



Standard Test Method for Analysis of Titanium and Titanium Alloys by Direct Current Plasma and Inductively Coupled Plasma Atomic Emission Spectrometry (Performance-Based Test Methodology)¹

This standard is issued under the fixed designation E2371; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method describes the analysis of titanium and titanium alloys, such as specified by committee B10, by inductively coupled plasma atomic emission spectrometry (ICP-AES) and direct current plasma atomic emission spectrometry (DCP-AES) for the following elements:

Element	Application Range (wt.%)	Quantitative Range (wt.%)
Aluminum	0–8	0.009 to 8.0
Boron	0–0.04	0.0008 to 0.01
Cobalt	0–1	0.006 to 0.1
Chromium	0–5	0.005 to 4.0
Copper	0–0.6	0.004 to 0.5
Iron	0–3	0.004 to 3.0
Manganese	0–0.04	0.003 to 0.01
Molybdenum	0–8	0.004 to 6.0
Nickel	0–1	0.001 to 1.0
Niobium	0–6	0.008 to 0.1
Palladium	0–0.3	0.02 to 0.20
Ruthenium	0–0.5	0.004 to 0.10
Silicon	0–0.5	0.02 to 0.4
Tantalum	0–1	0.01 to 0.10
Tin	0–4	0.02 to 3.0
Tungsten	0–5	0.01 to 0.10
Vanadium	0–15	0.01 to 15.0
Yttrium	0–0.04	0.001 to 0.004
Zirconium	0–5	0.003 to 4.0

1.2 This test method has been interlaboratory tested for the elements and ranges specified in the quantitative range part of the table above. It may be possible to extend this test method to other elements or broader mass fraction ranges as shown in the application range part of the table above provided that test method validation is performed that includes evaluation of method sensitivity, precision, and bias. Additionally, the validation study shall evaluate the acceptability of sample preparation methodology using reference materials or spike recoveries or both. Guide E2857 provides information on validation of analytical methods for alloy analysis.

¹ This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf, Re.

Current edition approved June 15, 2013. Published June 2013. Originally approved in 2004. Last previous edition approved in 2004 as E2371 - 04, which was withdrawn in January 2013 and reinstated in June 2013. DOI: 10.1520/E2371-13.

1.3 Because of the lack of certified reference materials (CRMs) containing bismuth, hafnium, and magnesium, these elements were not included in the scope or the interlaboratory study (ILS). It may be possible to extend the scope of this test method to include these elements provided that method validation includes the evaluation of method sensitivity, precision, and bias during the development of the testing method.

1.4 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.5 *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 safety hazards statements are given in Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

D1193 Specification for Reagent Water

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

E1097 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry

E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis

E1479 Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

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.

E1832 Practice for Describing and Specifying a Direct Current Plasma Atomic Emission Spectrometer
 E2027 Practice for Conducting Proficiency Tests in the Chemical Analysis of Metals, Ores, and Related Materials
 E2626 Guide for Spectrometric Analysis of Reactive and Refractory Metals
 E2857 Guide for Validating Analytical Methods

2.2 ISO Standards:³

ISO/IEC 17025 Requirements for the Competence of Calibration and Test Laboratories
 ISO Guide 31 Reference Materials—Contents of Certificates and Labels
 ISO Guide 34 General Requirements for the Competence of Reference Material Producers
 ISO Guide 98-3 Uncertainty of measurement Part 3: Guide to the Expression of Uncertainty in Measurement (GUM: 1995)—First Edition

3. Terminology

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

4. Summary of Test Method

4.1 A mineral acid solution of the sample is aspirated into an inductively coupled plasma (ICP) or direct current plasma (DCP) spectrometer. The intensities of emission lines from the spectra of the analytes are measured and compared with calibration curves obtained from solutions containing known amounts of pure elements.

5. Significance and Use

5.1 This test method for the chemical analysis of titanium and titanium alloys is primarily intended to test material for compliance with specifications of chemical composition such as those under the jurisdiction of ASTM Committee B10. It may also be used to test compliance with other specifications that are compatible with the test method.

5.2 It is assumed that all who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely and that the work will be performed in a properly equipped laboratory.

5.3 This is a performance-based test method that relies more on the demonstrated quality of the test result than on strict adherence to specific procedural steps. It is expected that laboratories using this test method will prepare their own work instructions. These work instructions will include detailed operating instructions for the specific laboratory, the specific reference materials used, and performance acceptance criteria. It is also expected that, when applicable, each laboratory will participate in proficiency test programs, such as described in Practice E2027, and that the results from the participating laboratory will be satisfactory.

6. Interferences

6.1 In Practice E1479, the typical interferences encountered during inductively coupled plasma spectrometric analysis of metal alloys are described. In Guide E1097, the typical interferences encountered during direct current plasma emission spectrometric analysis of metal alloys are described. The user is responsible for ensuring the absence of, or compensating for, interferences that may bias test results obtained using their particular spectrometer.

6.2 The use of an internal standard may compensate for the physical interferences resulting from differences between sample and calibration solutions transport efficiencies.

6.3 Shifts in background intensity levels because of recombination effects or molecular band contributions or both may be corrected by the use of an appropriate background correction technique. Direct spectral overlaps are best addressed by selecting alternative wavelengths. Spectral interference studies should be conducted on all new matrices to determine the interference correction factor(s) that shall be applied to concentrations obtained from certain spectral line intensities to minimize biases. Some instrument manufacturers offer software options that mathematically correct for direct spectral overlaps, but the user is cautioned to evaluate carefully this approach to spectral correction.

6.4 Modern instruments have software that allows comparison of a sample spectrum to the spectrum obtained from a blank solution. The user of this test method shall examine this information to ascertain the need for background correction and the correct placement of background points.

6.5 In Table 1, wavelengths that may be used for analysis of titanium alloys are suggested. Each line was used by at least one laboratory during the interlaboratory phase of test method development and provided statistically valid results. Additional elements and wavelengths may be added if proficiency is demonstrated. Information for the suggested analytical wavelengths was collected from each laboratory and has been converted to wavelengths as annotated in the NIST Atomic Spectra Database.⁴ In this database, wavelengths of less than 200 nm were measured in vacuum and wavelengths greater than or equal to 200 nm were measured in air. Additionally, the MIT Wavelength Tables⁵ were used. Tables for individual instruments may list wavelengths somewhat differently, as instrument optical path atmospheric conditions may vary.

