Designation: E1251 – 24

Standard Test Method for Analysis of Aluminum and Aluminum Alloys by Spark Atomic Emission Spectrometry[1]

This standard is issued under the fixed designation E1251; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method describes the analysis of aluminum and its alloys by spark-atomic emission spectrometry (Spark-AES). The aluminum specimen to be analyzed may be in the form of a chill cast disk, casting, foil, sheet, plate, extrusion, or some other wrought form or shape. The elements covered in the scope of this method are listed as follows.

Element	Tested Mass Fraction Range (Wt %)
Antimony	0.001 to 0.003
Arsenic	0.001 to 0.006
Beryllium	0.0004 to 0.24
Bismuth	0.03 to 0.6
Boron	0.0006 to 0.009
Calcium	0.0002 to 0.04
Chromium	0.001 to 0.23
Cobalt	0.4 to 1.60
Copper	0.001 to 5.5
Gallium	0.02 to 0.11
Iron	0.2 to 0.5
Lead	0.04 to 0.6
Lithium	0.0003 to 2.1
Magnesium	0.03 to 5.4
Manganese	0.001 to 1.2
Nickel	0.005 to 2.6
Phosphorus	0.003 to 0.017
Silicon	0.07 to 16
Sodium	0.003 to 0.02
Strontium	0.03 to 11.0
Tin	0.03 to 21.0
Titanium	0.001 to 0.12
Vanadium	0.002 to 0.022
Zinc	0.002 to 5.7
Zirconium	0.001 to 0.12

NOTE 1—The mass fraction ranges given in the scope were established through cooperative testing (ILS) of selected reference materials. The range shown for each element does not demonstrate the actual usable analytical range for that element. The usable analytical range may be extended higher or lower based on individual instrument capability, spectral characteristics of the specific element wavelength being used, and the availability of appropriate reference materials.

Warning—Mercury (Hg) is intentionally not included in the scope. Analysis of Hg in aluminum by Spark-AES is not recommended. Accurate analysis of Hg using this technique is compromised by the presence of an intense iron interference. Inaccurate reporting of Hg due to these interference effects can jeopardize the current designation of aluminum production as a mercury-free process. To demonstrate compliance with legislated Hg content limits, use of an alternate method capable of analysis with a minimum reporting limit of 0.0001% or lower is recommended. Suitable techniques include but are not limited to GD-MS, XRF, cold vapor AA, and ICP-MS.

1.2 This test method is suitable primarily for the analysis of chill cast disks as defined in Practices E716. Other forms may be analyzed, provided that: *(1)* they are sufficiently massive to prevent undue heating, *(2)* they allow machining to provide a clean, flat surface, which creates a seal between the specimen and the spark stand, and *(3)* reference materials of a similar metallurgical condition and chemical composition are available.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific safety and health statements are given in Section 10.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

B985 Practice for Sampling Aluminum Ingots, Billets, Castings and Finished or Semi-Finished Wrought Aluminum Products for Compositional Analysis

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[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.04 on Aluminum and Magnesium.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E305 Practice for Establishing and Controlling Spark Atomic Emission Spectrochemical Analytical Curves

E406 Practice for Using Controlled Atmospheres in Atomic Emission Spectrometry

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E716 Practices for Sampling and Sample Preparation of Aluminum and Aluminum Alloys for Determination of Chemical Composition by Spark Atomic Emission Spectrometry

E826 Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry (Withdrawn 2023)[3]

E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis (Withdrawn 2019)[3]

E1507 Guide for Describing and Specifying the Spectrometer of an Optical Emission Direct-Reading Instrument

E2972 Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials

2.2 *ANSI Standard:*[4]

ANSI H35.1/H35.1M American National Standard Alloy and Temper Designation Systems for Aluminum

3. Terminology

3.1 *Definitions*—For definitions of terms used in this Standard, refer to Terminology E135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *alloy-type calibration*—calibration curves determined using calibration materials from alloys with similar compositions.

3.2.2 *binary-type calibration*—calibration curves determined using binary calibration materials (primary aluminum to which has been added one specific element).

3.2.3 *global-type calibration*—calibration curves determined using calibration materials from many different alloys with considerable compositional differences.

3.2.4 *two-point drift correction*—the practice of analyzing high and low drift correction materials for each calibration curve and adjusting the intensities obtained back to the values obtained on those particular drift correction materials during the collection of the calibration data. The corrections are calculated mathematically and are applied to both the slope and intercept. Improved precision may be obtained by using a multi-point drift correction as described in Practice E1329.

3.2.5 *type standardization*—mathematical adjustment of the calibration curve's slope or intercept using a single reference material at or close to the nominal composition for the particular alloy being analyzed. For best results, the reference material being used should be within ±10 % of the composition (for each respective element) of the material being analyzed.

4. Summary of Test Method

4.1 A controlled electrical discharge is produced in an argon atmosphere between the prepared flat surface of a specimen and the tip of a counter electrode. The energy of the discharge is sufficient to ablate material from the surface of the specimen, break the chemical or physical bonds, and cause the resulting atoms or ions to emit radiant energy. The radiant energies of the selected analytical wavelengths and the internal standard wavelength(s) are converted into electrical signals by either photomultiplier tubes (PMTs) or a suitable solid state detector. The detector signals are electrically integrated and converted to a digitized value. The signals are ratioed to the proper internal standard signal and converted into mass fractions.

