



Designation: ~~E1999-99 (Reapproved 2004)~~ Designation: E1999 – 11

Standard Test Method for ~~Analysis of Cast Iron Using Optical Emission Spectrometry~~ Analysis of Cast Iron by Spark Atomic Emission Spectrometry¹

This standard is issued under the fixed designation E1999; 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 ~~optical emission spectrometric analysis of cast iron by use of the point-to-plane technique~~ spark atomic emission spectrometry for the following elements in the concentration ranges shown (Note 1):

Elements	Concentration Ranges, % Applicable Range, %	Quantitative Range, % ^A
Carbon	1.9 to 3.8	1.90 to 3.8
Chromium	0 to 2.0	0.025 to 2.0
Copper	0 to 0.75	0.015 to 0.75
Manganese	0 to 1.8	0.03 to 1.8
Molybdenum	0 to 1.2	0.01 to 1.2
Nickel	0 to 2.0	0.02 to 2.0
Phosphorus	0 to 0.4	0.005 to 0.4
Silicon	0 to 2.5	0.15 to 2.5
Sulfur	0 to 0.08	0.01 to 0.08
Tin	0 to 0.14	0.004 to 0.14
Titanium	0 to 0.12	0.003 to 0.12
Vanadium	0 to 0.22	0.008 to 0.22

^AQuantitative range in accordance with Practice E1601.

NOTE 1—The concentration ranges of the elements listed have been established through cooperative testing of reference materials. These concentration ranges can be extended by the use of suitable reference materials.

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 sufficient to prevent overheating during excitation. A heat sink backing may be used. The maximum thickness is limited only by the height that the stand will permit.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

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

E158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis

E172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis

E305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves

E351 Test Methods for Chemical Analysis of Cast Iron All Types

E406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis

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 Oct. 1, 2004. Published Nov. 2004. Originally approved in 1999. Last previous edition approved in 1999 as E1999-99^{ε1}. DOI: 10.1520/E1999-99R04.

Current edition approved May 15, 2011. Published July 2011. Originally approved in 1999. Last previous edition approved in 2004 as E1999-99 (2004). DOI: 10.1520/E1999-11

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

- E826 Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry
- E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
- ~~E1059 Practice for Designating Shapes and Sizes of Nongraphite Counter Electrodes~~
- 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

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2.2 Other Documents:

~~MNL 7~~MNL 7A Manual on Presentation of Data and Control Chart Analysis³

3. Terminology

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

4. Summary of Test Method

~~4.1 The most sensitive lines for carbon, phosphorus, sulfur and tin lie in the ultraviolet region. The absorption of the radiation by air in this region is overcome by flushing the spark chamber with argon or argon-hydrogen gas mixture and either evaluating all or portions of the spectrometer or filling all or portions of the spectrometer with an inert gas. 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 of a selected iron line, or at a predetermined time, and the relative radiant energies of the analytical lines are recorded and converted to concentration.~~

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 of a selected iron line, or at a predetermined time, and the relative radiant energies of the analytical lines are recorded and converted to concentration.

4.2 Carbon, phosphorus, sulfur and tin emit in the vacuum ultraviolet region. The absorption of the radiation by air in this region is overcome by flushing the spark chamber with argon or argon-hydrogen gas mixture and either evacuating the spectrometer or filling the spectrometer with an inert gas such as nitrogen or 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 of a selected iron line, or at a predetermined time, and the relative radiant energies of the analytical lines are recorded and converted to concentration.

NOTE 2—It is not within the scope of this test method to prescribe specific details of every instrument that could be used for the analysis of cast iron by spark atomic emission spectrometry. The parameters listed in this test method represent the parameters of the specific instruments used during the interlaboratory study to produce the precision and bias listed in this test method. Other spark atomic emission spectrometers with different parameters may be used provided that they produce equivalent or better precision and bias data

5. Significance and Use

5.1 The chemical composition of cast iron alloys must shall be determined accurately in order to insure the desired metallurgical properties. This procedure is suitable for manufacturing control and inspection testing.

6. Interferences

6.1 Interferences may vary with spectrometer design and excitation characteristics. Direct spectral interferences may be present on one or more of the wavelengths listed in a method. Frequently, these interferences must shall be determined and proper corrections made by the use of various reference materials. Refer to Table 1 for possible interferences. The composition of the sample being analyzed should match closely the composition of one or more of the reference materials used to prepare and control the calibration ~~curve which is employed.~~curve. Alternatively, mathematical corrections may be used to solve for interelement effects (refer to Practice E158). ~~Various mathematical correction procedures are commonly utilized. Any of these is acceptable, which will achieve analytical accuracy equivalent to that provided by this test method.~~Various mathematical correction procedures are commonly utilized. Any of these correction procedures that produce precision and accuracy results equal to or better than the results in the interlaboratory study for this test method are acceptable.

