



Standard Test Method for Analysis of Titanium Alloys by X-Ray Fluorescence Spectrometry¹

This standard is issued under the fixed designation E539; 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 method² covers the X-ray fluorescence analysis of titanium alloys for the following elements in the ranges indicated:

Element	Mass Fraction Range, %
Aluminum	0.041 to 8.00
Chromium	0.013 to 4.00
Copper	0.015 to 0.60
Iron	0.023 to 2.00
Manganese	0.003 to 9.50
Molybdenum	0.005 to 4.00
Nickel	0.005 to 0.80
Niobium	0.004 to 7.50
Palladium	0.014 to 0.200
Ruthenium	0.019 to 0.050
Silicon	0.014 to 0.15
Tin	0.017 to 3.00
Vanadium	0.017 to 15.50
Yttrium	0.0011 to 0.0100
Zirconium	0.007 to 4.00

1.2 *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 precautionary statements are given in Section 10.

2. Referenced Documents

2.1 ASTM Standards:³

[E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials](#)

[E1172 Practice for Describing and Specifying a Wavelength-Dispersive X-Ray Spectrometer](#)

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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² Supporting data for this test method as determined by cooperative testing has been filed at ASTM International Headquarters as three separate research reports RR:E02-1010, RR:E01-1061, RR:E01-1114.

³ 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.

[E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis](#)

[E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis](#)

[E1621 Guide for X-Ray Emission Spectrometric Analysis](#)

[E1724 Guide for Testing and Certification of Metal, Ore, and Metal-Related Reference Materials \(Withdrawn 2010\)⁴](#)

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology [E135](#).

4. Summary of Test Method

4.1 The specimen is finished to a clean, uniform surface and then irradiated by high-energy X-ray photons. Secondary X rays are produced and emitted from the sample. This radiation is diffracted by means of crystals and focused on a detector, which measures the count rates at specified wavelengths. The output(s) of the detector(s) is integrated or counted for a fixed time or until the counts reach a certain fixed number. Mass fractions of the elements are determined by relating the measured radiation of unknown samples to calibration curves prepared using reference materials of known compositions.

5. Significance and Use

5.1 This method is suitable for providing data on the chemical composition of titanium alloys having compositions within the scope of the standard. It is intended for routine production control and for determination of chemical composition for the purpose of certifying material specification compliance. Additionally, the analytical performance data included with this method may be used as a benchmark to determine if similar X-ray spectrometers provide equivalent precision and accuracy.

6. Interferences

6.1 Line overlaps, interelement effects and matrix effects may exist for some of the elements in the scope. A list of

⁴ The last approved version of this historical standard is referenced on www.astm.org.

potential line overlaps is provided in section 6.2. Modern X-ray spectrometers provide software for generation of mathematical corrections to model the effects of line overlaps, interelement and matrix interferences. The user of this method may choose to use these mathematical corrections for analysis. Guide E1621 provides a more extensive overview of mathematical interference correction methods.

6.2 Potential line overlaps may occur directly on the analyte line or may create problems with the background. Some listed interfering elements may not be present in significant mass fractions in the particular alloy being tested, but are listed for consideration. The magnitude of the overlap will be a function of the collimation on the analyte line. Line overlaps to consider:

Analyte	Interfering Element(s)
V	Ti (direct overlap)
Cr	V (direct overlap)
Cr	Mn (background overlap)
Ni	Nb, Cu (background overlaps)
Mo	Nb, Zr (background overlaps)
Pd	Mo (background overlap)
Ru	Mo, Nb (background overlap)
Y	Zr (background overlap)
Zr	Cu (background overlap)

7. Apparatus

7.1 Specimen Preparation Equipment:

7.1.1 *Surface Grinder*, with 60 to 600-grit silicon carbide belts or disks capable of providing test specimens with a uniform flat finish. For silicon determinations 60–600 grit aluminum oxide or aluminum zirconium oxide belts or disks capable of providing test specimens with a uniform flat finish should be used. A wet belt or wet disk grinder is preferred to prevent work hardening of the sample.

7.1.2 *Lathe*, as an alternative to abrasive surfacing of test specimens a lathe may be used to produce a uniform surface.