4.2 Three different methods of calibration defined in 3.2.1, 3.2.2, and 3.2.3 are capable of giving the same precision, accuracy, and detection limit.

4.2.1 *Binary calibration* employs calibration curves that are determined using a large number of high-purity binary calibration materials. This approach is used when there is a need to analyze almost the entire range of aluminum alloys. Because binary calibration materials may respond differently from alloy calibration materials, thus the latter are used to improve accuracy by applying a slope or intercept correction, or both, to the observed readings.

4.2.2 *Global calibration* employs calibration curves that are determined using many different alloy calibration materials with a wide variety of compositions. Mathematical calculations correct for both alloy difference and inter-element effects. Like 4.2.1, specific alloy calibration materials may be used to apply a slope or intercept correction, or both, to the observed readings.

4.2.3 *Alloy calibration* employs calibration curves that are determined using different alloy calibration materials that have similar compositions. Again, specific alloy calibration materials may be used to apply a slope or intercept correction, or both, to the observed readings.

5. Significance and Use

5.1 The metallurgical properties of aluminum and its alloys are highly dependent on chemical composition. Precise and accurate analyses are essential to obtaining desired properties, meeting customer specifications, and minimizing scrap due to off-grade material.

5.2 This test method is applicable to chill cast specimens as defined in Practices E716 and can also be applied to other types of samples provided that suitable reference materials are available. Also, other sample forms can be melted and cast into a disk, using an appropriate mold, as described in Practices E716. However, some elements (for example, magnesium) readily form oxides, while others (for example, sodium, lithium, calcium, and strontium) are volatile, and may be lost to varying degrees during the melting process.

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[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

6. Recommended Analytical Wavelengths and Potential Interferences

6.1 Table 1 lists the analytical wavelengths commonly used for aluminum analysis. Other lines may be used if they give comparable results. Also listed are recommended mass fraction ranges, background equivalent mass fractions, detection limits, useful linear ranges, and potential interferences. The values given in this table are typical; actual values obtained are dependent on instrument design.

NOTE 2—The background equivalent mass fraction and detection limits listed in Table 1 have been attained with a spectrometer that has a reciprocal dispersion of 54 nm/mm and a working resolution of 3.5 nm, using an entrance slit width of 25 µm and exit slit widths of 50 µm.

7. Apparatus

7.1 *Specimen Preparation Equipment:*

7.1.1 *Sampling Molds,* for aluminum, the techniques of pouring a sample disk are described in Practices E716. Chill cast samples, poured and cast as described within Practices E716, shall be the recommended form in this test method.

7.1.2 *Lathe,* capable of machining a smooth, flat surface on the reference materials and samples. A variable speed cutter, a cemented carbide or polycrystalline diamond tool bit, and an automatic cross feed are highly recommended. Proper depth of cut and desired surface finish are described in Practices E716.

7.1.3 *Milling Machine,* a milling machine can be used as an alternative to a lathe.

7.1.4 It is strongly recommended that the same preparation machinery used to prepare the reference materials is also used to prepare the samples. Differences in surface characteristics may influence the analysis.

7.2 *Excitation Source*—In today's instrumentation, the excitation source is computer controlled and is normally programmed to produce: *(1)* a high-energy pre-spark (of some preset duration), *(2)* a spark-type discharge (of some preset duration), *(3)* an arc-type discharge (of some preset duration), and *(4)* a spark-type discharge, during which, time-resolved measurements are made for improved detection limits (this may be optional on some instruments).

7.2.1 Typical parameters and times are given in Table 2. Note that the information presented is given as an example only and parameters may vary with respect to instrument model and manufacturer.

7.3 *Excitation Chamber,* shall be designed with an upper plate that is smooth and flat so that it will seal tightly with the prepared surface of the sample specimen. The seal that is formed between the two will prevent atmosphere from entering the discharge chamber. The excitation chamber will contain a mounting clamp to hold the counter electrode. The excitation stand assembly will also have some type of clamp or device designed to hold the sample firmly against the top plate. Some manufacturers may provide liquid cooling for the top plate to minimize sample heating during the excitation cycle. The excitation chamber will also be constructed so that it is flushed automatically with argon gas during the analytical burn cycle. The excitation chamber's design should allow for a flow of argon gas to prevent the deposition of ablated metal dust on the inner-chamber window(s). The excitation chamber will be equipped with an exhaust system that will safely dispose of the argon gas and the metal dust created during the excitation cycle. Considering health and cleanliness, the exhausted gas and dust should not be vented directly into the laboratory. Manufacturers have designed their instruments with some type of exhaust/filter system to minimize this problem. The exhaust can then be vented into an efficient hood system.

7.4 *Gas Flow System,* will be designed so that it can deliver pure argon gas to the excitation chamber. The purity of the argon gas will affect the precision of the results. Argon gas with a minimum purity of 99.995 % has been found acceptable. The gas shall be delivered by a flow system as described in Practice E406. The argon gas source can be from high-purity compressed gas cylinders, a cryogenic-type tank that contains liquid argon or possibly from a central supply (liquid only). It is essential that only argon gas meeting the minimum purity of 99.995 % be used. A lower purity grade of argon, such as a "welding grade," should not be used. The delivery system shall be composed of a two-stage type (high/low pressure) regulator of all-metal construction with two pressure gages. Delivery tubing must not introduce any contamination of the argon stream. Refrigerant-grade copper tubing is recommended. The gages on the regulator will allow for the adjustment of the gas pressure to the instrument. Delivery pressure specifications will vary with instrument manufacturer. Please note that the delivery tube connections should be made with all metal seals and the delivery tubing should be kept as short as possible. All metal connections are strongly recommended because the discharge is adversely affected by organic contamination, or by as little as 2 ug/g of oxygen or a few ug/g of water vapor. Argon supply shall be sufficient to support the required flow during analysis and bleed during idle periods. All connections must be leak-free.