7. Apparatus

7.1 When required, use sample preparation equipment as follows:

7.1.1 *Sample Mold*, to produce graphite-free white chilled iron samples that are homogeneous, free of voids or porosity in the region to be excited, and representative of the material to be analyzed. A chill-cast disk approximately 40 mm (1 ½ in.) in diameter and 3-mm to 12-mm (⅛-in. to ½-in.) thick is satisfactory. A sample mold made from copper with a low oxygen content has proven to be optimum for this purpose. Refer to Practice E1806 for iron sampling procedures.

7.1.2 *Surface Grinder or Sander with Abrasive Belts or Disks*, capable of providing a flat, clean, uniform surface on the reference materials and specimens.

7.2 *Excitation Source*, capable of providing sufficient energy to sample the specimen and excite the analytes of interest. See Practice E172. Any other excitation source whose performance has been proven to be equivalent may be used.

7.3 *Excitation Chamber*, ~~automatically flushed with argon or other inert support gas. Gases and electrodes are described in 8.1 and 8.2.~~, automatically flushed with argon or other inert gas. Clean the excitation chamber when the counter electrode is replaced.

NOTE 2—Clean the excitation chamber when the counter electrode is replaced. Clean the lens or protective window after approximately 200 to 300 excitations, or at a statistically determined time based on intensity loss, to minimize transmission losses. ~~3—Clean the lens or protective window as recommended by the instrument manufacturer.~~

³ ASTM Manual Series, ASTM, 6th Edition, 1990.

TABLE 1 Analytical and Internal Standard Lines, Possible Interferences

Element	Wavelength, nm	Reported Possible Interfering Elements
<u>Carbon</u>	<u>193.093</u>	<u>Al, Mo, Cu, S</u>
<u>Carbon</u>	<u>193.09</u>	<u>Al, Mo, Cu, S</u>
<u>Chromium</u>	<u>267.716</u>	<u>Mo, S, Mn</u>
<u>Chromium</u>	<u>267.72</u>	<u>Mo, S, Mn</u>
	<u>265.859</u>	
	<u>265.86</u>	
<u>Copper</u>	<u>211.209</u>	<u>Ni</u>
<u>Copper</u>	<u>211.21</u>	<u>Ni</u>
	<u>221.81</u>	
	<u>327.4</u>	<u>Mo, P</u>
	<u>327.40</u>	<u>Mo, P</u>
	<u>510.5</u>	<u>V</u>
	<u>510.55</u>	<u>V</u>
<u>Manganese</u>	<u>293.306</u>	<u>Cr, Mo, W</u>
<u>Manganese</u>	<u>293.31</u>	<u>Cr, Mo, W</u>
<u>Molybdenum</u>	<u>202.03</u>	<u>Ni</u>
	<u>281.61</u>	<u>Mn</u>
<u>Nickel</u>	<u>243.789</u>	<u>Mn</u>
<u>Nickel</u>	<u>243.79</u>	<u>Mn</u>
	<u>231.604</u>	<u>Mn</u>
	<u>231.60</u>	<u>Mn</u>
	<u>341.4</u>	
	<u>341.48</u>	
	<u>352.45</u>	<u>Mo</u>
<u>Phosphorus</u>	<u>178.287</u>	<u>Cr, Mn, Mo, Cu</u>
<u>Phosphorus</u>	<u>178.29</u>	<u>Cr, Mn, Mo, Cu</u>
<u>Silicon</u>	<u>212.411</u>	<u>Mo, Cu, Ni</u>
<u>Silicon</u>	<u>212.41</u>	<u>Mo, Cu, Ni</u>
	<u>251.612</u>	
	<u>251.61</u>	
	<u>288.16</u>	<u>Mo, Cr</u>
<u>Sulfur</u>	<u>180.731</u>	<u>Mn, Cu, Cr</u>
<u>Sulfur</u>	<u>180.73</u>	<u>Mn, Cu, Cr</u>
<u>Tin</u>	<u>189.989</u>	<u>Mn, Mo, Fe</u>
<u>Tin</u>	<u>189.99</u>	<u>Mn, Mo, Fe</u>
<u>Titanium</u>	<u>334.904</u>	<u>Cr</u>
<u>Titanium</u>	<u>334.90</u>	<u>Cr</u>
	<u>337.2</u>	<u>Fe</u>
	<u>337.28</u>	<u>Fe</u>
	<u>334.2</u>	
	<u>334.19</u>	
<u>Vanadium</u>	<u>310.23</u>	<u>Ni</u>
	<u>311.07</u>	
<u>Iron^A</u>	<u>273.074</u>	
<u>Iron^A</u>	<u>273.07</u>	
	<u>274.4</u>	
	<u>271.44</u>	
	<u>281.33</u>	
	<u>360.89</u>	

^AInternal standard.

