



Standard Test Method for Chemical Analysis of Zinc-5 % Aluminum-Mischmetal Alloys by ICP Emission Spectrometry¹

This standard is issued under the fixed designation E 1277; 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.

1. Scope

1.1 This test method covers the chemical analysis of zinc alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	3.0–8.0
Antimony	0.002 max
Cadmium	0.025 max
Cerium	0.03–0.10
Copper	0.10 max
Iron	0.10 max
Lanthanum	0.03–0.10
Lead	0.026 max
Magnesium	0.05 max
Silicon	0.015 max
Tin	0.002 max
Titanium	0.02 max
Zirconium	0.02 max

1.2 Included are procedures for elements in the following concentration ranges:

Element	Concentration Range, %
Aluminum	3.0–8.0
Cadmium	0.0016–0.025
Cerium	0.005–0.10
Iron	0.0015–0.10
Lanthanum	0.009–0.10
Lead	0.002–0.026

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific safety hazards statements are given in Section 7, 11.2, and 13.1.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

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 E01.05 on Zn, Sn, Pb, Be, and Other Metals.

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² *Annual Book of ASTM Standards*, Vol 11.01.

- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance With Specifications³
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁴
- E 55 Practice for Sampling Wrought Nonferrous Metals for Determination of Chemical Composition⁴
- E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition⁴
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁴
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data⁵
- E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method⁵

3. Summary of Test Method

3.1 The sample is dissolved in mixed acids. The sample solution is introduced into the plasma source of an ICP spectrometer and the intensities at selected wavelengths from the plasma emission spectrum are compared to the intensities at the same wavelengths measured with calibration solutions.

4. Significance and Use

4.1 This test method for the chemical analysis of metals and alloys is primarily intended to test such materials for compliance with compositional specifications. It is assumed that all those who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus

5.1 *Inductively-Coupled Argon Plasma (ICP) Atomic Emission Spectrometer*—The instrument is equipped with an argon-plasma source, a sample transport system for introducing the test sample and calibration solutions into the plasma. The monochromator or polychromator must be capable of isolating

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ *Annual Book of ASTM Standards*, Vol 3.05.

⁵ *Annual Book of ASTM Standards*, Vol 03.06.

the required wavelengths shown in Table 1 for measurement of their intensities by a linear photometer. Multielement programmed analysis including automatic data acquisition and computer-controlled calibration and analysis calculations may be used if available, provided that, in addition to calculated results, the instrument records intensity readings each time a test sample or calibration solution is presented to the instrument.

NOTE 1—All elements (including aluminum) are calibrated as linear functions of intensity. If the instrument cannot be set to measure aluminum and ignore other elements in calibration solutions No. 1 and No. 4, then a separate determination of aluminum must be made using calibration solutions No. 1, No. 2 and No. 4. The other elements can then be determined together in another run using only calibration solutions No. 2 and No. 3. Use the calibration solutions prepared in 10.1 in determining the instrument settings for the elements in this matrix. Follow the manufacturer's instructions to set the wavelengths and parameters to provide as large a difference between the intensity readings for the high and low calibration concentrations as is consistent with stable instrument readings. If there is a question of linearity of the instrument's response over the range of solution concentrations given, a third standard, equidistant between the two listed standards, must be measured to verify linearity.

6. Reagents

6.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in this test method shall conform to the "Reagent Grade" Specifications of the American Chemical Society.⁶ Other chemicals may be used provided that it is first ascertained that the reagent used is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6.3 *Aluminum, Standard Solution* (1 mL = 20.0 mg Al)—Transfer 2.0000 g of aluminum (purity: 99.999 % min) to a 250-mL beaker. Cover, add 50 mL of HCl (1 + 1) and a small crystal of mercuric nitrate. Heat gently to accelerate the reaction, but avoid temperatures high enough to cause a noticeable volume loss. If the reaction slows, add more mercuric salt as needed. A number of hours may be required to complete the dissolution (only a small droplet of mercury will

remain undissolved). Transfer the solution to a 100-mL volumetric flask, dilute to volume, and mix. Store in a polyethylene bottle.

