Designation: ~~E2465 – 11~~$^{\varepsilon1}$ E2465 – 13

Standard Test Method for
Analysis of Ni-Base Alloys by Wavelength Dispersive X-Ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation E2465; 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.

~~$^{\varepsilon1}$ NOTE—Editorial corrections were made in August 2011.~~

1. Scope

1.1 This test method covers the analysis of Ni-base alloys by wavelength dispersive X-ray Fluorescence Spectrometry for the determination of the following elements:

Element	~~Concentration~~ Range ~~%~~
~~Manganese~~	~~0.17 to 1.6~~
~~Phosphorus~~	~~0.005 to 0.015~~
~~Silicon~~	~~0.02 to 0.6~~
~~Chromium~~	~~11 to 22~~
~~Nickel~~	~~31 to 77~~
~~Aluminum~~	~~0.12 to 1.3~~
~~Molybdenum~~	~~0.045 to 10~~
~~Copper~~	~~0.014 to 2.5~~
~~Titanium~~	~~0.20 to 3.0~~
~~Niobium~~	~~1.43 to 5.3~~
~~Iron~~	~~2 to 46~~
~~Tungsten~~	~~0.016 to 0.50~~
~~Cobalt~~	~~0.014 to 0.35~~

Element	Composition Range
Manganese	0.06 % to 1.6 %
Phosphorus	0.008 % to 0.015 %
Silicon	0.08 % to 0.6 %
Chromium	1.6 % to 22 %
Nickel	23 % to 77 %
Aluminum	0.20 % to 1.3 %
Molybdenum	0.03 % to 10 %
Copper	0.007 % to 2.5 %
Titanium	0.11 % to 3.0 %
Niobium	0.55 % to 5.3 %
Iron	0.17 % to 46 %
Tungsten	0.06 % to 0.50 %
Cobalt	0.04 % to 0.35 %

NOTE 1—Unless exceptions are noted, concentration ranges can be extended by the use of suitable reference materials. Once these element ranges are extended they must be verified by some experimental means. This could include but not limited to Gage Repeatability and Reproducibility studies and/or Inter-laboratory Round Robin studies. Once these studies are completed, they will satisfy the ISO ~~17025~~17025 requirements for capability.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

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[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 E01.08 on Ni and Co and High Temperature Alloys.

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[2] 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.

E305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves
E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
E1622 Practice for Correction of Spectral Line Overlap in Wavelength-Dispersive X-Ray Spectrometry (Withdrawn 2006)[3]

2.2 *Other Documents:*

ISO 17025 General requirements for the competence of testing and calibration laboratories

2.3 *U.S. Government Standards:*[4]

10 CFR Part 19 Notices, Instructions and Reports to Workers: Inspection and Investigations
10 CFR Part 20 Standards for Protection Against Radiation

3. Terminology

~~3.1 *For definitions of terms used in this test method, refer to Terminology .*~~

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The test specimen is finished to a clean, uniform surface, then irradiated with an X-ray beam of high energy. The secondary X-rays produced are dispersed by means of crystals and the intensities are measured by suitable detectors at selected wavelengths. The outputs of the detectors in voltage pulses are 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 or kilocounts per unit time).

4.2 Concentrations of the elements are determined by relating the measured radiation of unknown specimens to analytical curves prepared with suitable reference materials. Either a fixed-channel (simultaneous) spectrometer or a sequential spectrometer, or an instrument combining both fixed-channels and one or more goniometers shall be used.

5. Significance and Use

5.1 This procedure is suitable for manufacturing control and for verifying that the product meets specifications. It provides rapid, multi-element determinations with sufficient accuracy to assure product quality. The analytical performance data included may be used as a benchmark to determine if similar X-ray spectrometers provide equivalent precision and accuracy, or if the performance of a particular spectrometer has changed.

6. Interferences

6.1 Interelement effects, or matrix effects, exist for some of the elements listed. Mathematical correction may be used to solve for these elements. Various mathematical correction procedures are commonly utilized. See Guide E1361 and Practice E1622. Any of these procedures that achieves analytical accuracy equivalent to that provided by this test method is acceptable.

7. Apparatus

7.1 *Specimen Preparation Equipment:*

7.1.1 *Surface Grinder or Sander With Abrasive Belts or Disks, or Lathe,* capable of providing a flat, uniform surface on the reference materials and test specimens. Aluminum oxide and zirconium oxide belts and discs with a grit size of between 60 and 180 have been found suitable.

7.2 *Excitation Source:*

7.2.1 *Tube Power Supply,* providing a constant potential or rectified power of sufficient energy to produce secondary radiation of the specimen for the elements specified. The generator may be equipped with a line voltage regulator and current stabilizer.

7.2.2 *X-ray Tubes,* with targets of various high-purity elements that are capable of continuous operation at required potentials and currents and that will excite the elements to be determined.

7.3 *Spectrometer,* designed for X-ray fluorescence analysis and equipped with specimen holders and a specimen chamber. The chamber shall contain a specimen spinner, and must be equipped for vacuum or helium-flushed operation for the determination of elements of atomic number 20 (calcium) or lower.