7.4 *Spectrometer*, having sufficient resolving power and linear dispersion to separate clearly the analytical lines from other lines in the spectrum in the spectral region 170.0 nm to 500.0 nm. The spectrometers used to test this method had a dispersion of 0.3 nm/mm to 0.6 nm/mm and a focal length of 0.5 m to 0.75 m. Spectral lines are listed in Table 1. The primary slit width is 15 μm to 50 μm. Secondary slit width is 15 μm to 200 μm. The spectrometer shall be provided with one or more of the following:

- 7.4.1 An air/gas inlet and a vacuum outlet. The spectrometer shall be operated at a vacuum of 25 μm of mercury or below.
- 7.4.2 A gas inlet and a gas outlet.

7.4.3 Sealed with nitrogen or other inert gas.

7.5 *Measuring System*, consisting of photomultipliers having individual voltage adjustment, capacitors on which the output of each photomultiplier is stored and an electronic system to measure voltages on the capacitors either directly or indirectly, and the necessary switching arrangements to provide the desired sequence of operation.

7.6 ~~Readout Console~~ *Readout Console or Computer*, capable of indicating the ratio of the analytical lines to the internal standard with sufficient precision to produce the accuracy of analysis desired.

7.7 ~~Flushing System~~, consisting of argon tanks or an argon-hydrogen gas mixture, a pressure regulator, and a gas flowmeter. Automatic sequencing shall be provided to actuate the flow of argon or argon-hydrogen mixture 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 or argon-hydrogen mixture shall be provided. The flushing system shall be in accordance with Practice Gas System, consisting of an argon or argon-hydrogen 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 gas system shall be in accordance with Practice E406.

7.8 *Vacuum Pump*, if required, capable of maintaining a vacuum of 25 μ m Hg or less.

NOTE 3—A 4—A pump with a displacement of at least 0.23 m³/min (8 ft³/min) is usually adequate.

8. Reagents and Materials

8.1 ~~Inert gas, argon, nitrogen, and hydrogen~~ *Gas (Argon, Nitrogen), or Hydrogen*, as required, ~~must~~ shall be of sufficient purity to permit proper excitation of the analytical lines of interest in the excitation chamber or light transmittance in the spectrometer chamber. Use in accordance with Practice E406.

8.2 ~~Counter Electrodes~~—A silver or thoriated tungsten rod of 2 to 6-mm diameter ground to a 30 to 90° included angle conical tip, which conforms to Practice E1059, has been found satisfactory. —A silver or thoriated tungsten rod of 2-mm to 6-mm diameter ground to a 30° to 90° conical tip. Other material may be used provided it can be shown experimentally that equivalent precision and accuracy are obtained.

NOTE 4—A 5—A black deposit may build up on the tip of the electrode, thus reducing the overall intensity of the spectral radiation. The number of acceptable excitations on an electrode varies from one instrument to another and should be determined in each laboratory. With a thoriated tungsten electrode, it has been reported that a hundred or more excitations usually can be made before replacement. Cleaning electrodes after each burn significantly reduces this buildup and gives more consistent results.

9. Reference Materials

9.1 ~~Certified Reference Materials~~, used as calibrants, for chill-cast iron alloys are available commercially. Calibrants

9.1 Calibrants can come in three forms: certified reference materials, reference materials, and analyzed production samples. In selecting calibrants, use caution with compositions that are unusual. One element may adversely influence the radiant energy of another element or its uniformity of distribution within the material. Tests should be made to determine if interrelations exist between elements in the calibrants. To compensate for inter-element effects, it is suggested that the calibrants approximate the composition of the material to be tested. The metallurgical history of the calibrants should be similar to that of the specimens being analyzed in accordance with the recommendations of Practice E305.

9.2 ~~Other Calibrants~~, shall be chemically analyzed test specimens taken from production heats. They shall cover the concentration ranges of the elements to be determined and shall include all of the specific types of alloys being analyzed. These calibrants shall be homogeneous and free of voids and porosity. The metallurgical history of the calibrants should be similar to that of the specimens being analyzed. Refer to Test Methods Certified Reference Materials (CRMs), used as calibrants for chill-cast iron alloys are available commercially.

