Standard Test Method for X-Ray Emission Spectrometric Analysis of 6AI-4V Titanium Alloy

1. Scope

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration Range, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>4.6 to 7.2</td>
</tr>
<tr>
<td>Vanadium</td>
<td>2.6 to 5.4</td>
</tr>
<tr>
<td>Iron</td>
<td>0.1 to 0.3</td>
</tr>
</tbody>
</table>

**Note 1**—The concentration ranges can be extended by use of suitable reference materials. The ranges for aluminum and vanadium represent the actual concentration ranges of the NIST\(^2\) Standard Reference Materials\(^6\) 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 Alloys\(^3\)
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials\(^5\)

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 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 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 6AI-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>
<thead>
<tr>
<th>TABLE 1 Operating Voltages and Currents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Aluminum</td>
</tr>
</tbody>
</table>

6.3 Spectrometer, designed for X-ray emission analysis using air 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 µm or less, controllable to ± 20 µm. 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 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 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, the booklet Radiation Safety Recommendations for X-Ray Diffraction and Spectrographic Equipment, #MORP 68-14, 1968, 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, 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.

8.3 Suitable monitoring devices, either film badges or dosimeters, shall be worn by all personnel using the equipment. 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. 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. Reference Materials

9.1 Certified Reference Materials may include NIST SRM® 653, 654, 655, 655a or their replacements.

9.2 Additional Certified Reference Materials are available from commercial sources. Select a minimum of three samples that contain vanadium, aluminum, and iron at the top and bottom of the concentration range and one 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:

\[ V_f = 12 \frac{350}{\lambda K_{\text{abs}}} \]  (1)

where:

- \( V_f \) = minimum voltage required for exciting the element, and
- \( \lambda K_{\text{abs}} \) = wavelength of the K absorption edge of the fluorescent element.

Ideally, the operating voltage, \( V \), should approximate or exceed:

\[ V = 3V_f \]  (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.

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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. 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 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 polished with 500 or 600-grit belt or disk.

### TABLE 2 Analytical Lines

<table>
<thead>
<tr>
<th>Element</th>
<th>Line Designation</th>
<th>2θ Angle, deg</th>
<th>Wave- ( \lambda ) A</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>( K_a )</td>
<td>57.52</td>
<td>1.937</td>
<td>LiF</td>
</tr>
<tr>
<td>Aluminum</td>
<td>( K_a )</td>
<td>144.67</td>
<td>8.338</td>
<td>PET</td>
</tr>
<tr>
<td>Aluminum</td>
<td>( K_b )</td>
<td>142.57</td>
<td>8.338</td>
<td>EDdt</td>
</tr>
<tr>
<td>Vanadium</td>
<td>( K_b )</td>
<td>69.12</td>
<td>2.284</td>
<td>LiF</td>
</tr>
<tr>
<td>Chromium</td>
<td>( K_b )</td>
<td>62.36</td>
<td>2.085</td>
<td>LiF</td>
</tr>
</tbody>
</table>

\( ^a \) 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 certified 6Al-4V titanium-alloy reference materials. Prepare an analytical curve for each element using the software package provided by the 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

<table>
<thead>
<tr>
<th>Specimen</th>
<th>V. Weight %</th>
<th>Counts, ( I V K_b )</th>
<th>( I K_a/\mu )</th>
<th>( I K_b/\mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>4.06</td>
<td>681</td>
<td>29</td>
<td>651</td>
</tr>
<tr>
<td>173A</td>
<td>5.28</td>
<td>424</td>
<td>18</td>
<td>406</td>
</tr>
<tr>
<td>653</td>
<td>5.38</td>
<td>621</td>
<td>17</td>
<td>604</td>
</tr>
</tbody>
</table>

\( ^a \) 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 16,000 counts for the lowest concentrations within the specification.

13.2.2 Correction for Vanadium-Chromium Line Overlap—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 \( K_b \) line at 69.12 deg with the Cr \( K_a \) line at 69.35 deg. The choice of the analytical line for determining V in titanium alloys is restricted to the V \( K_b \) line due to a more serious overlap of V \( K_b \) and Ti \( K_b \) lines. To correct for the overlap of the Cr \( K_a \) line with the V \( K_b \) line, measure the Cr \( K_p \) line and use the following empirical expression to subtract the overlapping Cr \( K_p \) line:

\[
I V K_b = (I V K_a + I Cr K_a meas.b (I Cr K_p meas. (3)
\]

where \( I Cr K_a = b (I Cr K_a meas) \) and the subscripts “o” and “meas” refer to overlap and measure, respectively.

13.2.2.1 Since \( b \) is a function of resolution, it must be determined for each spectrometer. If the overlap of the Cr \( K_a \) line on the V \( K_b \) 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 concentration of the 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 Bias

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 SRM’s® for calibration, these five laboratories analyzed the six unknowns once on five different days for vanadium, aluminum, and iron. In-house reference materials were employed for calibrating the instruments for iron. The precision data are shown in Table 4.

15.2 Supporting data for this test method as determined by cooperative testing have been filed at ASTM International Headquarters as RR:E2-1010.
15.2 Bias—Accurate chemical data were not available in all cases to determine the accuracy of this test method. Table 5 presents 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