6.6 Information on potential spectral interfering elements was provided by the laboratories participating in the interlaboratory study (ILS) and may have originated from sources such as recognized wavelength reference tables, instrument manufacturer's software wavelength tables, and/or an individual laboratory's wavelength research studies.

⁴ Ralchenko, Yu., Kramida, A. E., Reader, J., and NIST ASD Team, *NIST Atomic Spectra Database* (version 3.1.5), 2008, online. Available: <http://physics.nist.gov/asd3> [2008, October 28]. National Institute of Standards and Technology, Gaithersburg, MD.

⁵ Harrison, G. R., *MIT Wavelength Tables*, John Wiley & Sons, New York, New York, 1969.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

TABLE 1 Analytical Lines and Potential Interferences

Element	Wavelength (nm)	Potential Interference
Aluminum	176.639	
Aluminum	394.400	
Bismuth (see 1.4)	190.241	
Boron	182.579	Molybdenum, cobalt, chromium
Boron	249.678	Tin, chromium, iron
Boron	208.893	
Cobalt	230.786	
Cobalt	231.160	Antimony, nickel
Cobalt	235.342	
Cobalt	237.863	Iron
Cobalt	238.89	
Copper	224.701	
Copper	327.396	
Chromium	267.716	
Chromium	206.553	Tungsten
Chromium	266.602	Cobalt
Chromium	275.072	Iron, molybdenum
Hafnium (see 1.4)	277.336	
Hafnium (see 1.4)	232.247	
Iron	261.187	
Iron	259.940	
Magnesium (see 1.4)	280.270	
Manganese	257.611	Cerium, cobalt, tungsten
Manganese	260.568	
Molybdenum	201.510	
Molybdenum	202.030	
Nickel	231.604	
Niobium	288.318	
Niobium	295.088	Hafnium
Palladium	340.458	
Palladium	355.308	
Palladium	360.955	
Ruthenium	240.272	
Ruthenium	245.553	
Silicon	251.611	Hafnium, molybdenum
Silicon	288.160	Chromium
Tantalum	240.062	Iron
Tin	175.791	
Tin	242.949	
Titanium Internal Standard	191.391	
Titanium Internal Standard	247.417	
Titanium Internal Standard	326.369	
Titanium Internal Standard	348.966	
Titanium Internal Standard	358.713	
Titanium Internal Standard	372.459	
Titanium Internal Standard	431.506	
Tungsten	207.911	
Vanadium	292.402	Iron, molybdenum
Vanadium	326.770	
Vanadium	354.519	Niobium, tungsten
Vanadium	359.202	
Yttrium	360.073	Molybdenum
Zirconium	343.823	Nickel

6.7 The user shall verify that the selected wavelength performs acceptably in their laboratory, preferably during method validation (See Section 15). The user also may choose to use multiple wavelengths to help verify that line selection is optimized for the particular alloy being determined. It is recommended that when wavelengths and appropriate spectral corrections are determined, the user of this test method should

either specify this information or reference instrument programs that include this information in their laboratory analysis procedures.

7. Apparatus

7.1 Direct current plasma atomic emission spectrometers (DCP-AES) used in this test method may conform to the specifications given in Practice E1832. A differently designed instrument may provide equivalent measurements. Suitability for use is determined by comparing the results obtained with the precision and bias statements contained in this method.

7.2 Inductively coupled plasma atomic emission spectrometers (ICP-AES) used in this test method may conform to the specifications given in Practice E1479. A differently designed instrument may provide equivalent measurements. Suitability for use is determined by comparing the results obtained with the precision and bias statements contained in this test method.

7.3 The sample introduction system shall be constructed of materials resistant to all mineral acids including hydrofluoric acid (HF).

7.4 Each instrument shall be set up according to the manufacturer's instructions.

7.5 Machine tools capable of removing surface oxides and other contamination from the as-received sample may be used to produce uncontaminated and chemically representative chips or millings for analysis.

8. Reagents and Materials

8.1 Reagents:

8.1.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ 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.

8.1.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water is sufficiently purified to meet the requirements of Type II of Specification D1193 or equivalent. The water purification method used shall be capable of removal of all elements in concentrations that might bias the test results.

8.1.3 *Internal Standard*—The use of an internal standard is optional. However, the use of an internal standard may compensate for the physical interferences resulting from differences in sample and calibration solutions transport efficiency. They also help compensate for daily instrumental drift as a result of temperature changes and so forth.

8.2 Calibration Solutions:

8.2.1 In this test method, calibration is based on laboratory prepared, alloy matrix-matched calibration solutions. Alloy

⁶ *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 the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

matrix-matched calibration solutions are solutions that contain the approximate amounts of the major alloying elements such as aluminum, tin, vanadium, and zirconium found in typical sample solutions. They are intended to model the physical behavior of sample solutions in the plasma. The matrix solutions are prepared with starting materials of relatively pure materials, certified reference materials (CRMs) of known purity, or both. The solution can be spiked with aliquots of single or multi-element CRM solutions that contain the analytes to be quantified if not present in a pure metal form. It may be possible to analyze different alloys using common matrix-matched calibration solutions provided method validation studies demonstrate acceptable data. Care shall be exercised in the selection of commercial CRM solutions. Solutions designed for use in atomic absorption techniques, for example, may not be of sufficient purity for DCP or ICP-AES use. When ordering specify solutions intended for ICP-AES applications.

8.2.2 In 8.2.3 and the following paragraphs, the preparation of alloy matrix-matched calibration solutions for analysis of sample solutions that contain 1-g alloy/100-mL final dilution from pure metals is described. For the analysis of the matrix metals, further dilution may be required. It is acceptable to vary sample weight and final volume as long as the user's method demonstrates adequate sensitivity and precision (see 12.1).

8.2.3 Calculate the nominal amounts of the alloying metals in 1 g of the alloy to be analyzed. Use a source of each metal that contains a known, low concentration of residual elements.

8.2.4 Calculate the total amount of each residual element contained in each matrix metal. This quantity of residual elements will be present in the calibration solutions as added analyte(s). The total amount of each analyte must be adjusted to determine the actual concentration of each calibration solution accordingly.

NOTE 1—Powdered metals have been found acceptable for preparing matrix solutions. Select powdered metals that do not exhibit excessive surface oxidation. However, do not use powdered metals to make analyte additions as oxidation can lead to significant error in the amount of metal added.

