



Standard Test Method for Optical Emission Spectrometric Analysis of Aluminum and Aluminum Alloys by the Argon Atmosphere, Point-to-Plane, Unipolar Self-Initiating Capacitor Discharge¹

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1. Scope

1.1 This test method provides for the optical emission spectrometric analysis of aluminum and aluminum alloys, in cast or wrought form, for the following elements in the concentration ranges indicated:

Element	Concentration, Range, %
Silicon	0.001 to 24.0
Copper	0.001 to 20.0
Magnesium	0.001 to 11.0
Zinc	0.001 to 10.0
Tin	0.001 to 7.5
Nickel	0.001 to 4.0
Iron	0.001 to 3.5
Lithium	0.005 to 3.0
Manganese	0.001 to 2.0
Cobalt	0.001 to 2.0
Silver	0.001 to 1.5
Chromium	0.001 to 1.0
Zirconium	0.001 to 1.0
Lead	0.002 to 0.7
Bismuth	0.001 to 0.7
Cadmium	0.001 to 0.5
Beryllium	0.0001 to 0.5
Titanium	0.001 to 0.5
Antimony	0.001 to 0.5
Vanadium	0.001 to 0.15
Strontium	0.0001 to 0.07
Gallium	0.001 to 0.05
Sodium	0.0001 to 0.05
Boron	0.0001 to 0.05
Barium	0.0001 to 0.05
Calcium	0.001 to 0.05
Phosphorus	0.0001 to 0.01

1.2 This test method is suitable primarily for the control analysis of chill-cast specimens. Other forms may be analyzed, provided that (1) they are sufficiently massive to prevent undue heating, (2) they permit machining flat surfaces having a minimum diameter of approximately 15 mm, and (3) reference materials of similar metallurgical condition and chemical composition are available.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety hazard statements are given in 8.2 and Section 10.

2. Referenced Documents

2.1 ASTM Standards:

- 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 227 Test Method for Optical Emission Spectrometric Analysis of Aluminum and Aluminum Alloys by the Point-to-Plane Technique²
- E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves²
- E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)³
- E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis⁴
- E 607 Test Method for Optical Emission Spectrometric Analysis of Aluminum and Aluminum Alloys by the Point-to-Plane Technique, Nitrogen Atmosphere⁴
- E 716 Practices for Sampling Aluminum and Aluminum Alloys for Spectrochemical Analysis⁴
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data⁴

3. Terminology

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

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *alloy-type calibration*—the grouping of alloys of similar composition for the purpose of calibration so as to permit standardization with a minimum number of reference materials, for example, high silicon-aluminum casting alloys, American Aluminum Association alloy numbers 308 to 380, may be

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² *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 14.02 (excerpts in all other volumes).

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

standardized with 380 standardant.

3.2.2 *standardization*—See Terminology E 135. Two types of standardization are commonly used, as follows

3.2.2.1 *two-point standardization*—adjustment of a gain control of a channel for an individual spectral line in a manner that reproduces the readings that the high and low standardants displayed during the collection of calibration data. In computer applications, correction is done mathematically by applying a slope and intercept correction, that is, a multiplication to correct the amount of difference between the high and low standardant readings followed by the addition or subtraction of a constant to finally restore readings to expected values.

3.2.2.2 *single-point standardization*—adjustment of a channel for an individual spectral line using a single standardant. Usually the single standardant is a high reference material used to set the gain. If the analytical interest is just in low concentrations near the detection limit, a low standardant is used and either a gain or a background control may be adjusted.

4. Summary of Test Method

4.1 A unipolar self-initiating capacitor discharge is produced in an argon atmosphere between a prepared flat surface of the specimen and the tip of a semi-permanent thoriated-tungsten or other counter electrode. The radiant energies of selected analytical lines and an internal standard line are converted into electrical currents by photomultipliers. The currents are integrated during the exposure time either by charging integrating capacitors and measuring the cumulative voltages at the end of the exposure, or by interrogating the capacitors during the exposure and converting the voltages into digital counts by means of a computer. The ratios of the voltages of the analytical lines to the voltage of the internal standard line are converted into concentrations either manually

by graphs, tables, or X-Y recorders, or by a computer in accordance with Practice E 158.

4.2 Two alternative procedures for calibration may be employed. The two procedures can give the same precision, accuracy, and detection limits.

4.2.1 The first procedure, *Binary Calibration*, is used when there is a need to analyze almost the entire range of aluminum alloys. This procedure employs calibration curves for each element that cover the entire concentration range that has to be determined in all alloys. Fifty or more binary calibrants may be required for calibration. *Type* reference materials are used to adjust the concentrations read from the binary curves in order to report the correct concentrations for specific alloys.

4.2.2 The second procedure, *Alloy-Type Calibration*, is more appropriate for analyzing only a relatively few alloys of similar composition. It employs an analytical curve for each element that covers a relatively limited concentration range. Calibration may require only 5 to 20 calibrants.

5. Significance and Use

5.1 The physical and chemical properties of high-purity aluminum and aluminum alloys depend on chemical composition, which must be determined and controlled. Accurate, high-speed analysis of aluminum, before it is poured from the furnace, can prevent scrapped heats and minimize the cost of expensive alloying metals.

5.2 This test method is applicable to chill-cast specimens prepared for routine production control. It can be applied to other types of specimens if there are appropriate reference materials, or if the specimens are remelted.