7.3.1 *Analyzing Crystals,* flat or curved crystals with optimized capability for the diffraction of the wavelengths of interest. The use of synthetic multilayer structures can also be found in some state-of-the-art-equipment.

7.3.2 *Collimators or Slits,* for controlling the divergence of the characteristic X-rays. Use in accordance with the equipment manufacturer's recommendations.

7.3.3 *Detectors,* sealed-gas, gas-flow scintillation counters or equivalent.

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[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from the U.S. Nuclear Regulatory Commission, Public Document Room, ~~Mail Stop:OWFN-1 F13, Washington, DC 20555, (800) 397-4209, or via email at PDR.Resource@nrc.gov, or via the website at www.nrc.gov.~~One White Flint North, 11555 Rockville Pike, Rockville, MD 20852-2738, http://www.nrc.gov.

7.3.4 *Vacuum System,* providing for the determination of elements whose radiation is absorbed by air (for example, silicon, phosphorus, and sulfur). The system shall consist of a vacuum pump, gage, and electrical controls to provide automatic pump down of the optical path, and maintain a controlled pressure, usually ~~13Pa~~ 13 Pa (100 mm Hg) or less, controlled to ±3 Pa (20 mm Hg). A helium-flushed system is an alternative to a vacuum system.

7.4 *Measuring System,* consisting of electronic circuits capable of amplifying and integrating pulses received from the detectors. For some measurements, a pulse height selector in conjunction with the detectors may be used to remove high order lines and background. The system shall be equipped with an appropriate device.

8. Reagents and Materials

8.1 *Detector Gases*—Only gas-flow proportional counters require a detector gas. Use the gas and purity of gas specified by the instrument manufacturer. Typical gases specified include P-10 or P-5. P-10 consists of a mixture of 90 % argon and 10 % methane and P-5 consists of a mixture of 95 % argon and 5 % methane. Other gases may be specified as well.

9. Reference Materials

9.1 *Certified Reference Materials* are available from national metrology institutes, international research institutes, and commercial sources.

9.2 *Reference Materials* with matrices similar to that of the test specimens and containing varying amounts of the elements in the scope of this test method may be used provided they have been analyzed using validated standard methods of test. These reference materials shall be homogeneous and free of voids and porosity.

9.3 The reference materials shall cover the concentration ranges of the elements being sought. A minimum of three reference materials shall be used for each element. A greater number of calibrants may be required if the analyst chooses to perform mathematical corrections for interelement effects. See Guide E1361.

10. Hazards

10.1 U.S. Nuclear Regulatory standards for ionizing radiation as found in the Code of Federal Regulations, 10 CFR Part 19 and 10 CFR Part 20 shall be observed at all X-ray emission spectrometer installations in the United States. It is also recommended that operating and maintenance personnel follow the guidelines of safe operating procedures given in similar handbooks on radiation safety.

10.2 Exposure to excessive quantities of high energy radiation such as those produced by X-ray spectrometers is injurious to health. The operator should take appropriate actions to avoid exposing any part of their body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with the regulations governing the use of ionizing radiation. Manufacturers of X-ray fluorescence spectrometers generally build appropriate shielding/safety interlocks into X-ray equipment during manufacturing that minimize the risk of excessive radiation exposure to operators. Operators should not attempt to bypass or defeat these safety devices. Only authorized personnel should service X-ray spectrometers.

10.3 *Monitoring Devices,* either film badges or dosimeters[5] may be worn by all operating and maintenance personnel. Safety regulations shall conform to applicable local, state, and federal regulations.

11. Preparation of Reference Materials and Test Specimens

11.1 The analyst must choose a measurement area or diameter from the options built into the spectrometer. All test specimens and reference materials must have a flat surface of greater diameter than the chosen viewed area.

11.2 Prepare the reference materials and test specimens to provide a clean, flat uniform surface to be exposed to the X-ray beam. One surface of a reference material may be designated by the producer as the certified surface. The same preparation medium shall be used for all reference materials and test specimens.

11.3 Refinish the surface of the reference materials and test specimens as needed to eliminate oxidation.

12. Preparation of Apparatus

12.1 Prepare and operate the spectrometer in accordance with the manufacturer's instructions.

NOTE 2—It is not within the scope of this test method to prescribe minute details relative to the preparation of the apparatus. For a description and specific details concerning the operation of a particular spectrometer, refer to the manufacturer's manual.

12.1.1 *Start-up*—Turn on the power supply and electronic circuits and allow sufficient time for instrument warm-up prior to taking measurements.

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[5] Available from Siemens Gammasonics, Inc., 2000 Nuclear Drive, Des Plaines ~~Ill~~IL 60018.

12.2 *Tube Power Supply*—The power supply conditions should be set in accordance with the manufacturer's recommendations.

12.2.1 The voltage and current established as optimum for the X-ray tube power supply in an individual laboratory shall be reproduced for subsequent measurements.

12.3 *Proportional Counter Gas Flow*—When a gas-flow proportional counter is used, adjust the flow of the P-10 gas in accordance with the equipment manufacturer's instructions. When changing P-10 tanks, the detectors should be adequately flushed with detector gas before the instrument is used. After changing P-10 tanks, check the pulse height selector in accordance with the manufacturer's instructions.

