



Designation: E415–99a (Reapproved 2005) Designation: E 415 – 08

Standard Test Method for Optical Atomic Emission Vacuum Spectrometric Analysis of Carbon and Low-Alloy Steel¹

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 (ϵ) 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, % ^A	Quantitative Range, % ^B
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

^A Applicable range in accordance with Guide E 1763 for results reported in accordance with Practice E 1950.

^B Quantitative range in accordance with Practice E 1601.

NOTE 1—The concentration ranges of the elements listed have been established through cooperative testing² 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.

1.2 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 can vary significantly according to the design of the spectrometer stand, but a thickness between 10 mm and 38 mm has been found to be most practical.

1.3 This test method covers the routine control analysis in iron and steelmaking operations and the analysis of processed material. It is designed for chill-cast, rolled, and forged specimens. Better performance is expected when reference materials and specimens are of similar metallurgical condition and composition. However, it is not required for all applications of this standard.

1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility

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.

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² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: E2-1004.

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:³

- E30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E 158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis
- E 305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves
- E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron
- E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis
- E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys
- E 1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis
- E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
- E 1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods
- E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition
- E 1950 Practice for Reporting Results from Methods of Chemical Analysis

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.

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5. Significance and Use iteh.ai/catalog/standards/sist/f684a2ff-9ba5-4d53-b39d-0b00b60ac7b3/astm-e415-08

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 Sampling Devices:

6.1.1 Sample Mold, capable of producing castings that are homogeneous and free from voids and porosity. Refer to Practice E1806 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.

6.1.1 Refer to Practice E 1806 for devices and practices to sample liquid and solid iron and steel.

6.2 Excitation Source, capable of providing a triggered capacitor discharge having source parameters meeting the requirements of, capable of providing electrical parameters to spark a sample. See 11.1 for details.

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 counter 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. 2—Follow the manufacturer's recommendations for cleaning the excitation chamber (during continuous

³ 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.

operation, this typically should be done every 24 h). Follow the manufacturer's recommendations for cleaning the entrance lens or window (verifier data or other reference sample intensity data can typically indicate when this is necessary).

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 m to 3 m. Its approximate range shall be from 120.0 nm 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 3.33 Pa (25 μ m of mercury) or below. The primary slit width is 20 to 50 μ m. Secondary slit width is 50 to 200 μ m. Secondary slit widths can vary (normally between 37 μ m and 200 μ m) depending on the element wavelength and possible interfering wavelengths.

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 3.33 Pa (25 μ m Hg) or less.

NOTE 3—A pump with a displacement of at least 0.23 m³/min (8 ft³/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 E406 Gas System, consisting of an argon supply with pressure and flow regulation. Automatic sequencing shall be provided to actuate the flow at a given rate for a specific time interval. The flow rate may be manually or automatically controlled. The argon 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 (1/4-in.) in diameter, hard-drawn, fine, silver rods, 1.5-mm (1/16-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. The counter electrodes can be silver or thoriated tungsten rods, or other material, provided it can be shown experimentally that equivalent precision and bias is obtained. The rods can vary in diameter from 1.5 mm to 6.5 mm (depending on the instrument manufacturer) and typically are machined to a 90° or 120° angled tip.

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. A black deposit will collect on the tip of the electrode. This deposit should be removed between specimens (typically with a wire brush). If not removed, it can reduce the overall intensity of the spectral radiation or transfer slight amounts of contamination between specimens, or both. The number of acceptable excitations on an electrode varies from one instrument to another, and should be established in each laboratory. It has been reported that thousands of excitations can be performed on a thoriated tungsten electrode before replacement is necessary.

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

8. Reference Materials

8.1 *Certified Reference Materials (CRMs)*—These are available from the National Institute of Standards and Technology (NIST) and other sources. These cover sources and span 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 E30, E350, and E1019. They are used to calibrate the spectrometer for the elements of interest or to validate the performance of the test method. It is not recommended to use CRMs as verifiers or to establish the repeatability of the chemical measurement process. Differences can occur between CRMs and production samples prepared by the sampling procedures recommended in this test method. Certain element's (for example, sulfur) calibrations may need to be corrected with values from reference materials made by normal production sampling techniques and analyzed by Test Methods E 350 and E 1019.

NOTE 5—Certified Reference Materials manufactured by NIST are trademarked with the name, "Standard Reference Materials, SRMs."

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. Reference Materials (RMs)—These are available from multiple suppliers or can be developed in house. RMs are typically used to control (verifiers) and drift correct (standardants) the spectrometer. These reference materials shall be homogenous and contain appropriate concentrations of each element to be controlled or drift corrected, or both.

