



Designation: E2994 – 21

# Standard Test Method for Analysis of Titanium and Titanium Alloys by Spark Atomic Emission Spectrometry and Glow Discharge Atomic Emission Spectrometry (Performance-Based Method)<sup>1</sup>

This standard is issued under the fixed designation E2994; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes the analysis of titanium and its alloys by spark atomic emission spectrometry (Spark-AES) and glow discharge atomic emission spectrometry (GD-AES). The titanium specimen to be analyzed may be in the form of a disk, casting, foil, sheet, plate, extrusion, or some other wrought form or shape. The elements and ranges covered in the scope by spark-AES of this test method are listed below.

Element	Tested Mass Fraction Range (%)
Aluminum	0.008 to 7.0
Chromium	0.006 to 0.1
Copper	0.014 to 0.1
Iron	0.043 to 0.3
Manganese	0.005 to 0.1
Molybdenum	0.014 to 0.1
Nickel	0.006 to 0.1
Silicon	0.018 to 0.1
Tin	0.02 to 0.1
Vanadium	0.015 to 5.0
Zirconium	0.013 to 0.1

1.1.1 The elements oxygen, nitrogen, carbon, niobium, boron, yttrium, palladium, and ruthenium, were included in the ILS but the data did not contain the required six laboratories. Precision tables were provided for informational use only.

1.2 The elements and ranges covered in the scope by GD-AES of this test method are listed below.

Element	Tested Mass Fraction Range (%)
Aluminum	0.02 to 7.0
Carbon	0.02 to 0.1
Chromium	0.006 to 0.1
Copper	0.028 to 0.1

<sup>1</sup> 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.

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Element	Tested Mass Fraction Range (%)
Iron	0.09 to 0.3
Molybdenum	0.016 to 0.1
Nickel	0.006 to 0.1
Silicon	0.018 to 0.1
Tin	0.022 to 0.1
Vanadium	0.054 to 5.0
Zirconium	0.026 to 0.1

1.2.1 The elements boron, manganese, oxygen, nitrogen, niobium, yttrium, palladium, and ruthenium were included in the ILS, but the data did not contain the required six laboratories. Precision tables were provided for informational use only.

1.3 The elements and mass fractions given in the above scope tables are the ranges validated through the interlaboratory study. However, it is known that the techniques used in this standard allow the useable range, for the elements listed, to be extended higher or lower based on individual instrument capability, available reference materials, laboratory capabilities, and the spectral characteristics of the specific element wavelength being used. It is also acceptable to analyze elements not listed in 1.1 or 1.2 and still meet compliance to this standard test method. Laboratories must provide sufficient evidence of method validation when extending the analytical range or when analyzing elements not reported in Section 18 (Precision and Bias), as described in Guide E2857.

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 safety hazard statements are given in Section 9.*

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*:<sup>2</sup>

- E29** Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E135** Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E177** Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E305** Practice for Establishing and Controlling Spark Atomic Emission Spectrochemical Analytical Curves
- E406** Practice for Using Controlled Atmospheres in Atomic Emission Spectrometry
- E691** Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E1329** Practice for Verification and Use of Control Charts in Spectrochemical Analysis (Withdrawn 2019)<sup>3</sup>
- E1507** Guide for Describing and Specifying the Spectrometer of an Optical Emission Direct-Reading Instrument
- E1601** Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
- E2857** Guide for Validating Analytical Methods
- E2972** Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials

### 2.2 *ISO Standard*:<sup>4</sup>

- ISO/IEC Guide 98-3:2008** Uncertainty of Measurement—Part 3: Guide to the Expression of Uncertainty in Measurement (GUM:1995)—First Edition

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology **E135**.

### 3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *alloy-type calibration, n*—calibrations determined using reference materials from titanium alloys with generally similar compositions.

3.2.2 *global type calibration, n*—calibrations determined using reference materials from numerous different titanium alloys with considerable compositional variety.

