



Designation: **E539 – 11** **E539 – 19**

Standard Test Method for Analysis of Titanium Alloys by Wavelength Dispersive 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~~ safety, health, and ~~health~~ environmental practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in Section 10.

1.3 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:³

[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](#)

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

[E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis \(Withdrawn 2019\)](#)⁴

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

[E1621 Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry](#)

[E2857 Guide for Validating Analytical Methods](#)

~~[E1724](#)~~[E2972 Guide for Testing and Certification of Metal, Ore, and Metal-Related Reference Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials \(Withdrawn 2010\)](#)

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 May 1, 2011; March 1, 2019. Published July 2011; May 2019. Originally approved in 1975. Last previous edition approved in 2007 as E539 – 07; E539 – 11. DOI: 10.1520/E0539-11; 10.1520/E0539-19.

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.

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

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—Using analyzing crystals, this radiation is diffracted by means of crystals and focused on a detector, which~~ and directed towards a detector that 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.

5.2 Compositions outside the ranges in [1.1](#) may be reported if proper method validation is performed. Refer to Guide [E2857](#) for information on method validation.

6. Interferences

6.1 Line overlaps, interelement effects and matrix effects may exist for some of the elements in the scope. 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. 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—quantities~~ in the particular alloy being tested, but are listed for consideration. The magnitude of the overlap ~~will be~~ is a function of the collimation on the analyte ~~line—line~~ and the properties of the analyzing crystal. 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~~60-grit to 600-grit silicon carbide belts or disks capable of providing test specimens with a uniform flat finish. For silicon determinations ~~60–600-grit~~ 60-grit to 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, Lathe or Milling Machine~~, as an alternative to abrasive surfacing of test specimens ~~a lathe—specimens~~. A lathe or milling machine 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 ~~e commercially—available from both domestic and international sources~~. These should be used for the development of calibration curves—national laboratories and commercial producers. It may be necessary to use selected

certified reference materials as calibration standards for this test method. It is advisable to reserve one or more of the highest quality certified reference established materials to validate the calibrations.

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 [E1724E2972](#) for guidance in developing these reference materials.

9.3 ~~The reference materials used as calibration standards 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 corrections for interferences, especially when interference corrections are estimated using only empirical data. See Guide [E1361](#).~~

9.3.1 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, especially when interference corrections are estimated using only empirical data (see Guide [E1361](#)).

9.4 It is poor practice to use certified reference materials as routine control chart samples. When the goal is statistical process control, in-house reference materials are recommended.

NOTE 1—Valid calibration ranges do not end at the values for the highest and lowest calibration points. It is accepted practice to rely on calibration curves that extend 10 % beyond those values and possibly more, if consistent with the scope limits of the standard test method or otherwise validated.

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 or levels 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.

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.

12.8.1 For very low-level mass fractions, this may lead to excessive count times. In such cases, the requirement of minimum number of counts may be relaxed.

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.

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 12). 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 2—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.

13.1.1 X-ray fluorescence (XRF) spectrometers may be purchased with a factory calibration. Laboratories using such calibrations must validate these using Guide E2857 or similar.

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 3—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~~X-ray 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.

15.2 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.

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 and are presented for each material tested in Tables 15-29. The supporting data ~~is~~are found in RR:E01-1114.

17. Keywords

17.1 fluorescence; titanium; ~~X-ray~~X-ray; wavelength dispersive

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TABLE 2 Precision Data^A

Element	Sample	Number of Determinations	Average Concentration, Mass Fraction, %	Coefficient of Variation, v^B
Vanadium	Q	25	4.19	0.8
	R	25	4.12	0.9
	S	25	4.20	0.8
	T	25	4.21	0.7
Aluminum	Q	25	6.84	0.9
	R	25	6.33	1.0
	S	25	6.36	1.3
	T	25	6.36	0.8
Iron	Q	25	0.15	2.2
	R	25	0.15	2.4
	S	25	0.18	2.4
	T	25	0.18	2.2

^A These coefficient of variation values are reproducibility or multilaboratory data and were obtained by pooling data from the five cooperating laboratories. Repeatability data are on file at ASTM Headquarters.

