Designation: ~~E1999 – 18~~ E1999 – 23

Standard Test Method for
Analysis of Cast Iron by Spark Atomic Emission Spectrometry[1]

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 analysis of cast iron by spark atomic emission spectrometry for the following elements in the ranges shown (Note 1):

| | Ranges, % | |
Elements	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

[A]Quantitative range as directed in Practice E1601.

NOTE 1—The ranges of the elements listed have been established through cooperative testing of reference materials. These 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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 Spark Atomic Emission Spectrochemical Analytical Curves

E406 Practice for Using Controlled Atmospheres in Atomic Emission Spectrometry

E826 Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry (Withdrawn 2023)[3]

E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis (Withdrawn 2019)[3]

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 (Withdrawn 2015)[3]

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

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

2.2 *Other Documents:*

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

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 A capacitor discharge is produced between the flat, ~~ground~~prepared 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 mass fractions.

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 an argon-hydrogen gas mixture and either evacuating the spectrometer or filling the spectrometer with an inert gas such as nitrogen or argon.

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 shall be determined accurately in order to ~~insure~~ensure 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 this test method. Frequently, these interferences shall be determined and proper corrections made ~~by the use of~~ using 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.~~ calibrations. Alternatively, mathematical corrections may be used to solve for interelement effects. Various mathematical correction procedures are commonly utilized. Any of these correction procedures are acceptable that produce precision and accuracy results equal to or better than the results in the interlaboratory study for this test ~~method are acceptable.~~method.

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[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.

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

[4] ASTM Manual Series, ASTM International, 8th Edition, 2010.

**TABLE 1 Analytical and Internal Standard Lines,
Possible Interferences**

Element	Wavelength, nm	Reported Possible Interfering Elements
Carbon	193.09	Al, Mo, Cu, S
Chromium	267.72	Mo, S, Mn
	265.86	
Copper	211.21	Ni
	221.81	
	327.40	Mo, P
	510.55	V
Manganese	293.31	Cr, Mo, W
Molybdenum	202.03	Ni
	281.61	Mn
Nickel	243.79	Mn
	231.60	Mn
	341.48	
	352.45	Mo
Phosphorus	178.29	Cr, Mn, Mo, Cu
Silicon	212.41	Mo, Cu, Ni
	251.61	
	288.16	Mo, Cr
Sulfur	180.73	Mn, Cu, Cr
Tin	189.99	Mn, Mo, Fe
Titanium	334.90	Cr
	337.28	Fe
	334.19	
Vanadium	310.23	Ni
	311.07	
Iron[A]	273.07	
	271.44	
	281.33	
	360.89	

[A]Internal standard.

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. ~~Any other excitation source~~ Excitation sources whose performance has been proven to be equivalent may be used.

7.3 *Excitation Chamber,* automatically flushed with argon or other inert gas. Clean the excitation chamber when the counter electrode is replaced.

7.3.1 Clean the lens or protective window as recommended by the instrument manufacturer.

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 520.0 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 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 *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 meet the requirements of Practice E406.

7.8 *Vacuum Pump,* if required, capable of maintaining a vacuum of 25 μm 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.

8. Reagents and Materials

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

8.2 *Counter Electrodes*—A silver or 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.

8.2.1 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. Cleaning of the electrodes after each ~~burn~~ sample analysis significantly reduces this buildup and gives more consistent results.

9. Calibration Reference Materials (RMs)

9.1 These ~~can come~~ are available in three forms: certified reference materials, reference materials, and analyzed production samples. In selecting calibration RMs, 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 calibration RMs. To compensate for inter-element effects, it is suggested that the calibration RMs approximate the composition of the material to be tested. The metallurgical history of the calibration RMs should be similar to that of the specimens being analyzed as directed in Practice E305.

9.2 *Certified Reference Materials (CRMs),* used as calibration RMs for chill-cast iron alloys and are available commercially.

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

NOTE 4—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. Refer to Guide E2972 for additional information regarding reference materials.

9.4 *Analyzed Production Samples* shall be chemically analyzed test specimens taken from production ~~heats produced~~ material as directed in Practice E1806. They shall cover the mass fraction ranges of the elements to be determined and shall include all of the specific types of alloys being analyzed. These calibration RMs shall be homogeneous and free of voids and porosity. Refer to Practice E826 for information on homogeneity testing of reference materials using spark atomic emission spectrometry.

10. Preparation of Calibration RMs and Specimens

10.1 *Specimens,* cast graphite-free specimens from molten metal into a suitable mold and cool. Refer to Practice E1806 for information on the preparation of specimens for analysis.

10.2 *Preparation,* prepare the surface to be analyzed on a suitable belt or disk grinder. Prepare the surface of the specimens and calibration RMs in a similar manner. All specimens shall be 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.

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

11. Specimen Excitation Parameters

11.1 Operate the spectrometer as directed by the manufacturer's instructions. When the parameters in 11.1.1 are established, maintain them carefully. The variation of the power supply voltage shall not exceed ± 5 % and preferably should be held within ± 2 %.

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

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

11.2 *Spark ~~Conditions (Conditions—11.2.1)~~*—An example of spark parameters ~~is listed below:~~follows:

Flush period, s	2 to 10	
Preburn period, s	5 to 20	
Integration period, s	5 to 20	
Gas Flow	ft³/h	L/min
Flush	5 to 45	2.5 to 25
Preburn	5 to 45	2.5 to 25
Integration	5 to 30	2.5 to 15

11.2.1 Select preburn and integration periods after a study of volatization 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 or counter electrode is a 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, such as 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 as directed in 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~~alignment 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~~adjusting the alignment based on instrument performance.

