



Standard Test Method for Optical Emission Vacuum Spectrometric Analysis of Blast Furnace Iron by the Point-to-Plane Technique¹

This standard is issued under the fixed designation E 485; 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.

^{ε1} NOTE—Editorial changes were made in October 2000.

1. Scope

1.1 This test method describes the spectrochemical procedure for the analysis of blast furnace iron (hot metal) containing 4.2 to 5.0 % carbon for the following elements in the indicated ranges:

Elements	Concentration Range, %
Silicon	0.50 to 2.00
Manganese	0.20 to 1.50
Phosphorus	0.020 to 0.15
Titanium	0.02 to 0.10
Sulfur	0.010 to 0.050

1.2 *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:

- E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron²
- E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes²
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²
- E 158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis²
- E 172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis²
- E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves²
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data³

¹ This test method is under the jurisdiction of ASTM Committee E-1 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 Sept. 15, 1994. Published November 1994. Originally published as E 485 – 73. Last previous edition E 485 – 88.

² Annual Book of ASTM Standards, Vol 03.05.

³ Annual Book of ASTM Standards, Vol 03.06.

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E 135.

4. Summary of Test Method

4.1 The sample is excited in an inert gas atmosphere by a controlled triggered capacitor discharge using the point-to-plane technique. Using a vacuum spectrometer, the radiant energies of selected analytical lines and an internal standard line are measured by photomultipliers. The output current of each photomultiplier is accumulated and stored during the exposure period as a charge on an associated capacitor, where it appears as a measurable voltage. At the end of the exposure period the voltages corresponding to the analytical lines relative to the voltage for the internal standard line are measured. The measuring system may be calibrated in terms of percent concentration.

5. Apparatus

5.1 Sample Preparation Equipment:

5.1.1 *Sample Mold*, to produce gray 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 cast disk approximately 28 mm (1 1/2 in.) in diameter and 12 to 25 mm (1/2 to 1 in.) thick is satisfactory.

5.1.2 *Grinder*, to prepare a flat clean surface of the sample for analysis.

5.2 *Supporting Electrode*, to hold the sample in optical alignment and provide good electrical contact.

5.3 *Excitation Source*, providing a controlled triggered capacitor discharge with parameters described in 9.2. (See Practice E 172.)

5.4 *Spectrometer*, having the following representative characteristics:

	Vacuum	Air
Focal length, m	1	1 1/2
Concave grating, grooves/mm	2160	960
Reciprocal linear dispersion, Å/mm	4.6	6.9
Primary slit width, μm	25 to 75	25 to 75
Secondary slit width, μm	see Table 1	see Table 1

Wavelength coverage, nm	175.0 to 215.0	190.0 to 811.5
Pressure, torr	30×10^{-3} or less	

5.5 *Measuring System*, consisting of photomultipliers having individual voltage adjustment, capacitors on which the output of each photomultiplier is stored, an amplifier, a recorder system to register the voltages on the capacitors either directly or indirectly (as a ratio), and the necessary switching arrangements to provide the desired sequence of operation.

6. Materials

6.1 *Counter Electrode*—A rod of carbon, 6.15 mm (0.242 in.) in diameter. The shape of the rod tip shall be conical with the tip, 120 deg included angle, (ASTM Type C-2 described in Practice E 130) or flat (ASTM Type C-3 also described in E130). The analytical gap shall be 3 or 4 mm.

6.2 *Argon*, high-purity, 99.998 % pure.

7. Reference Materials

7.1 Primary calibration reference materials for the analysis of blast furnace iron are available from the National Institute of Standards and Technology. Other reference materials may be used which have been tested for homogeneity and which have been standardized in accordance with Test Methods E 30 to establish analytical curves. Other reference materials can be obtained by casting material from production.

7.2 In selecting other reference materials, observe caution with compositions that are unusual. Avoid using as reference materials cast iron that contains residual amounts of alloying elements in concentrations greater than normally found as residuals in blast furnace iron (greater than 0.20 %). One element may adversely influence the radiation of another element. If cast iron reference materials are used, tests shall be made to determine if interrelations exist between elements in the reference materials. To avoid interelemental effects, it is suggested that the reference materials closely match the composition of the blast furnace iron samples.

8. Preparation of Samples

8.1 *Sampling*—Observe the usual precautions when sampling blast furnace iron to assure that the sample represents as closely as possible the entire lot of material under test. Samples shall be free of pipe, blowholes, seams, occluded slag, flakes of graphite on the surface, and other physical imperfections. The samples shall be adequate to overlap the bore of the spark stand opening to affect an argon seal of sufficient bulk to prevent overheating during excitation. They shall weigh at least 40 g and be at least 12 mm (½ in.) thick. Samples and reference materials shall be similar in metallurgical condition.

