



Designation: E415 – 15

# Standard Test Method for Analysis of Carbon and Low-Alloy Steel by Spark Atomic Emission Spectrometry<sup>1</sup>

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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method covers the simultaneous determination of 21 alloying and residual elements in carbon and low-alloy steels by spark atomic emission vacuum spectrometry in the mass fraction ranges shown **Note 1**.

Element	Composition Range, %	
	Applicable Range, Mass Fraction % <sup>A</sup>	Quantitative Range, Mass Fraction % <sup>B</sup>
Aluminum	0 to 0.093	0.006 to 0.093
Antimony	0 to 0.027	0.006 to 0.027
Arsenic	0 to 0.1	0.003 to 0.1
Boron	0 to 0.007	0.0004 to 0.007
Calcium	0 to 0.003	0.002 to 0.003
Carbon	0 to 1.1	0.02 to 1.1
Chromium	0 to 8.2	0.007 to 8.14
Cobalt	0 to 0.20	0.006 to 0.20
Copper	0 to 0.5	0.006 to 0.5
Manganese	0 to 2.0	0.03 to 2.0
Molybdenum	0 to 1.3	0.007 to 1.3
Nickel	0 to 5.0	0.006 to 5.0
Niobium	0 to 0.12	0.003 to 0.12
Nitrogen	0 to 0.015	0.01 to 0.055
Phosphorus	0 to 0.085	0.006 to 0.085
Silicon	0 to 1.54	0.02 to 1.54
Sulfur	0 to 0.055	0.001 to 0.055
Tin	0 to 0.061	0.005 to 0.061
Titanium	0 to 0.2	0.001 to 0.2
Vanadium	0 to 0.3	0.003 to 0.3
Zirconium	0 to 0.05	0.01 to 0.05

<sup>A</sup> Applicable range in accordance with Guide E1763 for results reported in accordance with Practice E1950.

<sup>B</sup> Quantitative range in accordance with Practice E1601.

NOTE 1—The mass fraction ranges of the elements listed have been established through cooperative testing<sup>2</sup> of reference materials.

1.2 This test method covers analysis of specimens having a diameter adequate to overlap and seal the bore of the spark stand opening. The specimen thickness can vary significantly

<sup>1</sup> 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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<sup>2</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1122. Contact ASTM Customer Service at service@astm.org.

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 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:<sup>3</sup>

- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- 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

<sup>3</sup> 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.

Interlaboratory Testing of Chemical Analysis Methods (Withdrawn 2015)<sup>4</sup>

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

**E1950** Practice for Reporting Results from Methods of Chemical Analysis

**E2972** Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials

2.2 Other ASTM Documents

**ASTM MNL 7** Manual on Presentation of Data and Control Chart Analysis<sup>5</sup>

### 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 or by use of a vacuum ultraviolet (VUV) transparent gas 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.

6.3.1 Follow the manufacturer's recommendations for cleaning the spark 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).

6.4 *Spectral Lines*—**Table 1** lists spectral lines and internal standards usable for carbon and low alloy steel. The spectrometer must be able to measure at least one of the listed spectral lines for each of the listed elements. Spectral lines other than those listed in **Table 1** may be used provided it can be shown experimentally that equivalent precision and accuracy are obtained.

6.5 *Measuring System*, spectrometer capable of converting light intensities to measurable electrical signals. The measuring system may consist of one of the following configurations:

6.5.1 A photomultiplier (PMT) array 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.

6.5.2 A semiconductor detector array (CCD or CMOS), pixel selection electronics to reset the pixels and to transport the voltage of an individual pixel to one or more output ports of the detector arrays, and a voltage measuring system to register the voltage of said output ports.

6.5.3 A hybrid design using both photomultipliers and semiconductor arrays.

6.6 *Optical Path*—If the instrument is operated using a VUV transparent gas, check the manufacturer's suggested gas purity. It may be necessary to have a gas purification system consisting of a circulation pump and a cleaning cartridge to keep the O<sub>2</sub> (g) residual <500 ng/g and H<sub>2</sub>O (g) residual <1 µg/g and remove impurities of nitrogen and hydrocarbons. If the instrument is using a vacuum pump, it should be capable of maintaining a vacuum of 3.33 Pa (25 µm Hg) or less.

NOTE 2—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 *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 set. 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 are obtained. The rods can vary in diameter from 1.5 mm to 6.5 mm (depending on the instrument design) and typically are machined to a 90° or 120° angled tip.

7.1.1 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 burns on an electrode varies from one instrument to another, and should be established in each laboratory.