12.3 Exit slit ~~positioning~~alignment and alignment is normally performed by the manufacturer at spectrometer assembly. Under normal circumstances, further exit slit alignment is not necessary.

12.3.1 The manner and frequency of positioning or checking the position of the exit slits will depend on such factors as the type of spectrometer and the frequency of use. Each laboratory should establish a suitable check procedure.

13. Calibration, ~~Standardization (Drift Correction),~~Drift Correction (Standardization), and Verification

13.1 *Calibration*—Using the parameters in Section 11, excite each calibration RM and potential drift correction sample two times to four times in random sequence, bracketing these with excitations of any materials intended for use as verifiers (a verifier may be used as a calibration RM even though it is used principally as a verifier). There should be at least seven calibration RMs for each element, spanning the required mass fraction range. Repeat with different random sequences at least two times. Using the average intensity of the data for each point, determine ~~analytical curves~~the calibrations as described in Practice E305 (Note 5).

13.2 *~~Standardization (Drift Correction)~~—Drift Correction (Standardization)*—Following the manufacturer's recommendations, ~~standardize (drift correct)~~drift correct (standardize) on an initial setup or anytime that it is known or suspected that readings have shifted. Make the necessary corrections by applying arithmetic corrections. ~~Standardization (drift correction)~~Drift correction (standardization) shall be done anytime verifications indicate that readings have gone out of statistical control.

13.3 Verification shall be done at least at the beginning of instrument operation. A number of warm-up burns may be necessary. Analyze verifiers with duplicate burns to confirm that the average of the two burns falls within the control limits established in 17.1.

13.3.1 Check the verification after ~~standardizing.~~ drift correcting. Each laboratory should determine the frequency of verification necessary based on statistical analysis. Refer to 17.1. Typically, every 4 or 8 hours is practical and adequate. If results are not within the control limits established in 17.1, perform a ~~standardization~~ drift correction and then repeat verification. Repeat ~~standardization~~ drift correction as necessary so verifications are within control limits ~~or~~to investigate further for instrument problems.

NOTE 5—Modern instruments are very stable, and the software may not permit more than one set of intensity data to be averaged for the ~~calibration curves~~ calibrations since it is unnecessary.

14. Procedure for Excitation and Radiation Measurement

14.1 Check the ~~standardization (drift correction)~~drift correction (standardization) by verification as directed in 13.3.

14.2 Produce and record the radiation intensities for each element using the conditions given in Section 11.

14.3 *Replicate Excitation*—Make a minimum of two burns on each specimen. Average the replicate readings for each element if their difference does not exceed twice the established standard deviation for the element. If their difference exceeds this value, analyze the specimen two more times and average all four readings. In all cases, discard readings caused by observable defects in the specimen and replace it with another reading. When placing the freshly surfaced specimen on the excitation stand, position it to effect a gas tight seal and adequate gas flushing. Position the specimen so that there will be a uniform pattern of burns around its surface. For example, a disk-shaped specimen should have a ring of burn marks around its outer edge and approximately 6 mm (¼ in.) from the edge. Avoid burning the center of cast specimens where there is more likely to be quench cracks and segregation. Ensure that there is a good electrical connection between the specimen and the specimen ground. If required, cool the specimen after two burns to prevent overheating. Successive burns shall be sufficiently separated so that the burn patterns do not overlap.

14.4 Examine the specimen and instrument measurements after each burn to evaluate the quality of excitation. Cracks, voids, pits, moisture, or inclusions will invalidate the sampling and accuracy of a determination.

15. Calculation of Results

15.1 Average the readings obtained for each element.

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

16. Precision and Bias

16.1 *Precision:*

16.1.1 Seven laboratories cooperated in performing this test method and obtained the statistical information summarized in Table 2 through Table 4.[5] The interlaboratory data were evaluated in accordance with Practices E1601 and E1763. An approximate value for the expected reproducibility index, *R*, can be calculated for carbon with the following equation:

$$R = C_c \times 0.059 \tag{1}$$

where:

C_c = expected carbon content in the range 1.9 % to 3.8 %.

16.1.2 An estimate of the reproducibility index for the other analytes, R_A, can be calculated using the following equation:

$$R_A = \sqrt{\left[K_R^2 + \left(C_A \times K_{rel}\right)^2\right]} \text{ over the analyte range of 0 to } B \tag{2}$$

where:

C_A = expected analyte content, %,
B = upper limit of the analyte range, % (from Table 3), and
K_R and K_{rel} = constants for each analyte from Table 3.

16.1.3 Laboratories participating in the interlaboratory study used the same set of calibration RMs. Users are ~~warned~~cautioned that comparisons of results between laboratories using different sets of calibration RMs may experience greater differences in results than is implied by the calculated values for *R* from the equation or Table 2.

16.2 *Bias*—The accuracy of this test method at certain ~~concentration~~ mass fraction levels may be judged by comparing the accepted reference values with the arithmetic average obtained by interlaboratory testing (see Table 4). Users are cautioned that the accuracy of results from applying the method depend upon the accuracy of the calibration materials used and the care with which the calibration is performed.

17. Maintaining Analytical Credibility

17.1 Users are encouraged to include this test method in an accountability and quality control program. Refer to Practice E1329 for procedures to control analysis, including the use of control charts. Support for the use of control charts ~~with respect to a given standard~~ appear in MNL 7.

18. Keywords

18.1 cast iron; spark atomic emission; spectrometric analysis

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1027.