TABLE 1 Internal Standards and Analytical Lines

Element	Wavelength, nm	Exit slit Width, ^A μm
Iron ^B	271.441 (or 195.16)	75 to 300
Manganese	293.306	25 to 75
Phosphorus	178.287	25 to 75
Sulfur	180.731	25 to 75
Silicon	288.158 (or 251.61)	25 to 75
Titanium	324.20	150

^A Exit slit width is dependent on the optical characteristics of the spectrometer, and thus may be different from one instrument to another.

^B Internal standard.

8.2 *Surface Preparation*—Prepare samples and reference materials by grinding or machining to provide uniform flat surface areas. For speed and convenience, it is recommended that a belt or surface grinder with aluminum oxide abrasive be employed, and that a coarse grit, such as 40 or 50, be used.

9. Preparation of Apparatus

NOTE 1—The instructions given herein apply to most spectrometers; however, some settings and adjustments may need to be varied and, depending on the particular equipment, additional preparation of the equipment may be required. It is not within the scope of an ASTM method to prescribe the minute details of the apparatus preparation which differ not only for each manufacturer, but also often for different equipment from the same manufacturer. For a description of a spectrometer and further details of its operation, refer to the manufacturer's handbook.

9.1 Table 1 lists the recommended analytical and internal standard lines. Also given are the recommended exit slit widths. Align or test the position of the exit slits (Note 2) to ensure that peak radiation passes through each slit and is upon the photomultipliers. This shall be done initially, and as often as necessary thereafter to maintain proper optical alignment.

NOTE 2—The manner and frequency of positioning or checking the alignment of the exit slits will depend on factors such as: type of spectrometer, manufacturer, the variety of analytical problems encountered, and frequency of use. For details of setting and operating a particular spectrometer, refer to the manufacturer's handbook. Each laboratory should establish a suitable check procedure.

9.2 Electrical Parameters (Note 3):

Voltage, kV	1
Capacitance, μF	2
Inductance, μH	50
Damping resistance, Ω	0
Discharges/s	60
Current, r-f A	0.2
Type of discharge	triggered capacitor discharge

NOTE 3—The power supply voltage should be controlled within ±2 %.

9.3 Exposure Conditions:

Flush period, s	5 to 20
Preburn period, s	10 to 50 (Note 4)
Exposure period, s	20 to 25 (Note 4)
Argon flow,	
flush period, litres/s	0.20 to 0.40
preburn period, litres/s	0.16 to 0.40
exposure period, litres/s	0.16 to 0.40

NOTE 4—The exact preburn and exposure times required for the intensity ratios to reach reproducible values shall be established in each laboratory.

9.4 *Electrode System*—Insert the carbon counter electrode in the lower electrode position. Insert a calibrant sample in the upper electrode position and condition the counter electrode by one or two burns. Adjust the analytical gap to between 3 and 4 mm.

NOTE 5—The counter electrode must be regapped after four or five analyses.

9.5 *Preliminary Calibration*—Excite a low- and a high-concentration calibrant sample and set the photomultiplier sensitivity controls for the internal standard and each analytical photomultiplier to obtain the desired voltages on the capacitors.

NOTE 6—The voltages may be read directly, or one of a number of

different readout systems may be employed that yield linear or logarithmic functions of the voltages which may be displayed as relative numbers or as numbers calibrated directly in terms of percent.

10. Calibration, Standardization, and Verification

10.1 *Calibration*—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 will be at least three calibrants for each element, spanning the required concentration range. Repeat with different random sequences at least four times. Using the averages of the data for each point, determine analytical curves as directed in Practices E 305 and E 158.

10.2 *Standardization*—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 will be done any time verification indicates that readings have gone out of statistical control.

10.3 *Verification* shall be done at least at the beginning of a shift. Analyze verifiers in replicate to confirm that they read within the expected confidence interval, as defined in 10.4. The replication will be the same as that recommended in 11.1.

10.3.1 Check verification after standardizing. If confirmation is not obtained, run another standardization or investigate why instrument is malfunctioning.

10.3.2 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.

10.4 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 MNL 7.⁴ The latter is the preferable approach since it also monitors the consistency of the statistics of the measurements and provides a way of maintaining a record of performance.

11. Excitation and Radiation Measurement

11.1 Place the specimen in the electrode chamber and position the prepared surface over the counter electrode. Flush the excitation chamber with argon and excite the specimen (see 9.3). At the end of the instrument analysis cycle, record the readings obtained for each element. Reanalyze the specimen. Average the duplicate 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. Test the data to determine if there is an outlier as described in Practice E 876. If there is one outlier, average the other three results. If there are two outliers, average all four or repeat the test. (Two outliers may indicate sample inhomogeneity.)

