Designation: E322 – 12

Standard Test Method for
Analysis of Low-Alloy Steels and Cast Irons by Wavelength Dispersive X-Ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation E322; 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 method covers the X-ray fluorescence spectrometric analysis of low-alloy steels and cast irons for the following elements in the ranges indicated:

Elements	Mass Fraction Range, %
Manganese	0.20 to 1.50
Nickel	0.10 to 1.00
Chromium	0.10 to 1.00
Molybdenum	0.04 to 0.40
Copper	0.05 to 0.30
Vanadium	0.03 to 0.25

NOTE 1—These mass fraction ranges can be extended by the use of suitable reference materials. The detection limit for the elements is lower than the listed minimum value. The ranges represent the actual levels at which this test method was tested.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron
E351 Test Methods for Chemical Analysis of Cast Iron—All Types
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis
E1621 Guide for X-Ray Emission Spectrometric Analysis

3. Terminology

3.1 For definition of terms used in this test method, refer to Terminology E135.

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. The secondary X rays produced are dispersed by means of a crystal and the intensities are measured by a detector at selected wavelengths. The results are obtained by relating measured intensities to an appropriate calibration curve.

5. Significance and Use

5.1 This test method is comparative and intended for use as a routine method to test materials for compliance with compositional specifications. It is assumed that all who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices, such as those described in Guide E882.

6. Apparatus

6.1 *Specimen Preparation Equipment:*

6.1.1 *Disk or Belt Sander,* capable of providing test specimens with a uniform, clean surface finish, or other equivalent finishing device.

6.2 *Excitation Source:*

6.2.1 *X-ray Generator,* with a full-wave rectified power supply, or constant potential power supply.

6.2.2 *X-ray Tube,* with a high-purity tungsten target. Other targets may be used provided they produce data that meets the precision and bias in Section 14.

6.3 *Spectrometer:*

6.3.1 *Analyzing Crystal,* lithium fluoride LiF(200), flat or curved having a 2d spacing of 0.40276 nm; or LiF(220), flat or curved having a 2d spacing of 0.28473 nm.

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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 E01.01 on Iron, Steel, and Ferroalloys.

Current edition approved Aug. 1, 2012. Published September 2012. Originally approved in 1967. Last previous edition approved in 2004 as E322 – 96 (2004). DOI: 10.1520/E0322-12.

[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.

6.3.2 *Collimation*—Provide appropriate collimation to achieve the required resolution. For curved optics, no collimation is required; the use of entrance and exit slits might be required to reduce the intensity of background radiation.

6.3.3 *Goniometer*—A goniometer that provides an angular scan from 10° 2θ to 148° 2θ. Or alternatively, fixed channels for the analytes of interest, given in the scope of the method.

6.3.4 *Detectors,* gas-filled proportional counters or scintillation counter. Other detectors may be used provided they produce data that meets the precision and bias in Section 14.

6.4 *Measuring Unit*—An electronic circuit panel capable of amplifying, counting, or integrating pulses received from the detector tube. In addition, a pulse height analyzer should be available for pulse energy discrimination if needed. Good precision and accuracy have been obtained without the use of a pulse height analyzer.

7. Reference Materials

7.1 *Certified Reference Materials*—Low-alloy steel and cast iron certified reference materials are commercially available from a number of sources.

7.2 *Reference Materials*—Low-alloy steel and cast iron reference materials can be used. They should be analyzed and thoroughly evaluated in accordance with Test Methods E350 and E351.

8. Hazards

8.1 U.S Nuclear Regulatory standards for ionizing radiation as found in the Code of Federal Regulations 10 CFR Part 19, "Notices, Instructions and Reports to Workers: Inspection and Investigations" and 10 CFR Part 20, "Standards for Protection Against Radiation"[3] shall be observed at all X-ray emission spectrometer installations in the U.S. It is also recommended that operating and maintenance personnel follow the guidelines of safe operating procedures given in similar handbooks on radiation safety.

8.2 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 which 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.

9. Preparation of Reference Materials and Specimens

9.1 Prepare a clean, flat surface on the test specimen using an appropriate sander equipped with 240 grit or finer aluminum oxide abrasive paper. The abrasive paper shall have a greater diameter than the exposed specimen surface. If disks are used the disk radius shall be greater than the exposed specimen surface. The specimen shall be surfaced using the same grit paper as was used to prepare the surface of the calibrants. Other equivalent finish-machining methods may be used provided the data produced meets the precision and bias in Section 14.

NOTE 2—Any facets or imperfections in the flatness of the finished surface have been found to give marked changes in response.

9.2 Resurface the reference materials as needed to eliminate oxidized surfaces.

10. Preparation of Apparatus

10.1 Prepare the apparatus as follows:

Voltage, kV	50 (Note 3)
Current, mA	40 (Note 3)
Detector	Select the detector (or detector combination) according to the manufacturers' recommendation

NOTE 3—Different values for voltage and current may be used provided they produce data that meets the precision and bias in Section 14.

