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Designation: E 539 – 02

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.

^{ε1} ~~NOTE—Keywords were added editorially in December 1996.~~

¹ This test method is under the jurisdiction of ASTM Committee E-1 E01 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E1.06 on Ti, Zr, W, Mo, Ta, Nb, Hf.

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1. Scope

1.1 This test method covers the X-ray emission analysis of 6Al-4V titanium alloy for the following elements in the ranges indicated (Note 1):

Element	Concentration Range, %
Aluminum	4.6 to 7.2
Vanadium	2.6 to 5.4
Iron	0.1 to 0.3

NOTE 1—The concentration ranges can be extended by use of suitable standards, reference materials. The ranges for aluminum and vanadium represent the actual concentration ranges of the NIST² Standard Reference Materials[®] used when this method was tested. The maximum concentrations of the unknowns used in the cooperative test program were all lower than the reference materials. The iron concentration range was determined by in-house reference materials used by the cooperating laboratories.

1.2 This test method is designed for control analysis in the production of titanium alloys and for inspection testing of the product shipped to the consumer. It is applicable for analyzing cast or wrought samples having a diameter of approximately 32 mm and a thickness of approximately 25 mm.

NOTE 2—Samples of greater or lesser size than the size designed may be used with specially designed sample holders.

1.3 *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 8.

2. Referenced Documents

2.1 *ASTM Standards:*

E 120 Test Methods for Chemical Analysis of Titanium and Titanium Alloys³

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials³

3. Terminology

3.1 *Definitions:*

3.1.1 Refer to Terminology E 135.

4. Summary of Test Method

4.1 The sample is finished to a clean, uniform surface and then irradiated by an X-ray beam of high energy (short wavelength). The secondary X rays produced are dispersed by means of crystals and the intensities measured by detectors at selected wavelengths. The outputs of the detectors in voltage pulses are integrated or counted. Data are collected using time required to

² National Institute of Standards and Technology

² NIST Standard Reference Material Nos.[®] used when this study include NIST SRM[®] 653, 654, and 655, available 655 from National Institute of Standards and Technology, Washington, DC 20234. NIST SRM[®] Program, 100 Bureau Drive, Mail Stop 2322, Building 202, Room 204, Gaithersburg, MP 20899-2322.

³ *Annual Book of ASTM Standards*, Vol 03.05.

reach a fixed number of counts or using total counts for a fixed time. Concentrations of the elements are determined by relating the measured radiation of unknown samples to analytical curves or charts prepared from standard certified reference materials of known compositions. A fixed channel or polychromator system or a sequential system may be used to provide simultaneous or sequential determinations of elements.

5. Significance and Use

5.1 The chemical composition of 6Al-4V titanium alloy must be accurately determined to ensure the desired metallurgical properties. This test method is suitable for manufacturing control and inspection testing.

6. Apparatus

NOTE 3—It is not within the scope of this test method to prescribe all details of equipment to be used. Equipment varies between laboratories.

6.1 Sample Preparation Equipment :

6.1.1 *Surface Grinder*, with 60 to 600-grit silicon carbide belts or disks capable of providing test specimens with a uniform flat finish. A wet belt or wet disk grinder is preferred to prevent work hardening of the sample.

6.2 Excitation Source:

6.2.1 *X-Ray Generator*, providing constant potential or rectified power of sufficient energy to produce secondary radiation of the sample for the elements specified. The generator may be equipped with a line voltage regulator and current stabilizer, with voltage and current regulations up to 75 kV and 40 mA.

6.2.2 *X-Ray Tube*, with a high-purity tungsten or rhodium target capable of continuous operation up to potentials and currents shown in Table 1.

TABLE 1 Typical Operating Voltages and Currents

Element	Voltage, kV with Current, mA
Iron	60-32, 51-48, 48-48, 48-22
Aluminum	60-32, 51-48, 41-26, 48-22
Vanadium	48-24, 40-24, 51-48, 48-46, 48-22
Chromium	48-24, 40-24, 51-48, 48-48, 48-22

6.3 *Spectrometer*, designed for X-ray emission analysis using air and vacuum or helium, and equipped with specimen holders and specimen chamber. The chamber should contain a sample specimen spinner.

6.3.1 *Analyzing Crystals*, flat or curved lithium fluoride (LiF), pentaerythritol (PET), or ethylenediamine *d*-tartrate (EDdT).

