Designation: E 2209 – 02

Standard Test Method for Analysis of High Manganese Steel Using Atomic Emission Spectrometry[1]

1. Scope

1.1 This method provides for the analysis of high manganese steel by atomic emission spectrometry using the point-to-plane technique for the following elements in the concentration ranges shown:

Elements	Concentration 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.[2] These concentration ranges can be extended to higher concentrations by the use of suitable reference materials. Sulfur is not included because differences in results between laboratories exceeded acceptable limits at all analyte 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

A 128 Specification for Steel Castings; Austenitic Manganese[3]
E 135 Terminology Relating to Emission Spectrometry[4]
E 158 Practices for Fundamental Calculations to Convert Intensities into Concentrations of Optical Emission Spectrochemical Analysis[4]
E 172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis[4]
E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves[4]
E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and other Similar Chromium-Nickel-Iron Alloys[4]
E 406 Practice for Using Controlled Atmospheres Spectrometric Analysis[4]
E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data[5]
E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys[5]
E 1059 Practice for Designation of Shapes and Sizes of Non-Graphite Electrodes[5]
E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[5]
E 1806 Practice for Sampling Steel and Iron for the Determination of Chemical Composition[5]

2.2 *Other Document:*

ASTM Manual on Presentation of Data and Control Chart Analysis, ASTM STP 15D, fourth revision, 1976, Part 3, p. 71

3. Terminology

3.1 For definition of terms used in this method, refer to Terminology E 135.

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 photo-multiplier tubes and stored on capacitors. This discharge is terminated after a fixed exposure time. At the end of the exposure period, the charge on each capacitor is measured, and converted to concentration.

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.

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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.

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[2] Supporting data for this test method as determined by cooperative testing have been filed at ASTM International Headquarters. Request RR: E01-1035.

[3] *Annual Book of ASTM Standards*, Vol 01.02.

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] *Annual Book of ASTM Standards*, Vol 03.06.

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 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 curve that is employed. Alternatively, mathematical corrections may be used to solve for interelement effects (refer to Practice E 158). 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 representative of the material to be analyzed. Refer to Practice E 1806 for steel sampling procedures.

7.1.2 *Immersion Sampler,* to take a sample from the bath or from the metal stream when pouring can be used. The sample 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 and/or Disk
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 emission alignment, a flat surface for the specimen in opposition to a counter electrode. This stand shall provide an atmosphere of argon. The electrode and argon 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 to 450 nm. The spectrometer shall have a dispersion of at least 2 nm/mm and a focal length of at least 0.5 m. Gas purged spectrometers are an alternative to vacuum systems.

7.5 *Measuring System*, consisting of photo-multiplier tubes having individual voltage adjustment, capacitors on which the output of each photo-multiplier tube 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 *Vacuum Pump*, if required, capable of maintaining a vacuum of approximately 3 Pa. There are some equipment manufactures that will purge the optical portion of the spectrometer with argon or other inert gas rather than pull a vacuum on the optics. Either vacuum optics or purged optics are required to determine carbon and phosphorus in this method.

7.7 *Flushing System*, consisting of argon tanks, 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 flushing system shall be in accordance with Practice E 406.

8. Reagents and Materials

8.1 *Argon*, either gaseous or liquid, 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 E 406.

8.2 *Counter Electrode*—A Tungsten or Thoriated Tungsten rod ground to a 15, 30, 45 or 90° angle conical tip, which conforms to Practice E 1059, was found satisfactory.

9. Reference Materials

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

9.2 Calibrants shall be certified reference materials from recognized certification agencies. They shall cover the concentration ranges of the elements to be determined and shall include all of the specific types of alloys being analyzed. The 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 E 353 and E 1019 for chemical analysis of high manganese steel alloys.

9.2.1 In selecting calibrants, use caution with compositions that are unusual. One element may influence the radiant energy

TABLE 1 Wavelengths

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

[A] Interferences are dependent upon instrument design, and excitation conditions, and those listed require confirmation based upon specimens designed to demonstrate interferences. This standard method does not purport to address the interferences that these lines may have. Care should be taken to address the interferences when calibrating the instrument.

of another element. Tests should be made to determine if interrelations exist between elements in the calibrants.

10. Preparation of Calibrants and Specimens

10.1 Rough grind, either wet or dry, with a coarse grinding belt or disk. The final grind of the specimen must be the same grit as the calibrants. Dry the specimens, if wet, for proper excitation in the argon atmosphere. Make sure that the specimens are homogeneous and free from voids and pits in the region to be excited. Cast specimens from molten metal into a suitable mold and cool. Immersion and stream samplers are also suitable for use. Prepare the surface of the specimens and reference materials in a similar manner.