6. Interferences

6.1 Known line interferences due to other elements are listed in Table 1.

TABLE 1 Analytical Lines and Concentration Ranges

Element	Wavelength In Air, Å ^{A,B,C}	Recommended Concentration Range, %	Background Equivalent, % ^D	Detection Limit, % ^{E,F}	High- Concentration Index, % ^G	Interferences
						Element, λ, Å, and k, % ^H
Silicon	I 2881.58	0.001–1.5	0.01	0.0001	1.5	Cr 2881.93
	I 2516.12	0.001–1.5	0.006	0.0001	1.5	
	I 3905.53 ^B	0.05–24	0.25	0.01	>24	Cr 3905.66 0.09
	I 2124.15	0.05–24	0.5	0.05	>24	
Iron	II 2382.04	0.001–1.5	0.015	0.0008	1.0	
	II 2599.40	0.001–1.5	0.005	0.0004		
	I 2599.57					
	I 3749.49 ^B	0.001–3.5		0.0001 ^I		
	I 4415.12	0.01–3.5		0.0004		
Copper	I 4383.55	0.005–3.5	0.05			Fe 2961.28
	I 3273.96	0.001–1.5	0.005	<0.0001	0.7	
Manganese	I 2961.17	0.05–20	0.40	0.01 ^F	>20	
	II 2247.00	0.01–5	0.03	0.0005 ^F	5	
	I 5105.54	0.05–20	0.32	0.01 ^F	>20	
	I 4030.76 ^B	0.001–2	0.028	0.0001 ^F		
	II 2593.73	0.0005–0.5	0.004	0.00005	0.2	
Magnesium	II 2933.06	0.001–2	0.006	0.0002 ^F	>1.1	
	II 3460.33 ^B	0.01–2				
	II 2795.53	0.0005–0.3	0.0006	0.00003	0.04	
	I 2852.13	0.0005–0.3	0.008	<0.0001	0.25	
	I 2776.69	0.05–11	0.08	0.01	>11	
	I 3832.31 ^B	0.01–11	0.015	0.002 ^F	>11	
	I 5183.62	0.01–11	0.02	0.002 ^F	>11	

Element	Wavelength In Air, Å ^{A,B,C}	Recommended Concentration Range, %	Background Equivalent, % ^D	Detection Limit, % ^{E,F}	High- Concentration Index, % ^G	Interferences	
						Element, λ, Å, and k, % ^H	
Chromium	I 4254.35	0.001–1	0.015	<0.0001			
	II 2677.16	0.001–1	0.004	0.0005 ^F			
	II 2766.54	0.005–1					
Nickel	I 3414.76	0.001–2	0.02	<0.0001	>2.5		
	I 3101.88	0.005–4	0.05	0.001 ^F	>5		
	II 2316.04 (2nd)	0.001–2	0.015	0.0005 ^F	<2.5		
Zinc	I 2138.56 (2nd)	0.0005–0.1	0.035	0.0001 ^F	0.05		
	I 3345.02	0.001–10.0	0.065	0.0004	>8		
	I 4810.53	0.01–10	0.07	0.001 ^F	>10		
	I 4722.16	0.01–10	0.26	0.0015	>10		
Titanium	II 3349.04	0.0005–0.5	0.004	<0.0001			
	II 3372.80	0.001–0.5	0.002	<0.0001			
	I 3635.45	0.0005–0.05	0.030	0.0003 ^F			
Vanadium	I 3183.41	0.001–0.15	0.06	0.0003 ^F			
	II 3102.30	0.001–0.15	0.014	<0.0001			
Lead	I 4057.82	0.002–0.7	0.04	0.0001		Mn 4057.92	0.01
	I 2833.06	0.002–0.7	0.07	0.002			
Tin	I 3175.02	0.001–7.5	0.04	0.0001	>10		
Bismuth	I 3067.72	0.001–0.7	0.04	0.0002			
Gallium	I 2943.64	0.001–0.05	0.015	<0.0001			
	I 4172.06 ^B	0.001–0.05					
Boron	I 2497.73 (2nd)	0.0001–0.05	0.002	0.0001 ^F		Fe 2497.82	0.001
						Mn 2497.78	0.007
Beryllium	I 2089.59 (2nd)	0.0001–0.05				Mo 2089.52	0.13
	I 2348.61	0.0001–0.05	0.001	0.00003			
	II 3130.42	0.0005–0.05	0.0035	0.0001			
	I 3321.34	0.0001–0.05		0.0001			
	I 5889.95	0.0001–0.05	0.0015	<0.0001			
Sodium	II 3933.67 ^B	0.001–0.05	0.001	0.00005		Fe 3933.61	
Zirconium	II 3391.98	0.001–1	0.02	0.001 ^F			
	II 3496.21 ^B	0.001–1	0.006	<0.0001			
Cobalt	I 3453.51 ^B	0.0001–2		<0.0001			
Cadmium	I 2288.02	0.001–0.3	0.05	<0.0001		As 2288.12	
	I 4799.92	0.005–2	0.15	0.003			
Lithium	I 6707.84	0.0001–0.02	0.0005	<0.00005		Sb 3232.50	
	I 3232.61	0.01–3				Fe 3232.79	
	I 2311.47 (2nd)	0.001–0.5	0.17	0.0002		Co 2311.66	0.6
Antimony	I 2598.06	0.001–0.5		0.0002		Fe 2598.37	
	II 4215.52 ^B	0.0001–0.1	0.0004	0.0001			
Barium	II 4554.04	0.0001–0.1	0.0004	0.0001			
Phosphorous	I 1782.31 (2nd) ^{I,J}	0.0001–0.1	0.084	0.0001			
Silver	I 3280.68	0.0005–0.1					
	I 3382.89	0.0001–0.1			>10		
	I 4668.48	0.05–1.5					
Aluminum	I 2567.99	70–100					
	I 2660.39	70–100					
	I 2372.08	70–100					

^A I = atom line, II = ion line.

^B Useful analytical lines with improved signal to background ratios due to the complete removal of C-N background by the argon atmosphere.

^C Second (2nd) indicates that the second order shall be used, where available.

^D Background Equivalent—The concentration at which the signal due to the element is equal to the signal due to the background.

^E In this test method, the detection limit was measured by calculating the standard deviation of ten concentration printouts of a specimen between three and ten times the expected detection limit.

