



Designation: E2209 – 22

# Standard Test Method for Analysis of High Manganese Steel by Spark Atomic Emission Spectrometry<sup>1</sup>

This standard is issued under the fixed designation E2209; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the analysis of high manganese steel by spark atomic emission spectrometry for the following elements in the ranges shown:

Elements	Composition Range, %
Aluminum (Al)	0.02 to 0.15
Carbon (C)	0.3 to 1.4
Chromium (Cr)	0.25 to 2.00
Manganese (Mn)	8.0 to 16.2
Molybdenum (Mo)	0.03 to 2.0
Nickel (Ni)	0.05 to 4.0
Phosphorus (P)	0.025 to 0.06
Silicon (Si)	0.25 to 1.5

NOTE 1—The ranges represent the actual levels at which this method was tested.<sup>2</sup> These composition ranges can be extended by the use of suitable reference materials. Validation of these extensions may be conducted by following Practice E2587. Sulfur is not included because differences in results between laboratories exceeded acceptable limits at all sulfur levels.

1.2 *This test method may involve hazardous materials, operations, and equipment. 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.*

1.3 *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.*

<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 Ferrous Alloys.

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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:E01-1035. Contact ASTM Customer Service at service@astm.org

## 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 Spark Atomic Emission Spectrochemical Analytical Curves
- E406 Practice for Using Controlled Atmospheres in Atomic Emission Spectrometry
- E1059 Practice for Designating Shapes and Sizes of Non-graphite Counter Electrodes (Withdrawn 2013)<sup>4</sup>
- E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis (Withdrawn 2019)<sup>4</sup>
- E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
- E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition
- E2587 Practice for Use of Control Charts in Statistical Process Control

### 2.2 Other Document:

- ASTM MNL 7 ASTM Manual on Presentation of Data and Control Chart Analysis, 8th Edition, 2010.

## 3. Terminology

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

## 4. Summary of Test Method

4.1 A controlled discharge is produced between the flat surface of the specimen and the counter electrode. The radiant energies of selected analytical lines are converted into electrical energies by photomultiplier tubes and stored on capacitors.

<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.

<sup>4</sup> The last approved version of this historical standard is referenced on www.astm.org.

This discharge is terminated after a fixed integration time. At the end of the integration period, the charge on each capacitor is measured and converted to mass fraction percent.

**5. Significance and Use**

5.1 The chemical composition of high manganese steel alloys must be determined accurately to 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 method (Table 1). Frequently, these interferences may be determined and proper corrections made by the use of various reference materials. 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 that is utilized. Alternatively, mathematical corrections may be used to solve for interelement effects. Various mathematical correction procedures are commonly utilized. Any of these are acceptable that will achieve analytical accuracy equivalent to that provided by this method.

**7. Apparatus**

7.1 *Sample Preparation Equipment:*

7.1.1 *Sample Mold*, to produce chilled cast samples approximately 38 mm (1½ in.) in diameter that are homogeneous, free of voids or porosity in the region to be excited, and represen-

tative of the material to be analyzed. Refer to Practice E1806 for steel sampling procedures.

7.1.2 *Immersion Sampler*, to take a sample from the bath or from the metal stream when pouring cannot be used. The sampler should produce a sample of the same dimensions as listed in 7.1.1.

7.1.3 *Surface Grinder or Sander With Abrasive Belts or Disk*, capable of providing a flat uniform surface on the reference materials and specimens. The following table shows the various methods of sample preparation used in the Inter-Laboratory Study (ILS):

Type of Grinding Preparation	Belt or Disk, or Both
Grinding Medium	Aluminum Oxide, Zirconium Oxide
Grit of Grinding Medium	36 to 180

NOTE 2—Silicon carbide grinding medium may be used but it was not utilized by the laboratories in the Inter-Laboratory Study (ILS).

7.2 *Excitation Source*, capable of providing a triggered capacitor discharge having the source parameters meeting the requirements of 11.1.

7.3 *Excitation Stand*, suitable for mounting in optical alignment, a flat surface for the specimen in opposition to a counter electrode. This stand shall provide an atmosphere of argon. The argon and electrode are described in 8.1 and 8.2.

7.4 *Spectrometer*, having sufficient resolving power and linear dispersion to separate clearly the analytical lines from other lines in the spectrum of a specimen in the spectral region 170.0 nm to 450.0 nm. The spectrometer shall have a dispersion of at least 2 nm/mm and a focal length of at least 0.5 m.

NOTE 3—Many current spectrometer manufacturers utilize CMOS/CCD array technology and this enables equivalent resolution with a shorter focal length than specified in 7.4.

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

7.5.1 A photomultiplier (PMT) array having individual voltage adjustments, capacitors in which the output of each PMT 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.