7.5 *Measuring and Control System* of the instrument consists of either photomultiplier and integrating electronics or solid-state photosensitive arrays (CCD or CID) that convert observed light intensities to a digitizable signal. A dedicated computer or microprocessor is used to control burn conditions, source operation, data acquisition, and the conversion of intensity data to mass fractions. Data should be accessible to the operator throughout all steps of the calculation process. The instrument's control software should include functions for drift correction (standardization), type standardization, and the application of these functions to subsequent analyses.

8. Materials

8.1 *Counter Electrode*—The counter electrode and specimen surface are the two terminus points of the spark discharge. The counter electrode should be made from tungsten or other suitable material and have a pointed end. The gap distance between the specimen surface and the tip of the counter electrode is specified by the manufacturer. The diameter and geometry of the counter electrode is also application and manufacturer dependent. If different designs or configurations are offered, it is recommended that the prospective purchaser test each design to determine which performs best for the intended analytical task. The counter electrode configuration and auxiliary gap distance must not be altered subsequent to

TABLE 1 Recommended Analytical Lines

Element	Wavelength in Air (nm)^{A}	Recommended Mass Fraction Range, %	Background Equivalent, %^{B}	Calculated Detection Limit, %^{C,D}	High Mass Fraction Index, %^{E}	Interferences Element, λ(nm) and k, %^{F}	
Aluminum	256.799 I	70-100					
	266.039 I	70-100					
	237.208 I	70-100					
Antimony	231.147 I	0.001-0.5	0.17	0.0002		Co 231.166	0.6
	259.806 I	0.001-0.5		0.0002		Fe 259.837	
						Mn 259.817	0.01
Arsenic	234.984 I	0.005-0.1					
Beryllium	234.861 I	0.0001-0.05	0.001	0.00003			
	313.042 II	0.0001-0.05	0.0035	0.00001			
	332.134 I	0.0001-0.05		0.00001			
Bismuth	306.772 I	0.001-0.7	0.04	0.0002			
Boron	249.773 I	0.0001-0.05	0.002	0.0001*		Fe 249.782	0.001
						Mn 249.778	0.007
	249.678 I	0.0001-0.05					
	208.959 I	0.0001-0.05				Mo 208.952	0.13
Cadmium	228.802 I	0.001-1	0.05	<0.0001		As 228.812	
	479.992 I	0.005-2	0.15	0.003			
Calcium	393.367 II^{G}	0.001-0.05	0.001	0.00005		Fe 393.361	
Chromium	425.435 I	0.001-1	0.015	<0.0001			
	267.716 II	0.001-1	0.004	0.0005*			
	276.654 II^{G}	0.005-1					
Cobalt	345.351 I	0.0001-2		<0.0001			
Copper	327.396 I	0.001-1.5	0.005	<0.0001	0.7		
	324.754 I	0.001-0.5					
	296.117 I	0.05-20	0.40	0.01*	>20	Fe 296.128	
	224.700 II	0.01-5	0.03	0.0005*	5		
	510.554 I	0.05-20	0.32	0.01*	>20		
Gallium	294.364 I	0.001-0.05	0.015	<0.0001			
	417.206 I^{G}	0.001-0.05				Fe 417.213	
						Ti 417.190	
						Cr 417.167	
Iron	238.204 II	0.001-1.5	0.015	0.0008	1.0		
	259.940 II	0.001-1.5	0.005	0.0004			
	259.957 I						
	273.955 II	0.01-3.5					
	374.949 I^{G}	0.001-3.5		0.0001			
	441.512 I	0.01-3.5		0.0004			
	438.355 I	0.005-3.5					
Lead	405.782 I	0.002-0.7	0.04	0.0001		Mn 405.792	0.01
						Mg 405.763	0.001
	283.306 I	0.002-0.7	0.07	0.002			
Lithium	610.364 I	0.0001-3					
	670.784 I	0.0001-0.02	0.0005	<0.0005			
	323.261 I	0.01-3				Fe 323.279	
						Sb 323.250	
Magnesium	279.553 II	0.0005-0.3	0.0006	0.00003	0.04		
	285.213 I	0.0005-0.3	0.008	<0.0001	0.25		
	277.669 I	0.05-11	0.08	0.01	>11		
	383.231 I^{G}	0.01-11	0.015	0.002*	>11		
	383.826 I	0.1-11					
	518.362 I	0.01-11	0.02	0.002*	>11		
Manganese	403.076 I^{G}	0.001-0.1	0.028	0.0001*			
	259.373 II	0.0005-0.5	0.004	0.00005	0.2		
	293.306 II	0.001-2	0.006	0.0002*	>1.1		
	346.033 II	0.01-2					
Nickel	341.476 I	0.001-2	0.02	<0.0001	>2.5	Zr 341.466	0.01
	310.188 I	0.005-4	0.05	0.001*	>5		
	231.604 II	0.001-2	0.015	0.0005*	<2.5		
Phosphorus	178.231 I^{H}	0.0001-0.1	0.084	0.0001			
Silicon	288.158 I	0.001-1.5	0.01	0.0001	1.5	Cr 288.123	
	251.612 I	0.001-1.5	0.006	0.0001	1.5		
	390.553 I^{G}	0.05-24	0.25	0.01	>24	Cr 390.566	0.09
	212.415 I	0.05-24	0.5	0.05	>24		
Silver	328.068 I	0.0005-0.1					
	338.289 I	0.0001-0.1			>10		
	466.848 I	0.05-1.5					
Sodium	588.995 I	0.0001-0.05	0.0015	<0.0001			
Strontium	421.552 II^{G}	0.0001-0.1	0.0004	0.0001			
	460.733 I	0.0005-0.06					
Tin	317.502 I	0.001-7.5	0.04	0.0001	>10		
Titanium	334.904 II	0.0005-0.5	0.004	<0.0001			
	337.280 II	0.001-0.5	0.002	<0.00010			
	363.545 I	0.0005-0.05	0.030	0.003*			