3.2.3 *type standardization, n*—mathematical adjustment of the calibration curve's slope or intercept, or both, using a single reference material at or close to the nominal composition for the particular alloy being analyzed. For best results, the reference material being used should be of the same alloy family as the material being analyzed.

## 4. Summary of Test Method

4.1 *Spark-AES*—A controlled electrical discharge is produced in an argon atmosphere between the prepared flat surface

of a specimen and the tip of a counter electrode. The energy of the discharge is sufficient to ablate material from the surface of the specimen, break the chemical or physical bonds, and cause the resulting atoms or ions to emit radiant energy. The radiant energies of the selected analytical lines and the internal standard line(s) are converted into electrical signals by either photomultiplier tubes (PMTs) or a suitable solid-state detector. The detected analyte signals are integrated and converted to an intensity value. A ratio of the detected analyte intensity and the internal standard signal may be made. A calibration is made using a suite of reference materials with compositional similarity to the specimens being analyzed. Calibration curves plotting analyte intensity (intensity ratio) versus analyte mass fraction are developed. Specimens are measured for analyte intensity and results in mass fraction are determined using the calibration curves.

4.2 *GD-AES*—A glow discharge lamp creates a low-pressure Ar plasma above the sample surface by applying a high negative voltage between the sample (cathode) and an anode. Argon ions are accelerated into the specimen, which sputters material from the surface. The sputtered material diffuses into the argon plasma where it is dissociated into atoms and excited. The light emitted from these excited species is characteristic of the elements composing the sample and is converted into electrical signals by either photomultiplier tubes (PMTs) or a suitable solid-state detector. The detected analyte signals are integrated and converted to an intensity value. A ratio of the detected analyte intensity and the internal standard signal may be made. A calibration is made using a suite of reference materials with compositional similarity to the specimens being analyzed. Calibration curves plotting analyte intensity (intensity ratio) versus analyte mass fraction are developed. Specimens are measured for analyte intensity and results in mass fraction are determined using the calibration curves.

## 5. Significance and Use

5.1 This test method for the chemical analysis of titanium alloys is primarily intended to test material for compliance to compositional requirements of specifications such as those under 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 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 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 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 employed, and performance acceptance criteria.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>4</sup> Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandinnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

## 6. Recommended Analytical Lines and Potential Interferences

6.1 In Spark-AES or GD-AES atomic emission, when possible, select analytical lines which are free from spectral interferences. However, this is not always possible, and it may be necessary to apply background or inter-element corrections to account mathematically for the effect of the interference on the measured intensities. If interference corrections are necessary, refer to Practice E305 for detailed information on the various techniques used to calculate interference corrections.

6.2 Table 1 lists analytical lines routinely used for analysis of titanium alloys. For consistency of expression, the wavelengths are all listed as stated in the National Institute of Standards and Technology (NIST) Atomic Spectroscopy Database. In the NIST wavelength table, wavelengths < 200 nm are as determined in a vacuum and wavelengths ≥ 200 nm are as determined in air. Potential spectral interferences are also indicated. It is not implied that measurements for this standard test method must be made under the analytical conditions used by NIST. Refer to Section 7 for a discussion of appropriate spectrometer configurations.

## 7. Apparatus

### 7.1 Excitation Source:

7.1.1 *Spark Source*, unipolar, triggered capacitor discharge. In today's instrumentation, the excitation source is computer controlled and is normally programmed to produce: (1) a high-energy pre-spark (of some preset duration), (2) a spark-type discharge (of some preset duration), (3) an arc type discharge (of some preset duration), and (4) a spark-type discharge, during which, time resolved measurements are made for improved detection limits (this may be optional on some instruments).

7.1.2 *Glow Discharge Source*, capable of producing an argon plasma discharge. With current instrumentation, the excitation source may be direct current (DC) or radio frequency (RF) based.