⁴ Manual on Presentation of Data and Control Chart Analysis, ASTM Manual Series, ASTM, 6th ed., 1990.

NOTE 7—Establish the standard deviation from repeat analyses of production cast samples that cover the desired concentration ranges.

12. Calculation

12.1 Use the average readings obtained to read the concentration of the elements from the curves or from tables that have been prepared to relate the recorded numbers to concentration. A computer may be used to automatically convert the spectrometer output, either analog or digital signals, to digital percent concentration. No calculations are required if the readings are read directly in percent concentration.

13. Precision and Bias

13.1 *Precision*—The precision of the analyses data obtained in interlaboratory testing are shown in Table 2 and Table 3.

13.2 *Bias*—The bias data obtained in the interlaboratory testing are shown in Table 4.

14. Keywords

14.1 blast furnace iron; optical emission; point-to-plane technique; spectrometric analysis

TABLE 2 Precision Data (Reproducibility)

Element	Number of Analyses	Average Concentration, %	Standard Deviation ^{A,B,C}	Coefficient of Variation ^D
Silicon ^A	15	0.51	0.0414	8.1
	15	1.09	0.0337	3.1
	15	0.59	0.0330	5.6
	15	1.30	0.0407	3.1
Manganese ^A	15	0.66	0.0214	3.2
	15	0.71	0.0223	3.1
	15	1.13	0.0323	2.9
	15	1.00	0.0387	3.9
Phosphorus ^A	15	0.059	0.0040	6.8
	15	0.047	0.0030	6.4
	15	0.085	0.0064	7.5
	15	0.065	0.0060	9.2
Titanium ^B	9	0.028	0.0024	8.6
	9	0.050	0.0022	4.4
	9	0.040	0.0029	7.3
	9	0.085	0.0048	5.6
Sulfur ^A	15	0.035	0.0023	6.6
	15	0.020	0.0016	8.0
	15	0.024	0.0021	8.7
	15	0.009	0.0013	14.4

^A Three analyses from each of five laboratories.

^B Three analyses from each of three laboratories.

^C Estimate of standard deviation, *s*, calculated as follows:

$$s = \sqrt{\sum d^2 / (n - 1)}$$

where:

d = difference of determinations from the mean, and

n = number of determinations.

^D Coefficient of variation, *v*, is calculated as follows:

$$v = 100 s / \bar{X}$$

where:

S = standard deviation, and

\bar{X} = average concentration.

TABLE 3 Precision Data (Repeatability^A)

Element	Sample No.	Number of Analyses	Average Concentration, %	Standard Deviation	Coefficient of Variation
Silicon	1	21	1.30	0.013	1.00
	2	21	0.73	0.008	1.10
	3	21	0.78	0.011	1.41
Manganese	1	21	1.25	0.033	2.64
	2	21	1.13	0.011	0.97
	3	21	0.86	0.013	1.51
Phosphorus	1	21	0.097	0.011	11.34
	2	21	0.124	0.0033	2.66
	3	21	0.055	0.0014	2.54
Sulfur	1	21	0.036	0.001	2.78
	2	21	0.052	0.0023	4.42
	3	21	0.017	0.0005	2.94

^A Twenty-one repeat analyses of one sample in one laboratory.

TABLE 4 Bias Data

Element	Assumed True Value, % ^A	Average Spectrometer Value, %	Number of Laboratories	Deviation from Assumed True Value, %
Silicon	0.58	0.51	5	-0.07
	1.16	1.09	5	-0.07
	0.63	0.59	5	-0.04
	1.25	1.30	5	+0.05
Manganese	0.66	0.66	5	0.00
	0.69	0.71	5	+0.02
	1.14	1.13	5	-0.01
	0.95	1.00	5	+0.05
Phosphorus	0.057	0.059	5	+0.002
	0.049	0.047	5	-0.002
	0.085	0.085	5	0.000
	0.069	0.065	5	-0.004
Titanium	0.032	0.028	3	-0.004
	0.053	0.050	3	-0.003
	0.030	0.040	3	+0.010
	0.080	0.085	3	+0.005
Sulfur	0.035	0.035	5	0.000
	0.017	0.020	5	+0.003
	0.023	0.024	5	+0.001
	0.007	0.009	5	+0.002

^A Values established from duplicate analyses by methods as follows:

Silicon—perchloric acid dehydration
Manganese—photometric periodate
Phosphorus—photometric molybdenum-blue
Titanium—X-ray
Sulfur—combustion iodate titration

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).