^F See footnote E. For the values marked with an F, the available data was for a concentration greater than ten times but less than 100 times the expected detection limit.

^G High-Concentration Index—The concentration at which the tangent to the calibration curve plotted on log-log paper drops from 45° theoretical to 37°, that is, the response of I_a/I_s as ordinate versus % a as abscissa has dropped from approximately 1.0 to 0.75. It is recommended that a second, less sensitive line with close to 45° response be employed before this concentration is reached.

^H Interference Factor, k—The apparent increase in the concentration of the element being determined, expressed in percent, due to 1.0 % of the interfering element.

^I The detection limit for iron is determined more by possible segregation in the specimen and by contamination during machining than by spectrochemical sensitivity.

^J If phosphorous is to be determined, the most sensitive line appears to be 1782.31 Å in the second order and this requires a vacuum spectrometer. Optimum results are obtained by using as an internal standard a background channel profiled off the peak of phosphorous 1782 Å in the first order. The ratio of P1782.31 Å (2nd)/background near 1782 Å (1st) is plotted against % P. Even with this compensation for variability in background, alloys with highly different compositions of major alloying elements, particularly silicon, require separate reference materials and analytical curves.

7. Apparatus

7.1 Specimen Preparation Equipment:

7.1.1 *Specimen Molds* for aluminum and methods for pouring specimens are described in Practice E 716. Chill-cast

specimens, poured as described therein, shall be used in this test method.

7.1.2 *Lathe*, capable of machining a smooth, flat surface on the reference materials and specimens. A variable-speed cutter,

a cemented-carbide tool, and an automatic cross-feed are recommended.

7.1.3 Milling Machine—A vertical milling machine with *fly-cutter* and vise for holding the specimen can be used as an alternative to the lathe.

7.2 Excitation Source, capable of producing a unipolar self-initiating capacitor discharge, utilizing the parameters described in 13.2 or equivalent, and in accordance with Practice E 172. Each high-frequency wave train is fully rectified, so that the specimen is always the cathode, and only specimen material is introduced into the analytical gap. The counter electrode is not attacked, and can be used for analyzing many specimens.

7.3 Excitation Chamber, similar to that shown in Fig. 1, for mounting a machined, flat surface of the specimen so that it forms a seal to exclude atmospheric oxygen from the discharge. The excitation chamber shall be provided with a counter electrode holder and with a clamp to hold the specimen firmly against the upper plate. The upper plate shall be inclined at an angle of 10 to 15° to the light path. Depending upon the manufacturer, the excitation chamber may require water-cooling, or a diaphragm may be inserted in the chamber to occlude any radiation from the hot specimen or the counter electrode, or both may be required. The excitation chamber shall be designed so that it can be flushed automatically with argon gas. Argon gas shall be introduced just inside the fused quartz window, flowing toward the discharge, to prevent any of the metal powder produced at the discharge from coating the inside of the window. Argon also may be introduced around the counter electrode, but the flow rate shall not confine the discharge to an area less than 5 mm in diameter, to provide adequate sampling of the specimen. The argon, with most of the metal dust, shall be exhausted to the atmosphere from the back or side of the chamber.

7.4 Gas Flow System, to supply pure argon gas (99.995 %) to the excitation chamber. The gas shall be delivered by a flow system as described in Practice E 406 from either high-purity compressed gas, or liquid argon bottles, or from a welding

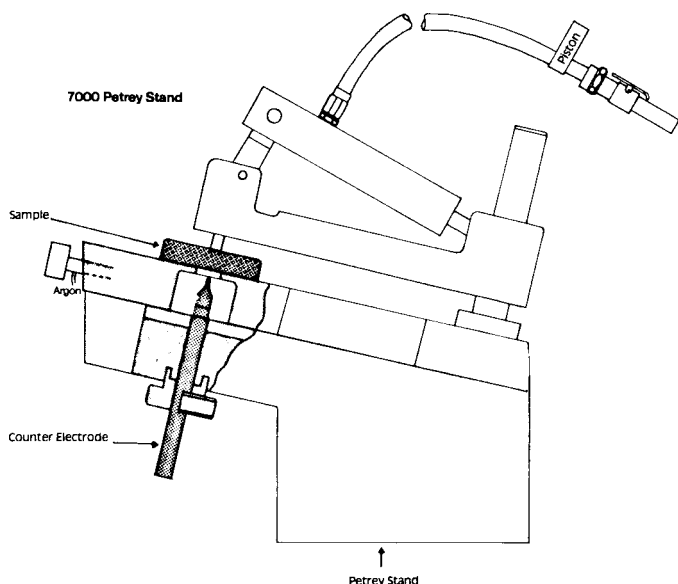


FIG. 1 Excitation Stand

grade supply that has been purified to the required 99.995 % level. The system shall include: a two-stage regulator of all-metal construction with two pressure gages; copper tubing with all-metal seals; a solenoid and valve operated automatically by the control system, to start the full argon flow for the *pre-flush* and stop it at the end of the exposure; and a needle valve to maintain a very slow bleed of argon through the excitation chamber when it is not in active use (Note 1). The copper tubing shall be kept as short as possible—preferably only a few feet. All connections shall be leak-free. A flow gage is required to check the flow rates. The flow gage need not be incorporated in the system permanently, but may be connected at the outlet temporarily while initiating adjusting the operating flow, and then can be removed. This keeps the system as simple as possible and eliminates a possible source of organic contaminants or leaks.

NOTE 1—All-metal connections are required because the discharge is adversely affected by organic contamination, or by as little as 2 ppm of oxygen or a few ppm of water vapor.

7.5 Spectrometer, with a reciprocal linear dispersion of 10 Å/mm, or better, and a combination of entrance and exit slit widths that provides a working resolution of at least 0.7 Å (Note 2). The wavelength coverage must include the analytical lines required for the needed concentration ranges, as listed in Table 1.