8.2.5 Determine the number and concentration of the calibration solutions needed to cover the concentration range for each element. Since most DCP software only allows a two-point calibration, it is suggested that, as a minimum, the calibration solutions have their highest concentration slightly above the highest expected sample concentration and their lowest concentration near the lowest expected sample concentration or the lower reporting limit, whichever is higher. If the instrument software allows for a 3-point calibration, a concentration near the midrange of the expected sample concentration range may be used.

8.2.6 Prepare the alloy matrix-matched solutions as follows:

8.2.6.1 Weigh the amounts of the pure metals calculated in 8.2.3, this includes the matrix metals and the analyte metals, into an HF-resistant dissolution vessel. Use one vessel for each calibration solution to be made.

8.2.6.2 Dissolve the pure metals in a sufficient amount of acid mixture to keep all analytes in solution. Select acid mixtures that will dissolve the metals used in the calibration solutions and the alloys to be analyzed using this method.

8.2.6.3 A mixture of HF+HNO₃ (2+1), HCl+HF+HNO₃ (1.5+2+1) or HCl+HF+HNO₃ (15+2+1) are examples of solutions that will dissolve many types of titanium alloys. Moderate the reaction with the addition of H₂O. For alloys containing molybdenum, palladium or ruthenium, first add concentrated HCl before the addition of H₂O or HF/HNO₃.

NOTE 2—If powdered metals, thin sheet, or small pins are used, add the acid cautiously as powdered metals tend to be very reactive.

8.2.6.4 Transfer the solutions into 100-mL HF-resistant volumetric flasks. If an internal standard is used, pipette the predetermined amount into each volumetric flask. Alternatively, titanium can be used as an internal standard. Proceed to 8.2.8.

8.2.6.5 Additional elements may be pipetted from liquid or aqueous CRMs if required.

8.2.7 As an alternative to using high-purity metals for preparing the alloy matrix solution, single or multi-element CRM solutions may be used according to the following steps:

8.2.7.1 Calculate the nominal amounts of titanium, alloying metals, in 1 g of the alloy to be analyzed.

8.2.7.2 Transfer appropriate quantities of the liquid CRMs into the appropriate number (see 8.2.5) of HF-resistant volumetric flask. Matrix metals solutions may be from CRM or solid metal digestions.

8.2.7.3 If an internal standard is used, pipette the predetermined amount into each volumetric flask. Alternatively, titanium can be used as an internal standard.

8.2.7.4 The solutions used to prepare the matrix solutions may contain analyte elements as residual elements in significant concentrations. Users may need to calculate the amount of residual elements contained in each matrix solution addition. The amount of relevant analyte from these sources should be totaled and used to adjust the stated concentration of each calibration solution accordingly.

8.2.8 Add the needed amount of single-element or multi-element CRM solutions into the flasks, making sure to leave one analyte free for use as a blank. Maintain the acidity necessary to assure solution stability. The acidity given on the solution CRM certificate of analysis will provide guidance on the necessary acid concentrations needed to do this. Typically, if these solutions are to match samples prepared using 1 g of alloy diluted to 100 mL, the quantity of acids used in 8.2.4 will be sufficient to hold all analytes in solution.

8.2.9 In the tables in Appendix X1, the calibration formulations used in ILS No. 0537 are illustrated.

8.3 Other Materials:

8.3.1 Argon—The purity of the argon shall meet or exceed the specifications of the instrument manufacturer.

8.3.2 Purge Gases—The purity of the purge gases shall meet or exceed the specifications of the instrument manufacturer.

8.3.3 Control Materials:

8.3.3.1 A laboratory may choose to procure, produce, or have manufactured a chip material containing analyte contents in the range of typical samples to be used as a control material.

These chips should be homogenous and well blended. Whenever possible, users of this test method are discouraged from using CRMs as routine control materials to preserve limited material supplies.

8.3.3.2 A laboratory may find it difficult to procure or have manufactured the materials described in 8.3.3.1 for all of the necessary analytes or alloys. If this is the case, then it is acceptable to prepare equivalent reference material solutions using the procedure described in 8.2 to use as control solutions.

9. Hazards

9.1 This test method involves the use of concentrated HF. Read and follow label precautions, material safety data sheets (MSDS) information, and Practices E50 for HF handling precautions, as well. For precautions to be observed in the use of certain other reagents in this test method, refer to Practices E50.

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

10. Sampling, Test Specimens, and Test Units

10.1 Laboratories shall follow written practices for sampling and preparation of test samples.

10.2 Test specimens should be obtained by milling or drilling chips that are clean and of sufficient size to allow the weighing of the appropriate sample for dissolution and analysis.

11. Preparation of Apparatus

11.1 Analytical instrumentation and sample preparation equipment shall be installed and operated in a manner consistent with manufacturer's recommendations.

12. Calibration

12.1 It will be necessary to establish that the instrument being used is capable of demonstrating acceptable sensitivity and precision for the elements being determined. Once this has been done, it will not be necessary to evaluate sensitivity and precision routinely. Evaluate equipment sensitivity and precision as described in 12.1.1 and 12.1.2.

12.1.1 *Sensitivity*—Sensitivity shall be evaluated by first establishing a calibration curve for each element being determined using calibration solutions prepared as described in 8.2. At a minimum, the calibration curve will contain two points. After thorough rinsing, the blank solution is analyzed ten times. Calculate three times the standard deviation of this determination as an approximation of the detection limit. Calculate ten times the standard deviation to approximate the limit of quantification. If the instrument/parameter selection does not produce an estimated detection limit equal to or better than the lower scope limit for the element(s) being determined, then it is probable the method will be unable to meet the lower scope limit. If the instrument/parameter selection does not produce a limit of quantification equal to or better than the lower scope limit for the element(s) being determined, then it is possible the method user will be unable to meet consistently the method's lower scope limit.

12.1.2 *Precision*—The short-term precision shall be determined as follows. Using the same calibration generated in 12.1.1, analyze the high calibration solution ten times using the selected instrument/parameters. Calculate the % relative standard deviation (% RSD) as follows:

$$\%RSD = \frac{100s}{\bar{C}} \quad (1)$$

where:

s = estimated standard deviation, and

$\bar{C}$ = average of the ten results for the measured concentration.

12.1.2.1 The calculated % RSD should be approximately 1 %. However, as concentrations decrease or as intensities approach detector saturation, % RSD may tend to increase, while not necessarily affecting the quality of the reported result. During the ILS, % RSD values were typically approximately 1 %, although some values approached 5 %. The user of this test method shall decide if precision is adequate for meeting data quality objectives. In Practice E1479, limited guidance as to the parameters that may have an effect on instrument precision is given. Instrument troubleshooting manuals provided by the manufacturer of the equipment may also provide guidance for optimizing performance for the specific instrument being used.

