



Designation: E 415 – 99a

# Standard Test Method for Optical Emission Vacuum Spectrometric Analysis of Carbon and Low-Alloy Steel<sup>1</sup>

This standard is issued under the fixed designation E 415; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the simultaneous determination of 20 alloying and residual elements in carbon and low-alloy steels in the concentration ranges shown (Note 1).

Element	Concentration Range, %	
	Applicable Range, % <sup>A</sup>	Quantitative Range, % <sup>B</sup>
Aluminum	0 to 0.075	0.02 to 0.075
Arsenic	0 to 0.1	0.05 to 0.1
Boron	0 to 0.007	0.002 to 0.007
Calcium	0 to 0.003	0.001 to 0.003
Carbon	0 to 1.1	0.08 to 1.1
Chromium	0 to 2.25	0.02 to 2.25
Cobalt	0 to 0.18	0.008 to 0.18
Copper	0 to 0.5	0.04 to 0.5
Manganese	0 to 2.0	0.10 to 2.0
Molybdenum	0 to 0.6	0.03 to 0.6
Nickel	0 to 5.0	0.02 to 5.0
Niobium	0 to 0.085	0.02 to 0.085
Nitrogen	0 to 0.015	0.004 to 0.015
Phosphorous	0 to 0.085	0.02 to 0.085
Silicon	0 to 1.15	0.07 to 1.15
Sulfur	0 to 0.055	0.01 to 0.055
Tin	0 to 0.045	0.01 to 0.045
Titanium	0 to 0.2	0.004 to 0.2
Vanadium	0 to 0.3	0.004 to 0.3
Zirconium	0 to 0.05	0.02 to 0.05

<sup>A</sup>Applicable range in accordance with Guide E 1763 for results reported in accordance with Practice E 1950.

<sup>B</sup>Quantitative range in accordance with Practice E 1601.

NOTE 1—The concentration ranges of the elements listed have been established through cooperative testing<sup>2</sup> of reference materials. Included, in addition to the original data of Test Method E 415 – 71, are data from cooperative testing of a broader range of reference materials to expand the element concentration ranges.

1.2 This test method covers analysis of specimens having a diameter adequate to overlap the bore of the spark stand opening (to effect an argon seal). The specimen thickness should be between 10 and 38 mm.

1.3 This test method covers the routine control analysis of preliminary and ladle tests from either basic oxygen, open-

hearth, or electric furnaces and analysis of processed material. It is designed for either chill-cast or rolled and forged specimens. The reference materials and specimens should be of similar metallurgical condition and composition.

1.4 *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:

- E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron<sup>3</sup>
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>4</sup>
- E 158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis<sup>4</sup>
- E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves<sup>4</sup>
- E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron<sup>4</sup>
- E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis<sup>5</sup>
- E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys<sup>5</sup>
- E 1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis<sup>5</sup>
- E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method<sup>5</sup>
- E 1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods<sup>5</sup>
- E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition<sup>5</sup>
- E 1950 Practice for Reporting Results from Methods of Chemical Analysis<sup>5</sup>

<sup>1</sup>This test method is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.

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<sup>2</sup>Supporting data for this test method have been filed at ASTM Headquarters as RR:E2-1004.

<sup>3</sup> Discontinued 1995, see 1994 *Annual Book of ASTM Standards*, Vol. 03.05.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol. 03.05.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol. 03.06

### 3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E 135.

### 4. Summary of Test Method

4.1 The most sensitive lines of arsenic, boron, carbon, nitrogen, phosphorus, sulfur, and tin lie in the vacuum ultraviolet region. The absorption of the radiation by air in this region is overcome by evacuating the spectrometer and flushing the spark chamber with argon. A capacitor discharge is produced between the flat, ground surface of the disk specimen and a conically shaped electrode. The discharge is terminated at a predetermined intensity time integral of a selected iron line, or at a predetermined time, and the relative radiant energies or concentrations of the analytical lines are recorded.