NOTE 2—According to Practice E 380, the Angstrom, Å, is a deprecated unit. However, it is employed here for the convenience of the users of this test method who may wish to refer to the wavelength tables which contain Angstrom units. An *Angstrom* is defined as 0.10 of a nanometre.

NOTE 3—If phosphorus is to be measured, the optimum line is 1782 Å, which is strongly absorbed by oxygen; therefore, a vacuum spectrometer is required, operating at a pressure of 25 microtorr or less.

NOTE 4—The background equivalents and detection limits listed in Table 1 can be attained with a reciprocal linear dispersion of 5.4 Å/mm and a working resolution of 0.35 Å, using an entrance slit width of 25 μm and an exit slit width of 50 μm.

7.6 Measuring System, consisting of photomultipliers having individual voltage adjustments, integrating capacitors, or digital counting circuitry, an amplifier and some form of readout system. The system also may contain the program circuitry that times the flush, pre-burn and exposure intervals, turns the source on and off, etc. The measuring system may read only intensity ratios (voltage ratios), which then have to be converted into concentrations manually, or the system may use a computer or programmable calculator to convert intensity ratios into concentrations.

7.6.1 Manual Measuring System, with an individual voltage or amplifier gain control and a zero adjustment control for each channel, to permit standardization as required. Note 5

NOTE 5—The gain and zero controls can be omitted if the analytical program is restricted to a few alloy types, the concentration ranges in each are restricted, and the gain and background levels do not vary widely from day to day. Then some mechanism for single point standardization, such as a calculating board with movable concentration scales, may be used to compensate for instrumental drift.

7.6.1.1 Intensity Readout System, which displays the ratio of the radiant energy of the analytical line to the radiation of the internal standard line, either as a digital number read visually or typed automatically, or as a deflection on a strip chart

recorder or X-Y recorder.

7.6.1.2 *Graphs, Flip Charts, or Calculating Boards*, used in conjunction with an intensity readout system, to convert digital intensity ratios into concentrations. With a strip chart or X-Y recorder, concentration scales may be preprinted on the paper, as illustrated in Test Method E 227.

7.6.2 *Computer Readout System or Programmable Calculator*, which stores the analytical curves in memory and converts the intensity ratios into concentrations (see X1.1 of Appendix X1). A printout of the analysis is recommended because it provides a permanent record and eliminates clerical errors, but display of results on a video scope is acceptable. Manual adjustments are not needed during standardization because gain and background adjustment factors can be calculated automatically.

8. Materials

8.1 *Counter Electrode*—The preferred counter electrode, consisting of a needle-point thoriated-tungsten wire mounted in a copper rod, is illustrated in Fig. 2(a). An alternative counter electrode, a 6.3-mm diameter tungsten or silver rod with a conical tip, is illustrated in Fig. 2(b).

8.2 *Argon Gas*, of 99.995 % purity. Cylinders of either compressed argon gas or liquid argon may be employed. Alternatively, argon gas of the requisite purity can be produced from a welding grade supply by passing it through a titanium furnace which removes oxygen, nitrogen, water, and oil vapors, and other impurities. See Practice E 406 for precautions to be used in handling gases.

NOTE 6—A magnesium furnace is not acceptable because it will introduce variable magnesium contamination.

9. Reference Materials

9.1 *Calibrants* shall be homogeneous and free of cracks or porosity, with a metallurgical condition similar to that of the unknown specimens to be analyzed. They shall be used to

produce the analytical curves for various elements being determined.

9.1.1 If an alloy-type calibration structure is used, it is desirable to have at least four calibrants for each element (see 3.2.1). The concentrations should be fairly evenly spaced over the anticipated analytical range, to establish a statistically sound smooth curve through all points.

9.1.1.1 If analytical lines are to be used above the concentrations at which they may start to self-absorb, it is necessary to have more calibration reference materials in the self-absorbed region, to define the shape of the curve.

9.1.2 The composition of the calibrants shall have been determined chemically at least to the accuracy required for the final analytical results. A few *benchmark Certified Reference Materials* are available from the National Institute of Standards and Technology⁵ and many other reference materials are available commercially in both chill-cast and wrought forms.⁶

9.1.3 For several trace elements, available reference materials contain variable concentrations of the trace element in a typical alloy of constant composition. These reference materials can be used for establishing an analytical curve, but will not reveal potential interferences from nearby lines of other elements, or matrix effects that change the background or response. For optimum usefulness, several of the calibrants should have concentrations of the other elements that cover the ranges to be expected in the unknown specimens.

NOTE 7—Fortunately with aluminum, there are relatively few interferences because the aluminum spectrum itself and the spectra of the major alloying elements (silicon, copper, magnesium, zinc, and tin) are simple. The alloying elements with complex spectra (nickel, manganese, iron, cobalt, chromium, zirconium, titanium, and vanadium) are present at concentrations so low that only the more intense lines can cause interferences.

NOTE 8—Reference materials and specimens modified with sodium may produce blacker burns with deeper penetration of the spark into the surface. This may result in a drop in the intensity of the aluminum internal standard below its normal level, and a corresponding increase in the intensity ratios for the analytical lines. This, in turn, may produce concentration readings for silicon that are too high by 0.3 % at the 5 % to 7 % level, and a similar increase for other elements. If nonmodified specimens are to be analyzed with calibration curves established with modified reference materials (or vice versa), corrections for such effects shall be applied.

9.2 Standardants:

9.2.1 *High-Concentration Standardants*— These may be selected commercially available reference materials or, preferably, reference materials prepared *in-house*, that have been tested for homogeneity and have among them concentration levels near or above the median concentration for each element. A single standardant for each matrix is preferable, but several may be used. The exact composition need not be known, since the standardants shall be used only to adjust the instrument to reproduce the intensity ratios which they produced at the time the analytical curves were established.

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

⁶ Aluminum reference materials are available from Aluminum Company of America, Technology Marketing Division, 18th Floor, Alcoa Building, Pittsburgh, PA 15219, and Analytical Reference Materials International, Inc., P.O. Box 2246, Evergreen, CO 80439-2246.