12.2 Calibration:

12.2.1 Set up the instrument for calibration in a manner consistent with the manufacturer's recommendations.

12.2.2 Specify calibration units consistent with the concentrations of the calibration solutions prepared in 8.2. The user may choose to specify units in the instrument software as a mass fraction such as % or mg/kg to simplify calculation and reporting of final results.

12.2.3 Define the number of replicate measurements to be made and averaged for a single reported result. Typically, a minimum of two replicates is specified.

12.2.4 Calibrate the instrument using the calibration solutions. Calibration curves for ICP-AES are generally linear over several orders of magnitude. Typical calibration methods include calculation of a linear function using a calculated intercept, calculation of a linear function while forcing the intercept through zero, and calculation of a linear function using concentration weighting. Method validation per Section 15 may help the laboratory in selecting an appropriate calibration algorithm.

12.2.5 The user of this test method shall verify the quality of the calibration fit. Typical instrument software will calculate a correlation coefficient for each calibration curve. It is acceptable to rely upon the correlation coefficient as a demonstration of calibration fit. Ideally, this coefficient should be 0.995 or better. The user of this test method may choose other methods to judge the quality of a calibration fit such as checking the residuals for trends and calculating a lack of fit parameter.

13. Procedure

13.1 Weigh a sample, consistent with the sample size selected for use in preparing the calibration solutions, to the nearest 0.001 g and place it into a HF-resistant vessel.

13.2 Add to the sample an appropriate volume of the same acid mixture used to prepare the calibration solutions (8.2.6) and cover.

13.3 If necessary, heat the vessel gently until the sample is dissolved.

13.4 Add an internal standard if used in the calibration solutions. Alternatively, titanium can be used as an internal standard.

13.5 Make any other necessary acid volume adjustments so that the acidity of the samples matches the acidity of the calibration solutions, noting that the sample mass to final sample solution volume shall be consistent with that of the calibration solutions. Dilute the vessel to volume and mix well.

NOTE 3—If sample preparation methods other than those specified are used, a validation study as specified in Section 15 should be used to evaluate the validity of the sample preparation method. Caution should be used when boiling solutions for the analysis of boron and silicon with HF as volatile fluorides may be lost. The reaction rate should be moderated with the addition of H₂O to the sample before the addition of HF, or a sealed digestion bomb may be used where method validation dictates their use.

13.6 Analyze the sample solution according to the instrument manufacturer's instructions and the laboratory's standard operating procedure, using the calibration generated in Section 12.

13.7 Analyze a control sample periodically throughout the run of the batch and at the end of the run. Use the control sample to evaluate the need for recalibration and reanalysis of samples. Refer to Section 14 for specific information on control sample analysis.

14. Control

14.1 The laboratory will establish procedures for calibration curve drift control. One suggested method involves the use of a control chart to monitor drift. Monitor each control sample. Refer to Practice E1329 for guidance on use of control charts. Users of this test method are strongly discouraged from using CRMs as routine control materials.

14.2 Most instrument manufacturer's software allows the use of programmable control sample tolerances. It is acceptable to calculate control limits and to use these as limits in the instrument software.

14.3 The individual laboratories' analysis procedures will typically specify reanalysis of affected samples if control samples indicate that the calibration is no longer valid.

15. Method Validation

15.1 A laboratory using this test method for the first time shall provide additional method validation data to demonstrate that the test method as applied in their laboratory is yielding unbiased, repeatable results.

15.2 Initially, the laboratory shall prepare and analyze solid CRMs or reference materials (RMs) or both using this test method to obtain these data. If there are no solid CRMs or RMs available for the alloys/analytes being determined, then spike recovery studies using alloy samples shall be part of the validation process. The precision and bias data obtained for

these materials shall be compared to the precision and bias data stated in this test method.

15.3 Any laboratory demonstrating precision and bias data outside of the laboratories measurement quality objectives should attempt to identify and correct any problems associated with their application of this test method.

15.4 The test method user shall weigh customer requirements and the laboratory's data quality objectives and justify acceptance of the test method validation data.

15.5 The test method validation study shall be documented.

16. Calculation

16.1 If the user chooses to specify units in the instrument software to express the concentration of analyte contained in the sample as a mass fraction, then no other calculations other than sample weight correction will be necessary. Results may be taken directly from the instrument readout.

16.2 If the user specified analyte concentration as a volume fraction into the software, it will be necessary to convert the analyte volume fraction concentrations obtained for the sample solution into analyte mass fractions contained in the sample. For example, if the sample is prepared as 1 g of sample diluted to a final volume of 100-mL solution, an analyte volume fraction of 1.00-mg analyte/L of solution corresponds to a mass fraction of 0.010 % analyte in the sample.

17. Report

17.1 Results shall be reported in a manner consistent with customer requirements. When uncertainty estimates are required, results should be reported in accordance with the guidance provided in ISO Guide 98-3. In this test method, it is explained that the analyst shall obtain an estimate of the overall uncertainty of the result and express that uncertainty as an expanded uncertainty, $U = ku_c$, where u_c is a combined uncertainty expressed at the level of 1s (one standard deviation) and k is an expansion factor typically chosen as $k = 2$. It is expected that the laboratory will include all significant sources of uncertainty in their estimate of the combined uncertainty. Express the value of U with two significant digits. Then, express the reported result to the same number of decimal places.

18. Precision and Bias

18.1 *Precision*—Originally, seven laboratories cooperated in testing this test method. In Tables 2-15 summaries of this precision information are presented. The interlaboratory data were evaluated in accordance with Practice E1601 and Guide E1763; the details are given in ASTM Research Report No. E01-1112.