### 5. Significance and Use

5.1 This test method for the spectrometric analysis of metals and alloys is primarily intended to test such materials for compliance with compositional specifications. It is assumed that all who use this test method will be analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

### 6. Apparatus

#### 6.1 Sample Preparation Equipment:

6.1.1 *Sample Mold*, capable of producing castings that are homogeneous and free from voids and porosity. Refer to Practice E 1806 for steel sampling procedures. The following mold types have been found to produce acceptable samples:

6.1.1.1 *Cast Iron Mold*—A mold 70 mm (2¾ in.) deep, 64 mm (2½ in.) in diameter at the top of the mold, and 57 mm (2¼ in.) in diameter at the bottom of the mold. The wall thickness of the mold is approximately 32 mm (1¼ in.).

6.1.1.2 *Refractory Mold Ring*—A mold that has a minimum inside diameter of 32 mm (1¼ in.) and a minimum height of 25 mm (1 in.). The ring is placed on a flat surface of a copper plate approximately 50 mm (2 in.) thick.

6.1.1.3 *Book-Type Steel or Copper Mold*, to produce a chill-cast disk 64 mm (2½ in.) in diameter and 13 mm (½ in.) thick.

6.2 *Excitation Source*, capable of providing a triggered capacitor discharge having source parameters meeting the requirements of 11.1.

6.3 *Spark Chamber*, automatically flushed with argon. The spark chamber shall be mounted directly on the spectrometer, and shall be provided with a spark stand to hold a flat specimen and a lower electrode of rod form.

NOTE 2—Clean the excitation chamber when the counter electrode is replaced. Clean the lens or protective window after approximately 200 to 300 excitations to minimize transmission losses.

6.4 *Spectrometer*, having a reciprocal linear dispersion of 0.60 nm/mm, or better, in the first order and a focal length of 0.75 to 3 m. Its approximate range shall be from 120.0 to 400.0 nm. Masks shall be provided in the spectrometer to eliminate scattered radiation. The spectrometer shall be provided with an air inlet and a vacuum outlet. The spectrometer shall be

operated at a vacuum of 25  $\mu\text{m}$  of mercury or below. The primary slit width is 20 to 50  $\mu\text{m}$ . Secondary slit width is 50 to 200  $\mu\text{m}$ .

6.5 *Measuring System*, consisting of photomultipliers having individual voltage adjustments, capacitors in which the output of each photomultiplier is stored, a voltage measuring system to register the voltages on the capacitors either directly or indirectly, and the necessary switching arrangements to provide the desired sequence of operation.

6.6 *Vacuum Pump*, capable of maintaining a vacuum of 25  $\mu\text{m}$  Hg.

NOTE 3—A pump with a displacement of at least 0.23 m<sup>3</sup>/min (8 ft<sup>3</sup>/min) is usually adequate.

6.7 *Flushing System*, consisting of argon tanks, a pressure regulator, and a gas flowmeter. Automatic sequencing shall be provided to actuate the flow of argon at a given flow rate for a given time interval and to start the excitation at the end of the flush period. Means of changing the flow rate of argon shall be provided. The flushing system shall be in accordance with Practice E 406.

### 7. Reagents and Materials

7.1 *Counter Electrodes*—The counter electrodes shall be 6.4-mm (¼-in.) diameter, hard-drawn, fine, silver rods, 1.5-mm (⅙-in.) thoriated, tungsten rods, or other material provided it can be shown experimentally that equivalent precision and bias is obtained. Machine the rods to a 90 or 120° cone.

NOTE 4—A black deposit builds up on the tip of the electrode, thus reducing the overall intensity of the spectral radiation. In general this condition will not affect analytical performance for the first 40 or 50 excitations, after which time a freshly prepared counter electrode should be installed. The number of acceptable excitations on an electrode varies from one instrument to another, and should be established in each laboratory. With a thoriated tungsten electrode, it has been reported that a hundred or more excitations can usually be made before replacement.