TABLE 1 *Continued*

Element	Wavelength in Air (nm)[A]	Recommended Mass Fraction Range, %	Background Equivalent, %[B]	Calculated Detection Limit, %[C,D]	High Mass Fraction Index, %[E]	Interferences Element, λ(nm) and k, %[F]
Vanadium	318.341 I	0.001-0.15	0.06	0.0003*		
	437.924 I	0.001-0.25				
	310.230 II	0.001-0.15	0.014	<0.0001		
Zinc	213.856 I	0.0005-0.1	0.035	0.0001*	0.05	
	334.502 I	0.001-10.0	0.065	0.0004	>8	
	481.053 I	0.01-10	0.07	0.001*	>10	
	472.216 I	0.01-10	0.26	0.0015	>10	
Zirconium	339.198 II	0.001-1	0.02	0.001*		
	349.621 II[G]	0.001-1	0.006	<0.0001		

[A] I = atom line, II = ion line.

[B] *Background Equivalent Mass Fraction*—The mass fraction at which the signal due to the element is equal to the signal due to the background.

[C] In this test method, the *calculated detection limit* was measured by calculating the standard deviation of ten consecutive burns on a specimen with element mass fraction(s) at levels *below* ten times the expected detection limit.

[D] See footnote C. For values marked with an asterisk (*) the available data were for a mass fraction greater than ten (10) times but less than a hundred (100) times the expected detection limit.

[E] *High Mass Fraction Index*—The mass fraction at which the slope of the calibration curve drops below 0.75.

[F] *Interference Factor, k*—The apparent increase in the mass fraction of the element being determined, expressed in percent, due to the presence of 1.0 % of the interfering element.

[G] Useful analytical wavelengths with improved signal to background ratios due to the complete removal of C-N background by the argon atmosphere.

[H] If phosphorus is determined, the most sensitive wavelength appears to be the 178.231 nm in the second order which requires either a vacuum or a gas filled spectrometer. The vacuum spectrometer should be operated at a pressure of 25 microtorr or less. The gas filled spectrometer will be charged with nitrogen to a positive pressure of slightly over one atmosphere (101 k pa). Optimum results are obtained by using a background channel that has been profiled “off peak” of the first order 178.231 nm phosphorus line as the internal standard. The ratio of P 178.231 nm (2nd) / background near the 178.231 nm (1st) is plotted against % phosphorus. 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.

TABLE 2 Typical Excitation Source Electrical Parameters

Parameter	High Energy Pre-spark	Spark	Arc
Resistance, Ω	1	1	15
Inductance, µH	30	130	30
Volts, V	400	400	400
Frequency, Hz	300	300	300
Capacitance, µF	12	3	5
Time, s	10	5	5

spectrometer calibration or calibration adjustments. Electrode maintenance (frequent brushing of the counter electrode) to maintain its configuration, gap distance, and minimize surface contamination are critical to accurate, precise analytical results. It is recommended that the instrument purchaser order several spare counter electrodes so that they can be replaced when necessary.

9. Reference Materials

9.1 *Calibration Materials*—All calibration materials shall be homogeneous and free of cracks or porosity. These materials should also possess a metallurgical condition that is similar to the material(s) that are being analyzed. The calibration materials shall be used to produce the analytical curves for the various elements being determined.

9.1.1 It is recommended that a calibration curve for any particular element be composed of a minimum of four calibration materials. The mass fractions of these calibration materials should be fairly evenly spaced over the calibrated analytical range so that a mathematically valid calibration curve can be established using all of the points.

9.1.1.1 The calibration materials used shall be of sufficient quality, purchased from a recognized reputable source, and have certified values to the required accuracy for the anticipated analytical tasks to be performed. A few SRMs are available from the National Institute of Standards and Technology (NIST). Also, there are other commercial sources for aluminum reference materials.

9.1.2 For trace elements, reference materials that contain variable mass fractions of the trace element in a typical alloy of constant or nearly constant composition are available. These reference materials can be used for establishing the analytical curve, but will not reveal potential interferences from nearby wavelengths of other elements, or matrix effects that change instrument response or background. For optimum usefulness, several of the calibration materials should have mass fractions for the other elements that vary over the expected ranges in the specimen to be analyzed.