(a) Needle-Point, Thoriated-Tungsten Wire Mounted in Copper Rod (b) Tungsten or Silver Rod with Conical Tip

FIG. 2 Counter Electrodes

9.2.2 *High-Purity or Blank Standardants*— These shall be homogeneous, with the lowest available concentrations of the elements being determined, but their exact compositions need not be known. Usually, the background readings of a spectrometer remain relatively constant. Therefore, a blank standardant for an element does not need to be used in routine standardization unless the lowest concentration that needs to be determined is within ten times the detection limit of that element. For specimens with such low concentrations, single point standardization, either with the blank or another specimen, may give more consistent results.

10. Safety Precautions

10.1 All high-voltage sources can give painful shocks if the operating personnel come in contact with the high voltage when the source is turned on. The excitation chamber shall be enclosed and shall be provided with a safety interlock so that the source cannot be turned on until the door is closed. Access to the power supply shall be permitted only by removing panels which contain safety interlocks or require the use of tools.

10.2 Fumes of fine metallic powders exhausted from the excitation chamber can be poisonous if specimens contain significant levels of heavy metals such as cadmium or lead. Such metals shall be trapped by bubbling the exhaust through water or a filter system, or the exhaust shall be vented to the atmosphere at a nonhazardous location.

11. Sampling

11.1 For the sampling of molten aluminum metal and the casting of disk specimens, see Practice E 716.

12. Preparation of Reference Materials and Specimens

12.1 *Preparation of Reference Materials*— The reference material shall be machined in the same manner as the specimens.

12.2 *Preparation of Specimens*—For the preparation of chill-cast disk specimens and other types of aluminum specimens, see Practice E 716.

NOTE 9—For optimum precision and accuracy, the reference materials and specimens shall have been freshly machined no longer than 1 h before use, to avoid the formation of aluminum oxide.

13. Preparation of Apparatus

13.1 Prepare and operate the spectrometer in accordance with the manufacturer’s instructions.

NOTE 10—It is not within the scope of this test method to prescribe minute details relative to the preparation of the apparatus. For a description and specific details concerning the operation of a particular spectrometer, refer to the manufacturer’s manual.

13.1.1 Program the spectrometer to accommodate the internal standard line or lines (or background settings) and the pertinent analytical lines listed in Table 1. Connect the photomultipliers, capacitors, and related measuring system.

NOTE 11—The argon atmosphere eliminates the molecular bands of cyanogen (CN) that are produced with excitations in air (see Test Method E 227) or nitrogen (see Test Method E 607). The absence of CN bands provides improved signal to background ratios for some analytical lines and permits the use of other lines. The lines listed have proven satisfactory for the elements and concentration ranges prescribed in the Scope. Other internal standard and analytical lines may be used, provided it is shown that the results obtained are comparable.

13.1.2 Profile the spectrometer in accordance with the manufacturer’s instructions (see 13.1).

13.1.3 Position or test the position of the spectrometer exit slits, secondary mirrors, if used, and photomultipliers to ensure that the peak radiation passes through each slit and illuminates the centers of the photomultipliers. This shall be done initially and as often as necessary thereafter to maintain proper alignment.

NOTE 12—Modern direct-reading spectrometers should show little drift in the response of channels with time. However, if at any time the gain adjustment of any channel drops below 0.5 or increases above 2, or if the background reading changes more than 0.5 to 2X, that channel should be checked for alignment or deterioration of components. It is recommended that all gains and backgrounds be checked 1 month after installation and thereafter at least once a year as a formal inspection procedure.

13.2 *Electrical Parameters*—Various sets of electrical parameters in a rectified-capacitor discharge source produce somewhat similar high-frequency oscillatory unidirectional waveforms. These have been found to give comparable analytical performance. Use one of the sets of electrical parameters given in Table 2.

13.3 *Typical Exposure Conditions*—Exposure conditions

TABLE 2 Electrical Parameters

	A-1	A-2	B-1	B-2	Preburn	C-1		C-2	
						High Alloys	99 + %	Al	
Secondary rms voltage, V	20 000	20 000
Peak volts, V						950			
Secondary capacitance, µF	0.010	0.015	10	10	7	0.5		0.25	
Main inductance, µH	300	210	100/200	1000/2000	55	55		5	
Rectifying bridge inductance, µH	15	20	
Resistance in series with gap, Ω	residual	residual	2.2	2.2	
Breakdown voltage of gap, V	13 500	13 500	
R-f current, A	4.2	4.6	
Peak current, A						100		275	
Discharges/s (60~ supply)	240	240	120	120		120		120	

will depend on the specific equipment, and a tradeoff that the individual laboratory selects between speed of analysis and slightly improved precision and accuracy with longer times. Typical time ranges are:

Flush period, s	2 to 7
Preburn period, s	2 to 10
Exposure period, s	5 to 20

13.4 *Gas Flow*—Gas flow rates will vary from laboratory to laboratory, but shall be in the following ranges:

Standby, L/min (standard ft ³ /h)	0.05 to 0.09 (0.1 to 0.2)
During exposure, L/min (standard ft ³ /h)	4.5 to 8 (9 to 15)

The compressed argon gas cylinder shall be replaced when the pressure falls to 7 kgf/cm² (100 psi). See Practice E 406 for precautions to be used in handling gases.

13.5 *Electrode System*—Position the flat, prepared surface of the specimen on the top of the excitation chamber so that the discharge will impinge on the area lying at least 5 mm from the edge of the specimen. The specimen shall seal the 8 to 15 mm opening in the top of the excitation chamber. The specimen serves as one electrode, the cathode. Mount the counter electrode opposite the specimen. Use only one type of counter electrode for measurements on all reference materials and specimens. The unidirectional discharge does not attack the counter electrode, so that it can be used for many burns before refinishing or replacement is necessary. Adjust the counter electrode to provide an analytical gap of 3.0 ± 0.1 mm.