6.4 *Cadmium, Standard Solution* (1 mL = 1.00 mg Cd)—Transfer 1.000 g of cadmium (purity: 99.95 % min) to a 250-mL beaker. Cover and add 40 mL of HNO₃ (1 + 1) and 10 mL of HCl. After dissolution is complete, heat to boiling to remove oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, add 240 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle.

6.5 *Cerium, Standard Solution A* (1 mL = 1.00 mg Ce)—Dry ceric ammonium nitrate ((NH₄)₂Ce(NO₃)₆, also known as ammonium hexanitrate cerate) (purity: 99.95 % min) for 4 h at 85°C and cool to room temperature in a desiccator. Dissolve 3.913 g of dry ceric ammonium nitrate in 100 mL of HCl (1 + 9). Transfer to a 1-L volumetric flask, add 240 mL of HCl and 20 mL of HNO₃, dilute to volume, and mix. Store in a polyethylene bottle.

6.6 *Cerium, Standard Solution B* (1 mL = 0.010 mg Ce)—Using a pipet, transfer 1.00 mL of Cerium Standard Solution A to a 100-mL volumetric flask. Dilute to volume with dilution solution and mix.

6.7 *Dilution Solution*—Half fill a 2-L volumetric flask with water. Add 500 mL of HCl and 40 mL of HNO₃, swirl to mix, dilute to the mark, and mix.

6.8 *Iron, Standard Solution A* (1 mL = 1.00 mg Fe)—Transfer 1.000 g of iron (purity: 99.95 % min) to a 250-mL beaker, cover, and add 100 mL of HCl (1 + 1). Boil gently to complete dissolution. Cool and transfer to a 1-L volumetric flask, add 200 mL of HCl and 20 mL of HNO₃, dilute to volume, and mix. Store in the polyethylene bottle.

6.9 *Iron, Standard Solution B* (1 mL = 0.010 mg Fe)—Using a pipet, transfer 1.00 mL of Iron Standard Solution A to a 100-mL volumetric flask. Dilute to volume with dilution solution and mix.

6.10 *Lanthanum, Standard Solution A* (1 mL = 0.010 mg La)—Ignite lanthanum oxide (La₂O₃) (purity: 99.9 % min) for 1 h at 1000°C and cool to room temperature in a desiccator. Dissolve 1.173 g of dry lanthanum oxide in 100 mL of HCl (1 + 9) and transfer to a 1-L volumetric flask. Add 240 mL of HCl and 20 mL of HNO₃, dilute to volume, and mix. Store in a polyethylene bottle.

6.11 *Lanthanum, Standard Solution B* (1 mL = 0.010 mg La)—Using a pipet, transfer 1.00 mL of Lanthanum Standard Solution A to a 100-mL volumetric flask. Dilute to volume with dilution solution and mix.

6.12 *Lead, Standard Solution* (1 mL = 1.00 mg Pb)—Transfer 1.000 g of lead (purity: 99.9 % min) to a 250-mL beaker, cover, and add 40 mL of HNO₃ (1 + 1). Boil gently to complete dissolution and to remove oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, add 250 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle.

6.13 *Zinc Matrix Solution* (50 mL = 3.75 g Zinc Matrix Standard)—Transfer 18.75 g ± 0.10 g of Zinc Matrix Standard to a 250-mL plastic beaker. Cover and add about 50 mL of water. Add 62.5 mL of HCl and heat enough to maintain the reaction but not enough to evaporate the solution. When most of the material has dissolved, add 5.0 mL of HNO₃. When all

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Wavelengths and Instrument Conditions^A