^B Coefficient of variation, v , in this method is calculated as follows:

$$v = \frac{(100/\bar{X}) \sqrt{\sum d^2 / (n-1)}}{\bar{X}}$$

$$v = \frac{(100/\bar{X}) \sqrt{\sum d^2 / (n-1)}}{\bar{X}}$$

where:

\bar{X} = average concentration, %;
 \bar{X} = average mass fraction, %;
 d = difference of determination from the mean, and
 n = number of determinations.

TABLE 3 Statistical Information for Aluminum (6-4 Ti Alloy Only)

Test Material	Number of Laboratories	Aluminum Found, %	Min SD (S_M , E1601)	Reproducibility SD (S_R , E1601)	Reproducibility Index (R, E1601)	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

TABLE 4 Statistical Information for Chromium (6-4 Ti Alloy Only)

Test Material	Number of Laboratories	Chromium Found, %	Min SD (S_M , E1601)	Reproducibility SD (S_R , E1601)	Reproducibility Index (R, E1601)	R_{rel}	Certified Chromium, %	Number	Source	Description
1	6	0.0241	0.00124	0.00259	0.00724	30.1	0.025	654B	NIST	Ti-6Al 4V
2	6	0.0180	0.00102	0.02796	0.00783	43.4	0.015	173C	NIST	Ti-6Al 4V
3	6	0.0125	0.00108	0.00292	0.00816	65.5	0.013	T5A	Brammer	Ti-6Al 4V
4	6	0.0272	0.00092	0.00465	0.01303	47.9	Not Cert.	HTL 601	TIMET	Ti-6Al 4V
5	6	0.0701	0.00127	0.00511	0.01430	20.4	Not Cert.	0240	Allvac	Ti-6Al 4V
6	6	0.0127	0.00099	0.00313	0.00877	68.8	0.013	175A	ARMI	Ti-6Al 4V
7	6	0.0071	0.00082	0.00378	0.01058	148.1	0.005	T20	Brammer	Ti-6Al 4V

TABLE 5 Statistical Information for Copper (6-4 Ti Alloy Only)

Test Material	Number of Laboratories	Copper Found, %	Min SD (S_M , E1601)	Reproducibility SD (S_R , E1601)	Reproducibility Index (R, E1601)	R_{rel}	Certified Copper, %	Number	Source	Description
1	6	0.0056	0.00016	0.00292	0.00818	145.2	0.004	654B	NIST	Ti-6Al 4V
2	6	0.0037	0.00029	0.00286	0.00800	214.0	0.0040	173C	NIST	Ti-6Al 4V
3	6	0.0015	0.00035	0.00270	0.00756	512.2	0.0025	T5A	Brammer	Ti-6Al 4V
4	6	0.0101	0.00036	0.00311	0.00870	86.3	Not Cert.	HTL 601	TIMET	Ti-6Al 4V
5	6	0.0655	0.00045	0.00236	0.00660	10.1	Not Cert.	0240	Allvac	Ti-6Al 4V
6	6	0.0034	0.00331	0.00264	0.00738	216.0	0.005	175A	ARMI	Ti-6Al 4V
7	6	0.0117	0.00035	0.00612	0.01713	146.1	0.016	T20	Brammer	Ti-6Al 4V

TABLE 6 Statistical Information for Iron (6-4 Ti Alloy Only)

Test Material	Number of Laboratories	Iron Found, %	Min SD (S_M , E1601)	Reproducibility SD (S_R , E1601)	Reproducibility Index (R, E1601)	R_{rel}	Certified Iron, %	Number	Source	Description
1	7	0.2293	0.00127	0.00443	0.01242	5.4	0.23	654B	NIST	Ti-6Al 4V
2	7	0.2253	0.00115	0.00577	0.01616	7.2	0.213	173C	NIST	Ti-6Al 4V
3	7	0.1745	0.00134	0.00718	0.02010	11.5	0.170	T5A	Brammer	Ti-6Al 4V
4	7	0.1998	0.00283	0.00635	0.01777	8.9	Not Cert.	HTL 601	TIMET	Ti-6Al 4V
5	7	0.2336	0.00108	0.00448	0.01254	5.4	Not Cert.	0240	Allvac	Ti-6Al 4V
6	7	0.1935	0.00138	0.00690	0.01933	10.0	0.20	175A	ARMI	Ti-6Al 4V
7	7	0.0845	0.00085	0.00996	0.02790	33.0	0.089	T20	Brammer	Ti-6Al 4V