11. Excitation and Exposure

11.1 Be certain the spectrometer is in optical alignment and has been calibrated according to the manufacturer's instructions.

11.1.1 *Electrical Parameters*—Electrical parameters within the following ranges were found acceptable.

Triggered Capacitor Discharge

Capacitance, :F	2.5 to 15
Inductance, :H	50 to 70
Resistance, Σ	residual to 5
Potential, V	940 to 1000
Peak Current, A	100 to 275
Current pulse duration, :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 to 2.16 nm/mm
Vacuum	1 to 25 Pa

11.3 *Exposure Conditions*:

Exposure Conditions

Flush Time	2 to 5 s
Preburn	10 to 30 s
Exposure	5 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. Normal values found to be adequate are listed as follows:

Capacitance (d-c charged) :F	1.2
Inductance, :H	residual
Resistance, Σ	residual
Potential, V	425

11.4.1 *Other Electrical Parameters*—Excitation units, on which the precise parameters given in 11.1.1 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, 4, 5, or 7 mm depending on the manufacturer's recommendations for that particular instrument.

11.6 *Discharge Source*—Most capacitor discharge sources in today's spectrometers are either the directional self-initiating capacitor discharge source or a triggered capacitor discharge source. Refer to Practice E 172 for a more detailed explanation of these sources.

12. Preparation of Instrumentation

12.1 Prepare the spectrometer in accordance with the manufacturer's instructions.

NOTE 3—It is not within the scope of this method to prescribe all details of equipment to be used. Equipment varies between laboratories.

13. Calibration, Standardization, and Verification

13.1 *Calibration*—Using the conditions given in 11.3, excite the calibrants and potential standardants in a random sequence, bracketing these burns 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 should be at least five calibrants for each element, spanning the required concentration range. Make replicate exposures in accordance with 14.2. Using the averages of the data for each point, determine analytical curves as described in Practices E 305 and E 158.

13.2 *Standardization*—Following the manufacturer's recommendations, standardize on an initial setup and anytime that is known or suspected that readings have shifted. Make the necessary corrections either by adjusting the controls on the readout or by applying mathematical corrections. 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 any analytical work. Analyze verifiers in replicate to confirm that they read within expected confidence interval, as defined in 13.4. The replication shall be the same as recommended in 14.2.

13.3.1 Check the verification after standardizing. If confirmation is not obtained, standardize again and/or investigate why confirmation is not obtained. Standardization is confirmed if the results are within two standard deviations from the mean of the standard.

13.3.2 Repeat the verification at least every 4 h or if the instrument has been idle for more than 1 h. If readings are not in conformance, repeat the standardization.

13.4 The confidence interval will be established from observations of the repeatability of the verifiers and determining the confidence interval for some acceptable confidence level as prescribed in Practice E 876 or by establishing the upper and lower limit of a control chart as prescribed in ASTM Manual STP 15D. The latter is the preferable approach since it also monitors the consistency of the statistics of the measurements and provides a means of maintaining a record of performance.

14. Measurement Procedure for Excitation and Radiation

14.1 Use the electrical 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. Make certain there is a good electrical ground between the specimen and the specimen holder device. Cool the specimen after two burns to prevent overheating, if required. One way of cooling the sample without water is to 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.

14.3 *Replicate Exposure*—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 instruments today will print out a statistical analysis of the burns for the analysis. If their difference exceeds this value, analyze the specimens two more times. Test the data to determine if there is an outlier as described in Practice E 876. If there is an outlier, average the other three results. If there are two outliers, average all four burns or repeat the test. (Two outliers may indicate sample inhomogeneity).

15. Calculation of Results

15.1 Average the readings obtained for each specimen. If the readout is not in direct concentration units, use this intensity to obtain the concentrations from the curves.

16. Precision and Bias

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 in accordance with Practice E 1601. Using reference materials supplied with the unknowns, calibration curves were established on the equipment and the corresponding 7 unknown samples were analyzed against the established curves. Precision data is found in Table 2.