18.2 A new study was performed in 2011 to demonstrate method precision and bias for an expanded scope. Additional analytes included cobalt, lead, niobium, palladium, ruthenium, tantalum, and tungsten. In Tables 16-21, the summaries of data for this additional study are presented. Nine laboratories were asked to report triplicate results, for six elements, obtained from five different titanium alloy samples. One laboratory

TABLE 2 Aluminum in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Aluminum Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
6	6	0.000383	0.000804	0.00161	0.00451	1177.
5	6	0.0339	0.000969	0.00299	0.00839	24.7
4	6	0.099	0.00168	0.00545	0.0152	15.4
1	6	3.136	0.0371	0.0632	0.177	5.6
3	6	6.435	0.0478	0.133	0.373	5.8
2	6	7.723	0.0589	0.128	0.359	4.6
Test Material	Certified Aluminum, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	3.08	0.083	NIST 649		Ti-15V-3Al-3Cr-3Sn (0.02)	
2	7.63	0.102	NIST 2433		Ti-8Al-1Mo-1V (0.05)	
3	6.36	0.075	NIST 173b		Ti-6Al-4V (0.04)	
4	0.096	0.003	HTL 572		TIMET ILT, Ti-CP (0.009)	
5	0.031	0.0029	HTL AA16#4		TIMET Internal, Ti-CP (0.001)	
6	0.0001	0.000283	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.1 % Al to a minimum of 5.2 %.

TABLE 3 Boron in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Boron Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
3	6	0.000095	0.000094	0.000137	0.000384	404.
4	5	0.00487	0.000458	0.000462	0.00129	26.6
1	7	0.00488	0.000076	0.000340	0.00095	19.5
2	5	0.00822	0.000393	0.000480	0.00134	16.3
Test Material	Certified Boron, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	0.0048	0.00007	HTL 572		TIMET ILT, Ti-CP (0.009)	
2	0.0093	-0.00108	HTL AA16#4		TIMET Internal, Ti-CP (0.001)	
3	<0.0001	0.0000	HTL 559		TIMET Electro-refined (no data)	
4	0.0052	-0.00033	HTL 573		TIMET ILT, Ti-6Al-4V (0.0003)	

Note—The General Analytical Error model estimates relative errors decrease above 0.002 % to a minimum of 18.5 %.

TABLE 4 Chromium in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Chromium Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	5	0.00035	0.000335	0.000862	0.00241	692.
3	5	0.0149	0.000191	0.000600	0.00168	11.3
2	5	0.0245	0.000203	0.001633	0.00457	18.7
1	5	3.809	0.01878	0.03363	0.0942	2.47
Test Material	Certified Chromium, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	3.84	-0.031	NIST 648		Ti-5Al-2Sn-2Zr-4Cr-4Mo (0.03)	
2	0.025	-0.0005	NIST 173b		Ti-6Al-4V (NIST 654B, 0.002)	
3	0.0145	0.0004	HTL 572		TIMET ILT, Ti-CP (0.0005)	
4	0.0003	0.00005	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.1 % Cr to a minimum of 2.5 %.

TABLE 5 Copper in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Copper Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	5	0.000353	0.00038	0.00066	0.00185	524.
1	7	0.00410	0.00033	0.00170	0.00476	116.
3	7	0.0206	0.00057	0.00281	0.00786	38.2
5	6	0.0211	0.00058	0.00215	0.00601	28.5
2	6	0.473	0.00938	0.0218	0.0610	12.9
Test Material	Certified Copper, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	0.008	-0.0039	NIST 173b		Ti-6Al-4V(0.001) NIST 654B(0.004±0.001)	
2	0.49	-0.017	IARM-178A		ARM I RM Ti-6Al-6V-2Sn (0.028)	
3	0.025	-0.0044	HTL 572		TIMET ILT, Ti-CP (0.003)	
4	<0.0001	<0.0003	HTL 559		TIMET Electro-refined (no data)	
5	0.025	-0.0039	HTL 573		TIMET ILT, Ti-6Al-4V (0.001)	

Note—The General Analytical Error model estimates relative errors decrease above 0.015 % Cu to a minimum of 13 %.

TABLE 6 Iron in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Iron Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	6	0.00188	0.00015	0.00073	0.00203	108.
3	6	0.0444	0.00092	0.00144	0.00404	9.1
2	6	0.227	0.00196	0.00696	0.0195	8.6
1	6	1.706	0.0108	0.0205	0.0575	3.37
Test Material	Certified Iron, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	1.77	-0.064	NIST 2432		Ti-10V-2Fe-3Al (0.05)	
2	0.23	-0.003	NIST 173b		Ti-6Al-4V (0.01)	
3	0.048	-0.0036	HTL 572		TIMET ILT, Ti-CP (0.003)	
4	0.0011	0.00078	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.06 % Fe to a minimum of 3.5 %.

TABLE 7 Manganese in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Manganese Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	5	-0.00071	0.000008	0.00056	0.00157	219.
3	5	0.00388	0.000030	0.00046	0.00128	33.0
1	5	0.00420	0.000043	0.00050	0.00140	33.3
2	5	0.01277	0.000124	0.00041	0.00115	9.0
Test Material	Certified Manganese, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	0.0048	-0.0006	HTL 572		TIMET ILT, Ti-CP (0.0006)	
2	0.013	-0.00023	HTL AA16#4		TIMET Internal, Ti-CP (0.002)	
3	0.0044	-0.00052	HTL 573		TIMET ILT, Ti-6Al-4V (0.0008)	
4	0.0001	-0.00081	HTL 559		TIMET Electro-refined (no data)	

Note—All laboratories reported negative concentrations for Material 4. Three materials cover the range of 0.004 to 0.013 % Mn. Within that range, the Constant Analytical Error [KC] model estimates the Reproducibility Index is 0.0013 % Mn.

TABLE 8 Molybdenum in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Molybdenum Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	4	0.00065	0.000417	0.00063	0.00175	268.
3	4	0.0149	0.000499	0.00312	0.0087	58.7
2	5	0.981	0.0172	0.0363	0.1017	10.4
1	5	5.889	0.0442	0.207	0.580	9.9
Test Material	Certified Molybdenum, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	6.01	-0.12	NIST 2431		Ti-6Al-2Sn-4Zr-6Mo (0.07)	
2	0.99	-0.009	NIST 2433		Ti-8Al-1Mo-1V (0.02)	
3	0.013	0.0019	NIST 173b		Ti-6Al-4V (0.004)	
4	<0.0001	<0.00055	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.02 % Mo to a minimum of 9.9 %.

TABLE 9 Nickel in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Nickel Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	6	0.00035	0.00021	0.00021	0.00059	171.
3	5	0.00242	0.00020	0.00028	0.00078	32.5
1	6	0.0271	0.00042	0.00099	0.00276	10.2
2	7	0.795	0.00707	0.0103	0.0287	3.61
Test Material	Certified Nickel, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	0.028	-0.0009	NIST 173b		Ti-6Al-4V; NIST 654B (0.002)	
2	0.811	-0.016	HTL 526		TIMET Internal, Ti-0.8Ni-0.3Mo (0.006)	
3	0.0035	-0.00108	HTL 572		TIMET ILT, Ti-CP (0.0012)	
4	0.0002	0.00015	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.016 % Ni to a minimum of 3.6 %.