11. Excitation and Radiation Measurement

11.1 *Excitation*—Place the specimen into the instrument, taking care not to contaminate the specimen surface. Generate the secondary fluorescence using the settings listed in Section 10.

11.2 *Radiation Measurements*—Make radiation measurement of the analytical lines listed in Table 1 using the settings listed in Section 10.

NOTE 4—In Table 1, the listed degree 2θ peaks represent the theoretical values for lithium fluoride crystals LiF(200) and LiF(220) with 2d spacings of 0.40267 nm and 0.28473 nm respectively.The actual goniometer setting for these peaks must be determined experimentally within each laboratory. Periodic checks to verify this setting are advisable.

11.2.1 Obtain the radiation measurement for each element. Collect sufficient counts to produce the required statistical precision. Use the data in the following Table to determine the minimum number of counts required:

Element	Total Counts
Nickel	64 000
Manganese	64 000
Chromium	64 000
Molybdenum	32 000
Copper	32 000
Vanadium	16 000

TABLE 1 Analytical Peaks

Element	Line	Wave-length, nm	Crystal	° 2θ (Note 4)	Alternative Crystal	° 2θ for Alternative Crystal (Note 4)
Nickel	Kα (K-L3)	0.1659	LiF(200)	48.61	LiF(220)	71.27
Manganese	Kα (K-L3)	0.2103	LiF(200)	62.91	LiF(220)	95.20
Chromium	Kα (K-L3)	0.2291	LiF(200)	69.29	LiF(220)	107.11
Molybdenum	Kα (K-L3)	0.0710	LiF(200)	20.28	LiF(220)	28.90
Copper	Kα (K-L3)	0.1542	LiF(200)	44.96	LiF(220)	65.56
Vanadium	Kα (K-L3)	0.2505	LiF(200)	76.84	LiF(220)	123.17

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[3] Available from the 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.

TABLE 2 Precision Data[A]

Element	Mass Fraction Range, %	Relative Standard Deviation, RSD %[B]
Manganese	0.52 to 1.41	0.60
Nickel	0.23 to 0.79	0.83
Chromium	0.21 to 0.86	0.88
Molybdenum	0.05 to 0.35	1.02
Copper	0.06 to 0.27	1.04
Vanadium	0.03 to 0.22	1.16

[A] The values were obtained by pooling data from five laboratories.

[B] Relative standard deviation, RSD, in this method, is calculated as follows:

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

where:

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

NOTE 5—Larger numbers than the above listed total counts have been accumulated within a reasonable counting time by various instruments.

12. Calibration and Standardization

12.1 *Calibration*—Make measurements on a sufficient number of reference materials to establish the calibration curve. Prepare the calibration curves for each element by plotting the intensity versus mass fraction values. Refer to Guide E1361and Guide E1621 for additional information relating to sound calibration practices.

12.2 *Standardization*—Before testing samples, standardize the spectrometer calibration following the manufacturer's instructions.

13. Calculation

13.1 The mass fractions are determined from the prepared calibration curves.

14. Precision and Bias

14.1 *Precision*—Precision data are shown in Table 2.

14.2 *Bias*—Representative bias data are shown in Table 3.

TABLE 3 Bias Data

Element	Established Value,[A] mass fraction %	Deviation of X-ray Value[B] from Established Value, relative %	Maximum Observed Deviation from Established Value, mass fraction %
Manganese	0.640	1.14	0.03
	0.910	0.55	0.02
	1.120	0.96	0.025
Nickel	0.325	1.42	0.01
	0.520	0.23	0.005
	0.695	0.07	0.007
Chromium	0.350	0.49	0.01
	0.515	2.35	0.015
	0.700	0.74	0.03
Molybdenum	0.100	1.90	0.005
	0.195	3.33	0.008
	0.295	0.58	0.005
Copper	0.060	3.83	0.005
	0.080	0.63	0.004
	0.175	0.97	0.007
Vanadium	0.045	12.44	0.01
	0.145	0.68	0.008

[A] The samples used for this program are secondary standards whose values are averages from chemical analyses performed by eight laboratories.

[B] These values were calculated from the total results reported from three separate days of study, and five participating laboratories.

14.2.1 It is unlikely that any results using this test method will deviate more than the maximum deviation shown in Table 3, provided the operating parameters are as specified.

NOTE 6—The analyst must verify the absence of or accurate correction of interferences such as zirconium on molybdenum Kα, the absence of or accurate correction of inter-element effects such as molybdenum and nickel on chromium, and the absence of differences due to metallurgical history or condition of the sample.

15. Keywords

15.1 cast iron; low-alloy steel; spectrometric analysis; X-ray fluorescence