NOTE 13—Physically cleaning the counter electrode after each exposure, using a motor-driven wire brush, can prolong the time before a major cleaning or replacement is needed.

NOTE 14—It is essential that the operator learns to distinguish between *good burns* and *bad burns*, which are usually due to an air leak between the specimen and the top of the excitation chamber or sometimes to air included in a crack in the specimen. A *good* burn will have a deeply pitted area in the center, surrounded by a blackish ring, usually wider opposite the argon inlet. A *bad* burn will have shallow pittings, surrounded by a whitish or silvery ring. Reject all bad burns.

13.5.1 Except for the few seconds required to change specimens, the opening in the top of the excitation chamber shall be covered with a scrap specimen or other seal at all times.

NOTE 15—When the relative humidity is greater than 80 %, an excitation chamber left uncovered for several minutes may have to be flushed for a quarter of an hour or more before excitations will return to normal.

13.6 *Warm-Up*—After any prolonged intervals of nonuse of the instrument, warm up the source, excitation chamber, and gas flow system by burning an expendable specimen until repeatable readings are obtained.

14. Calibration

14.1 *Obtaining Calibration Data*—The following procedure is designed to minimize the effects of any possible instrumental drift on the consistency of the data used for preparing analytical curves. See Appendix X1 for additional information concerning the acquisition of calibration data.

14.1.1 Profile and warm up the instrument.

14.1.2 Normalize the instrument for the elements to be calibrated with the first five or six calibrants, using at least six

and preferably eight burns for each standardization reference material. Then burn each calibrant four times. Burn the standardants for the next five or six calibrants. Normalize for any element that has shown a drift greater than $2s$ (as measured in Note 18), or for any element not covered by the first normalization. Burn the next five or six calibrants. Repeat the process of burning the standardants, normalizing where appropriate, and burning the next five or six calibrants, until all calibrants have been burned.

14.1.3 Repeat the procedure described in 14.1.2, except burn the calibrants in the reverse order.

14.1.4 Repeat the procedure described in 14.1.2, except this time start each group of five or six calibrants with the third or fourth calibrant in that group.

14.1.5 Repeat the procedure described in 14.1.2, except burn the calibrants in the reverse order starting each group of five or six calibrants with the fourth or third calibrant in that group.

14.1.6 Average the intensity ratio readings for all sixteen burns of each calibrant.

NOTE 16—Normalizing the instrument while burning the calibrants has been helpful in establishing analytical curves that will provide concentrations accurate to better than 1 % of the stated value for concentrations above 1 %. It is not required if less accuracy is acceptable.

14.2 *Calibrating the Instrument:*

14.2.1 For an instrument with a manual readout, for each element plot the measured intensity ratio readings against the stated concentrations or concentration ratios. Draw the optimum theoretical analytical curve through the plotted points. Refer to Practices E 158 and E 305 for guidance.

14.2.1.1 Use these curves to prepare the flip charts, calculating boards, or calibrated strip charts or X-Y recorders that will be used to convert intensity ratios into concentrations.

14.2.1.2 For an instrument with a computer or programmable calculator that requires the manual drawing of analytical curves, follow the manufacturer's instructions to make the appropriate entries.

14.2.2 For an instrument with a computer that calculates the analytical curves from the measured intensity ratios and the stated concentrations or concentration ratios, follow the manufacturer's instructions to enter the data and obtain the analytical curves.

14.2.2.1 With such a computer, particularly if the software permits use of a fourth or higher power polynomial, recognize that accurate analysis of unknown specimens requires more than a report of a good fit between the calculated and stated concentrations for the calibration reference materials. The computer may have calculated a curve that weaves in and out between the points for the calibrants. With such a curve, seriously erroneous analyses may be obtained for unknown specimens with concentrations between the calibrants. If the computer has a graphics feature, use it to plot the curve it has calculated; otherwise, plot manually the curves the computer has calculated to ensure that they are theoretically correct. Refer to Practice E 158.

14.3 *Verifying the Accuracy of Calibration*—Standardize the instrument and reburn the calibrants as unknowns and compare the measured concentrations with the stated values.

Check for and correct clerical errors and biases.

14.3.1 If individual calibrants give consistently high readings for an element, check for possible interferences from other elements. Calculate and enter appropriate correction factors in accordance with Practice E 158.

15. Standardization

15.1 *Preparation for Standardization*—All future accuracy of analyses will depend on self-consistent intensity ratio readings, free from drift with time, for all the reference materials used for calibration. Therefore, the instrument shall be normalized as needed while the calibration data are being generated (see Appendix X1).

NOTE 17—Unfortunately, direct readers are usually calibrated shortly after they have been installed in the laboratory. Usually they have not yet become as stable as they will be after a month or so, and consequently, the readings obtained may show significant drift. The process of calibration will probably take several days. Accordingly, to correct for drift, it is essential to select prospective standardants and determine their uniformity before starting the calibration process.

15.2 *Checking Homogeneity of the Standardants*—Using the conditions given in Section 13, burn the standardants selected in accordance with 9.2 at least ten times each and preferably sixteen times. The relative standard deviations of the internal standard intensities shall be less than 1.5 %, while the relative standard deviations of the intensity ratios of the analytical lines divided by the internal standard shall be less than 1 % (Note 18). If one or more of the standardants do not meet these criteria, this is an indication that they are not sufficiently homogeneous. Select alternative reference materials and qualify them.

NOTE 18—The *standard deviation* (s) and the *relative standard deviation* (RSD %) are calculated as follows (see Practice E 876):

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

where:

d = difference between individual measurements and the mean, and

n = number of individual measurements.

$$RSD \% = \frac{100}{\bar{X}} s \quad (2)$$

where:

\bar{X} = the average of the individual measurements.