7.2 *Gas Flow System*—Designed to deliver pure argon gas to the excitation/sample interface region. Use the minimum argon purity specified by the instrument manufacturer. Refer to Practice E406 for practical guidance on the use of controlled atmospheres.

7.3 *Spectrometer*—Having acceptable dispersion, resolution, and wavelength coverage for the determination of titanium alloys. As described in Guide E1507.

7.4 *Optional Optical Path Purge or Vacuum System*—Designed to enhance vacuum wavelength sensitivity by either purging the optical path with a UV-transparent gas or by evacuating the optical path to remove air. The UV-transparent gas must meet the manufacturer's minimum suggested purity requirements.

7.5 *Measuring and Control Systems*—Designed to convert emitted light intensities to a measurable electrical signal. These systems will consist of either a series of photomultiplier tubes (PMT) or solid-state photosensitive arrays ((Charge Coupled

**TABLE 1 Analytical Lines for the Analysis of Titanium Alloys and Potential Interferences**

Elements	Wavelength, λ (nm)	Potential Interferences, λ (nm)
Aluminum	236.70	
	256.799	Zr 256.764
	394.401	
	396.152	
Boron	182.64	
	208.957	
	249.678	Fe 249.678
Carbon	165.701	
	165.812	
	193.027	Al 193.041
Chromium	284.325	Zr 284.352
	425.433	
Copper	200.3	
	327.396	
	510.554	
Iron	371.993	
	259.940	Ti 259.992
	259.957	
Manganese	293.31	
	403.076	
	403.307	
	403.449	
Molybdenum	202.02	
	290.91	
	386.411	Zr 386.387
Nickel	341.476	Zr 341.466
	231.604	
	316.34	W 316.342
Niobium	319.50	
	405.89	
	149.26	
Nitrogen	174.272	
	130.22	
Oxygen	340.458	Mo 340.434, Zr 340.483
Palladium	363.470	
Ruthenium	349.894	
Silicon	372.803	
	212.415	
	251.611	
	288.158	Cr 288.123
Tin	140.0454	
	147.5	
	189.989	
Titanium	303.41	
	317.505	Fe 317.544
	337.279	
	367.16	
Tungsten	374.16	
	239.71	
Vanadium	429.461	Zr 429.479
	214.01	
	326.770	
	411.179	W 411.182
Yttrium	437.924	Zr 437.978
	360.073	Zr 360.119
	371.029	Ti 370.996
	339.198	Fe 339.23, Nb 339.234
Zirconium	343.823	
	357.247	Fe 357.200, W 357.240
	360.119	Cr 360.167
	306.77	
Bismuth <sup>A</sup>	165.70	
Carbon <sup>A</sup>	228.62	
Cobalt <sup>A</sup>	383.05	
Europium <sup>A</sup>	227.33	
Hafnium <sup>A</sup>	296.33	
Tantalum <sup>A</sup>	239.71	
Tungsten <sup>A</sup>		

<sup>A</sup> Suggested wavelength as data for the analyses of these elements by this test method is very limited.

Device (CCD) or Charge Injection Device (CID)) and integrating electronics. A dedicated computer is used to control analytical method conditions, source operation, data acquisition, and the conversion of intensity data to mass fraction.

**7.6 Other Software**—Designed to coordinate instrument function. At a minimum, the instrument’s software should include functions for calibration, routine instrument drift correction (standardization) and routine analysis. Additional software features may include functionality for tasks such as control charting.

**7.7 Specimen Preparation Equipment:**

**7.7.1 Lathe**, capable of machining a smooth, flat surface on the reference materials and samples. A variable speed cutter, a cemented carbide or polycrystalline diamond tool bit, and an automatic cross-feed are highly recommended.

**7.7.2 Milling Machine**, a milling machine can be used as an alternative to a lathe.

**7.7.3 Belt/Disk Sanding**, a belt sander may be used to prepare the surface for analysis.

NOTE 1—Spectrometer manufacturers may have specific specimen preparation guidelines which may influence the selection of specimen preparation equipment.

