



Standard Test Method for Optical Emission Vacuum Spectrometric Analysis of Stainless Steel by the Point-to-Plane Excitation Technique¹

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1. Scope

1.1 This test method² provides for the optical emission vacuum spectrometric analysis of stainless steel in solid form by the point-to-plane excitation technique for the following elements in the concentration ranges shown:

Element	Concentration Range, %
Chromium	17.0 to 23.0
Nickel	7.5 to 13.0
Molybdenum	0.01 to 3.0
Manganese	0.01 to 2.0
Silicon	0.01 to 0.90
Copper	0.01 to 0.30
Carbon	0.005 to 0.25
Phosphorus	0.003 to 0.15
Sulfur	0.003 to 0.065

1.2 This test method is designed for the routine analysis of chill-cast disks or inspection testing of stainless steel samples that have a flat surface of at least 13 mm (0.5 in.) in diameter. The samples must be sufficiently massive to prevent overheating during the discharge and of a similar metallurgical condition and composition as the reference materials.

1.3 Analytical curves are plotted using the concentration ratio method as shown in Practice E 158. One or more of the reference materials must closely approximate the composition of the specimen. The technique of analyzing reference materials along with unknowns and performing the indicated mathematical corrections may also be used to correct for interference effects and to compensate for errors resulting from instrument drift. A variety of such systems are commonly used. Any of these that will achieve analytical accuracy equivalent to that reported for this test method are acceptable.

1.4 *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.*

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.

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² Supporting data for this test method are on file at ASTM Headquarters. Request Research Report RR: E02-1023.

2. Referenced Documents

2.1 ASTM Standards:

- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials³
- E 158 Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis³
- E 172 Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis³
- E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves³
- E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys³
- E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis⁴
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data⁴
- E 1060 Practice for Interlaboratory Testing of Spectrochemical Methods of Analysis⁴

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 A controlled discharge is produced between the flat surface of the specimen and the counter electrode. The radiant energy of selected analytical lines are converted into electrical energies by photomultiplier tubes and stored on capacitors. The discharge is terminated at a predetermined level of accumulated radiant energy from the internal standard iron line or after a fixed exposure time. At the end of the exposure period, the charge on each capacitor is measured, and displayed or recorded as a relative energy or concentration.

5. Significance and Use

5.1 The chemical composition of stainless steels must be determined accurately in order to ensure the desired metallurgical properties. This procedure is suitable for manufacturing

³ *Annual Book of ASTM Standards*, Vol 03.05.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

control and inspection testing.

6. Apparatus

6.1 Sample Preparation Equipment:

6.1.1 *Sample Mold*, capable of producing castings that are homogeneous and free of voids and porosity. The following mold types have been found to produce acceptable samples.

6.1.1.1 *Refractory Mold Ring*, having a minimum inside diameter of 32 mm (1.25 in.) and a minimum height of 25 mm (1.0 in.). The ring is placed on a flat surface of a copper plate approximately 50 mm (2.0 in.) thick.

6.1.1.2 *Book-Type Steel Mold*, to produce a chill-cast disk 64 mm (2.5 in.) in diameter and 13 mm (0.5 in.) thick. The wall thickness of the mold should be 32 mm (1.25 in.) to aid chill casting.

6.1.2 *Abrasive Grinder*, a suitable belt grinder, horizontal disk grinder, or similar grinding apparatus. The resulting surface should be uniformly plane and free of defects. These may be either wet or dry grinding devices. Grinding materials with grit sizes ranging from 60 to 180 have been found satisfactory.

6.2 *Excitation Source*, with parameters capable of producing a usable spectrum as described in 10.2 and conforming to Practice E 172.

6.3 *Excitation Stand*, suitable for mounting in optical alignment, a flat surface of the specimen in opposition to a counter electrode. The stand shall provide an atmosphere of argon and may be water cooled. Electrode and argon are described in 7.1 and 7.2.

6.4 *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 500.0 nm. Spectrometer characteristics for two of the instruments used in this test method are described as having dispersion of 0.697 nm/mm (first order), the focal length of 1 m. Spectral lines are listed in Table 1.

6.5 *Measuring System*, consisting of photomultiplier tubes having individual voltage adjustment, capacitors on which the output of each photomultiplier 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.