7.2 *Inert Gas, Argon*, in accordance with Practice E 406.

### 8. Reference Materials

8.1 Certified Reference Materials (CRMs) are available from the National Institute of Standards and Technology and other sources. These cover all or part of the concentration ranges listed in 1.1. They are valuable in establishing preliminary working curves and determining the precision of the instrument. However, because of differences between these CRMs and the production specimens prepared by the sampling procedures recommended for this test method, curves based on CRMs may (in very unusual circumstances) need to be corrected with values from reference materials made by normal production sampling techniques and analyzed in accordance with Test Methods E 30, E 350, and E 1019.

8.2 *Reference Materials*—Periodically check the instrument for drift. For this purpose, verifiers and standardants are employed. These reference materials shall be homogeneous and contain appropriate amounts of each element, covering the concentration range of elements contained in the specimens.

## 9. Preparation of Specimens and Reference Materials

9.1 Use cast or rolled and forged samples. Cut a 13 to 25-mm (½ to 1-in.) thick slice from the sample or obtain an initial smooth flat surface by machining at least 1.3 mm (0.05 in.) off the original surface using a lathe or grinder. Make certain that the specimens are homogeneous and free from voids and pits in the region to be excited (Note 5). Rough grind the cut surface by grinding on a belt sander, either wet or dry, with 50 to 80-grit abrasive belt. Obtain the final surface by dry grinding. A finer abrasive belt, such as 120-grit, may be used for final dry grinding, but is not essential (Note 6).

NOTE 5—Specimen porosity is undesirable because it leads to the improper “diffuse-type” rather than the desired “concentrated-type” discharge. The specimen surface should be kept clean because the specimen is the electron emitter, and electron emission is inhibited by oily, dirty surfaces.

NOTE 6—Reference materials and specimens shall be refinished dry on a belt sander before being re-excited on the same area.

## 10. Preparation of Apparatus

NOTE 7—The instructions given herein apply to most spectrometers; however, some settings and adjustments may need to be varied, and additional preparation of the equipment may be required. It is not within the scope of an ASTM test method to prescribe the minute details of the apparatus preparation which may differ not only for each manufacturer, but also for different equipment from the same manufacturer. For a description of and further details of operation of a particular spectrometer, refer to the manufacturer’s handbook.

10.1 Program the spectrometer to accommodate the internal standard lines and one of the analytical lines for each element listed in Table 1.

NOTE 8—The lines listed in Table 1 have proven satisfactory for the elements and concentration ranges described in the scope. Other internal standard and analytical lines, such as those listed in Table 2, may be used provided that it can be shown experimentally that equivalent precision and accuracy are obtained.

10.2 Position or test the position of the spectrometer exit slits to ensure that peak radiation passes through each slit and is incident on the photomultiplier. This shall be done initially and as often as necessary thereafter to maintain proper alignment.

NOTE 9—The manner and frequency of positioning or checking the position of the exit slits will depend on factors such as: the type of spectrometer, the variety of analytical problems encountered, and the frequency of use. Each laboratory should establish a suitable check procedure.

## 11. Excitation and Exposure

### 11.1 Electrical Parameters (Note 10)

11.1.1 Select excitation parameters within the following ranges

	Triggered Capacitor Discharge
Capacitance, $\mu\text{F}$	10 to 15
Inductance, $\mu\text{H}$	50 to 70
Resistance, $\Omega$	3 to 5
Potential, V	940 to 1000
Current, A, r-f	0.3 to 0.8
Number of discharge/s	60

NOTE 10—When parameter values are established, maintain them carefully. The variation of the power supply voltage shall not exceed