9.1.3 Atomic emission analysis is a comparative technique that requires a close match of the metallurgy, structure, and composition between the reference material and the test material. Differences in structure, such as result from the sodium modification of high silicon alloys, or differences in metallurgical history, due to extruding, rolling, or heat treating, induce a variety of effects that can influence the analytical results. To ensure analytical accuracy, care must be taken to match the characteristics of the reference material to that of the test material or suitable corrections to adjust for these influences must be established.

9.2 *Drift Correction (Standardization) Materials:*

9.2.1 *Materials for Drift Correction*—Both high and low mass fraction materials are available from several commercial sources or may be developed in-house. The low material is usually high-purity aluminum. The high material(s) should have mass fractions near or above the median mass fraction for the calibrated range of each wavelength. The commercially available materials are tested for homogeneity and reproducibility of spectral response but are not necessarily certified for composition of individual elements. Composition certification is not required because these materials are only used to adjust intensity ratios back to those obtained during the initial calibration of the instrument. Care should be exercised when replacing depleted materials with new ones that are from different heats or lots, since the actual mass fraction of the individual element(s) may be different from the material currently in use. Whenever materials are replaced, appropriate procedures must be followed to reference the intensities obtained from the new material to the intensities obtained from the material being replaced. See 14.3 for details.

9.2.2 *High-Purity Drift Correction Materials*—These shall be homogeneous and shall consist of aluminum with the lowest available mass fraction of the elements being determined. These materials are used to establish the background readings of the spectrometer for most elements. Their exact compositions need not be known.

9.2.3 *Blank Drift Correction Materials*—These materials shall be homogeneous and of similar composition to the alloy type calibration materials as described in 9.1 but will contain the lowest available mass fractions of the trace elements being determined. They may be used if the lowest mass fraction of the element being determined is within ten times the detection limit of that element.

9.2.4 *Type Standardization Materials*—These should be reference materials or equivalent materials that closely match the metallurgical history and composition of the unknown(s). These usually provide a nominal mass fraction reference point which the instrument's computer software can use to calculate a slope or intercept correction to the observed readings to fine-tune the instrument's calculated response for each element of interest. This correction is then applied to each subsequent analysis. When using this approach it is assumed that the composition(s) of the unknown(s) will be essentially similar to the composition of this material.

10. Hazards

10.1 The spark discharge presents a potential electrical shock hazard. The spark stand or the sample clamping device, or both, shall be provided with a safety interlock system to prevent energizing the electrode whenever contact can be made with the electrode. The instrument should be designed so access to the power supply is restricted by the use of safety interlocks.

10.2 Fumes of the fine metallic powder that are exhausted from the excitation chamber can be poisonous if the sample specimens contain significant levels of hazardous elements. Therefore, the instrument shall be designed with an internal exhaust system that is equipped with its own set of filters. Additionally, the instrument exhaust (after being filtered), may be vented directly to a safe area. The filters should be cleaned or changed according to the manufacturer's recommendations to enable correct instrument operation.

11. Sampling

11.1 *Chill Cast Disks and Other Aluminum Forms*—For the techniques used to sample, melt, and cast molten aluminum metal into a chill cast disk suitable for analysis, refer to Practices E716.

12. Preparation of Reference Materials and Specimen

12.1 *Preparation of Reference Materials*—All reference materials shall have their surfaces prepared for analysis according to Practices E716 with the cutting depth usually limited to that required to produce a fresh surface (about 0.010 in. or 250 µm). The surfaces of the reference materials and the surfaces of the test specimens shall be prepared in the same manner. See Practices E716 for details.

12.2 *Preparation of Specimens*—For techniques to select and prepare both chill cast samples and other forms of aluminum, such as sheet, plate, extrusions, and castings refer to Practices E716.

12.3 To achieve the best analytical results, both reference materials and sample specimens should have fresh surfaces. Surfaces should not be tested that: *(1)* are freshly prepared, *(2)* appear oxidixed, *(3)* have porosity, inclusions or other foreign substances, or *(4)* have been contaminated by handling.

13. Preparation of Apparatus

13.1 Prepare the spectrometer for operation in accordance with the manufacturer's instructions.

NOTE 3—It is not within the scope of this method to prescribe all of the details that are associated with the correct operation of any spectrometer. The reader is referred to the manufacturer's manual. Additionally, it is recommended that the purchaser of the spectrometer determine if training courses are offered by the manufacturer. Frequently manufacturer's will offer specific spectrometer training courses several times yearly.

13.1.1 *Instrument Configuration*—Instruments are usually pre-configured for the analytical program (elements), mass fraction ranges, and alloy families according to specifications that have been requested by the purchaser. Optionally, the purchaser may also choose to specify that the instrument is completely pre-calibrated for all alloys and all intended analytical tasks. The purchaser also has the option of completely configuring and calibrating the instrument. When this is done, careful attention is required in the selection of the correct analytical conditions, analytical channels, internal standard channels, calibration ranges, and calibration materials to meet the specific analytical tasks. Whether the manufacturer or the end user calibrates an instrument, it is the responsibility of the end user to verify that the instrument is performing according to the specifications that have been defined in the initial agreement or according to the performance as stated by the manufacturer. It is beyond the scope of this test method to describe the intricacies of complete instrument configuration. The user should consult the manufacturer's hardware and software manuals for specific configuration requirements.

13.1.2 *Profiling the Instrument*—Profile the instrument according to the manufacturer's instructions. If the instrument is newly installed, it is recommended that the profile be checked several times during the first few weeks of operation to determine the stability of the unit. Compare the differences in the settings to the tolerance variability allowed by the manufacturer.