TABLE 10 Silicon in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Silicon Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
5	5	0.0024	0.000595	0.00390	0.0109	460.
4	6	0.0109	0.000651	0.00444	0.0124	114.
2	5	0.0457	0.00253	0.00385	0.0108	23.6
1	4	0.090	0.00342	0.00342	0.00959	10.6
3	7	0.404	0.01212	0.0237	0.0665	16.5
Test Material	Certified Silicon, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	0.088	0.002	NIST 2431		Ti-6Al-2Sn-4Zr-6Mo (0.005)	
2	0.046	-0.0003	NIST 173b		Ti-6Al-4V (0.005)	
3	0.429	-0.025	HTL 525		TIMET Internal, Ti-4Al-4Mo-2Sn (0.006)	
4	0.012	-0.0011	HTL 572		TIMET ILT, Ti-CP (0.003)	
5	0.0001	0.0023	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.07 % Si to a minimum of 15.8 %.

TABLE 11 Tin in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Tin Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
4	5	0.0016	0.00036	0.00309	0.0087	554.
3	6	0.0221	0.00221	0.00390	0.0109	49.5
2	6	2.001	0.0125	0.0202	0.0566	2.83
1	5	3.025	0.0192	0.0224	0.0628	2.08
Test Material	Certified Tin, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	3.04	-0.015	NIST 649		Ti-15V-3Al-3Cr-3Sn (0.04)	
2	1.98	0.021	NIST 2431		Ti-6Al-2Sn-4Zr-6Mo (0.05)	
3	0.023	-0.0009	NIST 173b		Ti-6Al-4V; NIST 654B (0.002)	
4	<0.0001	<0.0015	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.4 % Sn to a minimum of 2.3 %.

TABLE 12 Vanadium in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Vanadium Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
5	6	0.00111	0.00246	0.00258	0.00721	649.
4	5	0.0094	0.00232	0.00254	0.00712	75.9
2	7	0.964	0.00960	0.0314	0.0880	9.1
3	6	4.366	0.0304	0.0968	0.271	6.2
1	7	15.01	0.0681	0.204	0.572	3.81
Test Material	Certified Vanadium, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	15.1	-0.09	NIST 649		Ti-15V-3Al-3Cr-3Sn (0.1)	
2	0.98	-0.016	NIST 2433		Ti-8Al-1Mo-1V (0.02)	
3	4.31	0.056	NIST 173b		Ti-6Al-4V (0.05)	
4	0.010	-0.0006	HTL 572		TIMET ILT, Ti-CP (0.002)	
5	0.0007	0.0004	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.2 % V to a minimum of 4.1 %.

TABLE 13 Yttrium in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Yttrium Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	$R_{rel}\%$
3	6	0.000007	0.0000536	0.0000623	0.000175	2663.
2	7	0.000331	0.0000873	0.0000875	0.000245	73.9
1	7	0.004087	0.0000532	0.000206	0.000578	14.1
Test Material	Certified Yttrium, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	0.0040	0.000087	HTL AA16#4		TIMET Internal, Ti-CP (no data)	
2	0.0007	-0.000369	HTL 573		TIMET ILT, Ti-6Al-4V (0.0002)	
3	0.0000	0.000007	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.012 % Y to a minimum of 14.1 %.

TABLE 14 Zirconium in Titanium and Titanium Alloys by Atomic Emission Spectrometry

Test Material	Number of Laboratories	Zirconium Found, %	Minimum SD (s_M , E1479)	Reproducibility SD (s_R , E1479)	Reproducibility Index (R , E1479)	R_{rel} %
4	5	0.00060	0.00017	0.00056	0.00158	261.
3	6	0.0080	0.00023	0.00083	0.00232	29.0
1	7	1.836	0.0223	0.0472	0.132	7.2
2	7	4.083	0.0189	0.0329	0.092	2.26
Test Material	Certified Zirconium, %	Bias, %	Material Identification (Source)		Description (Uncertainty or Standard Deviation)	
1	1.84	-0.004	NIST 648		Ti-5Al-2Sn-2Zr-4Cr-4Mo (0.04)	
2	4.06	0.023	NIST 2431		Ti-6Al-2Sn-4Zr-6Mo (0.05)	
3	0.008	0.000	NIST 173b		Ti-6Al-4V; NIST 654B (0.001)	
4	0.0003	0.0003	HTL 559		TIMET Electro-refined (no data)	

Note—The General Analytical Error model estimates relative errors decrease above 0.05 % Zr to a minimum of 3.6 %.

TABLE 15 Constants for Predicting Reproducibility Index, R_C

Analyte	K_F (%)	K_{rel} (%)	K_C (%)
Aluminum	0.0045	5.20	0.0013
Boron	0.00038	18.5	
Chromium	0.0024	2.47	
Copper	0.0019	13.1	
Iron	0.0020	3.52	
Manganese	0.0018	9.9	
Molybdenum	0.00060	3.63	
Nickel	0.011	15.8	
Silicon	0.0087	2.31	
Tin	0.0072	4.08	
Vanadium	0.00017	14.1	
Yttrium	0.0016	3.60	
Zirconium			

TABLE 16 Cobalt (%)

Material	Average ^A $\bar{x}$	Certified Value ^B	Avg. Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Low Level	0.001 339	-	-	0.000 129	0.001 037	0.000 361	0.002 905
BS T 80	0.014 745	0.0146	100.99	0.000 157	0.000 616	0.000 439	0.001 724
BS T 81	0.039 515	0.0395	99.89	0.000 358	0.001 623	0.001 004	0.004 545
CR 252	0.067 312	-	-	0.000 760	0.002 792	0.002 129	0.007 816
CR 237	0.065130	-	-	0.000 383	0.004 294	0.001 073	0.012 023

^A The average of the laboratories' calculated averages.

^B As reported on the Certificate of Analysis provided by Brammer Standard Company, Inc. for BST80 and BST81 and on the Certificate of Analysis provided by Analytical Reference Materials International for the low level sample.