NOTE 3—It has been reported that thousands of burns can be performed on a thoriated tungsten electrode before replacement is necessary.

<sup>4</sup>The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>5</sup>ASTM Manual Series, ASTM International, 8th edition, 2010.

**TABLE 1 Internal Standard and Analytical Lines**

Element	Wavelength, $\lambda$ , nm	Line Classification <sup>A</sup>	Possible Interference <sup>B</sup>
Aluminum	396.15	I	Mo
	394.40	I	V, Mn, Mo, Ni
	308.22	I	V, Mn
Antimony	217.6	I	Ni, Nb, Mn, W
Arsenic	189.04	I	V, Cr
	197.20	I	Mo, W
	193.76	I	Mn
Boron	345.13	II	
	182.64	I	S, Mn, Mo
	182.59	I	W, Mn, Cu
Calcium	393.37	II	
	396.85	II	Nb
Carbon	165.81	I	Cr
	193.09	I	Al
Chromium	312.26	II	V
	313.21	II	
	425.44	I	
	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
	258.03	II	Fe, Mn, W
Copper	212.3	II	Si
	324.75	I	Mn, Nb
	327.40	I	Nb
	224.26	II	W, Ni
	213.60	II	Mo, Cr
	510.55	I	W
	136.14	II	
	157.40	II	
	172.24	II	
	174.28	II	
	179.34	I	
	182.88	II	
	205.13	I	
	216.20	I	
	217.81	I	
	218.65	II	
	226.76	II	
	235.12	II	
	239.15	I	
	277.21	I	
	281.33	I	
	285.18	I	
	296.69	II	
297.05	I		
299.95	I		
300.81	I		
303.74	I		
304.76	I		
Iron (IS)	305.91	I	
	316.79	I	
	517.16	I	
	321.33	II	
	487.21	I	
	458.38	II	
	413.70	I	
	410.75	I	
	383.63	I	
	363.83	I	
	339.93	I	
	328.68	I	
	308.37	I	
	282.33	I	
	249.59	I	

**TABLE 1** *Continued*

Element	Wavelength, $\lambda$ , nm	Line Classification <sup>A</sup>	Possible Interference <sup>B</sup>
	226.76	II	
	218.65	II	
	216.20	I	
	193.53	II	
	190.48	I	
	187.75	II	
	149.65	II	
	271.44	II	
	273.07	II	
	492.39	I	Co
Lead	405.75	I	Mn
Manganese	293.31	II	Cr, Mo, Ni
	255.86	II	Zr
	263.82	II	Al, W
Molybdenum	379.83	II	
	202.03	II	Mn
	277.54	I	Cu, V, Co, Mn
	281.61	II	Mn
	386.41	I	V, Cr
Nickel	471.44	I	
	227.73	II	
	341.48	I	
	352.45	I	
	231.60	II	Co, Ti
	227.02	II	Nb, W
	243.79	II	Co, Fe, Ni
Niobium	313.08	II	Ti, V
	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
	212.41	I	Mo, Ni, V, Cu, Nb
	390.55	I	Cr, Cu, W, Ti
Sulfur	180.73	I	Mn
Tin	147.52	II	
	189.99	II	Mn, Mo, Al
Titanium	308.80	I	Cu, Co
	337.28	II	Nb
Tungsten	324.20	II	Nb
	400.88	I	
	202.99	II	Ti, V, Mn
	220.50	II	Co
Vanadium	437.92	I	
	310.23	II	Fe, Mo, Nb, Ni
Zirconium	468.78	I	
	349.62	II	
	343.82	II	W
	206.19	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.

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 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.

NOTE 4—Certified Reference Materials manufactured by NIST are trademarked with the name, “Standard Reference Material.”

8.2 *Reference Materials (RMs)*—These are available from multiple suppliers or can be developed in house. Reference Materials are typically used in control procedures (verifiers) and in drift correction (standardization) of the spectrometer, and they may be useful in calibrations. These reference materials shall be homogenous and contain appropriate mass fractions of each element for the intended purpose. Refer to Guide E2972 for production of your own reference materials.

8.3 Several issues can impact the selection and use of CRMs and RMs:

8.3.1 Samples and reference materials may exhibit differences in metallurgical structure, in particular having different sizes, compositions, and distributions of inclusions. Inhomogeneous distribution of inclusions can worsen repeatability of individual measurements of elements found in the inclusions. Some inclusions may be removed during preburn steps prior to integration of intensities, causing low results. Typical samples can be used to determine repeatability of individual measurements to yield estimates consistent with performance for actual samples.