**TABLE 1 Internal Standard and Analytical Lines**

Element	Wavelength, nm	Line Classification <sup>A</sup>	Possible Interference <sup>B</sup>
Aluminum	394.40	I	V, Mn, Mo, Ni
	308.22	I	V, Mn
Arsenic	197.20	I	Mo, W
	193.76	I	Mn
Boron	182.64	I	S, Mn, Mo
	182.59	I	W, Mn, Cu
Calcium	396.85	II	Nb
Carbon	193.09	I	Al
Chromium	298.92	II	Mn, V, Ni, Nb, Mo
	267.72	II	Mn, Mo, W
Cobalt	345.35	I	Cr, Mo
	228.62	II	Ni, Cr
Copper	327.40	I	Nb
	213.60	II	Mo, Cr
Iron (IS)	271.44	II	
	273.07	II	Co
Manganese	293.31	II	Cr, Mo, Ni
	255.86	II	Zr
Molybdenum	379.83	II	Mn
	277.54	I	Cu, V, Co, Mn
	386.41	I	V, Cr
Nickel	231.60	II	Co, Ti
	227.02	II	Nb, W
Niobium	319.50	II	Mo, Al, V
Nitrogen	149.26	I	Fe, Ti, Si, Mn, Cu, Ni and nitride forming elements such as Ti
Phosphorus	178.29	I	Mo
Silicon	288.16	I	Mo, Cr, W
	251.61	I	Fe, V
Sulfur	180.73	I	Mn
Tin	189.99	II	Mn, Mo, Al
Titanium	337.28	II	Nb
	324.20	II	Nb
Vanadium	310.23	II	Fe, Mo, Nb, Ni
	311.07	II	Mn, Ti, Fe
Zirconium	343.82	II	W

<sup>A</sup> The numerals I or II in the line classification column indicate that the line has been classified in a term array and definitely assigned to the normal atom (I) or to the singly ionized atom (II).

<sup>B</sup> Interferences are dependent upon instrument design, spectrum line choices, and excitation conditions, and those listed require confirmation based upon specimens selected especially to demonstrate suspected interferences.

**TABLE 2 Other Analytical Lines**

Element	Wavelength, nm	Line Classification <sup>A</sup>	Possible Interference <sup>B</sup>
Arsenic	189.04	I	V, Cr
Carbon	165.81	I	
Copper	224.26	II	Ni
	324.75	I	Mn, Nb
Molybdenum	202.03	II	
	281.62	II	Mn
Silicon	212.415	II	Mo, Ni, V, Cu, Nb

<sup>A</sup> The numerals I or II in the line classification column indicate that the line has been classified in a term array and definitely assigned to the normal atom (I) or to the singly ionized atom (II).

<sup>B</sup> Interferences are dependent upon instrument design, dispersion, spectrum line choices, and excitation conditions, and those listed require confirmation based upon specimens selected especially to demonstrate suspected interferences.

$\pm 5\%$  and preferably should be held within  $\pm 2\%$ .

11.1.2 *Initiation Circuit*—The initiator circuit parameters shall be adequate to uniformly trigger the capacitor discharge. Nominal values found to be adequate are listed as follows:

Capacitance, $\mu\text{F}$	0.0025
Inductance, $\mu\text{H}$	residual
Resistance, $\Omega$	2.5
Peak voltage, V	18 000

11.1.3 *Other Electrical Parameters*—Excitation units, on which the precise parameters given in 11.1.1 and 11.1.2 are not available, may be used provided that it can be shown experimentally that equivalent precision and accuracy are obtained.

11.2 *Exposure Conditions* (Note 11)—Use the following exposure conditions:

Preflush period, s	5 to 15
Preburn period, s	5 to 20
Exposure period, s	3 to 30

Argon flow (Note 12)	$\text{ft}^3/\text{h}$	L/min
Flush	5 to 45	2.5 to 25
Preburn	5 to 45	2.5 to 25
Exposure	5 to 30	2.5 to 15

NOTE 11—Select preburn and exposure periods after a study of volatilization rates during specimen excitations. Once established, maintain the parameters consistently.

NOTE 12—A high-purity argon atmosphere is required at the analytical gap. Molecular gas impurities, nitrogen, oxygen, hydrocarbons, or water vapor, either in the gas system or from improperly prepared specimens should be minimized.