TABLE 17 Niobium (%)

Material	Average ^A $\bar{x}$	Certified Value ^B	Avg. Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Low Level	0.004 050	0.009	45.00	0.000 269	0.001 413	0.000 753	0.003 957
BS T 80	0.037 958	0.0367	102.90	0.000 706	0.001 774	0.001 978	0.004 967
BS T 81	0.019 573	0.0191	102.48	0.000 170	0.001 092	0.000 475	0.003 058
CR 252	0.068 636	-	-	0.000 591	0.004 535	0.001 654	0.012 698
CR 237	0.069090	-	-	0.000 711	0.006 003	0.001 990	0.016 807

^A The average of the laboratories' calculated averages.

^B As reported on the Certificate of Analysis provided by Brammer Standard Company, Inc. for BST80 and BST81 and on the Certificate of Analysis provided by Analytical Reference Materials International for the low level sample.

reported three sets of data using one ICP and two different DCP spectrometers. These three sets of data all used independent sample preparations and calibration materials. Every “test result” reported represents an individual determination. Prac-

tice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. E01-XXXX.

TABLE 18 Palladium (%)

Material	Average ^A $\bar{x}$	Certified Value ^B	Avg. Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Low Level	0.000 477	-	-	0.000 526	0.003 048	0.001 472	0.008 533
BS T 80	0.133 748	0.1424	93.92	0.001 163	0.013 596	0.003 255	0.038 069
BS T 81	0.039 973	0.0398	100.43	0.000 628	0.003 446	0.001 759	0.009 649
CR 252	0.136 888	-	-	0.002 213	0.013 194	0.006 197	0.036 945
CR 237	0.134 485	-	-	0.002 006	0.012 182	0.005 615	0.034 111

^A The average of the laboratories' calculated averages.

^B As reported on the Certificate of Analysis provided by Brammer Standard Company, Inc. for BST80 and BST81 and on the Certificate of Analysis provided by Analytical Reference Materials International for the low level sample.

TABLE 19 Ruthenium (%)

Material	Average ^A $\bar{x}$	Certified Value ^B	Avg. Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Low Level	0.000 175	-	-	0.000 297	0.000 636	0.000 832	0.00 1780
BS T 80	0.041 733	0.0469	88.98	0.000 230	0.006 632	0.000 644	0.018 569
BS T 81	0.028 389	0.0310	91.58	0.000 561	0.002 807	0.001 570	0.007 860
CR 252	0.065 726	-	-	0.000 669	0.001 732	0.001 874	0.004 850
CR 237	0.070 081	-	-	0.000 581	0.003 643	0.001 626	0.010 201

^A The average of the laboratories' calculated averages.

^B As reported on the Certificate of Analysis provided by Brammer Standard Company, Inc. for BST80 and BST81 and on the Certificate of Analysis provided by Analytical Reference Materials International for the low level sample.

TABLE 20 Tantalum (%)

Material	Average ^A $\bar{x}$	Certified Value ^B	Avg. Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Low Level	-0.000 01	-	-	0.000 703	0.001 626	0.001 967	0.004 552
BS T 80	0.000 522	-	-	0.000 598	0.001 097	0.001 674	0.003 072
BS T 81	0.000 374	-	-	0.000 361	0.001 213	0.001 010	0.003 397
CR 252	0.089 637	-	-	0.001 998	0.004 008	0.005 595	0.011 223
CR 237	0.084 290	-	-	0.001 365	0.004 206	0.003 823	0.011 778

^A The average of the laboratories' calculated averages.

^B As reported on the Certificate of Analysis provided by Brammer Standard Company, Inc. for BST80 and BST81 and on the Certificate of Analysis provided by Analytical Reference Materials International for the low level sample.

TABLE 21 Tungsten (%)

Material	Average ^A $\bar{x}$	Certified Value ^B	Avg. Recovery %	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Low Level	0.001 104	-	-	0.001 026	0.001 388	0.002 872	0.003 888
BS T 80	0.015 556	0.0174	89.40	0.000 503	0.002 037	0.001 407	0.005 703
BS T 81	0.036 274	0.0372	97.51	0.001 413	0.002 830	0.003 955	0.007 924
CR 252	0.068 730	-	-	0.001 093	0.001 571	0.003 062	0.004 399
CR 237	0.070 346	-	-	0.001 316	0.002 293	0.003 685	0.006 422

^A The average of the laboratories' calculated averages.

^B As reported on the Certificate of Analysis provided by Brammer Standard Company, Inc. for BST80 and BST81 and on the Certificate of Analysis provided by Analytical Reference Materials International for the low level sample.

18.2.1 Repeatability Limit (r)—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the “ r ” value for that material; “ r ” is the interval representing the critical difference between two test results for the same material obtained by the same operator using the same equipment on the same day in the same laboratory.

18.2.1.1 Repeatability limits are listed in **Tables 2-7**.

18.2.2 Reproducibility Limit (R)—Two test results shall be judged not equivalent if they differ by more than the “ R ” value for that material; “ R ” is the interval representing the critical difference between two test results for the same material obtained by different operators using different equipment in different laboratories.

18.2.2.1 Reproducibility limits are listed in **Tables 16-21**.

18.2.3 The terms repeatability limit and reproducibility limit are used as specified in Practice E177.

18.2.4 Any judgment in accordance with **18.2.1** would have an approximate 95 % probability of being correct.

18.3 An approximate value for the expected reproducibility index, R_C , at any concentration, C , within the quantitative range of this test method (see **1.1**) can be calculated by **Eq 2**. The constants, K_R and K_{rel} , are presented in **Table 16** (see **Note 4**).

$$R_C = (K_R^2 + (C \cdot K_{rel})^2)^{1/2} \quad (2)$$

NOTE 4—Manganese within this quantitative range follows the constant error model (see **Table 8**).

18.4 *Bias*—The accuracy of this test method has been deemed satisfactory on the basis of the bias information in **Tables 2-21**. The bias data from the original study are expressed in terms of the difference (in mass fraction) of the ILS study mean from the certified value of the RM studied. The bias of the data obtained in the 2011 study is expressed as the average recovery in % of the ILS study mean versus the RM certified value. Users are encouraged to use these or similar RMs to assure proper analytical performance.