8.3.2 For certain elements, there may be no available reference materials with metallurgical structure similar to typical samples. Therefore, calibrations may be biased. It is recommended to validate results using typical samples analyzed using Test Methods E350 and E1019.

## 9. Preparation of Specimens and Reference Materials

9.1 The specimens and reference materials shall be prepared in the same manner. A specimen cut from a large sample section shall 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 that the specimens are free from voids and pits in the region to be measured (Note 5). Initially, grind the surface with a 50-grit to 80-grit abrasive belt or disc (wet or dry) or mill the surface. If wet grinding, 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 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.

9.2.1 Reference materials and specimens shall be refinished dry on an abrasive belt or disc before being remeasured on the same area.

## 10. Preparation of Apparatus

NOTE 6—The instructions given in this test method apply to most spectrometers. However, some settings and adjustments may require modification, 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 for a particular spectrometer, refer to the manufacturer’s manual(s).

10.1 Program the spectrometer to use 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 mass fraction range and the individual spectrometer software.

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 7).

NOTE 7—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. Burn and Exposure

### 11.1 Electrical Parameters:

11.1.1 Burn 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, $\mu\text{F}$	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 discharges	60

11.1.2 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  $\pm 2\%$ .

11.1.3 *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, $\mu\text{F}$	0.0025
Inductance, $\mu\text{H}$	residual
Resistance, $\Omega$	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 11.1.3 are not



available, may be used provided that it can be shown experimentally that equivalent precision and accuracy are obtained.

**11.2 Burn and Measurement Conditions**—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	ft <sup>3</sup> /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

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

**11.2.2** A high-purity argon atmosphere is required at the analytical gap. Molecular gas impurities, such as 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 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 ( $\pm 0.1$  mm) analytical gap. Condition a fresh counter electrode with two burns to six burns using the operating conditions described in **11.1** and **11.2**.

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

**11.5 Semiconductor Detector Array**—In newer instruments semiconductor detector arrays are replacing PMTs. The width of the individual pixels shall be similar to the width of the exit slits used in conventional instruments equipped with PMTs.

## 12. Calibration, Standardization, and Verification

**12.1 Calibration**—Using the conditions given in **11.1** – **11.3**, measure calibrants and potential drift correction samples in a random sequence, bracketing these with measurements of any materials intended for use as verifiers. (A calibrant may be used later as a verifier. See **8.1**.) There shall be at least three calibrants for each element, spanning the required mass fraction range. Measure each calibrant, drift correction sample, and verifier two times to four times and use the average value. If the spectrometer system and software permit, repeat with different random sequences at least two times. Using the averages of the data for each point, determine analytical curves as directed in the 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 shall be done anytime verification indicates that readings have gone out of statistical control. In the case of automatic corrections conducted by the spectrometer software, observe the standardization factors and/or offsets. The factors and/or

offsets are often presented in the spectrometer software after standardization and/or stored in log files. Refer to your instrument manual or instrument manufacturer for access to this information.

**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 necessary frequency of verification 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 verification results are within control limits or investigate further for instrument problems.

**12.4 Quality Control**—Establish control limits in accordance with ASTM MNL 7, Practice **E1329**, or other equivalent quality control procedure.

## 13. Measurements

**13.1** Place the prepared surface of the specimen on the sample stand so that measurement shall impinge on a location approximately 6 mm ( $\frac{1}{4}$  in.) from the edge of the specimen.

**NOTE 8**—With certain spectrometers, a properly burned specimen usually exhibits a dark ring around the pitted sparked area. With that equipment, a smooth texture, white burn without the characteristic dark ring indicates an improperly burned specimen. If boron nitride disks are used to mechanically restrict the burned area of the sample, a properly burned specimen may not exhibit a dark ring.

**13.2** Measure 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 mass fractions of the elements from the analytical curves developed in **12.1**.

**14.2** Rounding of test results obtained using this test method shall be performed in accordance with the Rounding Method of Practice **E29**, unless an alternative rounding method is specified by the customer or applicable material specification.

## 15. Precision and Bias

**15.1** Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:E01-1122.<sup>2</sup> The interlaboratory test data summarized in **Table 2** have been evaluated in accordance with Practice **E1601**.

**15.2 Precision**—Up to eight laboratories cooperated in performing this test method with thirteen unknown samples and obtained the statistical information summarized in **Table 2**.

**15.3 Bias**—Differences between average composition determined by this method and the certified compositions provides the bias found in the interlaboratory study. Bias information is found in **Table 2**.