7.2 X-ray Spectrometer:

7.2.1 Practice E1172 describes the essential components of a wavelength-dispersive spectrometer and should be used as a reference source for considerations in selection of a suitable spectrometer for testing to this method.

8. Reagents and Materials

8.1 *Detector Gas*—As specified by the spectrometer manufacturer for use with flow proportional detectors.

9. Reference Materials

9.1 Certified reference materials are commercially available from both domestic and international sources. These should be used for the development of calibration curves.

9.2 It may be necessary to produce additional reference materials to supplement the certified reference materials used in the development of calibration curves. Refer to Guide E1724 for guidance in developing these reference materials.

9.3 The reference materials shall cover the mass fraction ranges of the elements being determined. A minimum of three reference materials shall be used to develop the calibration curve for each element. A greater number of calibration materials may be required to calculate mathematical correc-

tions for interferences, especially when interference corrections are estimated using only empirical data. See Guide E1361.

10. Hazards

10.1 X-ray spectrometers produce ionizing radiation. This method does not purport to address all safety considerations relating to the installation and use of an X-ray spectrometer to perform this method. In general, however, OSHA guidelines for use of ionizing radiation producing equipment must be met, as well as state and local regulations relating to radiation hygiene must be followed. Additionally, the safety guidelines established by the instrument manufacturer should be followed. Appropriate safety practices should be used with sample preparation equipment. Refer to Guide E1621 for additional information on hazards.

11. Preparation of Reference Materials and Test Specimens

11.1 The reference materials and test specimens must be of an appropriate size for fabrication into a flat surfaced piece that will fit into the cup utilized to perform the test with the flat surface completely covering the aperture of the cup. Grind or lathe/mill the reference materials/specimens to provide a flat, clean area for testing. All reference materials and test specimens must receive the same surface preparation. Care must be used in selecting the grinding media, in order to minimize the potential for surface contamination from the media. For instance, aluminum oxide and aluminum zirconium oxide grinding belts/disks may introduce aluminum and/or zirconium contamination and silicon carbide belts/disks may introduce silicon contamination. The 2010 ILS study indicated that grinding using an aluminum based media may be an unsuitable preparation method for aluminum determination of mass fractions of less than 1.0 % as statistically significant aluminum pickup was observed for labs using grinding for preparation of CP type materials.

12. Preparation of Apparatus

12.1 Install and operate the spectrometer in accordance with the manufacturer's instructions. Also refer to Guide E1621 for additional considerations for preparing the spectrometer.

12.2 The tube power supply conditions (kV/mA) should be optimized according to the manufacturer's recommendations. Once established the optimized current and voltage settings shall be used for generation of calibration curves and for all subsequent specimen measurements.

12.3 Check pulse height discrimination for each detector per the manufacturer's recommendations to verify that the limit voltages are properly established for each element being determined.

12.4 The crystals and X-ray lines specified in Table 1 have been found to provide acceptable performance. Set up the instrument in accordance with manufacturer's recommendations to analyze using these X-ray lines. Other lines may be used provided performance criteria using the alternative lines compare favorably to the precision and bias stated for this method.

TABLE 1 Suggested X-Ray Lines

Element	Line Designation ^A	2 θ Angle, deg ^B	Wavelength, (nm)	Crystal
Aluminum	K α	144.67	0.8339	PET
Aluminum	K α	142.57	0.8339	EDDT
Chromium	K β	62.36	0.2085	LiF 200
Chromium	K α	69.36	0.2291	LiF 200
Copper	K α	45.03	0.1542	LiF 200
Iron	K α	57.52	0.1937	LiF 200
Manganese	K α	62.97	0.2103	LiF 200
Molybdenum	K α	20.33	0.0710	LiF 200
Nickel	K α	48.67	0.1659	LiF 200
Niobium	K α	21.40	0.0748	LiF 200
Palladium	K α	16.76	0.0587	LiF 200
Ruthenium	K α	18.42	0.0644	LiF 200
Silicon	K α	109.21	0.7126	PET
Tin	L α	126.77	0.3600	LiF 200
Vanadium	K β	69.13	0.2285	LiF 200
Vanadium	K α	76.94	0.2505	LiF 200
Yttrium	K α	23.80	0.0831	LiF 200
Zirconium	K α	22.55	0.0788	LiF 200

^A Line designations listed in this method are based on the Siegbahn system, which has been superseded by the IUPAC Nomenclature System for X-Ray Spectrometry, Jenkins, R., Manne, R., Robin, R., and Senemaud, C., *Pure & Appl. Chem.*, 63(5), 1991, pp. 735-746.