Element	Wavelength	Time, s	No. Integ.	BCor1	BCor2
Al	3092.7	1.0	3
Cd	2265.02	.5	3	2264.46	2265.58
Ce	4186.6	.5	2
Fe	2599.4	.5	2
La	3988.5	.5	2	3987.54	3989.06
Pb	2832.97	1.0	3	...	2833.36

^A The tabulated conditions were those found satisfactory on one instrument. Wavelengths are expressed in angstroms. Time = seconds for each integration. No. Integ. = number of integrations averaged for each reading, and BCor1 and BCor2 are off-peak background correction wavelengths.

solids have dissolved, remove from the heat and allow to cool. Transfer to a 250-mL plastic volumetric flask, dilute to the mark, and mix.

6.14 *Zinc Matrix Standard*—Use a zinc reference material⁷ of known composition with respect to the elements listed in the scope of this test method.

7. Hazards

7.1 For precautions to be observed in the use of certain reagents in this test method, refer to Practices E 50.

8. Sampling

8.1 For procedures for sampling the material, refer to Practices E 55 and E 88.

9. Interlaboratory Studies and Rounding of Calculated Values

9.1 Only four laboratories were available to test this method, therefore, the interlaboratory test does not comply with the protocol for Practice E 173. However, the statistics were calculated according to Practice E 173.

9.2 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

9.3 E 173 has been replaced by Practice E 1601. The reproducibility Index R, corresponds to the Reproducibility Index R₂ of Practice E 1601. Likewise the Repeatability Index R₁ of E 173 corresponds to the Repeatability Index r of Practice E 1601.

10. Calibration

10.1 Prepare calibration and test sample solutions before calibration measurements are started.

10.2 *Calibration Solutions*—All calibration solutions contain the same concentration of zinc as the test sample solutions. The aluminum content of calibration solutions No. 2 and No. 3 must be equal to the midpoint of the calibrated aluminum range. Using a pipet, transfer 50.0 mL of the Zinc Matrix Solution into each of four 100-mL plastic volumetric flasks marked Cal No. 1 through Cal No. 4. Add the volumes of standard solutions specified in Table 2 (also see Table 3), dilute to volume with dilution solution, and mix:

10.3 *Test Sample Solution*—Transfer a 3.8 to 4.2-g portion of the test sample weighed to the nearest 0.02 g to a 250-mL polytetrafluoroethylene beaker. Add about 30 mL of water, cover, and cautiously add 25 mL of HCl in increments. Heat gently to maintain the reaction, if necessary, but do not boil. When most of the material has dissolved, add 2.0 mL of HNO₃, let the solution cool for about 20 min, transfer to a 100-mL plastic volumetric flask, dilute to volume, and mix.

10.4 *Automatic Calibration Mode*—(If the instrument does not have the capability to take data from calibration solutions and calculate and store the equations needed to convert instrument readings from test samples directly into concentration values automatically, or if that capability is not to be used,

proceed in accordance with 10.5.) Set up the instrument parameters as directed in Section 5. If one of the parameters is a “lower limit” (used to establish a printed “less than” value), set it to 0 for each element. Enter the concentrations of the elements to be found in each calibration solution. Table 4 gives the concentration table for solutions based upon NBS SRM 728⁷ as Zinc Matrix Standard. If a different Zinc Matrix Standard is used, Table 4 must be revised to reflect the different composition of that material. Using the calibration solutions, follow the manufacturer’s procedure to perform the instrument calibration at the wavelengths specified in Table 1. Without undue delay, proceed in accordance with 11.2.

10.5 *Nonautomatic Mode*—No separate calibration run is required if intensity readings only are recorded. Set up the instrument to measure intensities at the wavelengths specified in Table 1 according to the manufacturer’s instructions and proceed to 11.3 .

TABLE 2 Standard Solution Volumes Added, mL^{A,B}

Element	No. 1	No. 2	No. 3	No. 4
Aluminum	6.00	11.0	11.0 ^B	16.0
Cadmium	1.00	...
Cerium	...	2.00(B)	4.00(A)	...
Iron	...	1.00(B)	4.00(A)	...
Lanthanum	...	2.00(B)	4.00(A)	...
Lead	1.00	...