6.3.2 *Collimator*, for limiting the characteristic X rays to a parallel bundle when flat crystals are used in the instrument. For curved crystal optics, no collimation is necessary.

6.3.3 *Detectors*—Sealed or gas-flow proportional counters, or equivalent.

6.3.4 *Vacuum System*, providing for the determination of elements whose radiation is absorbed by air. The system should consist of a vacuum pump, gage, and electrical controls to provide automatic pump-down of the optical path and to start the analysis at a pressure of 100 μ m or less, controllable to \pm 20 μ m. A helium system can also be used.

6.4 *Measuring System*—An electronic circuit capable of amplifying, counting, and integrating pulses received from the detector tube. The system should be equipped with visual and automatic recording devices and have a pulse height analyzer, which is used for pulse energy voltage discrimination.

7. Reagents

7.1 *Detector Gas* (P-10), consisting of a mixture of 90 % argon and 10 % methane.

8. Safety Precautions

8.1 *Occupational Health and Safety Standards*⁴ on ionizing radiation shall be observed at all X-ray emission spectrometer installations. It is also recommended that personnel follow the guidelines of safe operating procedures given in the NIST Handbook *X-Ray Protection, HB76*,⁵ the booklet *Radiation Safety Recommendations for X-Ray Diffraction and Spectrographic Equipment, #MORP 68-14*, 1968,⁶ by T. M. Moore and D. J. McDonald, and the U. S. Government Handbook 93, *Safety Standard for Non-Medical X-Ray and Sealed Gamma-Ray Sources*, Part 1, General,⁵ or similar handbooks of latest issue.

8.2 X-ray equipment should be used only under the guidance and supervision of a responsible, qualified person.

⁴ A two-stage mechanical pump meeting the requirements can be purchased from Precision Scientific Co., Chicago, IL 60647.

⁴ Federal Register, Vol 36, No. 105, May 29, 1971, Sec. 1910.96 or Sargent-Welch Scientific Co., Skokie, IL 60076, of latest issue of Subpart G; Superintendent of Documents, U. S. Government Printing Office, NBS Handbook III.

⁵ Federal Register, Vol 36, No. 105, May 29, 1971, Sec. 1910.96 or of latest issue of Subpart G;

⁵ Available from Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20025; National Institute of Standards and Technology Handbook 111; ANSI N43.2-1971: 20025.

⁶ Available from Superintendent of Documents; U. S. Government Printing Office, Washington, DC 20025; Department of Health, Education and Welfare, Rockville, MD 20850.

8.3 Suitable monitoring devices, either film badges or dosimeters, shall be worn by all personnel using the equipment.⁷ ~~To~~ To meet local, state, and national radiation standards, periodic radiation surveys of the equipment for leaks and excessive scattered radiation shall be made by a qualified person using an ionization-chamber detector.⁸ The personal film badge survey record, the radiation survey record, and a maintenance record shall be available upon request.

8.4 Special precautions for the operator shall be posted.

8.5 X-ray caution signs shall be posted near the X-ray equipment and at all entrances to the radiation area.

8.6 Fail-safe “X-ray On” warning lights shall be used at the X-ray tube.

9. Standards

~~9.1 Primary Standards shall be~~ Reference Materials

9.1 Certified Reference Materials may include NIST-6Al-4V titanium reference materials identified as Nos. SRM[®] 653, 654,

655, and 654a, 655a or their replacements. These shall be used for calibration of the instrument for the determination of aluminum and vanadium.⁷

9.2 Additional Certified Reference material NIST No. 173 could be melted in a button furnace to obtain a disk.

⁷Radiation Film Badge Service, available from Nuclear Chicago, 200 Nuclear

⁷NIST SRM® Program, 100 Bureau Drive, Des Plaines, IL 60018, has been found satisfactory. Mail Stop 2322, Room 204, Gaithersburg, MD 20899-2322.

~~9.2 Secondary Standards are not Materials are available from commercial sources.⁸ Produce a series of standards in the laboratory to cover the analytical concentration ranges. Select a minimum of three samples that contain vanadium, aluminum, and iron at the top and bottom of the concentration range and one intermediate. Analyze portions of these samples in accordance with Test Methods E 120, preferably by more than one analyst and assign the average analysis. intermediate.~~

10. Preparation of Standards and Samples

10.1 Grind the specimens to provide a flat, clean area over the entire surface to be exposed to the X-ray beam. Adhere rigorously to the preparation technique established.

