



Designation: **E2994 – 16** 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)¹

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 (ϵ) 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
Iron	0.09 to 0.3
Molybdenum	0.016 to 0.1

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.

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Element	Tested Mass Fraction Range (%)
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 and 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-Validating Analytical Methods.

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:²

- [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 \(Withdrawn 2019\)³](#)
- [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:⁴

- [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~~, practice, refer to Terminology [E135](#).

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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

⁴ Available from American National Standards Institute (ANSI), 25 W. 42nd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>; International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

3.2.2 *global type calibration, n—~~calibration curves~~ 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~~ 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~~ 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~~ intensity and results in mass fraction are determined using the calibration curves.

4.2 *GD-AES*—A glow discharge lamp creates a ~~low pressure~~ 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~~ 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~~ 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~~ 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.

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.

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	
Chromium	193.027	Al 193.041
	284.325	Zr 284.352
Copper	425.433	
	200.3	
Iron	327.396	
	510.554	
	371.993	
	259.940	Ti 259.992
Manganese	259.957	
	403.076	
Manganese	293.31	
	403.076	
	403.307	
	403.449	
Molybdenum	202.02	
	290.91	
Molybdenum	386.411	Zr 386.387
	386.411	Zr 386.387
Nickel	341.476	Zr 341.466
	231.604	
Niobium	316.34	W 316.342
	319.50	
Nitrogen	405.89	
	149.26	
Oxygen	174.272	
	130.22	
Palladium	340.458	Mo 340.434, Zr 340.483
	363.470	
Ruthenium	349.894	
	372.803	
Silicon	212.415	
	251.611	
Tin	288.158	Cr 288.123
	147.5	
Tin	140.0454	
	147.5	
	189.989	
	303.41	
Titanium	317.505	Fe 317.544
	337.279	
	367.16	
Tungsten	374.16	
	239.71	
Vanadium	429.461	Zr 429.479
	214.01	
Vanadium	326.770	
	411.179	W 411.182
	437.924	Zr 437.978
	360.073	Zr 360.119
Yttrium	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
Bismuth ^A	306.77	
Carbon ^A	165.70	
Cobalt ^A	228.62	
Europium ^A	383.05	
Hafnium ^A	227.33	
Tantalum ^A	296.33	
Tungsten ^A	239.71	

^A Suggested wavelength as data for the analyses of these elements by this test method is very limited.

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~~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~~measurable electrical signal. These systems will consist of either a series of photomultiplier tubes (PMT) or solid-state photosensitive arrays ((Charge Coupled 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 ~~and/or alloy 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~~ [Guide E2972—Standard Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials.](#)

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)*—(*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 – Validating Analytical Methods](#).

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.