7.5.2 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. However, this method was tested with spectrometers equipped with PMTs. If a spectrometer is utilized that is equipped with CCD or CMOS, the user should validate that the precision and bias equivalent to that specified in Section 16 can be obtained.

7.5.3 A hybrid design using both PMTs and semiconductor arrays.

7.6 *Vacuum Pump*, if required, capable of maintaining a vacuum of approximately 3 Pa. There are some equipment manufacturers that will purge the optical portion of the spectrometer with argon or other inert gas rather than apply a

TABLE 1 Wavelengths

Element	Wavelength (nm)	Line Classification	Possible Interferences <sup>A</sup>
Aluminum	394.4	I	V, Mn, Mo
	396.152	I	Mo
Carbon	193.09	I	Al
	298.92	II	Mn, V, Ni, Nb, Mo
Chromium	267.72	II	Mn, Mo, V
	425.435	I	
	273.07	I	
Iron (Internal Standard)	271.44	II	
	263.81	II	
Manganese	290.02	II	
	293.31	II	Cr
	202.03	II	
Molybdenum	263.876	II	
	281.61	II	Al, Mn
	386.41	I	V, Cr
	231.60	II	Co, Ti
Nickel	218.54	II	
	352.45	I	
	341.476	I	
Phosphorus	178.29	I	Mo
	212.41	I	
Silicon	288.16	I	Mo, Cr, W
	251.61	I	Fe, V
	180.73	I	Mn

<sup>A</sup> Interferences are dependent upon instrument design, and excitation conditions, and those listed require confirmation based upon specimens designed to demonstrate interferences. This method does not purport to address all the interferences that these lines may have. Take care to address the interferences when calibrating the instrument.

vacuum on the optics. Either vacuum optics or purged optics are required to determine carbon and phosphorus in this method.

7.7 *Gas System*, consisting of an argon supply, a pressure regulator, and a gas flow meter. Automatic sequencing shall be provided to actuate the flow of argon at a given flow rate for a given time interval and to start the excitation at the end of the required flush period. The gas system shall be in accordance with Practice E406.

## 8. Reagents and Materials

8.1 *Argon* (supplied from gas cylinders or liquid tanks), must be of sufficient purity to permit proper excitation of the analytical lines of interest. Argon of 99.998 % purity has been found satisfactory. Refer to Practice E406.

8.2 *Counter Electrode*—A tungsten rod ground to a 15°, 30°, 45° or 90° angle conical tip, which conforms to Practice E1059, was found satisfactory. The instrument manufacturer will define the material and geometry. Other material may be used, provided it can be shown experimentally that equivalent precision and bias are obtained.

## 9. Reference Materials

9.1 *Certified Reference Materials*, for high manganese steel are commercially available.

9.2 Calibration Reference Materials (RMs) shall be certified reference materials from recognized certification agencies. 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. They shall be homogeneous and free of voids and porosity. Their metallurgical history should be similar to that of the specimens being analyzed.

9.2.1 When selecting calibration RMs, use caution with compositions that are unusual. One element may influence the radiant energy of another element. Tests should be made to determine if interrelations exist between elements in the calibration RMs.

## 10. Preparation of Calibration RMs and Specimens

10.1 Rough grind, either wet or dry, with a coarse grinding belt or disk. Dry the specimens, if wet, for proper excitation in the argon atmosphere. Ensure that the specimens are homogeneous and free from voids and pits in the region to be excited. Refer to 7.1.1 and 7.1.2. Prepare the surface of the specimens and reference materials in a similar manner.

## 11. Excitation and Instrument Parameters

11.1 *Electrical Parameters*—Electrical parameters within the following ranges were found acceptable. 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, $\mu\text{F}$	2.5 to 15
Inductance, $\mu\text{H}$	50 to 70
Resistance, $\Omega$	residual to 5
Potential, V	940 to 1000
Peak Current, A	100 to 275
Current pulse duration, $\mu\text{s}$	130 to 250
Number of discharges/s	60 to 120

## 11.2 Spectrometer Configurations:

Spectrometer Parameters	
Focal Length	0.5 m to 1.2 m
Dispersion	0.5 nm/mm to 2.16 nm/mm
Vacuum	1 Pa to 25 Pa

## 11.3 Excitation Conditions:

Flush Time	2 s to 5 s
Preburn	10 s to 30 s
Integration	5 s to 20 s

11.4 *Initiation Circuit*—The initiator circuit parameters shall be adequate to uniformly trigger the capacitor discharge. The values for these parameters will vary with the instrument. Values found to be adequate are as follows:

Capacitance (d-c charged) $\mu\text{F}$	1.2
Inductance, $\mu\text{H}$	residual
Resistance, $\Omega$	residual
Potential, V	425

11.4.1 *Other Electrical Parameters*—Excitation units, on which the precise parameters given in 11.1 and 11.4 are not available, may be used, provided that it can be shown experimentally that equivalent precision and accuracy are obtained.