9. Preparation of Specimens and Reference Materials

9.1 Use cast or rolled and forged samples. Cut a 13 to 25-mm (1/2 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 (

9.1 The specimens and reference materials must be prepared in the same manner. A specimen cut from a large sample section must be of sufficient size and thickness for preparation and to properly fit the spectrometer stand. A 10 mm to 38-mm thick specimen is normally most practical.

9.2 Ensure the specimens are free from voids and pits in the region to be excited (Note 6). Initially grind the surface with a 50-grit to 80-grit abrasive belt or disc (wet or dry). Perform the final grind with a dry abrasive belt or disc. A finer abrasive grinding media (for example, 120-grit) may be used for the final grind, but is not essential (Note 7).

NOTE 56—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. 7—Reference materials and specimens must be refinished dry on an abrasive belt or disc before being re-excited on the same area

10. Preparation of Apparatus

NOTE 7—The 8—The instructions given in this test method 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. Multiple lines may be used for a given element (for example, nickel) depending on the concentration range and the individual spectrometer software.

TABLE 1 Internal Standard and Analytical Lines

Element	Wavelength, nm	Line Classification ^A	Possible Interference ^B
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
Nickel	386.41	I	V, Cr
	231.60	II	Co, Ti
Niobium	227.02	II	Nb, W
	319.50	II	Mo, Al, V
Nitrogen	149.26	I	Fe, Ti, Si, Mn, Cu, Ni and nitride forming elements such as Ti
	178.29	I	Mo
Phosphorus	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

^A 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).

^B 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.

~~NOTE 8—The 9—~~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.

10.2 Test the positioning of the spectrometer entrance slit to ensure that peak radiation is entering the spectrometer chamber. This shall be done initially and as often as necessary to maintain proper entrance slit alignment. Follow the manufacturer’s recommended procedures. The laboratory will determine the frequency of positioning the alignment based on instrument performance.

10.3 Exit slit positioning and alignment is normally performed by the manufacturer at spectrometer assembly. Under normal circumstances, further exit slit alignment is not necessary (Note 10).

~~NOTE 9—The 10—~~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 utilizing qualified service engineers.

11. Excitation and Exposure

11.1 ~~Electrical Parameters (Note 10)~~(Note 11):

~~11.1.1~~Select excitation parameters within the following ranges

11.1.1 Excitation parameters are normally established by the spectrometer manufacturer. The following ranges are historical guidelines and newer instruments may vary from these.

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<https://standards.iteh.ai/catalog/standards/sist/f684a2ff-9ba5-4d53-b39d-0b00b60ac7b3/astm-e415-08>

TABLE 2 Other Analytical Lines

Element	Wavelength, nm	Line Classification ^A	Possible Interference ^B
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

^A 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).

^B 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.

Triggered Capacitor Discharge

Capacitance, μF	10 to 15
Inductance, μH	50 to 70
Resistance, Ω	3 to 5
Potential, V	940 to 1000
Current, A, r-f	0.3 to 0.8
Number of discharge/s	60
Number of discharges	60

~~NOTE 10—When 11—When~~ parameter values are established, maintain them carefully. The variation of the power supply voltage shall not exceed $\pm 5\%$ 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:—The initiator circuit parameters shall be adequate to uniformly trigger the capacitor discharge. The following settings are historical guidelines and newer instruments may vary from these:~~

Capacitance, μF	0.0025
Inductance, μH	residual
Resistance, Ω	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)~~

~~11.2 Excitation Conditions (Note 12)—Use the following exposure conditions:—The following ranges are normally adequate:~~

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

Argon flow (Note 12)	ft^3/h	L/min
Argon flow (Note 13)	ft^3/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 12—Select~~ preburn and exposure periods after a study of volatilization rates during specimen excitations. Once established, maintain the parameters consistently.

~~NOTE 12—A 13—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~~machined to a ~~45 to 120° included angle~~ 90° or 120° angled cone. Use either a 3 mm, 4 mm, or 5-mm (± 0.1 -mm) gap. ~~Center the analytical gap on the optical axes of the spectrometer gap.~~ Condition a fresh counter electrode with two to six excitations using the operating conditions ~~described 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. Photomultiplier Potentials —The sensitivity of the photomultipliers is normally established and set by the spectrometer manufacturer based on the particular wavelengths selected.~~

~~NOTE 13—The 14—The~~ range of anode to cathode potentials for a given tube should be specified, that is 650 V dc 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—Excite each calibrant, standardant, and verifier two to four times and use the average value. If the spectrometer system and software permits, 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, standardization~~ 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.