**8. Reagents and Materials**

**8.1 Reference Materials:**

**8.1.1 Certified reference materials (CRMs)** should be used as calibration reference materials, if available. These certified reference materials shall be of similar composition to the alloys being analyzed. In cases where CRMs are not available for the element or alloy, or both, being analyzed or if available CRMs do not adequately cover the intended analytical range, it is acceptable to use other reference materials for calibration.

**8.2 Other Reference Materials:**

**8.2.1 In-House Reference Materials**—Some laboratories may have the resources to produce in-house reference materials for titanium alloys. It is acceptable to use these reference materials for calibration of Spark-AES and GD-AES instruments provided that the in-house reference materials have been developed following technically sound development protocols and are accompanied with appropriate documentation. Refer to Guide **E2972**.

**8.3 Instrument Manufacturer Provided Reference Materials**—Some manufacturers perform factory calibrations which may include reference materials owned by the manufacturer. The laboratory should make reasonable attempts to secure certificates of analysis for each of these reference materials and to evaluate the acceptability of these certificates in conjunction with the laboratory’s quality policies.

**8.4 Drift Correction (standardization) Materials**—This suite of materials should be of similar composition to the alloys being analyzed and should contain analyte levels near the extremes of the calibration range for each analyte. Refer to Practice **E305** for a more detailed discussion of the use of drift correction (standardization) materials with AES analysis.

**8.5 Type Standards:**

**8.5.1 Reference Materials for Type Standardization**—Certified reference materials, reference materials and in-house reference materials may be used for type standardization. Because the materials are used to adjust the slope or intercept or both of a calibration curve, the materials used for this purpose should have values traceable to higher order reference materials. In-house reference materials are acceptable for use in type standardization provided that these have been developed following technically sound development protocols, such as those described in Guide **E2972**.

**8.6 Process Control (Verifiers)**—Process control material should be of similar composition to the unknowns. Additionally, they should contain analytes in sufficient quantity as to display a significant intensity response when analyzed, in order to verify instrument drift.

**9. Hazards**

**9.1** The excitation sources present a potential electrical shock hazard. The sample stand or lamp shall be provided with a safety interlock system to prevent energizing the source whenever contact with the electrode is possible. The instrument should be designed so access to the power supply is also restricted by the use of safety interlocks.

**9.2** Exhaust gas containing fine metallic dust generated by the excitation process may be a health hazard. Therefore, the instrument should be designed with an exhaust system to remove this dust in a safe manner. Some instruments are equipped with a filtration system designed for this purpose. An acceptable alternative to the filtration system would be a ventilation system that exhausts the powder to a “safe” area outside of the laboratory. If a filtration system is used, it should be maintained according to the manufacturer’s recommendations.

**9.3** If the filtration system includes filters, the filters used to collect the internal dust are likely exposed to an oxygen-depleted atmosphere. Sudden exposure of the filter to air may create a fire hazard. The lab should assess the risks associated with used filter disposal.

**10. Sampling, Test Specimens, and Sample Preparation**

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

**10.2** Check specimens for porosity or inclusions. Porosity or inclusions or both need to be removed during the preparation process.

**10.3** The specimen configuration must also be amenable to machining using the sample preparation equipment selected. Prepare the specimen surface by either sanding, milling, or lathe turning to produce a clean, flat analytical surface. Reference materials and samples should be prepared in a similar manner.

**10.4** Test specimens should be of a configuration that will fit the sample stand being used. The prepared specimen surface must be large enough to cover the sample orifice on the sample stand of the instrument.

10.5 Depending on sample size, geometric shape, or alloy, it may be required to prepare the surface of samples and reference materials in different manners. When multiple sample preparations techniques are proposed, the user should evaluate the equivalence of results obtained from all proposed preparation techniques during method validation.