15.3 *Number of Standardization Burns*—It is recommended that the number of burns of the standardants be at least twice the number of burns for the reference materials or specimens

that are being standardized. For unknown specimens where usually two burns are used, this means at least four burns of the standardants. During calibration, eight burns of the standardants are recommended.

15.4 *Recording or Entering the Standardization Readings:*

15.4.1 For readout systems that have to be standardized manually, record the average readings for each element.

15.4.2 For computer readout systems, enter the high and low readings into computer memory.

16. Procedure for Analyzing Specimens

16.1 *Excitation*—Burn the specimens in accordance with the conditions given in 13.2-13.5.

16.2 *Replicate Burns*—Burn the specimens one to five times, depending upon the homogeneity of the metal and the confidence level required. A single burn frequently is employed for primary aluminum or for low-concentration alloys, where the specimens usually are homogeneous. Two to four burns are recommended for most alloys, where homogeneity is fair and accuracy becomes important. In alloys that are noted for segregation, as many as five burns may be needed.

16.2.1 The determinations from all burns should be averaged unless a burn produces a really abnormal internal standard count, or appears visually to be *bad* (that is, having a silvery rather than a blackish ring surrounding the pitted area). When a burn is rejected, it may be replaced with another burn in order to maintain the normal number of burns to be averaged.

17. Calculation of Results

17.1 If the readout is manual, record the intensity ratios and convert them into elemental concentrations from the analytical curves, flip charts, a calculating board, or preprinted concentration scales. If a computer readout is available, read or print the concentrations directly.

18. Precision and Bias

18.1 *Precision:*

18.1.1 *Repeatability*—Precision data based on ten successive measurements on a single reference material within one laboratory are given in Table 3 for some of the analytical lines.

18.1.2 *Reproducibility*—Testing for precision between laboratories is currently being conducted.

18.2 *Bias*—Interlaboratory testing for bias is currently being conducted.

19. Keywords

19.1 aluminum and aluminum alloys; analysis; spectrochemical; spectrochemical analysis

TABLE 3 Precision Data (Repeatability)

Element	Wavelength in Air, A ^A	Low Concentration		High Concentration	
		Concentration, %	RSD, % ^B	Concentration, %	RSD, % ^B
Silicon	I 2881.58	0.005	8.6	1.2	0.86
	I 2516.12	0.005	9.1	1.2	0.93
	I 3905.53	1.1	0.96	11.3	0.51
	I 2124.15	0.052	3.0	11.3	0.46
Iron	II 2382.04	0.20	1.2	1.2	1.5
	I 2599.57				
Copper	II 2599.40	0.10	1.5	0.60	0.53
	I 3247.54	0.0034	3.0		
Manganese	I 3273.96	0.001	7.9	4.8	0.76
	I 5105.54	0.50	1.7		
	I 2961.17			4.8	0.49
	II 2247.00			4.8	0.45
Magnesium	I 4030.76	0.0015	4.0		
	II 2593	0.10	0.6	0.40	1.1
	II 2933.06	0.035	0.69	1.10	0.45
Chromium	II 2795.53	0.001	2.6	0.20	1.4
	I 2852.13	0.15	0.40	1.6	1.5
	I 2776.69			3.0	0.70
	I 3832.31	0.20	0.95	3.0	0.50
Nickel	I 5183.62	1.6	0.31	3.0	0.86
	I 4254.35	0.0012	4.7	0.3	0.31
Zinc	II 2677.16			0.31	0.68
	I 3414.76	0.0019	3.6	0.40	0.52
Titanium	II 2316.04 (2nd)	0.039	1.4	0.40	1.3
	I 2138.56	0.10	0.82		
	I 3345.02	0.001	36	6.6	0.52
	I 4810.53	0.0023	8.7	3.52	0.40
Vanadium	I 4722.16	0.003	5.1	6.11	0.33
	II 3349.04	0.028	0.65	0.45	0.66
	II 3372.80	0.0037	0.61		
Lead	I 3635.45			0.10	0.22
	I 3183.41	0.04	0.75		
Tin	II 3102.30	0.0057	1.4	0.018	0.84
	I 4057.82	0.0018	13	0.03	1.6
Bismuth	I 3175.02	0.04	1.2	7.42	2.2
	I 3067.72	0.001	18	0.1	1.9
Gallium	I 2943.64	0.015	0.48	0.04	0.75
	I 2497.73	0.0002	2.7	0.019	1.5
Beryllium	I 2348.61	0.001	1.2	0.005	1.2
	II 3130.42	0.002	3.6	0.01	1.0
Sodium	I 5889.95	0.0006	19	0.015	5.6
	Calcium	II 3933.67	0.013	5.9	
Zirconium	II 3391.98	0.05	1.3	0.11	0.70
	II 3496.21	0.001	4.0		
Cadmium	I 2288.02	0.0006	17		
	Lithium	I 6707.84	0.0001	14	
Antimony	I 3232.61				
	I 2311.47 (2nd)	0.0007	18	0.0041	8.8
Phosphorous	I 1782.31 (2nd)	0.0004	27		

^A I = atom line, II = ion line.

^B The relative standard deviation (RSD %) is calculated as follows:

$$RSD \% = \frac{100 \sqrt{\sum d^2 / (n - 1)}}{\bar{X}}$$

where:

 \bar{X} = average concentration, %,

 d = difference between the individual results and \bar{X} , and

 n = number of determinations. The data are based on ten successive readings.

APPENDIX

(Nonmandatory Information)

X1. CALIBRATION AND STANDARDIZATION

X1.1 Advantages of Computer Readout Systems

X1.1.1 Computers or programmable calculators make it practical to employ concentration ratio plots for calibration curves, which compensate for significant variations in the intensity of the aluminum internal standard line as major alloying elements vary over wide concentration ranges (see Practice E 158). Concentration ratio calculations make it possible to report the concentration of the aluminum as well as the major, minor, and trace elements, which can be valuable for high-purity aluminum.