6.6 *Readout Console*, capable of indicating the ratio of the analytical lines to the internal standard with sufficient precision to produce the accuracy of analysis desired.

6.7 *Vacuum Pump*, capable of maintaining a vacuum of 25 μ m Hg.

6.8 *Flushing System*, consisting of argon tanks, a pressure regulator, and a gas flowmeter. 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.

NOTE 1—It is not within the scope of this test method to prescribe all details of equipment to be used. Equipment varies among laboratories.

7. Reagents and Materials

7.1 *Argon*, either gaseous or liquid, must be of sufficient purity to permit proper excitation of the analytical lines of

TABLE 1 Analytical and Internal Standard Lines

Element	Wavelength, nm	Concentration Switch Over Points
Chromium	298.919	
Nickel	243.789	
	227.021	
	218.549	
	216.910	
Molybdenum	202.030	<1 %
	281.615	
	308.561	>1 %
	369.265	
Manganese	293.306	
Silicon	251.612 ^A	
	288.158	
Copper	327.396	<0.10 %
	224.699	>0.10 %
Carbon	193.092	
Phosphorus	178.287 ^A	
Sulfur	180.731	
Iron ^B	271.441	
	322.706	

^A Silicon 251.612 can have a small but significant interference from molybdenum 251.611. Phosphorus 178.287 may show small but significant interferences from unlisted lines or background due to molybdenum, chromium, and manganese. Interference corrections will not be necessary if: separate silicon and phosphorus curves are used for 316 and 317 alloys; the manganese content varies only between 0.7 and 1.5 %; and the chromium concentration is held between 17 and 20 %.

^B Either iron line 271.441 or 322.775 with narrow entrance and exit slits to avoid interference from manganese 322.809 can be used as internal standard with any of the listed analytical lines. Iron 271.441 is not appropriate for tungsten tool steels or super alloys with high cobalt because of interference from cobalt 271.442.

interest. Argon of 99.998 % purity has been found satisfactory. Refer to Practice E 406.

7.2 *Electrodes*, may be 3 to 6 mm (0.125 to 0.25 in.) in diameter ground to a 90° tip or whatever the instrument manufacturer recommends for the particular source. Hard-drawn, fine, silver rods, thoriated-tungsten rods, or other material may be used provided it can be shown experimentally that equivalent precision and accuracy are obtained.

8. Reference Materials

8.1 *Certified Reference Materials* are available from the National Institute of Standards and Technology⁵ and other international certification agencies.

8.2 *Reference Materials* with matrices similar to that of the test specimen and containing varying amounts of the elements to be determined may be used provided they have been chemically analyzed in accordance with ASTM standard test methods. These reference materials shall be homogeneous, and free of voids or porosity.

8.3 The reference materials shall cover the concentration ranges of the elements being sought. A minimum of three reference materials shall be used for each element.

9. Preparation of Samples

9.1 Cast samples from molten metal into a suitable mold and cool. Prepare the surface to be analyzed on a suitable belt or disk grinder. Prepare the surface of the specimens and reference materials in a similar manner. If wet surfacing

⁵ National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, MD 20899.

procedure is used, dry the specimens for proper excitation in the argon atmosphere.

10. Excitation and Exposure

10.1 Be certain the spectrometer is in optical alignment and has been calibrated in accordance with the instructions of the manufacturer.

10.2 *Electrical Parameters*—Two different types of sources were employed in the testing of this test method.

10.2.1 *Directional Self-Initiating Capacitor Discharge Source:*

Capacitance, μF	0.015
Inductance, L_1 , μH	310
Inductance, L_2 , μH	20
Resistance, Ω	residual
Potential, V	13 500
Peak Current, A	90
First Valley Current, A	60
Current pulse duration, μs	120
Number of discharges/s	240

10.2.1.1 *Exposure Conditions:*

Flush, s	7	Argon Flow 0.42 m^3/h
Preburn, s	20	Argon Flow 0.42 m^3/h
Integration, s	20	Argon Flow 0.42 m^3/h

10.2.2 *Triggered Capacitor Discharge Source:*

	Preburn	Exposure
Pulse Output:		
Capacitance, μF (d-c charged)	7.5	2.5
Inductance, μH	50	50
Resistance, Ω	residual	residual
Potential, V	950	950
Peak Current, A	275	100
Current pulse duration, μs	250	130
Number of discharges/s	120	120
Trigger:		
Capacitance (d-c charged), μF	1.2	...
Inductance, μH	residual	...
Resistance, Ω	residual	...
Potential, V	425	...