## 11. Preparation of Apparatus

11.1 Analytical instrumentation and specimen preparation equipment shall be installed in a manner consistent with manufacturer recommendations.

11.2 Specify the following parameters into the instrument software.

11.2.1 The excitation source conditions.

11.2.2 The analytical lines and measurement conditions to be used for measurement.

11.2.3 The internal standards and associated measurement parameters, if intensity ratio is to be used as the expression for the measurement response. Titanium is typically used as the internal standard for the analysis of titanium alloys.

11.2.4 Drift correction (standardization) sample identification and associated measurement parameters. If possible, each analyte should be assigned a drift correction (standardization) sample containing analyte mass fractions near the anticipated calibration extremes. If the software supports the use of multiple point drift correction (standardization), specify additional drift correction (standardization) samples, as necessary.

11.2.5 Calibration reference materials identification, analyte mass fractions and associated measurement parameters.

11.2.6 Appropriate reporting parameters such as result format, unit of measure, reporting order, report destination, etc.

11.2.7 Optimize source operating conditions, analyte lines, and measuring conditions by performing test measurements on calibration reference materials in order to assess the sensitivity and precision of the selected measuring conditions.

11.2.8 A cursory examination of intensity data from the test measurements should suggest that the selected measurement conditions are acceptable. Examine the intensity data for these attributes.

11.2.8.1 There is a change in response for increasing analyte mass fraction.

11.2.8.2 The % RSD of the intensity multiplied by the analyte concentration of a standard in the analytical range yields an estimated analyte standard deviation that is consistent with the laboratories measurement quality objectives.

11.2.8.3 Ultimately, the acceptability of the selected measurement method parameters will be demonstrated by the method validation study.

11.2.9 The laboratory should make a copy of the analytical parameters offline in order to recover in the event of instrument database corruption. Analytical instrumentation and sample preparation equipment shall be installed and operated in a manner consistent with manufacturer and laboratory procedures.

## 12. Calibration

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

12.2 Specify the following parameters, as necessary for calibration, into the instrument software. If the manufacturer has provided a factory calibration and associated information, check that the steps have been done correctly, with help from the manufacturer as appropriate. For manufacturer provided calibrations, laboratories should perform method validation to ensure all results are correct. Refer to Guide [E2857](#).

12.2.1 The excitation source conditions determined during method development.

12.2.2 The analytical lines and measurement conditions to be used for analysis as determined during method development.

12.2.3 The internal standards and associated measurement parameters if intensity ratio is to be used as the expression for the measurement response. Typically, titanium is used as the internal standard for the analysis of titanium alloys.

12.2.4 Drift correction (standardization) material identification and associated measurement parameters. If possible, each analyte should be assigned a drift correction (standardization) material containing analyte contents near the anticipated calibration extremes. If the software supports the use of multiple point drift correction (standardization), specify additional drift correction (standardization) materials as necessary.

12.2.5 Calibration reference materials identification, analyte mass fraction and associated measurement parameters. The calibration reference materials should be of similar composition to the alloys being analyzed and contain the analyte mass fraction necessary for adequately deriving the calibration curves. Refer to Practice [E305](#) for additional guidance in selection of reference materials necessary for calibration.

12.2.6 Appropriate reporting parameters such as result format, unit of measure, reporting order, report destination, etc.

12.3 Prepare the drift correction (standardization) materials and test specimens using the same technique.

12.4 Measure each drift correction (standardization) material for a minimum of three excitation cycles. Measurements should be made in a radial pattern, slightly away from the edge of the drift correction (standardization) material. If measurements are to be made near the center of the material, then consideration should be given to the metallurgical condition of the material, since cast or wrought materials may have physical imperfections or chemical segregation near the center. Laboratories should determine acceptable levels of precision for the analyte being measured.