^B The 2 θ angles represent the theoretical values for the crystals indicated. The actual positions for the peak count rates of the elements should be experimentally determined for each spectrometer.

12.5 Choose a sample cup size that is suitable for the expected specimen sizes.

12.6 Use the spinner if available on the spectrometer. The orientation of the grinding striations on the reference materials must be situated the same as the striation pattern on the specimens if a sample spinner is not employed.

12.7 Determine and specify background correction, if available and necessary, by following the manufacturer's recommendations.

12.8 Optimize counting times to obtain adequate precision for the determinations being made. A minimum of 10 000 counts is required for one percent precision in the counting statistics, 40 000 for one-half percent.

13. Calibration and Standardization

13.1 *Calibration (Preparation of Analytical Curves)*—Using the conditions given in Section 12, measure a series of reference materials that cover the required mass fraction ranges. Use at least three reference materials for each element. Prepare a calibration curve for each element being determined using the instrument manufacturer's recommendations. It will be necessary to analyze more than three reference materials to generate mathematical interference corrections from the empirical data. It is acceptable to use matrix corrections generated from fundamental parameter calculations such as those provided in some instrument manufacturer's software (Note 1). Because the number of calibration materials available for generation of titanium alloy calibrations for some elements is very limited, it may be preferable to use matrix corrections generated from fundamental parameters. Refer to Practices E1361 and E1621 for more detailed information on X-ray calibration curve generation and corrections.

NOTE 1—Two approaches may be taken for the use of fundamental parameters. In one case, fundamental parameters calculations are used to create a set of influence coefficients that are used in a specific mathematical model to fit the measured calibration data. The second approach is full fundamental parameters software in which all calculations are based on theory and internal to the software. The analyst is not required to choose an algorithm and no coefficients are reported.

13.2 As X-ray tubes and detectors age, it is normal for count rates to change and standardization (drift correction) or recalibration will be necessary to maintain analytical quality. Control charting per Practice E1329 may be used to verify continuing calibration curve performance and to establish the need for recalibration or standardization (drift correction). If standardization (drift correction) is to be used, establish a protocol at the time that the calibration curves are established.

13.3 *Calibration Verification*—The performance of a calibration curve must be verified after establishment. This is accomplished by re-analyzing enough reference materials to establish that the calibration curve is performing as desired.

NOTE 2—The user of this method is strongly cautioned to use calibration reference materials that fully cover the mass fraction ranges expected to be analyzed.

14. Procedure

14.1 *Specimen Loading*—If the spectrometer is equipped with a sample spinner, it shall be used. If a sample spinner is not available, the grinding striation orientation on all specimens and reference materials must be the same when they are placed in the spectrometer.

14.2 *Excitation*—Expose the specimens to X radiation in accordance with the conditions specified in Section 12 by following the instrument manufacturer's recommendations.

14.3 *Radiation Measurements*—Refer to Guide E1621 for guidance on obtaining enough counts to be statistically meaningful.

15. Calculation of Results

15.1 Using the count rates measured in 14.3 and the calibration curves generated in 13.1, determine the mass fractions of the elements in the specimen.

16. Precision and Bias

16.1 The data presented in Tables 2-14 were determined in prior studies made to demonstrate method performance for the method as historically scoped for Titanium 6Al-4V analysis only. The data in Table 2 and Table 14 are supported by the research report RR:E02-1010. The data in Tables 3-13 are supported by the research report RR:E01-1061.

16.2 A new study was performed in 2010 in order to demonstrate method precision and bias for an expanded scope of alloys. Six laboratories participated in this interlaboratory study. Two of the six laboratories submitted datasets from two instruments. Up to eight total datasets per analyte were collected from the laboratories for twelve different materials. The twelve different materials were selected to represent a range of titanium alloys, as well as a range of concentrations for the elements that may be determined using this method. Precision and bias were calculated in accordance with E1601