11.5 *Electrode System*—Insert the counter electrode in the lower electrode position. Adjust the analytical gap to 3 mm, 4 mm, 5 mm, or 7 mm depending on the manufacturer's recommendations for that particular instrument.

11.6 *Discharge Source*—Most capacitor discharge sources in current spectrometers are of either two types: directional self-initiating capacitor discharge, or triggered capacitor discharge.

## 12. Preparation of Instrumentation

12.1 Prepare the spectrometer as directed in the manufacturer's instructions.

NOTE 4—It is not within the scope of this method to prescribe all details of equipment to be used. Equipment varies between laboratories.

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

13.1 *Calibration*—Using the conditions given in Section 11, excite the calibration RMs and potential drift correction samples in a random sequence, bracketing these burns with excitations of any materials intended for use as verifiers. (A verifier may be used as a calibration RM even though it is burned only as a verifier.) There should be at least five calibration RMs for each element, spanning the required mass fraction range. Make replicate excitations as directed in 14.2. Using the averages of the data for each point, determine calibrations as described in Practice E305 or the instrument manufacturer's instructions.

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

13.3 *Type Standardization*—After calibration and drift correction, type standardization is an analytical technique that

may be employed by some laboratories. This is usually performed utilizing the instrument manufacturer's software and recommendations. A type reference material is selected that is similar in composition to the expected composition of the unknown samples. Type standardization should be performed at a frequency interval determined by the laboratory. The type standardization should be verified by analyzing a control sample that is similar in composition to the expected composition of the unknown sample and applying an approval criterion to the results before analysis of unknown samples.

13.4 *Verification*—Shall be done at least at the beginning of any analytical work. Analyze verifiers in replicate to confirm that they read within expected confidence interval, as defined in 13.5. The replication shall be the same as directed in 14.2.

13.4.1 Check the verification after drift correction. If confirmation is not obtained, drift correct again or investigate why confirmation is not obtained, or both. Drift correction is confirmed if the results are within two standard deviations from the mean of the verifier.

13.4.2 Repeat the verification at least every 4 h or if the instrument has been idle for more than 1 h. If results are not in conformance, repeat the drift correction.

13.5 The confidence interval will be established from observations of the repeatability of the verifiers and establishing the upper and lower limit of a control chart as directed in Practice E1329 or ASTM MNL 7.

## 14. Measurement Procedure for Excitation and Radiation

14.1 Use the conditions given in Section 11.

14.2 Place the freshly-surfaced specimen on the excitation stand. Position it to effect a gas-tight seal and adequate argon flushing. Position the specimen so that there will be a uniform pattern of burns around its face. For example, a disk-shaped specimen should have a ring of burn marks around its outer edge and approximately 6 mm (0.25 in.) from the edge. Avoid burning the center of cast specimens where quench cracks and segregation are more likely to be present. Ensure there is a good electrical ground between the specimen and the specimen holder device. Cool the specimen, if required, after two burns to prevent overheating. To cool the sample without water, place it on a solid piece of copper to act as a heat sink. Examine the specimen after each burn to evaluate the quality of the excitation. Cracks, voids, pits, moisture, or inclusions will limit the sampling and accuracy of a determination. Successive burns shall be sufficiently separated so that the burn patterns do not overlap.

14.2.1 Burns are permitted to overlap on sample specimens that are used for conditioning the spectrometer from one material type to another as these are not used for analytical data. Also, it is not required to prepare the surface of sample specimens completely when used for these conditioning procedures.

14.3 *Replicate Excitations*—As a minimum, make duplicate burns on each specimen. Average the duplicate readings for each element if their difference does not exceed twice the established standard deviation for that element. Most modern instruments will display statistical calculations of the burns. If their difference exceeds this value, analyze the specimens two more times. Examine the data to determine if there is an outlier. If there is an outlier, average the other three results. If there are two outliers, average all four burns or repeat the analysis. (Two outliers may indicate sample inhomogeneity).

## 15. Calculation of Results

15.1 Average the results obtained for each specimen. If the display is not in direct mass fraction units, use this intensity to obtain the mass fractions from the calibrations.

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<sup>5</sup>

16.1 *Precision*—The precision of this test method was determined by submitting 7 unknown samples to 9 different laboratories. The interlaboratory testing was conducted as directed in Practice E1601. Using reference materials supplied with the unknowns, calibrations were established on the equipment and the corresponding 7 unknown samples were analyzed against the established calibrations. Precision data are found in Table 2.

16.2 *Bias*—The difference between the certified mass fraction and the average mass fraction determined by this test method indicates the bias encountered in the interlaboratory test. Bias data are found in Table 2.

## 17. Keywords

17.1 high manganese steel; spark atomic emission spectrometry

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1031. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).