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

17. Keywords

17.1 high manganese steel; atomic emission; point-to-plane technique; spectrometric analysis

TABLE 2 Precision and Bias Data

Certified Concentration, %	Average Concentration, %	No. of Labs	Min SD (s_M, E 1601)	Reproducibility SD (s_R, E 1601)	Reproducibility Index (R, E 1601)	R_{rel}%	Material Test Number
Aluminum							
0.01	0.0044	5	0.0005	0.0037	0.0103	237	7
0.004	0.0047	7	0.0005	0.0034	0.0096	203	5
0.042	0.0470	6	0.0012	0.0024	0.0067	14.2	3
0.103	0.1073	8	0.0012	0.0056	0.0158	14.7	6
0.14	0.1220	6	0.0018	0.0131	0.0367	30.0	4
Carbon							
0.303	0.338	9	0.00425	0.1070	0.2997	88.0	1
0.79	0.804	9	0.00562	0.0258	0.0722	8.99	7
0.82	0.813	9	0.00802	0.0132	0.0371	4.56	6
0.92	0.908	7	0.00707	0.0121	0.0338	3.72	3
1.24	1.241	9	0.00934	0.0165	0.0462	3.72	5
1.22	1.263	9	0.00804	0.0244	0.0682	5.40	2
1.4	1.395	7	0.01028	0.0163	0.0457	3.28	4
Chromium							
0.27	0.2770	9	0.0036	0.0214	0.0600	21.7	7
0.474	0.5098	9	0.0064	0.0568	0.1589	31.2	1
0.56	0.5439	9	0.0037	0.0234	0.0655	12.0	5
0.62	0.5842	9	0.0070	0.0286	0.0799	13.7	2
1.02	0.9621	7	0.0094	0.0741	0.2075	21.6	4
1.45	1.446	7	0.0173	0.0539	0.1509	10.4	3
1.93	1.924	9	0.0165	0.0296	0.0828	4.30	6
Manganese							
8.28	8.115	7	0.0886	0.1896	0.5310	6.54	4
9.25	8.990	9	0.0749	0.3416	0.9566	10.6	7
12.4	12.409	8	0.0562	0.2527	0.7076	5.70	2
13.6	13.582	8	0.0819	0.1375	0.3849	2.83	6
13.5	13.584	9	0.0927	0.1426	0.3992	2.94	5
15.6	15.784	9	0.1045	0.3754	1.051	6.66	1
16.1	16.152	7	0.1529	0.1819	0.5094	3.15	3
Molybdenum							
0.023	0.0166	6	0.0019	0.0058	0.0163	98.2	2
0.01	0.0173	5	0.0016	0.0106	0.0298	172	4
0.035	0.0346	9	0.0111	0.0158	0.0444	128	6
0.078	0.0690	9	0.0130	0.0192	0.0538	77.9	5
0.6	0.5807	9	0.0180	0.0373	0.1044	18	3
1.55	1.543	7	0.0221	0.0849	0.2379	15.4	7
1.91	1.992	9	0.0367	0.2444	0.6843	34.3	1
Nickel							
0.05	0.0506	6	0.0028	0.0035	0.0097	19.2	3
0.118	0.1132	8	0.0027	0.0145	0.0405	35.8	2
0.58	0.6193	8	0.0044	0.0185	0.0517	8.36	7
0.69	0.6923	8	0.0076	0.0130	0.0363	5.24	5
1.05	1.0555	8	0.0190	0.0375	0.1051	9.96	6
3.13	3.030	8	0.0302	0.0809	0.2266	7.48	1
3.9	3.966	6	0.0167	0.0740	0.2073	5.23	4
Phosphorus							
0.024	0.0242	9	0.0006	0.0028	0.0078	32.2	1
0.026	0.0247	7	0.0008	0.0016	0.0045	18.1	3
0.03	0.0299	9	0.0007	0.0023	0.0063	21.2	7
0.036	0.0341	9	0.0010	0.0015	0.0043	12.6	6
0.033	0.0377	9	0.0006	0.0016	0.0046	12.2	2
0.04	0.0378	9	0.0010	0.0017	0.0048	12.6	5
0.06	0.0523	7	0.0014	0.0030	0.0085	16.2	4
Silicon							
0.25	0.2593	9	0.0028	0.0059	0.0164	6.34	5
0.374	0.3801	9	0.0040	0.0142	0.0397	10.4	2
0.46	0.4599	9	0.0031	0.0076	0.0214	4.65	6
0.67	0.6669	9	0.0046	0.0368	0.1030	15.4	1
0.9	0.9164	7	0.0078	0.0215	0.0602	6.57	3
0.98	0.9290	7	0.0098	0.0484	0.1355	14.6	4
1.65	1.477	9	0.0140	0.0475	0.1330	9.00	7
Sulfur							
0.001	0.0019	4	0.0006	0.0019	0.0052	272	2
0.002	0.0030	7	0.0005	0.0008	0.0022	73.3	1
0.005	0.0039	5	0.0007	0.0007	0.0020	51.9	5
0.008	0.0064	8	0.0005	0.0024	0.0068	107	7
0.012	0.0087	7	0.0007	0.0028	0.0080	91.4	3
0.014	0.0129	9	0.0011	0.0026	0.0074	57.0	6
0.03	0.0202	7	0.0011	0.0041	0.0115	56.8	4

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