12.4 *Measurement Conditions*—The K-$L_{2,3}$ ~~(Kα)~~(Kα) lines for each element are used, except for tungsten. For tungsten, the L_3-M_5 ~~(Lα)~~(Lα) line is used. When using a sequential spectrometer, measurement angles shall be calibrated in accordance with the manufacturer's guidelines.

12.4.1 *Crystals and Detectors*—The following crystals and detectors are suggested for the elements indicated:

Element	Crystal	Detector
Chromium	L1,L2	SP,Sc,FP
Cobalt	L1,L2	SP,Sc,FP
Copper	L1,L2	SP,Sc,FP
Manganese	L1,L2	SP,Sc,FP
Molybdenum	L1,L2	Sc
Nickel	L1,L2	SP,Sc,FP
Niobium	L1,L2	Sc
Phosphorus	Ge	FP,SP
Silicon	PET,InSb	FP,SP
Titanium	L1,L2	SP,Sc,FP
Aluminum	PET	Sc,FP
Iron	L1,L2	SP,Sc
Tungsten	L1,L2	SP,Sc
	L1 = LiF200	SP = Sealed Proportional
	L2 = LiF220	Sc = Scintillation
		FP = Flow Proportional

12.4.2 *Counting Time*—Collect a sufficient number of counts so that the precision of the analysis will not be affected by the variation in the counting statistics. A minimum of 10,000 counts is required for one percent relative precision of the counting statistics and 40,000 for one-half percent relative. If fixed time measurements are used, the measurement times can be derived from the measured intensity (counts per second) and the minimum number of required counts (that is, 10,000 or 40,000). Alternatively, measurement times of 10 s for each of the elements are a good starting point.

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 an analytical curve for each element being determined (refer to Practice E305). For information on correction of interelement effects in X-ray Spectrometric Analysis refer to Guide E1361. Information on correction of spectral line overlap in wavelength dispersive X-ray spectrometry can be found in Practice E1622.

13.2 *Standardization (Analytical Curve Adjustment)*—Using a control reference material, check the calibration of the X-ray spectrometer at a frequency consistent with SPC practice or when the detector gas or major components have been changed. If the calibration check indicates that the spectrometer has drifted, make appropriate adjustments in accordance with the instructions in the manufacturers' manual. Refer to Practice E305 for frequency of verification of standardization.

14. Procedure

14.1 *Specimen Loading*—Place the reference materials and test specimens in the appropriate specimen holding container. If the spectrometer is equipped with an automated loading device, loading and unloading all specimens from the same holder may improve repeatability. The container shall have a suitable opening to achieve the required precision in an acceptable amount of time. The holder must be equipped to keep the specimen from moving inside the holder.

14.2 *Excitation*—Expose the specimen to primary X radiation in accordance with Section 12.

14.3 *Radiation Measurements*—Obtain and record the counting rate measurement for each element. Either fixed count or fixed time modes may be used. Obtain at least the predetermined minimum counts for all specimens.

14.4 *Spectral Interferences*—Some X-ray spectrometers will not completely resolve radiation from several element combinations (for example, molybdenum and sulfur; molybdenum and phosphorus, and iron and cobalt). Therefore care must be exercised in the interpretation of intensities when both elements are present. Mathematical calculations must be used to correct for interferences.

14.5 *Replicate Measurements*—Make a single measurement on each test specimen. The performance of an X-ray spectrometer is not improved significantly by making multiple measurements on the same surface of the specimen. Confidence in the accuracy of analysis will improve by making multiple measurements on freshly prepared surfaces of the same specimen.

15. Calculation of Results

15.1 Using the radiation measurements for the test specimen and the appropriate analytical curves, determine the concentrations of the various elements.

15.1.1 If mathematical calculations must be made to correct the concentrations for interelement effects, any of a number of correction procedures may be employed. Refer to the equipment manufacturer's manual for the recommended procedure for the instrument being used. See Guide E1361.

16. Precision and Bias[6]

16.1 *Precision*—An acceptable number of laboratories tested this method in accordance with Practice E1601. Precision data, including R and R_{rel} are provided in Tables 1-13.

16.2 *Bias (Accuracy)*—A number of certified reference materials were tested in the development of this test method. The accuracy of this test method has been deemed satisfactory based on the bias data in Tables 14-26. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

17. Keywords

17.1 Ni-base alloys; spectrometric analysis; X-ray ~~emission;~~ emissionsX-ray fluorescence

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1060.

TABLE 1 Statistical Information for Manganese

Test Matl.	No. of Labs	% Mn (mean)	R	R_{rel} (%)
J	7	1.5862	0.2319	14.6
D	7	0.7693	0.0505	6.6
G	7	0.5000	0.0268	5.4
B	5	0.4473	0.0380	8.5
O	6	0.3039	0.0153	5.0
P	7	0.2660	0.0159	6.0
E	7	0.2181	0.0965	44.3
H	6	0.2096	0.0172	8.2
I	6	0.1693	0.0116	6.9