X1.1.2 A computer makes it possible to correct for interferences from other elements, such as the interference of iron, 2598.37 Å, on antimony, 2598.06 Å.

X1.2 Universal Calibration Versus Matrix Calibration

X1.2.1 Either calibration procedure can be employed with this test method, as described in X1.3.

X1.2.1.1 *Universal Calibration Curves* are a set of curves covering the complete range of concentrations expected for each element in all the aluminum alloys to be analyzed. For standardization, several reference materials are employed to ensure that the high ends of each calibration curve will be returned to their original readings, and a single high-purity reference material is used to set the low ends of the curves. For each major alloy type, the calibration curves are adjusted by burning a *type* reference material in order to obtain the correct concentrations for various alloys.

X1.2.1.2 With the *Alloy-Type Calibration* procedure, a set of calibration curves covers a limited range of concentrations for a few specific alloys. Different but simple curves covering a relatively short concentration range are used for each major alloy. Usually ten matrices will encompass all the present commercial aluminum alloys, organized so that one or two standardants are sufficient for each of the matrices described in X1.4.

X1.3 Four Different Methods of Calibration and Standardization

X1.3.1 For the analysis of aluminum and aluminum alloys, four different methods of calibration and standardization are being used, as listed below. Equivalent accuracy can be obtained with each method, when properly employed. The first two are used primarily for relatively simple analytical programs, covering only a few alloy types. The second two are appropriate for more complex analytical programs.

X1.3.1.1 The instrument may have been precalibrated by the manufacturer, using a wide range of reference materials and concentration or concentration ratio calibration plots, or using sets of binary alloys for the different elements and concentrations or concentration ratio plots. A single standardant is employed for each alloy type, with a composition near the normal or target concentrations for all elements. The computer applies the displacement appropriate to that alloy over the relatively short portion of the overall calibration curve that will be used. Standardization becomes a short and simple process.

X1.3.1.2 For the analysis of a few alloys with closely similar compositions, such as the 319, 355, and 356 casting alloys, or the 1000 and 6000 Series wrought alloys with 97 + % aluminum, it may be possible to employ only eight to

twelve calibrants which will define the calibration curves for all required elements over their relatively restricted concentration ranges. Standardization may be possible with one or two reference materials of the highest concentration alloy which have the major elements near the top of their range and the minor and trace elements near or above the middle of their normal ranges. Alternatively, it may be desirable to use separate standardization reference materials for each alloy type within the matrix. In either case, standardization requires only two or three minutes and can be repeated easily if there is reason to suspect significant drift.

X1.3.1.3 Sets of binary calibrants or a wide range of calibrants can be used to establish a calibration curve for each element that will cover the entire concentration range expected in all samples. Concentration or concentration ratio plots can be employed. The computer stores a single curve for each element. Standardization is practiced customarily at the start of each new shift (or operator), using several high reference materials that between them cover the high ranges for all elements. Usually a single high-purity reference material suffices to standardize the low ends of the curves for all elements. Normally standardization will require ten to fifteen minutes. In routine use, whenever a different alloy type has to be analyzed, a *type* reference material will be burned and the computer will apply lateral shifts to the standardized curves, appropriate to each element in that alloy. This will require only a minute or two.

X1.3.1.4 The whole array of aluminum alloys can be divided into eight or ten matrices, as listed in X1.4. Each matrix is calibrated as in X1.3.1.2 and the computer stores a different set of calibration curves for each matrix. Standardization for each matrix is similar to that described in X1.3.1.2 and usually will be practiced during each shift normally just before the first specimen of a particular matrix is expected in the laboratory.

X1.4 Matrix Structures Appropriate for Aluminum Alloys

X1.4.1 Appropriate matrix calibration structures for use as described in X1.3.1.2 and X1.3.1.4 are as follows:

X1.4.1.1 *High-Purity Aluminum*, with all impurity elements less than 0.6 %, including the 1000 Series wrought alloys.⁷

X1.4.1.2 *High-Copper (up to 10 %), Relatively Low Silicon (up to 4 %) Aluminum Alloys*, consisting of the 2000 Series wrought alloys or 200 Series casting alloys⁷ (except for the 242 alloy with high magnesium and nickel, which requires a separate standardant). Two separate matrices will be required if both the 2000 Series wrought alloys and 200 Series casting alloys have to be analyzed.

X1.4.1.3 *High-Silicon (up to 12 %), Relatively Low Copper (up to 4.5 %) Aluminum Alloys*, consisting of the 300 and 400 Series casting alloys (except for the 332 alloy with high magnesium and nickel, which requires a separate standardant).

X1.4.1.4 *High-Silicon Aluminum Alloys*, with silicon in the 12 to 24 % range.

⁷ The 1000 to 7000 Series wrought alloys and 200 to 800 Series casting alloys specified throughout X1.4 are in accordance with the American Aluminum Association numbering system.

X1.4.1.5 *The 242 and 382 High-Temperature Aluminum Alloys* can be combined into a single matrix, with a 382 standardization reference material, but two separate matrices give better accuracy.

X1.4.1.6 *High-Magnesium (up to 10 %) Aluminum Alloys*, with low concentrations of other elements, consisting of the 5000 Series wrought alloys and 500 Series casting alloys.

X1.4.1.7 *Low-Alloy Aluminum*, with all alloying elements less than 2.5 %, consisting primarily of the 6000 Series wrought alloys.

X1.4.1.8 *High-Zinc Aluminum Alloys*, consisting of the 7000 Series wrought alloys and 700 Series casting alloys.

X1.4.1.9 *High-Tin (above 6 %) Aluminum Alloys* consisting of the 800 Series casting alloys.

X1.4.1.10 *Identification Matrix*, with all elements from 0.01 % to the highest concentration likely to be encountered for each element, which can be useful for identifying scrap, mixed stock, or a completely unknown specimen.

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