analysis procedure (Section 17) is performed. However, the laboratory must use a calibration control strategy such as described in 16.6.

16.1.2 The laboratory must document the calibration control strategy in the local operating procedure. The calibration control strategy may consider one or more of the following factors:

16.1.2.1 A specific time interval that has elapsed since prior calibration;

16.1.2.2 A drift verifier indicates that the calibration has drifted (see 16.5); and

16.1.2.3 A non-exhaustive list of operational events which will necessitate calibration or drift correction include: changing instrument reagents, changing carrier gas supply, or a significant service event.

16.2 Prior to making calibration measurements, condition the instrument by making the number of analyses determined per item (5) in 14.2.2.3.

16.3 Blank Determination Procedure:

16.3.1 Follow the instrument manufacturer's guidelines to establish whether the blank or the calibration slope should be determined first.

16.3.1.1 If the calibration slope is determined first, proceed to 16.4 and perform the reference material determination procedure, then proceed to 16.3.2. If the blank determination procedure is performed first, proceed directly to 16.3.2.

16.3.2 Perform a minimum of three blank determinations using the analysis protocol developed in Section 14. The blank determination must include the empty crucible, including any accelerator to be used for analysis.

16.3.3 Apply the average determined in 16.3.2 to the calibration using the instrument software. Depending upon its design, the software may automatically compensate for a blank value in subsequent calibration and sample analyses, or it may be used as the zero point for the calibration.

16.3.4 If the blank is determined after the calibration slope has been set, verify that the blank has been set correctly.

bias results unacceptably with respect to the laboratory's data quality objectives. If the blank has changed significantly, repeat 16.3.2.

16.4 Reference Material Determination Procedure:

16.4.1 Following the analysis protocol developed per Section 14, measure the reference materials selected for calibration. Reference materials selected should exhibit measurement uncertainties similar to those selected for the interlaboratory study (reference 19.1).

16.4.2 Each calibration reference material shall be analyzed in duplicate, at a minimum. Adding more replicates when the uncertainty stated on the certificate is high relative to the stated analyte content, may improve the calibration.

16.4.3 Following the software's protocols for generating the calibration, establish the calibration using the calibration protocol developed per Section 14. The calibration must be developed as a first order line fit as described in Section 14.

16.4.4 If a single point calibration is selected (see item (1) in 14.2.1.5), the calibration line shall be developed using the mass fractions and instrument responses observed for a blank (determined in 16.3) and a reference material with a high analyte mass fraction.

16.4.5 If a multiple point calibration is selected (see item (2) in 14.2.1.5), the calibration line shall be developed using the mass fractions and instrument responses observed for a low analyte mass fraction reference material, a high analyte mass fraction reference material, and additional reference materials with intermediate analyte mass fractions as selected by the laboratory. The calibration may include the blank based on the system design.

16.4.6 The calibration lines developed using the protocols of 16.4.4 or 16.4.5 may be calculated to force the line intercept through zero or by calculating the intercept of the calibration line. See Section 18 for further information on calibration line calculations.

16.4.7 The highest calibration point in either the single point or multiple point calibration line should contain an analyte mass fraction near the highest expected sample analyte mass fraction.

16.4.8 Some manufacturers use dual detectors to enable analyses of broader mass fraction ranges. It may be necessary to establish more than one calibration line to calibrate the instrument for the full mass fraction range required. Follow the manufacturer's protocol for establishing calibrations for the two measurement ranges. These calibrations must comply with 16.4.4 or 16.4.5. If a dual range instrument will only be used to analyze samples falling into one of the ranges, it is not mandatory that both ranges be calibrated.

16.4.9 Take note of the calibration factor calculated by the software. Consult the operator's manual for guidance on the allowable range for this factor. A slope exceeding this range may indicate a problem with calibration settings, the reference materials used for calibration, or the instrument's operation. Investigate and correct any underlying causes of the calibration issue. Re-determine the blank and calibration before proceeding.

16.5 Calibration Bias Determination Procedure:

16.5.1 After the calibration is established, demonstrate the potential calibration bias as follows. It is not necessary to perform this procedure routinely, unless a significant change has been made which could impact the calibration (see 16.1.2.3).

16.5.1.1 Analyze a reference material having a mass fraction near the mid-range of the calibration range. If the analysis of the reference material is within the uncertainty of the reference material, there is evidence that the calibration is not biased. The laboratory may choose to analyze additional reference materials to give additional confidence in the calibration in other composition ranges. If the uncertainty of the reference material selected to demonstrate calibration bias is relatively large, it is possible that a calibration with significant bias could go undetected.

16.5.1.2 If the bias determination reference material analysis does not fall within the reference material uncertainty, the lab may decide to determine if the confidence interval of the reference material analysis overlaps the uncertainty of the reference material in order to demonstrate calibration bias.

(1) Analyze three to five replicates of the reference material(s) selected to examine calibration bias.

(2) Using the results of these reference material measurements, calculate a one-sided 95 % confidence interval (CI) using Eq 1:

$$CI = t^*s/\sqrt{n} \quad (1)$$

where:

CI = one-sided 95 % confidence interval,
 n = number of replicates used in 16.5.1.1,
 s = sample standard deviation of n replicates, and
 t = student's t critical value chosen for a one-sided interval for the requisite degrees of freedom ($df = (n - 1)$) and $\alpha=0.05$.

The values are:

$t = 2.92$ for $n = 3$ ($df = 2$);
 $t = 2.353$ for $n = 4$ ($df = 3$); and
 $t = 2.132$ for $n = 5$ ($df = 4$).

(3) The calculated s should be comparable to S_r , the repeatability standard deviation, given in the Precision and Bias Tables of this method (see Section 19). If $s \gg S_r$, there is evidence that there may be an instrument precision issue or that the particular instrument may not perform the same as the instruments used in the interlaboratory study of this test method. The user should determine the cause of the imprecision and correct it, if possible. If $s \gg S_r$ and it cannot be corrected, the laboratory may not be able to reliably verify the calibration bias.

(4) Compare the uncertainty interval around the assigned value to the confidence interval. If the two intervals overlap to any extent, there is evidence that the calibration is not biased. If this check fails, there may be calibration bias.

16.5.1.3 If potential calibration bias is noted during this verification, the laboratory should determine whether or not this bias is related to an instrument problem. It has been observed that bias between the different reference materials selected for calibration and verification may give the appearance that the instrument response is not within bias.