Designation: E 404 – 95 (Reapproved 2000)ε1

Standard Test Method for Spectrographic Determination of Boron In Carbon and LowAlloy Steel by the Point-To-Plane Technique[1]

This standard is issued under the fixed designation E 404; 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.

ε[1] NOTE—Editorial changes were made in October 2000.

1. Scope

1.1 This test method covers the spectrographic determination of boron in carbon and low-alloy steel for boron in the concentration range from 0.001 to 0.01 %.

NOTE 1—The concentration range of the element listed has been established through cooperative testing[2] of reference materials. The scope is underwritten by available spectrochemical reference materials.

1.2 This test method is applicable for the analysis of carbon and low-alloy steel samples, chill-cast, rolled, or forged, of miscellaneous sizes and shapes on which a flat surface at least 12.7 mm in diameter can be prepared, and which are sufficiently massive to prevent overheating during the discharge. Thin samples less than 3.2 mm but greater than 0.79 mm thick, may be analyzed if these samples are soldered to steel plate having a thickness of at least 3.2 mm.

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:*

E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron[3]

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis[4]

E 116 Practice for Photographic Photometry in Spectrochemical Analysis[4]

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes[4]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[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 327 Test Method for Optical Emission Spectrometric Analysis of Stainless Type 18-8 Steels by the Point-to-Plane Technique[5]

E 409 Practice for Description and Performance of the Microphotometer[4]

3. Terminology

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

4. Summary of Test Method

4.1 A flat sample surface is excited by a controlled arc discharge using the point-to-plane technique. The intensity ratio of a boron line and an iron line is determined photometrically. The concentration of boron is read from an analytical curve relating log intensity ratio to log concentration.

5. Significance and Use

5.1 Some hot-worked surfaces may be severely deboronized (up to⅛ in.) into the sample. Tests should be performed to establish the amount of sample for each process that needs to be removed to allow a correct boron analysis.

6. Apparatus

6.1 *Sample Preparation Equipment*:

6.1.1 *Cut-off Machine*, capable of cutting test specimens 63.5 mm in diameter.

6.1.2 *Belt Sander*, with 36 and 60-grit aluminum oxide belts.

6.2 *Electrode Cutter*, for shaping electrodes to the configurations described in Section 7.

6.3 *Excitation Source*, providing a controlled arc with the parameters described in 11.1.1. (See Practice E 172.)

6.4 *Spark Stand*, suitable for mounting in optical alignment a flat surface of the specimen in opposition to a graphite counter electrode. The stand may be water-cooled.

[1] This test method is under the jurisdiction of the 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 have been filed at ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103, as RR:E2-1000.

[3] Discontinued 1995; see *1994 Annual Book of ASTM Standards*, Vol 03.05.

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

[5] Discontinued 1999; see *1998 Annual Book of ASTM Standards*, Vol 03.06.

6.5 *Spectrograph*—Any of the commercially available instruments may be used provided they have sufficient resolving power to resolve the line B 249.678 nm from the neighboring iron lines Fe 249.653 nm and Fe 249.699 nm.

6.6 *Microphotometer*, capable of measuring the transmittances of the selected analytical lines in accordance with Practice E 409.

6.7 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations and conforming to the requirements of Practice E 115.

6.8 *Calculating Equipment*, capable of converting microphotometer readings to intensity ratios from the emulsion calibration curve.

7. Materials

7.1 *Electrodes*, of 6.4-mm high-purity graphite rod, the end of which is machined to the shapes designated in Table 1.

7.2 *Photographic Emulsion*[6]

7.3 *Photographic Processing Solutions*, as described in Practice E 115.

8. Reference Materials

8.1 *Certified Reference Materials* are available from the National Institute of Standards and Technology[7] and other sources. These have a diameter of 32 mm and a thickness of 19 mm and cover the concentration range listed in 1.1.

8.2 *Reference Materials* shall be free from voids and porosity. They shall be analyzed in accordance with Test Methods E 30, or equivalent.

9. Preparation of Reference Materials and Samples

9.1 Cast samples from molten metal in a sample mold, remove from the mold and allow to air cool in accordance with Test Method E 327. Cut a 12.7 to 25.4-mm thick slice from the bottom of the test sample or obtain a smooth, flat surface by machining or grinding at least 1.6 mm off the original cast surface. Rough polish the cut or machined surface by grinding on a belt surface, either wet or dry, with a 36-grit aluminum oxide abrasive belt. Obtain the final surface by grinding with a 60-grit aluminum oxide abrasive belt.

9.2 Solder thin samples less than 3.2 mm but greater than 0.79 mm thick that would overheat during the discharge to a steel plate having a thickness of at least 3.2 mm.

10. Preparation of Apparatus

10.1 *Electrode System*:

[6] The sole source of supply of photographic emulsion, Eastman SA No. 1 known to the committee at this time is the Eastman Kodak Co., 343–T State St., Rochester, NY 14650. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Y:our comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[7] National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, MD 20899.

TABLE 1 Electrode Configurations

Noncapacitive AC Arc	Triggered Capacitor Discharge	Spark-Ignited Unidirectional Arc
C-2[A]	Pointed tip with an included angle of 15°	Pointed tip with an included angle of 90°

[A] Shape given in Practice E 130.

10.1.1 Insert a freshly cut counter electrode in the spark stand and adjust to the prescribed analytical gap (Note 2). Place the specimen, freshly ground surface down on the spark stand, so that the discharge will pass between the tip of the counter electrode and the freshly ground surface.

NOTE 2—The analytical gap for the spark-ignited unidirectional arc is 2 mm. A 3-mm analytical gap is used for the other electrical parameters.