19. Keywords

19.1 atomic emission spectrometry; DCP; direct current plasma; ICP; inductively coupled plasma; performance-based test method; titanium; titanium alloys

APPENDIXES

(Nonmandatory Information)

X1. ICP SYNTHETIC CALIBRATION STANDARD FORMULATION

TABLE X1.1 ICP Synthetic Calibration Standard Formulation

Element	Standard B			Standard C			Standard D			Standard E			Standard F			Standard G		
	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.
Al	--	--	--	--	--	--	20.0	4.00	8.5.3.1	40.0	8.00	8.5.3.1	--	--	--	--	--	--
B	1.0	0.020	8.5.3.2	2.0	0.040	8.5.3.2	--	--	--	--	--	--	--	--	--	--	--	--
Cr	--	--	--	--	--	--	10.0	2.00	8.5.3.3	25.0	5.00	8.5.3.3	--	--	--	--	--	--
Cu	2.0	0.040	8.5.3.5	3.0	0.600	8.5.3.4	--	--	--	--	--	--	--	--	--	--	--	--
Fe	--	--	--	--	--	--	5.0	1.00	8.5.3.6	15.0	3.00	8.5.3.6	--	--	--	--	--	--
Mn	1.0	0.020	8.5.3.7	2.0	0.040	8.5.3.7	--	--	--	--	--	--	--	--	--	--	--	--
Mo	--	--	--	--	--	--	--	--	--	--	--	--	15.0	3.00	8.5.3.8	40.0	8.00	8.5.3.8
Ni	2.0	0.040	8.5.3.10	5.0	1.00	8.5.3.9	--	--	--	--	--	--	--	--	--	--	--	--
Si	--	--	--	--	--	--	--	--	--	--	--	--	10.0	0.200	8.5.3.11	25.0	0.500	8.5.3.11
Sn	--	--	--	--	--	--	10.0	2.00	8.5.3.12	20.0	4.00	8.5.3.13	--	--	--	--	--	--
V	--	--	--	--	--	--	--	--	--	--	--	--	25.0	5.00	8.5.3.13	75.0	15.00	8.5.3.13
Y	1.0	0.020	8.5.3.14	2.0	0.040	8.5.3.14	--	--	--	--	--	--	--	--	--	--	--	--
Zr	--	--	--	--	--	--	--	--	--	--	--	--	15.0	3.00	8.5.3.15	25.0	5.00	8.5.3.15
Ti (g) ^B		4.99 g	8.6		4.90 g	8.6		4.55 g	8.6		4.00 g	8.6		4.44 g	8.6		3.58 g	8.6
HCl ^C	150 mL			149 mL			144 mL			143 mL			139 mL			122 mL		
HNO ₃ ^C	9.7 mL			9.9 mL			9.5 mL			8.5 mL			9.0 mL			7.3 mL		
HF	20 mL			20 mL			20 mL			20 mL			20 mL			20 mL		
I.S.	Ref 8.7			Ref 8.7			Ref 8.7			Ref 8.7			Ref 8.7			Ref 8.7		

^A Element addition can also be accomplished by weighing if the purchased solution has certified values for the concentration in mg/g along with the mg/mL designation. Appropriate conversions will have to be made.

^B Base Material of 99.99 % minimum purity (metals basis) and analyzed by GDMS or suitable method to determine the level of purity. Each element should not exceed 10 ppm. Appropriate adjustments must be made to the elemental % content that takes into account base material elemental content.

^C The HCl and HNO₃ acidities given are based on the formulations of **8.2.6.3**. They would be adjusted accordingly if purchased standard solutions contain different acidities.

X2. DCP SYNTHETIC CALIBRATION STANDARD FORMULATION

TABLE X2.1 DCP Synthetic Calibration Standard Formulation

Element	Standard B			Standard C			Standard D			Standard E			Standard F			Standard G		
	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.	mL ^A	%	Ref.
Al	--	--	--	--	--	--	40.0	4.00	8.5.3.1	80.0	8.00	8.5.3.1	--	--	--	--	--	--
B	2.0	0.020	8.5.3.2	4.0	0.040	8.5.3.2	--	--	--	--	--	--	--	--	--	--	--	--
Cr	--	--	--	--	--	--	20.0	2.00	8.5.3.3	50.0	5.00	8.5.3.3	--	--	--	--	--	--
Cu	4.0	0.040	8.5.3.5	6.0	0.600	8.5.3.4	--	--	--	--	--	--	--	--	--	--	--	--
Fe	--	--	--	--	--	--	10.0	1.00	8.5.3.6	30.0	3.00	8.5.3.6	--	--	--	--	--	--
Mn	2.0	0.020	8.5.3.7	4.0	0.040	8.5.3.7	--	--	--	--	--	--	--	--	--	--	--	--
Mo	--	--	--	--	--	--	--	--	--	--	--	--	30.0	3.00	8.5.3.8	80.0	8.00	8.5.3.8
Ni	4.0	0.040	8.5.3.10	10.0	1.00	8.5.3.9	--	--	--	--	--	--	--	--	--	--	--	--
Si	--	--	--	--	--	--	--	--	--	--	--	--	20.0	0.200	8.5.3.11	50.0	0.500	8.5.3.11
Sn	--	--	--	--	--	--	20.0	2.00	8.5.3.12	40.0	4.00	8.5.3.12	--	--	--	--	--	--
V	--	--	--	--	--	--	--	--	--	--	--	--	50.0	5.00	8.5.3.13	150.0	15.00	8.5.3.13
Y	2.0	0.020	8.5.3.14	4.0	0.040	8.5.3.14	--	--	--	--	--	--	--	--	--	--	--	--
Zr	--	--	--	--	--	--	--	--	--	--	--	--	30.0	3.00	8.5.3.15	50.0	5.00	8.5.3.15
Ti (g) ^B	9.98 g	8.6		9.80 g	8.6		9.10 g	8.6		8.00 g	8.6		8.88 g	8.6		7.15 g	8.6	
HCl ^C	150 mL			148 mL			137 mL			117 mL			128 mL			94 mL		
HNO ₃ ^C	13.8 mL			13.3 mL			14.0 mL			12.0 mL			13.0 mL			9.6 mL		
HF	20 mL			20 mL			20 mL			20 mL			20 mL			20 mL		
I.S.	Ref 8.7			Ref 8.7			Ref 8.7			Ref 8.7			Ref 8.7			Ref 8.7		

^A Element addition can also be accomplished by weighing if the purchased solution has certified values for the concentration in mg/g along with the mg/mL designation. Appropriate conversions will have to be made.

^B Base Material of 99.99 % minimum purity (metals basis) and analyzed by GDMS or suitable method to determine the level of purity. Each element should not exceed 10 ppm. Appropriate adjustments must be made to the elemental % content that takes into account base material elemental content.

^C The HCl and HNO₃ acidities given are based on the formulations of 8.2.6.3. They would be adjusted accordingly if purchased standard solutions contain different acidities.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).