10.2.2.1 *Exposure Conditions:*

Flush, s	2	Argon Flow 0.56 m^3/h
Preburn, s	10	Argon Flow 0.56 m^3/h
Exposure, s	10 or 15	Argon Flow 0.56 m^3/h

11. Calibration, Standardization, and Verification

11.1 *Calibration*—Using the conditions given in 10.2, excite 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 shall be at least three calibrants for each element, spanning the required concentration range. Repeat with different random sequences at least four times. Follow the procedure for the concentration-ratio method as described in Practice E 158. Using the averages of the data for each point, determine analytical curves as described in Practice E 305.

11.2 *Standardization*—Following the manufacturer's recommendations, 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 anytime verification indicates that readings have gone out of statistical control.

11.3 *Verification*—Shall be done at least at the beginning of a work shift. Analyze verifiers in replicate to confirm that they read within expected confidence interval, as defined in 11.4.

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

11.3.2 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.

11.4 The confidence interval will be established from observations of the repeatability of the verifiers and determining the confidence interval for some acceptable confidence level in accordance with Practice E 876 or by establishing the upper and lower limit of a control chart in accordance with ASTM Manual MNL7.⁶ 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.

12. Procedure for Excitation and Radiation Measurement

12.1 Produce and record the spectra using the conditions in 10.2.

12.2 *Replicate Exposure*—Make duplicate exposures of each specimen and report the average. Place the freshly surfaced specimen on the excitation stand in a manner to effect a gas-tight seal and adequate argon flushing. Position the specimen so there will be a uniform pattern of excitations around its face. For example, a disk-shaped specimen should have a ring of excitation marks around its outer edge and approximately 6 mm (0.25 in.) from the edge. Avoid the center of cast specimens because there is more chance of quench cracks and segregation. Make a good electrical ground. Cool the specimen after two excitations to prevent overheating, if required. Examine the specimen after each excitation to evaluate the quality of excitation. Cracks, voids, pits, moisture, or inclusions will limit the sampling and the accuracy of a determination. Successive excitations shall be sufficiently separated so that the discharge patterns do not overlap.

13. Calculation of Results

13.1 Average the readings obtained for each specimen. If the readout is not in direct concentration units, use this value to obtain the concentrations from the curves, or related scale values and concentration by reference to a table that has been previously prepared.

14. Precision and Bias²

14.1 *Precision*—The precision of this test method was determined by submitting three stainless alloys to five different laboratories. The interlaboratory testing was conducted in accordance with Practice E 1060. Using reference materials supplied with the unknowns, in-house reference materials,

⁶ MNL 7 Manual on Presentation of Data and Control Chart Analysis, ASTM Manual Series, ASTM, 6th edition, 1990.

NBS and British Certified Reference Materials for calibration, the unknowns, and in-house reference materials were run on three separate days. The precision data for the three unknowns is shown in Table 2.

14.1.1 *Accuracy*—The three unknowns were analyzed by alternate chemical methods by two laboratories independent of the testing of this test method. The agreement between the

results obtained by chemical methods and those obtained by this test method is displayed in Table 3. These data were obtained by procedures outlined in Practice E 1060.

14.2 *Bias*— There is no known bias in this test method.

15. Keywords

15.1 optical emission; point-to-plane technique; spectrometric analysis; stainless steel