12.5 Prepare the calibration reference materials and test specimens using the same technique; see [10.5](#).

12.6 Measure each calibration reference materials a minimum of three times. Measurement should be made in a radial pattern, slightly away from the from the edge of the calibration material. If measurements are to be made near the center of the material, then consideration should be given as to the metallurgical condition of the material, since cast or wrought materials may have physical imperfections or chemical segregation near the center. Laboratories should determine acceptable levels of precision for the analyte being measured.

12.7 Create calibrations using multivariate regression analysis. As necessary, use background corrections and inter-element corrections to mathematically correct for spectral interferences. See Practice E305 for a detailed discussion on calculating calibrations for atomic emission analyses, particularly as the discussion relates to the use of non-linear models with higher order polynomials.

12.8 Laboratories may wish to analyze samples by type standardization to improve accuracy of the current calibrations.

12.8.1 Laboratories must be aware that reference materials used for type standardization update must be compositionally very similar to that of the unknowns. When improperly performed, type standardization may produce errant results.

12.9 Set up the type standard as required by the software. Analyze the reference material a minimum of three excitations as in 12.6.

12.10 Verify the type standardization by analyzing a reference material to ensure statistical control. The laboratory may analyze the reference material used for type standardization but a higher confidence of acceptability may be obtained by analyzing an independent reference material. During and upon completion of a period of continuous analyses, laboratories should perform additional verifications with a frequency to be established by the laboratory.

12.11 Laboratories choosing to use type standardization should perform method validation. Refer to Guide E2857.

### 13. Procedure

13.1 Prepare the specimens for analyses per Section 10.

13.2 Place a prepared specimen over the orifice in the instrument sample stand or lamp. There should not be any gaps between the specimen and the orifice.

13.3 Perform a minimum of two separate excitation cycles (measurements) on the specimen, repositioning or re-preparing the specimen between measurements so that the centers of the ablated areas of the measurements do not overlap.

13.3.1 The complexity of the alloy, specimen homogeneity, and the level of confidence required should be considered when determining the number of repeat measurements. Two to four measurements are recommended for most alloys where homogeneity is fair and accuracy becomes important. In very complex alloys or in alloy systems that are noted for their segregation, additional measurements may be required.

13.3.2 The determinations from all measurements should be averaged unless one or more individual measurements produces an abnormal internal standard intensity, can be statistically invalidated, or appears visually to be bad (see Notes 2 and 3). When an analysis is rejected, it should be replaced in order to maintain the normal number of measurements to be averaged and reported as a single test result.

NOTE 2—With spark excitation, it is essential that operators learn the difference between “good” measurement and “bad” measurement. Bad measurements can be caused by an air leak between the sample and the top plate, a poor quality sample, poor quality argon and various other reasons. A “good” measurement will have a deeply pitted area in the center surrounded by a blackish ring. The actual appearance of an analysis will vary with source conditions and alloy. A “bad” measurement will tend to

have shallow pits surrounded by a white or silver colored ring. Usually the intensity of the titanium internal standard channel for a “bad” measurement will be considerably lower than a good measurement.

NOTE 3—With GD-AES excitation, the differences between “good” and “bad” measurements are commonly determined by the quality of the sputter spots. Because GD-AES uses vacuum to hold the sample to the lamp, a seal leak can cause non-uniform sputtering or prevent the sample from being held to the lamp. A “good” measurement should be uniform with no ring or marks around the spot where the O-ring seal was present. A “bad” measurement may have uneven sputtering or a discoloration around the sputter spot.

13.4 Examine the calculated % RSD for the average of the usable measurements. Laboratories should determine acceptable levels of precision for the analyte being measured.

13.5 Analyze process control material as detailed in laboratory procedure(s).

### 14. Maintaining Statistical Process Control

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

14.2 Some instrument 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 laboratory’s analysis procedures will typically specify reanalysis of affected samples, if control samples indicate that the calibration is no longer valid.

14.4 The laboratory shall establish a frequency of analysis for the verifier. Once a verifier control strategy is established, analyze the verifier periodically to evaluate instrument response drift.