^A Use standard solution A or B as indicated in parentheses.

^B Added to match solution No. 2, not for calibration purposes.

TABLE 3 Solution Concentrations Added, mg/L^A

Element	No. 1	No. 2	No. 3	No. 4
Aluminum	1200	2200	...	3200
Cadmium	10.0	...
Cerium	...	0.2	40.0	...
Iron	...	0.1	40.0	...
Lanthanum	...	0.2	40.0	...
Lead	10.0	...

^A Table 4 is derived from this table by adding the trace element contributions from the zinc matrix solution to the concentrations shown in this table and converting the resulting sum to weight percent.

11. Procedure

11.1 *Measurement Sequences*—To reduce the distortion of data if instrument drift occurs while measurements are taken, solutions are presented to the instrument in a specified order and only a single reading (or, if desired, the average of several integrations) is recorded each time a solution is presented to the

TABLE 4 Concentration Table for Calibration Solutions^{A,B}

Element	No. 1	No. 2	No. 3	No. 4
Aluminum	3.00	5.50	...	8.00
Cadmium00011	.0251	...
Cerium00050	.1000	...
Iron00052	.1003	...
Lanthanum00050	.1000	...
Lead00104	.0260	...

^A The values in this table assume SRM 728 as zinc matrix, a sample weight of 4.00 g, and results reported in %.

^B To calculate the concentration table for a different zinc matrix material, add the parts per million contributed from 3.75 g of that material in a volume of 100 mL to the parts per million shown in Table 3. Calculate the percent element by dividing the parts per million by 400.

⁷ SRM 728, Intermediate Purity Zinc, available from The Office of Standard Reference Materials, National Institute of Standards and Technology, Gaithersburg, MD 20899, has been found suitable.

instrument. Repeat the following sequence of solution presentations four times to obtain the required four replicate readings: calibration solution No. 1, calibration solution No. 2, test sample solution, calibration solution No. 3, and calibration solution No. 4. More than one test sample solution may be presented to the instrument between calibration solutions No. 2 and No. 3. Many instruments do not require a rinse between each solution presentation, but it is advisable to rinse the system periodically. A rinse with dilution solution after each completed sequence is the minimum recommended frequency.

11.2 Automatic Mode—Calibrate the instrument in accordance with 10.4. Without undue delay, proceed to analyze the solutions as directed in 11.1. (**Warning**—Attempting to shorten the measurement time by substituting four readings taken during a single solution presentation instead of the prescribed sequences may lead to an improper calibration even though the precision of the measurements appears satisfactory. Be sure that the instrument has been set to record intensities as well as concentrations for both calibration and test solutions. Proceed in accordance with 12.1.)

11.3 Nonautomatic Mode—With the instrument set up in accordance with Section 5, measure the calibration and test sample solutions as directed in 11.1, recording the intensity readings for each solution presentation. Solution presentation may be performed manually, or, if the instrument is provided with the necessary equipment, by automatic solution presentation. The proper sequencing of the replicate readings must be followed in either case. Proceed in accordance with 12.2.

12. Calculation

12.1 Automatic Mode—The instrument record includes calibration and test solutions results in both intensity and concentration units. To test the accuracy of the recorded concentrations, calculate the average concentrations of the sample and the appropriate calibration solutions. For each calibration solution, determine the difference between the average recorded concentration and the value listed in the concentration table. The automatically calculated concentration values are acceptable if the differences are less than 5 % (relative) for the high and 10 % (relative) for the low calibration solution. The requirement for aluminum is that the average error for the three calibration results must be within 2 % (relative). If the results for an element meet these criteria, record the average test sample concentration (C_s), and proceed in accordance with Section 13. Otherwise, use the intensity readings for the element to calculate results as directed in 12.2.

