Designation: ~~E415 – 08~~ E415 – 14

Standard Test Method for ~~Atomic Emission Vacuum Spectrometric~~ Analysis of Carbon and Low-Alloy Steel by Spark Atomic Emission Spectrometry[1]

This standard is issued under the fixed designation E415; 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~~ by spark atomic emission vacuum spectrometry in the mass fraction ranges shown (Note 1).

	~~Concentration Range, %~~ Composition Range, %	
Element	Applicable Range, Mass Fraction %[A]	Quantitative Range, Mass Fraction %[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 E1763 for results reported in accordance with Practice E1950.
[B] Quantitative range in accordance with Practice E1601.

NOTE 1—The ~~concentration~~ mass fraction ranges of the elements listed have been established through cooperative testing[2] of reference materials. Included, in addition to the original data of Test Method E415 – 71, are data from cooperative testing of a broader range of reference materials to expand the element ~~concentration~~ mass fraction ranges.

1.2 This test method covers analysis of specimens having a diameter adequate to overlap and seal the bore of the spark stand ~~opening (to effect an argon seal).~~ opening. 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.

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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 ~~June 1, 2008~~March 1, 2014. Published ~~July 2008~~April 2014. Originally approved in 1971. Last previous edition approved in ~~2005~~2008 as ~~E415 – 99a (2005).~~E415 – 08. DOI: 10.1520/E0415-08.

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

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:*[3]

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

~~E158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis (Withdrawn 2004)[4]~~

E305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves

E350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron

E406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis

E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques

E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

E1950 Practice for Reporting Results from Methods of Chemical Analysis

2.2 *Other ASTM Documents*

ASTM MNL 7 Manual on Presentation of Data and Control Chart Analysis[4]

3. Terminology

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

4. Summary of Test Method

4.1 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 of the analytical lines are recorded. 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.

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 *Sampling Devices:*

6.1.1 Refer to Practice E1806 for devices and practices to sample liquid and solid iron and steel.

6.2 *Excitation Source,* 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—Follow the manufacturer's recommendations for cleaning the excitation chamber (during continuous 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).~~

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[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.

~~[4] The last approved version of this historical standard is referenced on www.astm.org.~~

[4] ~~MNL 7A *Manual on Presentation of Data and Control Chart Analysis*, ASTM Manual Series, ASTM International, 7th ed., 2002.~~ ASTM Manual Series, ASTM International, 8th edition, 2010.

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~~145.0 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 μm of mercury) or below. The primary slit width can range from 20 μm to 50 μm. Secondary slit widths can vary (normally between 37 μm and 200 μm) depending on the element wavelength and possible interfering wavelengths.

6.5 *Measuring System,* consisting of photomultipliers (Note 2) 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.

NOTE 2—Spectrometers equipped with CCD and/or CID detectors may be used provided the user can verify that the data obtained are equivalent to the precision and bias statistics in this method.

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 m^3/min (8 ft^3/min) is usually adequate.

6.7 *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 E406.

7. Reagents and Materials

7.1 *Counter Electrodes*—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 °~~90° or ~~120 °~~120° angled tip.

~~NOTE 4—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.~~

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NOTE 4—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 E406.

8. Reference Materials

8.1 *Certified Reference Materials (CRMs)*—These are available from the National Institute of Standards and Technology (NIST) and other sources and span all or part of the ~~concentration~~ mass fraction ranges listed in 1.1. 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 E350 and E1019.

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

8.2 *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~~compositions of each element to be controlled or drift corrected, or both.

9. Preparation of Specimens and Reference Materials

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 (~~essential. ~~Note 7).~~

NOTE 6—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 7—Reference materials and specimens must be refinished dry on an abrasive belt or disc before being re-excited on the same area~~

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
	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

[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.

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.

9.2.1 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 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~~ mass fraction range and the individual spectrometer software.

NOTE 8—The lines listed in Table 1 have proven satisfactory for the elements and ~~concentration~~ mass fraction 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 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~~9).

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 utilizing qualified service engineers.

11. Excitation and Exposure

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

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.

	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 discharges	60

~~NOTE 11—When parameter values are established, maintain them carefully. The variation of the power supply voltage shall not exceed ±5 % and preferably should be held within ±2 %.~~

11.1.2 When parameter values are established, maintain them carefully. The variation of the power supply voltage shall not exceed ± 5 % and preferably should be held within ± 2 %.

11.1.3 *Initiation Circuit*—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

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

11.2 *Excitation ~~Conditions~~ Conditions—~~(Note 12)—~~*The following ranges are normally adequate:

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

~~Argon flow (Note 13)~~	~~ft^3/h~~	~~L/min~~
Argon flow	ft^3/h	L/min
~~Flush~~	~~5 to 45~~	~~2.5 to 25~~
Flush	5 to 45	2.5 to 25
~~Preburn~~	~~5 to 45~~	~~2.5 to 25~~
Preburn	5 to 45	2.5 to 25
~~Exposure~~	~~5 to 30~~	~~2.5 to 15~~
Exposure	5 to 30	2.5 to 15

~~NOTE 12—Select preburn and exposure periods after a study of volatization rates during specimen excitations. Once established, maintain the parameters consistently.~~

11.2.1 Select preburn and exposure periods after a study of volatization rates during specimen excitations. Once established, maintain the parameters consistently.

~~Note 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.~~

11.2.2 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 machined to a 90 ° or 120 ° angled cone. Use either a 3 mm, 4 mm, or ~~5-mm (±0.1-mm)~~ 5 mm (± 0.1 mm) analytical gap. Condition a fresh counter electrode with two to six excitations using the operating conditions described in 11.1 and 11.2.

11.4 *Photomultiplier Potentials*—The sensitivity of the photomultipliers is normally established and set by the spectrometer manufacturer based on the particular wavelengths selected.

~~Note 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.~~

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12. Calibration, Standardization, and Verification

12.1 *Calibration*—Using the conditions given in 11.1 – 11.3, excite calibrants and potential ~~standardants~~ drift correction samples in a random sequence, bracketing these 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. Excite each calibrant, ~~standardant,~~ drift correction sample, 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~~the ~~E158 and~~ spectrometer manufacturer's software or Practice E305.

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 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 Each laboratory shall determine the frequency of verification necessary based on statistical analysis. Typically every 4 h to 8 h is practical and adequate. If the results are not within the control limits established in 12.4, perform a standardization and repeat verification. Repeat standardization as necessary so verifications are within control limits or investigate further for instrument problems.

12.4 *Quality Control*—Establish control limits in accordance with ASTM MNL ~~7A,~~7, Practice E1329, 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 a location approximately 6 mm (¼ in.) from the edge of the specimen.

Note 10—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 Using the average results obtained in 13.2, calculate the ~~concentration~~ mass fraction % of the elements from the analytical curves developed in 12.1.