



Designation: E 539 – 06

Standard Test Method for X-Ray Emission Spectrometric Analysis of 6Al-4V Titanium Alloy¹

This standard is issued under the fixed designation E 539; 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 emission analysis of 6Al-4V titanium alloy for the following elements in the ranges indicated:

Element	Concentration Range, %
Aluminum	4.6 to 7.2
Chromium	0.023 to 0.071
Copper	0.015 to 0.066
Iron	0.1 to 0.3
Manganese	0.009 to 0.068
Molybdenum	0.018 to 0.072
Nickel	0.026 to 0.073
Tin	0.016 to 0.076
Vanadium	2.6 to 5.4
Zirconium	0.009 to 0.064

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

- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E 1172 Practice for Describing and Specifying a Wavelength-Dispersive X-Ray Spectrometer
- E 1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis
- E 1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis
- E 1621 Guide for X-Ray Emission Spectrometric Analysis
- E 1622 Practice for Correction of Spectral Line Overlap in

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

Current edition approved Dec. 1, 2006. Published December 2006. Originally approved in 1975. Last previous edition approved in 2002 as E 539 – 02.

² Supporting data for this test method as determined by cooperative testing has been filed at ASTM International Headquarters as two separate research reports RR:E2-1010 and RR: RR: E01-1061.

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.

Wavelength-Dispersive X-Ray Spectrometry⁴

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology E 135.

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 analyzing crystals and focused on a detector which measures the count rates at specified wavelengths. The outputs of the detectors in voltage pulses are integrated or counted. Radiation measurements are made based on the time required to reach a fixed number of counts, or on the total counts obtained for a fixed time (generally expressed in counts per unit time). Concentrations 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 6Al-4V titanium alloys for the scope elements. It is intended to be used 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 scope elements. A list of 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. Guides

⁴ Withdrawn.

E 1621 and **E 1622** provide 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 concentrations in 6-4 titanium, 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)
Ni	Nb, Cu (background overlaps)
Mo	Nb, Zr (background overlaps)
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 **E 1172** 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 of similar composition to 6Al-4V titanium alloy and are to be used for the development of calibration curves.

9.2 Reference materials of similar composition to 6Al-4V titanium alloy may also be produced or obtained. These reference materials may be used to supplement the certified reference materials used in the development of calibration curves.

9.3 The reference materials shall cover the concentration 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 corrections for interferences. See Guide **E 1361**.

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 **E 1621** 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 to be used 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.

12. Preparation of Apparatus

12.1 Install and operate the spectrometer in accordance with the manufacturer's instructions. Also refer to Guide **E 1621** 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 determinations.

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

TABLE 1 Suggested X-Ray Lines

Element	Line Designation ^A	2θ Angle, deg ^B	Wavelength, (nm)	Crystal
Aluminum	Kα	144.67	0.8339	PET
Aluminum	Kα	142.57	08339	EDDT
Chromium	Kβ	62.36	0.2085	LiF 200
Chromium	Kα	69.36	0.2291	LiF 200
Copper	Kα	45.03	0.1542	LiF 200
Iron	Kα	57.52	0.1937	LiF 200
Manganese	Kα	62.97	0.2103	LiF 200
Molybdenum	Kα	20.33	0.0710	LiF 200
Nickel	Kα	48.67	0.1659	LiF 200
Ruthenium	Kα	18.42	0.0644	LiF 200
Silicon	Kα	109.21	0.7126	PET
Tin	Lα	126.77	0.3600	LiF 200
Vanadium	Kα	69.13	0.2285	LiF 200
Vanadium	Kα	76.94	0.2505	LiF 200
Yttrium	Kα	23.80	0.0831	LiF 200
Zirconium	Kα	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 2θ 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.

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.

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 concentration 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. Refer to Practices E 1361, E 1621, and E 1622 for more detailed information on X-ray calibration curve generation and corrections.

13.2 As 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 E 1329 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 standardization (drift correction) protocol at the time that a calibration curve is 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 1—The user of this method is strongly cautioned to use calibration reference materials that fully cover the concentration ranges expected to be analyzed. It was found during interlaboratory testing that interlabo-

ratory reproducibility tended to get worse for elements that had concentration values near the extremes of typical calibrations.

14. Procedure

14.1 *Specimen Loading*—If the spectrometer is equipped with a sample spinner, proceed to 14.2. If a sample spinner is not employed, the grinding striation orientation on the specimens must match the orientation on the reference materials used to generate the calibration curves.

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 E 1621 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 concentration of the elements in the specimen.

16. Precision and Bias

16.1 *Precision*—When this test method was originally developed, the precision was determined by submitting four 6A1-4V titanium alloys to five different laboratories. Using their own equipment, and NIST SRMs for calibration, these five laboratories analyzed the six unknowns once on five different days for aluminum, vanadium, and iron. In-house reference materials were employed for calibrating the instruments for iron. The precision data is shown in Table 2. The supporting data for the original work is filed at ASTM as RR: E02-1010.

16.1.1 The interlaboratory study that was performed to demonstrate the acceptability of the revised scope included seven laboratories. The precision data obtained in this study is summarized in Tables 3-12. The complete research report has been filed at ASTM as EE: E01-1061.

16.2 *Bias*—When this method was originally developed, accurate chemical data was not available in all cases to determine the accuracy of this test method. Table 13 presents a comparison between the x-ray values obtained for the unknown samples in the cooperative test program and values obtained by one analyst using conventional chemical analysis.

16.2.1 The interlaboratory study performed to demonstrate the acceptability of the revised scope included analysis of several certified reference materials. The accuracy of this method had been determined satisfactory based upon the bias data in Tables 3-12. Users are encouraged to use these or

TABLE 3 Statistical Information for Aluminum

Test Material	Number of Laboratories	Aluminum Found, %	Min SD (S_M , E 1601)	Reproducibility SD (S_R , E 1601)	Reproducibility SD (R , E 1601)	R_{rel}	Certified Aluminum, %	Number	Source	Description
1	7	6.371	0.0155	0.0299	0.08375	1.3	6.34	654B	NIST	Ti-6Al 4V
2	7	6.288	0.0108	0.0335	0.09279	1.5	6.245	173C	NIST	Ti-6Al 4V
3	7	6.287	0.0247	0.0357	0.0999	1.6	6.33	T5A	Brammer	Ti-6Al 4V
4	7	6.244	0.0178	0.0512	0.1433		Not Cert.	HTL 601	TIMET	Ti-6Al 4V
5	7	6.031	0.0125	0.0655	0.1834	3.0	Not Cert.	0240	Allvac	Ti-6Al 4V
6	7	6.198	0.0176	0.0376	0.1054	1.7	6.20	175A	ARMI	Ti-6Al 4V
7	7	5.889	0.0132	0.0636	0.1780	3.0	5.90	T20	Brammer	Ti-6Al 4V