13.1.3 *Checking Optical Alignment*—Position or test the position of the spectrometer exit slits, secondary mirrors (if used) or refractor plates (if used), and photomultipliers to ensure that the peak radiation passes through each slit and illuminates the centers of the phototubes. This shall be done by a trained expert initially and as often as necessary thereafter to ensure proper alignment.

13.1.4 Modern direct reading spectrometers should show little drift in the response 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 changes by more than 0.5 to 2 times, that channel should be checked for alignment or deterioration of components.

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 produce comparable analytical performance. Refer to 7.2 for typical parameters.

13.3 *Spark Conditions*—These conditions vary with the manufacturer of the equipment and may require selection by the user. A longer integration may result in better precision and accuracy with less sample through-put, while a shorter integration will increase sample through-put but may decrease precision and accuracy. Typical time ranges are:

Flush period, s	2 to 7
Pre-burn period, s	2 to 20
Integration (spark) period, s	2 to 10
Integration (arc) period, s	2 to 10

13.4 *Gas Flow*—Argon flow rate requirements may vary between manufacturers and between laboratories. The following ranges are presented as a guide.

Standby, L/min	0.03 to 0.5
During Integration, L/m	3.0 to 10

13.4.1 The high-pressure compressed gas cylinder should be changed when the pressure falls below 7 kg/cm^2 (100 kPa). If the gas is supplied from a cryogenic tank, caution should be exercised so that the tank is not allowed to completely empty. Consult with the gas supplier for their recommendation regarding cryogenic tank changes. See Practice E406 for precautions when handling gases.

13.5 *Electrode System*—The sample specimen serves as one electrode, the cathode. The tungsten or other suitable electrode serves as the counter electrode. Since the discharge is essentially unidirectional, the counter electrode is not attacked and therefore can be used for many burns. Because the electrode is moveable, continual adjustment of the analytical gap is required. It is recommended that this gap be checked periodically. The adjustment frequency is dependent on the number of burns. Consult the manufacturer to determine the optimum adjustment frequency for each instrument type. However, material ablated from the sample surface tends to accumulate on the tip of some types of electrodes, and can change the gap and may adversely affect results. Therefore the counter electrode should be cleaned (brushed) with a wire brush that is normally supplied with the instrument. For best performance it is strongly recommended that the counter electrode be cleaned after every burn. Also, with continued use the shape of the electrode may change due to this buildup of material. Frequent close inspection of the electrode is recommended. Some instruments use pin type electrodes that are not affected by an accumulation of ablated material. Pin electrodes tend to erode faster and the gap should be checked more frequently and the electrode may need replaced more frequently.

13.6 *Reference Material/Sample Placement*—Reference materials and samples should be placed on the spark stand so that the hole in the top plate is completely covered. Completely covering the hole will prevent air leaks into the discharge area. Air can cause “bad” burns and adversely affect precision and accuracy. The hole should be covered during idle periods for the same reason. Samples and reference materials should be sparked approximately 7 mm to 10 mm from their outer edge. This can be best accomplished by placing them so that the outer edge of the machined surface just covers the hole in the top plate. Overlapping the burns may adversely affect precision and accuracy.

13.7 It is essential that operators learn the difference between a “good” burn and a “bad” burn. Bad burns can be caused by an air leak between the sample and the top plate, a poor quality sample, poor quality argon, and various other reasons. A “good” burn will have a deeply pitted area in the center surrounded by a blackish ring. The actual appearance of a burn will vary with source conditions and alloy. A “bad” burn will tend to have shallow pits surrounded by a white or silver colored ring. Usually the intensity of the aluminum internal standard channel for a “bad” burn will be considerably lower than a good burn. All “bad” burns should be rejected and replaced.

13.8 *Warm-Up*—After any prolonged interval of instrument non-use, several warm-up burns should be taken. Generally two to four burns are sufficient to check for proper gas flow and consistency of results.

14. Drift Correction

14.1 *Need for Drift Correction*—Spark Atomic emission spectrometric analyses depend upon relative measurements that are subject to drift over time. To correct for drift, a suite of reference materials that includes both high and low mass fractions of the elements is used to drift correct the intensities whenever a correction is required. Failure to routinely correct for instrument drift will adversely affect analysis results. The frequency for drift correction should be determined by statistical process control methods based on periodic measurement of a control sample.

14.2 *Drift Correction*—Select a suite of reference materials that will cover the analytical array and anticipated element mass fraction ranges of the instrument to be drift corrected. It is highly recommended that the purchaser of a new instrument specify that the appropriate drift correction materials be included with the purchase of the spectrometer. If the instrument comes pre-calibrated, then these materials should automatically be included with the instrument. It is the responsibility of the purchaser to ensure that the correct drift correction materials are included with the instrument. Follow the manufacturer’s instructions when drift correcting. The spectrometer’s software should have a program that will guide the operator through the drift correction process. If the instrument is newly installed, give the unit sufficient time to stabilize in its new environment before proceeding with a drift correction. It is recommended that the spectrometer be allowed to stabilize under vacuum (if so equipped) and to adapt to the final controlled environment surroundings for at least two days before a drift correction is performed. Note, the instrument must be profiled before performing a drift correction. Refer to Practice E1329 for further details.

14.3 *Number of Burns*—It is recommended that four burns be taken on each of the drift correction materials during the drift correction process.