10.2 *Excitation and Exposure*—Produce and record the spectra in accordance with the following conditions:

10.2.1 *Electrical Parameters*—Select one of the following excitation parameters:

Noncapacitive a-c Arc

Radio-frequency, current, A	3.9
Potential, V, rms	2400
Frequency, Hz	60

Triggered Capacitor Discharge

Capacitance, μF	40
Inductance, μH	360
Resistance, Ω	50
Potential, V	1000
Radio-frequency, current, A	2
Number of discharges/s	60
Sample polarity	negative

Spark-Ignited Unidirectional Arc

Peak voltage, V	423
Current, A	10
Number of discharges/s	60
Sample polarity	positive

10.2.2 *Other Electrical Parameters*—Excitation units on which the precise parameters given in 10.2.1 are not available may be used provided that it can be shown experimentally that equivalent precision and accuracy are obtained.

10.2.3 *Exposure Conditions*—Use the following exposure conditions:

Preburn period, s	0
Exposure period, s	20 to 60 (Note 3)
Spectral region, Å	2300 to 3000 (Note 4)
Slit width, μm	20
Filters	(Note 5)

NOTE 3—Exposure time shall be selected to give suitable line density.

NOTE 4—The spectral region from 450.0 to 550.0 nm may be used to resolve the boron analytical line B249.678 (second order) from the neighboring iron lines.

NOTE 5—Fixed or removable filters may be used to obtain more favorable intensity ratios. A removable filter may be used to provide a dual concentration range.

10.2.4 *Emulsion Calibration Exposure*— Expose the emulsion for calibration by exciting plain carbon steel as described in 10.2.1 and 10.2.3.

10.2.5 *Replicate Exposures*—Use sufficient reference materials to compensate for curve shifts. Expose reference materials and specimens in duplicate.

11. Photographic Processing

11.1 Process the emulsion in accordance with Practice E 115.

12. Photometry

12.1 Using a microphotometer make transmittance measurements for analytical line pairs and lines of the calibration

TABLE 2 Analytical Lines

Analytical Line, nm	Internal Standard Line, nm	Concentration Index, %	Excitation
B 249.678	Fe 250.657	0.004	Noncapacitive ac arc
B 249.678 (second order)	Fe 248.16 (second order)[A]	None; however, maintain the transmittance of the iron internal standard line at 15 to 50 %	Triggered capacitor discharge
B 249.678 (second order)	Fe 248.16 (second order) Fe 249.586 (second order)	None; however, maintain the transmittance of the iron internal standard line at approximately 30 %	Spark-ignited unidirectional arc

[A] These lines are corrected for background in accordance with 13.2 of Practice E 116.

TABLE 3 Precision Data[A]

	Number of Determinations	Average Concentration, %	Standard Deviation, *s*	Relative Standard Deviation, RSD %
Noncapacitive a-c arc	6	0.0024	±0.00017	±6.97
	6	0.0067	±0.00030	±4.62
	6	0.0012	±0.00010	±8.87
	6	0.0018	±0.00010	±5.64
Triggered capacitor discharge	6	0.0027	±0.00004	±1.49
	6	0.0070	±0.00050	±6.98
	6	0.0010	±0.00010	±11.04
	6	0.0019	±0.00016	±8.50
Spark-ignited unidirectional arc	6	0.0029	±0.00020	±6.85
	6	0.0076	±0.00015	±2.01
	6	0.0010	±0.00004	±4.06
	6	0.0017	±0.00014	±8.18

[A] Standard deviation, *s*, in this test method is calculated as follows:

$$s = \sqrt{[\Sigma X^2 - (\Sigma X)^2/n]/(n-1)}$$

where:
X = individual determinations, and
n = number of determinations.

Relative standard deviation, RSD, in this test method is calculated as follows:

$$RSD = (100/\bar{X})s$$

where:
s = standard deviation, and
$\bar{X}$ = average concentration, %.

TABLE 4 Accuracy Data

	Assumed True Value, %	Average Calculated Value, %	Deviation from Assumed True Value, %
Noncapacitive a-c arc	0.0025	0.0024	0.0001
	0.0065	0.0067	0.0002
	0.0012	0.0012	0.0000
	0.0018	0.0018	0.0000
Triggered capacitor discharge	0.0025	0.0027	0.0002
	0.0065	0.0070	0.0005
	0.0012	0.0010	0.0002
	0.0018	0.0019	0.0001
Spark-ignited unidirectional arc	0.0025	0.0029	0.0004
	0.0065	0.0076	0.0011
	0.0012	0.0010	0.0002
	0.0018	0.0017	0.0001

spectrum. The analytical line pairs are shown in Table 2.

13. Calibration

13.1 *Emulsion Calibration*—Calibrate the emulsion in accordance with Practice E 116.

13.2 *Preparation of Analytical Curve*— Make sufficient exposures of the reference materials to establish the analytical curve. Convert the percent transmittances obtained with the microphotometer to intensity ratios by means of the emulsion calibration curve. Plot intensity ratio of the calibration reference materials on log-log paper as a function of concentration in percent of boron. Refer to Practice E 305.

14. Calculation

14.1 Convert the transmittance measurements of the analytical line pair of the unknown to intensity ratios by means of the emulsion calibration curve. Refer these ratios to the analytical curve prepared in 13.2 and read the concentration of boron in percent from the curve.

15. Precision and Bias

15.1 *Precision*—The precision of the test method was established by analyzing four samples each six times on separate days in three different laboratories with the source parameters and operating conditions listed herein. Precision data are given in Table 3.

15.2 *Bias*—The bias of this test method was obtained by comparing the average of duplicate determinations to the assumed true value. Accuracy data are given in Table 4.

16. Keywords

16.1 boron in carbon and low-alloy steels; optical emission; point-to-plane technique; spectrographic analysis