11. Preparation of Apparatus

11.1 *Start Up*—Energize the power supply and electronic circuits for at least ½ h prior to taking measurements.

11.2 *Power Supply*—Adjust the voltage of the power supply to produce secondary fluorescence according to the expression:

$$V_f = 12\ 350/\lambda_{K_{ABS}} \quad (1)$$

where:

V_f = minimum voltage required for exciting the element, and

$\lambda_{K_{abs}}$ = wavelength of the K absorption edge of the fluorescent element.

Ideally, the operating voltage, V , should approximate or exceed:

$$V = 3V_f \quad (2)$$

Adjust the current to produce a rate of secondary fluorescence within the desired limits of statistical precision and detector linearity (Note 4). Typical operating voltage and current used by different laboratories for the determination of iron (Fe), aluminum (Al), vanadium (V), and chromium (Cr) in titanium alloys are shown in Table 1. These values should be used as a guide only.

NOTE 4—The voltage and current established as optimum for the X-ray emission power supply in an individual laboratory is reproduced for subsequent measurements.

11.3 *Detector Gas Flow*—Adjust the flow of P-10 gas in accordance with the equipment manufacturer's instructions. ~~Some detectors require a rapid flow rate and others only a bubble a second.~~ Optimum rate should be determined by each laboratory, and the detectors should be adequately flushed with detector gas before the instrument is used.

11.4 *Pulse Height Analyzer*—Threshold discrimination should be set as slow as possible, consistent with the removal of noise with respect to the detector employed.

11.5 *Loading Samples*—Rotate the ~~standards~~ reference materials and samples in the sample chamber so that the relationship between the X-ray beam and the grinding striations are the same for all measurements. The precaution need not be taken when a sample spinner is utilized or when the sample surface is ~~highly~~ polished with a 400, 500, 500 or 600-grit belt or disk.

TABLE 2 Analytical Lines

Element	Line Designation	2θ Angle, deg ^A	Wave-length, Å	Crystal
Iron	K _α	57.52	1.937	LiF
Aluminum	K _α	144.67	8.338	PET
Aluminum	K _α	142.57	8.338	EDdt
Vanadium	K _β	69.12	2.284	LiF
Chromium	K _β	62.36	2.085	LiF

^A The 2θ angles represent the theoretical values for the crystals indicated. The actual position for the peak intensities of the elements should be experimentally determined for each spectrometer.

12. Calibration and Standardization

12.1 *Analytical Curves*—Take radiation measurements on at least three ~~primary certified~~ 6Al-4V titanium-alloy standards, at least twice on each of three separate days. ~~reference materials.~~ Prepare an analytical curve for each element by plotting on rectangular coordinate paper, using the radiation energy in counts per second or integrated intensity on the abscissa and the concentrations of the elements in the standards on the ordinate. Another method can be used. The ratio of the time required to accumulate predetermined counts for one of the standards, and the time required to accumulate the same number of counts for the other standards is plotted as a function of concentration expressed in percent. ~~In some cases, the counts obtained on an unknown is divided software package provided by the counts obtained on a reference material; then this ratio is plotted as a function of concentration. instrument manufacturer.~~

12.2 *Analytical Curve Adjustment*—Check the calibration of an instrument when it has been idle for more than 1 h or when the detector gas has been changed by analyzing a certified reference material.

TABLE 3 Data for Determination of Vanadium in Titanium Alloy^A

Specimen	V, Weight %	Counts,		I V K _β ^B	
		I V K _β + I ₀ Cr K _α	I Cr K _β	(w/b = 1.0)	(w/b = 1.5)
64	...	680	29	651	636
173A	4.06	666	22	644	633
653	2.58	424	18	406	397
654	3.83	621	17	604	595
655	5.38	881	18	863	854

^A Background corrected intensities in counts per second were made using the average of four runs.

^B Corrected vanadium data for a spectrometer with $b = 1.0$ and for a spectrometer where $b = 1.5$.

13. Procedure for Excitation and Radiation Measurements

13.1 *Excitation*—Expose the sample to primary X radiation in accordance with the conditions described in Section 10.

13.2 *Radiation Measurements*—Measure radiation intensities of the analytical lines listed in Table 2.

13.2.1 *Recording*—Obtain and record the radiation measurement for each element in terms of sufficient total counts for optimum statistical counting precision. Obtain a minimum of 16–2000 counts for the lowest concentrations within the specification.