11.3 *Electrode System*—The specimen, electrically negative, serves as one electrode. The opposite electrode is a thoriated tungsten or silver rod, the tip of which has been sharpened to a 45 to 120° included angle cone. Use either a 3, 4, or 5-mm ( $\pm 0.1$ -mm) gap. Center the analytical gap on the optical axes of the spectrometer. Condition a fresh counter electrode with two to six excitations using the operating conditions in accordance with 11.1 and 11.2.

11.4 *Preliminary Calibration*—Excite a low- and a high-composition reference material and set the dynode potentials (photomultiplier sensitivity controls) for the internal standard line and each element line to obtain the desired voltages on the capacitors.

NOTE 13—The range of anode to cathode potentials for a given tube should be specified, that is 650 to 1000 V dc. If within the potential range the tube is either too sensitive or too insensitive for the element concentration range, select another photomultiplier. The potentials on the capacitors may be read directly, or a number of different readout systems may be employed which yield linear or logarithmic functions of the potentials and which may be displayed as relative numbers or as numbers calibrated directly in terms of percent.

## 12. Calibration, Standardization, and Verification

12.1 *Calibration*—Using the conditions given in 11.1-11.3, excite calibrants and potential standardants in a random sequence, bracketing these burns with excitations of any materials intended for use as verifiers. (A verifier may be used as a calibrant even though it is burned only as a verifier.) There shall be at least three calibrants for each element, spanning the required concentration range. Repeat with different random sequences at least two times. Using the averages of the data for each point, determine analytical curves as directed in Practices E 158 and E 305.

12.2 *Standardization*—Following the manufacturer's recommendations, standardize on an initial setup or anytime that it is known or suspected that readings have shifted. Make the necessary corrections either by adjusting the controls on the readout or by applying arithmetic corrections. Standardization will be done anytime verification indicates that readings have gone out of statistical control.

12.3 *Verification*—Verify that the instrument's standardization is valid immediately after each standardization, at the beginning of each shift, and as required in accordance with 12.3.2.

12.3.1 Analyze verifiers in accordance with Section 13. If results do not fall within the control limits established in 12.4, run another standardization or investigate why the instrument may be malfunctioning.

12.3.2 Repeat the verification at least every 4 h or if the instrument has been idle for more than 1 h. If readings are not in conformance, repeat the standardization.

12.4 *Quality Control*—Establish control limits in accordance with MNL 7,<sup>6</sup> Practice E 1329, or other equivalent quality control procedure.

## 13. Excitation and Radiation Measurements

13.1 Place the prepared surface of the specimen on the excitation stand so that excitation will impinge on an area at least 6 mm ( $\frac{1}{4}$  in.) from the edge of the specimen.

NOTE 14—With certain spectrometers, a properly excited specimen usually exhibits a dark ring around the pitted sparked area. With that equipment, a smooth, white, texture burn without the characteristic dark ring indicates an improperly excited specimen. However, if boron nitride disks are used to mechanically restrict the excited area of the sample, a properly excited specimen may not exhibit a dark ring.

13.2 Excite specimens in duplicate and report the average of the duplicate results.

## 14. Calculation

14.1 Average the duplicate percent concentration readings obtained for each specimen from a direct readout system, or use the average scale or clock reading to obtain the concentrations of constituents from the curves or from tables which have been prepared to relate scale values and concentrations.

## 15. Precision and Bias

15.1 *Precision*—Up to eight laboratories cooperated in performing this test method and obtained the statistical information summarized in Table 3. Additional data for within-laboratory variability of results, obtained by analyzing three specimens of one material in seven laboratories in accordance with source conditions specified in this method, are given in Table 4. Other specimens may exhibit greater or less variability using the same instrument and excitation conditions.

<sup>6</sup> MNL 7 *Manual on Presentation of Data and Control Chart Analysis*, ASTM Manual Series, ASTM, 6th ed., 1990.