



Designation: **E2371--21** **E2371 - 21a**

# 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)<sup>1</sup>

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 ( $\epsilon$ ) 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 in 1.1. 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.

1.3 Because of the lack of certified reference materials (CRMs) containing bismuth, hafnium, and magnesium, these elements

<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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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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific safety hazards statements are given in Section 9.

1.6 *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>

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

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

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

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 (Withdrawn 2019)<sup>3</sup>

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 (Withdrawn 2015)<sup>3</sup>

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

E2857 Guide for Validating Analytical Methods

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

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.

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

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 ICP spectrometric emission analysis of metal alloys are described. In Guide E1097, the typical interferences encountered during DCP 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.<sup>5</sup> 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 Tables<sup>6</sup> 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, an individual laboratory's wavelength research studies, or a combination of these.

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 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.

<sup>5</sup> 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.

<sup>6</sup> Harrison, G. R., *MIT Wavelength Tables*, John Wiley & Sons, New York, New York, 1969, <https://mitpress.mit.edu/books>.

**TABLE 1 Analytical Lines and Potential Interferences**

Element	Wavelength (nm)	Potential Interference
Aluminum	176.639	
Aluminum	394.400	
Bismuth (see 1.3)	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	238.892	
Copper	224.701	
Copper	327.396	
Chromium	267.716	
Chromium	206.553	Tungsten
Chromium	266.602	Cobalt
Chromium	275.072	Iron, molybdenum
Hafnium (see 1.3)	277.336	
Hafnium (see 1.3)	232.247	
Iron	261.187	
Iron	259.940	
Magnesium (see 1.3)	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

7.2 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.<sup>7</sup> 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 mean reagent water sufficiently purified to meet the requirements of Type II of Specification D1193 or equivalent. Equivalency is defined as water quality that does not adversely affect test results. Laboratories shall establish and document water quality requirements. 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. It also helps compensate for daily instrumental drift as a result of changes in temperature and other parameters.

### 8.2 Calibration Solutions:

8.2.1 In this test method, calibration is based on laboratory prepared, alloy matrix-matched, calibration solutions. Alloy matrix-matched calibration solutions are solutions that contain approximate amounts of the major alloying elements, such as aluminum, tin, vanadium, and zirconium found in typical sample solutions. These additions 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), or both. Reference materials may be either digested solid materials or purchased single or multi-element standard solutions. 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 the reference materials or 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 contain sufficient purity for DCP or ICP-AES use. Take care when using reference materials designated for atomic absorption techniques.

8.2.2 Calculate the nominal amounts of titanium and alloying metals present in the samples to be analyzed, based on specimen mass and final dilution volume.

8.2.2.1 Transfer appropriate volumes of the CRMs or matrix metals into a HF-resistant volumetric flask. Matrix metals solutions may be from CRM or solid metal digestions.

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

8.2.2.3 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.

8.2.3 Add the needed amount of single-element or multi element CRM solutions into the flasks, ensuring to leave one analyte free

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<sup>7</sup> *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, [www.chemistry.org](http://www.chemistry.org) and [www.usp.org](http://www.usp.org)

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 required. 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.

8.2.4 Laboratories must determine acid mixtures that will dissolve the metals used in the matrix-matched calibration solutions and the alloys to be analyzed using this method. Acid mixtures shall be documented within laboratory quality systems documentation.

8.2.4.1 A mixture of HF+HNO<sub>3</sub> (2+1), HCl+HF+HNO<sub>3</sub> (1.5+2+1) or HCl+HF+HNO<sub>3</sub> (15+2+1) are examples of acid matrices that will dissolve many types of titanium alloys. Moderate the reaction with the addition of reagent water. For alloys containing molybdenum, palladium, or ruthenium, first add concentrated HCl before the addition of H<sub>2</sub>O or HF/HNO<sub>3</sub>.

8.2.4.2 Use caution 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 water to the sample before the addition of HF, or a sealed digestion bomb may be used where method validation dictates their use.

8.2.5 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 so, then it is acceptable to develop control solutions by preparing equivalent reference material solutions using the procedure described in 8.2.

## 9. Hazards

ASTM E2371-21a

<https://standards.iteh.ai/catalog/standards/sist/fc90111a-db02-4dc7-8fe3-7da1ab2b0e09/astm-e2371-21a>

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.

## 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 may be obtained by milling or drilling chips or shearing pieces that are clean and of sufficient size to allow the weighing of the appropriate specimen 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 Laboratories must establish that the instrument being used can demonstrate acceptable sensitivity and precision for the elements being analyzed. Once completed, it is not necessary to evaluate sensitivity and precision routinely. Methods to evaluate equipment sensitivity and precision are described in 12.1.1 and 12.1.2. Other methods to evaluate sensitivity and precision are acceptable. A description of the evaluation method and results shall be documented within the laboratory's quality documentation. Refer to Section 14 (Control) for routine drift control.



12.1.1 *Sensitivity*—Sensitivity can 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 limit of detection (LOD). Calculate ten times the standard deviation to approximate the limit of quantification (LOQ). If the instrument/parameter selection does not produce an estimated LOD 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 LOQ 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 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 regarding the parameters that may have an effect on instrument precision is given. Instrument troubleshooting manuals—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—calibration. It is acceptable to rely upon the correlation coefficient as a demonstration of calibration fit. Ideally, this coefficient should be 0.995 or better to 1.000. 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 specimen, consistent with the specimen 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 specimen an appropriate volume of the same acid mixture used to prepare the calibration solutions (8.2) and cover.