13.2.2 *Integration Time*—When integration of pulses is used to measure intensities, a minimum of 30-s integration time for the lowest concentrations is necessary.

13.2.3 *Correction for Vanadium-Chromium Line Overlap⁸*—When the residual chromium concentration in the titanium alloy is greater than 0.1 % chromium, it is necessary to correct for the overlap of the V K_β line at 69.12 deg with the Cr K_α line at 69.35 deg. The choice of the analytical line for determining V in titanium alloys is restricted to the V K_β line due to a more serious overlap of V K_α and Ti K_β lines. To correct for the overlap of the Cr K_α line with the V K_β line, measure the Cr K_β line and use the following empirical expression to subtract the overlapping Cr K_α line:

$$I V K_{\beta} = (I V K_{\beta} + I_0 Cr K_{\alpha})_{\text{meas}} - b(I Cr K_{\beta})_{\text{meas}} \quad (3)$$

where $I_0 Cr K_{\alpha} = b (I Cr K_{\beta})_{\text{meas}}$, and the subscripts “o” and “meas” refer to overlap and measure, respectively.

13.2.3.1 Since b is a function of resolution, it must be determined for each spectrometer. If the overlap of the Cr K_α line on the V K_β line was total, with regard to an instrument resolution, then the value of b would be approximately 8. The value of b decreases with increasing spectrometer resolution and becomes zero at full resolution of the overlapping lines. Because b is a function of resolution, it must be determined for each spectrometer and at specific wavelengths. The determination can be done by least-squares fitting or the graphical procedure. A typical summary of counting data obtained for the determination by a laboratory is given in Table 3.

14. Calculation

NOTE 5—For sequential and fixed-channel instruments, the integrated voltages or pulses can be automatically printed on an electric typewriter. The output signals can be entered directly into a computer so that concentrations can be read directly.

14.1 ~~The instrument's data processing system will calculate the percent concentration of each element from the appropriate analytical curve, unknown sample based on the calibration curves and display the answers on the output.~~

14.1.1 Concentrations can be read from tables prepared from the analytical curves relating counts per second and concentrations.

15. Precision and Bias⁹

15.1 *Precision*—Precision of this test method was determined by submitting four 6Al-4V titanium alloys to five different laboratories. Using their own equipment, and NIST reference materials SRM's[®] for calibration, these five laboratories analyzed the six unknowns once on five different days for vanadium, aluminum, and iron. ~~In-house standards reference materials~~ were employed for calibrating the instruments for iron. The precision data are shown in Table 4.

⁸ A survey meter called

⁸ Rasberry, S. D., Caul, H. J., and Yezer, A., “X-Ray Fluorescence Analysis of Silver Dental Alloys with Correction for a Cutie-Pie, which will meet the requirements, can be purchased from Nuclear Chicago. Line Interference,” *Spectrochimica Acta*, SAASB, Vol 23B, 1968, pp. 347–350.

⁹ Available from National Institute of Standards and Technology, U. S. Department of Commerce, Washington, DC 20234.

⁹ Supporting data for this test method as determined by cooperative testing have been filed at ASTM International Headquarters as RR:E2-1010.

TABLE 4 Precision Data^A

Element	Sample	Number of Determinations	Average Concentration, %	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:

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

where:

\bar{X} = average concentration, %,

d = difference of determination from the mean, and

n = number of determinations.

15.2 *Bias*—Accurate chemical data were not available in all cases to determine the accuracy of this test method. Table 5 presents

TABLE 5 Comparison of Data from X-ray and Chemical Analysis

Element	Sample	Concentration, % ^A	
		X-ray	Chemical
Vanadium	Q	4.19	4.20
	R	4.12	4.05
	S	4.20	4.09
	T	4.21	4.09
Aluminum	Q	6.84	6.70
	R	6.33	6.43
	S	6.36	6.28
	T	6.36	6.28
Iron	Q	0.15	0.15
	R	0.15	0.17
	S	0.18	0.16
	T	0.18	0.16

^A The X-ray values are pooled data from the five cooperating laboratories. Data for each of the five individual laboratories are on file at ASTM Headquarters.

a comparison between the X-ray values obtained for the unknown samples in the cooperative test program and values obtained by one analyst by conventional chemical analysis.

16. Keywords

16.1 emission; titanium; X-ray

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