14.5 Drift correct (standardize) the instrument when the verifier measurement indicates that the spectrometer has drifted to the point that one or more elements exceed the established 2 s or 3 s control limits. Update the drift correction (standardization) using the drift correction (standardization) samples established in 12.3.

14.6 Users of this test method are discouraged from using certified reference materials as drift correction samples or routine verifiers.

### 15. Method Validation

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

15.2 Guide E2857 suggests multiple means of validating analytical methods. For this standard test method, the minimum expectation is that the laboratory will prepare and analyze solid CRMs or RMs, or both, using the method to obtain the necessary validation data. Ideally, these will be reference materials that are independent of the calibration. The precision and bias data obtained for these materials must then be

compared to the precision and bias data stated in this test method. See Guide E2857 for some guidance in making this comparison.

15.3 If the validation exercise yields precision and bias data worse than the Precision and Bias section of this test method, the laboratory should attempt to identify and correct any problems associated with their application of this test method.

15.4 Ultimately, the method user must weigh customer requirements and the laboratory’s data quality objectives and justify acceptance of the method validation data.

15.5 The method validation study shall be documented.

**16. Calculations**

16.1 Calibration curves are calculated by plotting an expression of intensity (raw intensity or intensity ratio to internal standard intensity) versus analyte mass fraction for the calibration reference materials. Refer to Practice E305 for a detailed discussion of calibration curve calculations.

16.2 Analyte results for the unknowns are determined by comparing the intensity (raw or ratio) obtained for the specimen measurements to the calibration curve.

16.3 All calculations may be performed using the instrument software. Results shall be expressed as a mass fraction, either as % or mg/kg.

16.4 Calculate the mean of the results of the individual measurements of each sample.

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

**17. Report**

17.1 Results shall be reported in a manner consistent with laboratory internal requirements.

17.2 When uncertainty estimates are required, the lab must use a procedure created following guidance in ISO Guide 98-3.

**18. Precision and Bias**

18.1 The precision of this test method is based on an interlaboratory study conducted in 2013. A total of 14 laboratories participated in this study, 7 utilizing GD-AES, and 7 utilizing Spark AES, analyzing up to 4 different materials for 19 elemental components. Every “test result” represents an individual determination, and all participants were asked to

report triplicate test results. Practice E691 was followed for the design and analysis of the data; the details are given in RR:E01-1123.<sup>5</sup>

18.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

18.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

18.1.1.2 Repeatability limits are listed in Tables 2-39 below.

18.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

18.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

18.1.2.2 Reproducibility limits are listed in Tables 2-39 below.

18.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

18.1.4 Any judgment in accordance with statements 18.1.1 and 18.1.2 would have an approximate 95 % probability of being correct.

18.2 *Bias*—Assigned values for certified reference materials are listed in Table 40, and the bias has been determined using these values. Copies of the certificates of analysis have been included in the Research Report.

18.3 The precision statement was determined through a statistical examination of all usable test results reported by 14 laboratories, for 19 elements, in 4 different samples, by 2 methodologies.

18.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1123. Contact ASTM Customer Service at service@astm.org.

**TABLE 2 Spark-AES – Aluminum (%)**

Material	Number of Labs n	Certified or Reference Value	Average <sup>A</sup> $\bar{x}$	Repeatability Standard Deviation $s_r$	Reproducibility Standard Deviation $s_R$	Repeatability Limit $r$	Reproducibility Limit $R$	Bias %
MBH 101xTi6	6	5.99	6.0365	0.0371	0.0793	0.1038	0.2219	0.2
ARMI 174C	6	0.003	0.0016	0.0001	0.0013	0.0002	0.0038	- 46.7
ARMI 176C	1	5.97	5.7338	0.0109	...	0.0305	...	- 4.3
ARMI 261A	6	3.00	2.8475	0.0157	0.1294	0.0439	0.3622	- 5.1

<sup>A</sup> The average of the laboratories’ calculated averages.