9.3 *Reference Materials (RM's)*, used as calibrants for chill-cast iron alloys are available commercially.

NOTE 6—The distinction is made between CRMs and production materials because there are commercially available RMs produced by reputable producers that do not claim to be CRMs but in all other respects fit the definition of CRMs.

9.4 *Analyzed Production Samples* shall be chemically analyzed test specimens taken from production heats produced according to Practice E1806. They shall cover the concentration ranges of the elements to be determined and shall include all of the specific types of alloys being analyzed. These calibrants shall be homogeneous and free of voids and porosity. Refer to Test Methods E351 and E1019 or other nationally accepted test methods for chemical analysis of iron base alloys. Refer to Practice E826 for information on homogeneity testing of reference materials.

9.2.1 In selecting calibrants, use caution with compositions that are unusual. One element may influence adversely the radiant energy of another element or its uniformity of distribution within the material. Tests should be made to determine if interrelations exist between elements in the calibrants. To compensate for interelement effects, it is suggested that the calibrants approximate the composition of the material to be tested.

10.

10. Preparation of Calibrants and Specimens

10.1 ~~Cast~~ 10.1 *Specimens*, cast graphite-free specimens from molten metal into a suitable mold and cool. ~~The molten metal must~~

be at a high enough temperature. Refer to Practice E1806 for information on the preparation of specimens for all carbon to be in solution. Prepare analysis.

10.2 Preparation, prepare the surface to be analyzed on a suitable belt or disk grinder. Prepare the surface of the specimens and reference materials calibrants in a similar manner. All specimens must ~~shall~~ be moisture-free for proper excitation in the argon atmosphere.

~~NOTE 5—Specimen free of moisture, oil, and residue for proper excitation.~~

10.3 Specimen porosity is undesirable because it leads to the “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~~

10.4 Calibrants and specimens shall be refinished dry on a belt or disc sander before being re-excited on the same area.

11. Excitation and Exposure

~~11.1 Operate the spectrometer according to the manufacturer’s instructions.~~ Specimen Excitation Parameters

11.1 Operate the spectrometer according to the manufacturer’s instructions.

NOTE 7—When parameters are established, maintain them carefully. The variation of the power supply voltage shall not exceed $\pm 5\%$ and preferably should be held within $\pm 2\%$.

11.1.1 An example of excitation parameters for a high-energy unidirectional spark source is listed below:

	Preburn	Exposure
Capacitance, μF	10	10
Inductance, μH	20	20
Resistance, Ω	0	4.4
Potential, V	550	350
Number of discharges/s	120	60

11.2 Exposure Spark Conditions (Note 8)—An example of exposure spark parameters is listed below:

Preflush period, s	2 to 10	
Flush period, s	2 to 10	
Preburn period, s	5 to 20	
Exposure period, s	5 to 20	
Argon Flow (Note 9)	ft^3/h	L/min
Gas Flow	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 8—Select preburn and exposure periods after a study of volatilization rates during specimen excitation. Once established, maintain the parameters consistently.~~

~~NOTE 9—A high-purity argon atmosphere is required for 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.~~ 8—Select preburn and exposure periods after a study of volatilization rates during specimen excitation. Once established, maintain the parameters consistently. The instrument manufacturer can normally provide this information.

11.3 Electrode System—For conventional capacitor discharge excitation systems, 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 30 to 90° included angle cone. Use a 3 to 6-mm (0.125 to 0.25-in.) gap. Once a gap size is selected, maintain a consistent gap. Center the analytical gap on the optical axes of the spectrometer. Condition a fresh counter electrode with 2 to 6 excitations using the conditions given in 11.1 and 11.2. — For conventional capacitor discharge excitation systems, the specimen, electrically negative, serves as one electrode. The opposite electrode or counter electrode is a thoriated tungsten or silver rod. Use a 3-mm to 6-mm (0.125-in. to 0.25-in.) analytical gap. Once a gap size is selected, maintain it consistently. Condition a fresh counter electrode with 2 excitations to 6 excitations. A high-purity argon atmosphere is required for 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.

12. Preparation of Apparatus

12.1 Prepare the spectrometer in accordance with the manufacturer’s instructions. Program the spectrometer to accommodate the internal standard lines and one of the analytical lines for each element listed in Table 1.

12.2 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 shall determine the frequency of positioning the alignment based on instrument performance.

12.3 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 9).

NOTE 10—It is not within the scope of this test method to prescribe all details of equipment to be used. Equipment varies between laboratories.