TABLE 2 Precision Data

Element	Sample ^A	Average Concentration, %	Standard Deviation, Single Value		Range of Duplicates, 95 %	
			Within Laboratory, %	Between Laboratories, %	(R_1) ^B , %	(R_2) ^C , %
Carbon	CT-304	0.062	0.0011	0.0033	0.0035	0.0100
	CT-305	0.067	0.0015	0.0052	0.0046	0.0159
	CT-316	0.061	0.0013	0.0015	0.0040	0.0047
Manganese	CT-304	0.765	0.0038	0.0212	0.0120	0.0643
	CT-305	1.84	0.016	0.037	0.049	0.111
	CT-316	1.66	0.012	0.022	0.036	0.067
Phosphorus	CT-304	0.025	0.0004	0.0025	0.0014	0.0077
	CT-305	0.025	0.0004	0.0010	0.0011	0.0029
	CT-316	0.031	0.0004	0.0012	0.0014	0.0036
Sulfur	CT-304	0.022	0.0007	0.0017	0.0021	0.0052
	CT-305	0.022	0.0007	0.0018	0.0023	0.0054
	CT-316	0.024	0.0006	0.0011	0.0018	0.0034
Silicon	CT-304	0.55	0.005	0.006	0.015	0.019
	CT-305	0.56	0.004	0.008	0.013	0.026
	CT-316	0.72	0.008	0.016	0.025	0.047
Copper	CT-304	0.33	0.005	0.022	0.016	0.067
	CT-305	0.29	0.005	0.022	0.016	0.019
	CT-316	0.24	0.003	0.012	0.011	0.038
Nickel	CT-304	9.63	0.055	0.237	0.17	0.72
	CT-305	11.97	0.105	0.191	0.33	0.58
	CT-316	12.54	0.073	0.242	0.23	0.73
Chromium	CT-304	18.65	0.075	0.148	0.24	0.45
	CT-305	18.55	0.107	0.108	0.34	0.33
	CT-316	17.48	0.053	0.150	0.17	0.46
Molybdenum	CT-304	0.316	0.0035	0.0082	0.0109	0.0250
	CT-305	0.470	0.0020	0.0116	0.006	0.0366
	CT-316	2.44	0.016	0.019	0.052	0.057

^A This is a composite of each of the five one-week daily results. This represents a total of 15 determinations. The results reported by each laboratory are on file at ASTM Headquarters.

^B Within-laboratory, repeatability, degrees of freedom = 10.

^C Between-laboratories, reproducibility, degrees of freedom = 14.

TABLE 3 Accuracy Data

Element	Sample	Concentration, %		Accuracy, % (95 % Confidence)		
		Determined ^A	Assumed	S_a	$S_{(W)}$	$S_{(SR)}$
Carbon	CT-304	0.062	0.063	0.0025	0.0011	0.0033
	CT-305	0.067	0.067	0.0052	0.0015	0.0052
	CT-316	0.061	0.061	0.0026	0.0013	0.0015
Manganese	CT-304	0.765	0.78	0.025	0.0038	0.0212
	CT-305	1.84	1.85	0.027	0.016	0.037
	CT-316	1.66	1.67	0.022	0.012	0.022
Phosphorus	CT-304	0.025	0.026	0.0015	0.0004	0.0025
	CT-305	0.025	0.025	0.0009	0.0004	0.0010
	CT-316	0.031	0.029	0.0021	0.0004	0.0012
Sulfur	CT-304	0.022	0.023	0.0021	0.0007	0.0017
	CT-305	0.022	0.022	0.0017	0.0007	0.0018
	CT-316	0.024	0.023	0.0018	0.0006	0.0011
Silicon	CT-304	0.55	0.56	0.013	0.005	0.006
	CT-305	0.56	0.55	0.014	0.004	0.008
	CT-316	0.72	0.69	0.013	0.008	0.016
Copper	CT-304	0.33	0.34	0.023	0.005	0.022
	CT-305	0.29	0.29	0.007	0.005	0.006
	CT-316	0.24	0.25	0.017	0.003	0.012
Nickel	CT-304	9.63	9.60	0.223	0.055	0.237
	CT-305	11.97	11.95	0.181	0.105	0.191
	CT-316	12.54	12.61	0.78	0.073	0.242
Chromium	CT-304	18.65	18.57	0.165	0.075	0.148
	CT-305	18.55	18.58	0.114	0.107	0.108
	CT-316	17.48	17.60	0.184	0.053	0.150
Molybdenum	CT-304	0.316	0.33	0.017	0.0035	0.0082
	CT-305	0.470	0.45	0.019	0.0020	0.0116
	CT-316	2.44	2.45	0.020	0.016	0.019

^A All percent concentrations consist of a 15-determination average, the "apparent" outliers were left in because a statistical evaluation of the data is not a satisfactory reason for eliminating the data values. The results for each individual laboratory is on file at ASTM Headquarters.

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