14.4 *Checking Homogeneity of Candidate Drift Correction Materials*—If the homogeneity of the material(s) being used is questionable; the material(s) can be tested for homogeneity.

14.5 *Recording the Drift Correction Readings:*

14.5.1 Instruments that come pre-calibrated will have the initial drift corrected response factors entered into the instrument's software.

14.5.2 If the instrument does not come pre-calibrated, then follow the manufacturer's instructions regarding establishing the initial drift correction responses/factors. Initial drift correction responses should be established immediately after calibration.

14.5.3 If one of the drift correction materials must be replaced because it has become unusable (too thin), follow the instructions listed in the instrument's manual regarding the replacement and recording of the new drift correction material's responses. Failure to properly replace drift correction materials may adversely affect analysis accuracy.

15. Calibration

15.1 *Obtaining Calibration Data*—The following procedure is designed to allow the user to collect accurate data for the purpose of generating calibration curves. For details on establishing and controlling spectrochemical calibration curves, refer to Practice E305. Any recently installed, laboratory-grade spectrometer should show minimal drift over an 8-h to 24-h time period when placed in a laboratory with a carefully controlled environment.

15.1.1 Select the reference materials for use as the calibration materials.

15.1.2 Follow the manufacturer's operating manual and use the instrument's software to design, and name the analytical program. Using the software, enter the identities of the selected calibration materials and their associated mass fractions for the elements to be calibrated in this calibration.

15.1.3 Before starting the collection of calibration data, thoroughly clean the excitation chamber and check the analytical gap or replace the electrode as needed. Prepare fresh surfaces on the selected calibration materials.

15.1.4 Profile the instrument.

15.1.5 Burn the calibration materials and collect the data.

15.2 Refer to Practice E305 and calibrate the instrument using the instrument's software, following the instructions in the manufacturer's manual. Use the appropriate program that allows for the calculation of the calibration curves. Take care when using third and fourth order regressions that enough calibration materials are available to adequately cover the entire range.

15.3 *Verifying the Accuracy of Calibration*—After completing a calibration, re-burn several of the calibration materials as unknowns and compare the measured mass fractions for each element with the certified values. Check for clerical errors, elemental interferences, or biases if results do not compare favorably.

15.3.1 If individual calibration materials give consistently high readings for an element, check for possible interferences from other elements. Manually calculate or, using the instrument's software, have the software calculate the appropriate factors for the interference(s).

16. Procedure for Analyzing Specimens

16.1 *Excitation*—Burn the specimens using the parameters and conditions in 13.2, 13.3, 13.4, and 13.5.

16.2 *Replicate Burns*—Burn the specimens from one to eight times, depending on the complexity of the alloy, specimen homogeneity, and the level of confidence required. A single burn is frequently employed for qualitative analysis of primary aluminum to detect major changes in the composition of aluminum from individual Hall cells to assess performance. A single burn shall not be used for determining compliance with composition specifications. Two to four burns are recommended for most alloys where homogeneity is acceptable and accuracy becomes important. In very complex alloys or in alloy systems that are noted for their segregation, additional burns may be required.

16.2.1 The determinations from all burns should be averaged unless a burn produces a very abnormal internal standard intensity or appears visually to be bad (see 13.7). When a burn is rejected, it should be replaced in order to maintain the normal number of burns to be averaged.

17. Calculation of Results

17.1 After performing the test material analyses, the instrument software will calculate the mass fractions of the elements based on the calibration curves. Further manipulation of the data should not be necessary.

17.2 Rounding of test results obtained using this test method shall be performed as directed in Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

18. Data Reporting

18.1 *Number of Significant Figures*—The composition of alloys shall not be reported with more significant figures or higher precision than that of the materials used to calibrate the spectrometer. As a general guideline, labs should report results at least to the number of decimal places given in ANSI H35.1/H35.1M if possible. Footnote 3 in Section 2 of ANSI H35.1/H35.1M provides the following:

TABLE 3 Summary of Interlaboratory Tests

Test Sample	Mass Fraction		S_T	S_R	R	2R
	Certified	Observed				
Antimony						
WA1199	0.0013	0.0012	0.00041	0.00041	0.0011	0.0022
SS1075	0.0033	0.0036	0.00024	0.00024	0.00067	0.0013
Arsenic						
L1	0.0014	0.0012	0.00021	0.00021	0.00059	0.0012
L5	0.0064	0.0055	0.00083	0.00083	0.0023	0.0046
Beryllium						
3004-3	0.0004(4)	0.00046	0.000010	0.000040	0.00011	0.0002
5056	0.004	0.0037	0.000011	0.00037	0.0010	0.002
358	0.24	0.237	0.0021	0.0034	0.0095	0.02
Bismuth						
1000	0.034	0.0335	0.0005	0.0010	0.0029	0.006
2011	0.56	0.567	0.0048	0.021	0.058	0.12
Boron						
1075	0.0006	0.00055	0.000024	0.00006	0.00016	0.0003
18	0.009	0.0107	0.00026	0.0012	0.0033	0.007
Calcium						
3004-3	0.0002(5)	0.00027	0.000012	0.000072	0.0002	0.0004[A]
Chromium						
3003	0.001	0.00146	0.00009	0.0023	0.0064	0.013
1000	0.036	0.0347	0.00025	0.0033	0.0092	0.018
5056	0.12	0.1208	0.00093	0.0050	0.0140	0.028
7075	0.23	0.2264	0.0036	0.0067	0.0189	0.038
Cobalt						
7091	0.44	0.4423	0.0054	0.0054	0.015	0.030
Copper						
1075	0.001	0.00084	0.00014	0.00061	0.0017	0.0034
1000	0.030	0.0306	0.00027	0.00123	0.0035	0.007
3003	0.15	0.154	0.00074	0.00435	0.0122	0.024
7075	1.58	1.564	0.0179	0.0388	0.109	0.22
2011	5.49	5.492	0.0231	0.0538	0.151	0.30
Gallium						
1075	0.022	0.0219	0.00030	0.00053	0.0015	0.0030
Iron						
5056	0.20	0.195	0.00532	0.01655	0.046	0.09
2011	0.53	0.530	0.00264	0.01275	0.036	0.07
Lead						
1000	0.036	0.035	0.0003	0.0009	0.003	0.005
2011	0.56	0.580	0.0060	0.0461	0.129	0.26
Lithium						
3004-3	0.0003(4)	0.00034	0.000006	0.000025	0.00007	0.00014
2090	2.14	2.13	0.023	0.041	0.114	0.23
Magnesium						
1000	0.030	0.0317	0.00044	0.00158	0.0044	0.009
356	0.36	0.354	0.00426	0.00860	0.024	0.05
7075	2.61	2.596	0.0219	0.0283	0.079	0.16
5056	5.36	5.364	0.0400	0.0441	0.123	0.25
Manganese						
1075	0.001	0.00102	0.00008	0.00024	0.001	0.013[A]
1000	0.032	0.0316	0.00022	0.00131	0.0037	0.007
5056	0.10	0.1006	0.00044	0.0039	0.0109	0.022
3003	1.21	1.208	0.00850	0.0139	0.039	0.08
Nickel						
3003	0.005	0.00474	0.00007	0.00028	0.0008	0.0016
1000	0.031	0.0299	0.00028	0.00177	0.0050	0.0099
850	1.21	1.219	0.0044	0.0082	0.023	0.048
336	2.60	2.596	0.0216	0.0247	0.069	0.139
Phosphorus						
AP-4	0.003	0.00269	0.00016	0.00028	0.0008	0.0016
Silicon						
1075	0.068	0.0699	0.0004	0.00266	0.0074	0.015
2011	0.28	0.288	0.00194	0.00784	0.022	0.044
356	7.18	7.16	0.0414	0.0811	0.23	0.45
390A	16.36	16.29	0.13	0.242	0.68	1.35
Sodium						
3004-3	0.0002(9)	0.00026	0.000011	0.000017	0.00005	0.00010
18	0.021	0.024	0.0016	0.0036	0.010	0.020
Strontium[B]						
336	0.027	0.0271	0.0005	0.0008	0.00229	0.00458
356	0.028	0.0277	0.0003	0.0016	0.00435	0.00870
Tin						
1000	0.028	0.0287	0.0002	0.0011	0.003	0.006
Titanium						
1075	0.001	0.00083	0.000031	0.000341	0.0010	0.0019[A]

TABLE 3 *Continued*

Test Sample	Mass Fraction		S_T	S_R	R	2R
	Certified	Observed				
2011	0.003	0.00321	0.000041	0.000185	0.0005	0.0010[A]
1000	0.031	0.0318	0.000161	0.000799	0.0022	0.0045
356	0.12	0.1176	0.00058	0.00353	0.010	0.020
Vanadium						
1075	0.002	0.00195	0.000055	0.00016	0.0005	0.0009
1000	0.022	0.0218	0.000237	0.00058	0.0016	0.0033
Zinc						
1075	0.002	0.00229	0.00040	0.00069	0.0019	0.004
1000	0.030	0.0302	0.00065	0.00071	0.0020	0.004
356	0.01	0.1001	0.00059	0.00111	0.0031	0.006
7075	5.74	5.741	0.0285	0.0927	0.26	0.52
Zirconium						
1075	0.001	0.00093	0.00007	0.00017	0.0005	0.0009
2090	0.12	0.120	0.012	0.0023	0.006	0.013

[A] Values are below minimum quantifiable limit calculated based on the data in this ILS.
[B] Supporting data for strontium have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1113.

Standard limits for alloying elements and impurities are expressed to the following places:

Less than 0.001 %	0.000X
0.001 but less than 0.01 %	0.00X
0.01 but less than 0.10 % unalloyed aluminum made by a refining process	0.0XX
Alloys and unalloyed aluminum not made by a refining process	0.0X
0.10 through 0.55 percent (It is customary to express limits of 0.30 % through 0.55 % as 0.X0 or 0.X5)	0.XX
Over 0.55 % (Except that combined Si + Fe limits for 1XXX designations must be expressed as 0.XX or 1.XX)	0.X, X.X, etc.

19. Precision and Bias[5]

19.1 *Precision*—Eight laboratories cooperated in the inter-laboratory study using either the binary calibration approach or the alloy-type calibration technique. Since an attempt was made to include all general alloy types, not all laboratories could analyze all materials or all mass fraction ranges. Testing was done in accordance with Practice E691. A summary of the inter-laboratory test is shown in Table 3.

19.2 *Bias*—There is no evidence of bias since all acceptable individual test results are within one *R* of the assumed mass fractions.

20. Keywords

20.1 aluminum; aluminum alloys; Spark Atomic Emission Spectrometry (Spark-AES)

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1113. Contact ASTM Customer Service at www.astm.org/contact.