12.2 Nonautomatic Mode—The measurement data consists of four intensity readings for each calibration and test sample solution. Calculate the average intensity values for the high calibration solution (R_h), the low calibration solution (R_l), and the test sample solution (R_s). For aluminum, also determine the average intensity (R_m) for the middle calibration solution. Determine the test sample concentration as directed in either 12.3 or 12.4.

12.3 Graphical Calibration—Plot R_h and R_l (also R_m for aluminum) as the y -variable (measured along the vertical axis) against the corresponding concentrations from the concentration table as the x -variable (horizontal axis). Draw the calibration curve, a line which (except for aluminum) extends through

both points back to intersect the vertical axis. For aluminum, the calibration curve is a straight line plotted from the concentration value for the low calibration solution to the concentration value of the high calibration solution in such a manner that the positive and negative differences between the line and all points is minimized. Note that no calibration curve can be extended above the concentration of its high end. In addition, the aluminum curve cannot be used for concentrations below its low end. The concentration of the test sample (C_s) is read from the x -axis corresponding to the intersection of the average sample reading (R_s) with the calibration curve. In the same manner, read the concentrations corresponding to all of the individual intensity readings for the low calibration solution. Proceed in accordance with Section 13.

12.4 Calculator Calibration—Use a calculator or computer least-squares curve fit program that also calculates predicted values for x and y from given values of the other variable. Enter the intensity readings for calibration solutions as the y -variable with concentrations from the concentration table as the associated x -values. Enter the average intensity reading of the test sample solution and use the program to predict its concentration (C_s). In the same manner, calculate the concentrations corresponding to all of the individual intensity readings for the low calibration solution. Proceed as directed in Section 13.

12.5 Determination Limit, is calculated in accordance with Practice E 876. For this application, it is defined as the concentration below which the relative error of the calculated concentration is predicted to be greater than 15 % at the 95 % confidence level. The determination limit concept does not apply to the aluminum determination because the calibration curve for that element does not extend lower than approximately 3 % aluminum. For all other elements, the determination limit establishes the lowest practical concentration that can be reported by the use of this test method. This test method specifies four replicate readings for both calibration and sample solutions. Use the standard deviation of the low calibration solution readings to calculate the determination limit:

$$DL = 10.6 \times s \text{ where } s = \text{the standard deviation.} \quad (1)$$

12.6 Test Sample Concentration, (C)—Calculate by correcting for the sample weight if different from 4.00 g:

$$C = C_s \times (4/A) \quad (2)$$

where:

C_s = the average recorded test sample concentration, and
 A = the test sample weight, g.

13. Report

13.1 Report the aluminum content as $C \% A1$ if the calculated value falls within the range of 3.0 % to 8.0 %. Otherwise, do not report the results for aluminum *or any other element* because the test sample is not within the scope of this test method. For each other element, calculate the determination limit as directed in 12.5. Compare this value with the lower scope limit and use the greater of the two as the lower reporting limit (LRL). If the calculated concentration, C , of the element is less than the value of LRL, report the concentration of the element as “less than” LRL. If C is greater than the value of LRL, report the element concentration as $C \% \text{ Element}$.

(**Warning**—Do not report any element whose concentration is more than 10 % (relative) higher than the high calibration concentration for that element.)

14. Precision and Bias

14.1 *Precision*—Precision calculations have been done in accordance with Practice E 173. The results are summarized in Table 5.

14.2 *Bias*—The bias of this test method could not be evaluated because adequate certified standard reference materials were unavailable at the time of testing. The user is cautioned to verify by the use of certified reference materials, if available, that the accuracy of this test method is adequate for the contemplated use.

15. Keywords

15.1 ICP emission; mischmetal; rare earths; spectrometry; zinc alloys

TABLE 5 Statistical Information

Element	Sample	Number of Laboratories	Mean	R_1	R_2
Aluminum	Gal-5	4	4.88	0.139	0.273
	Gal-6	4	5.31	0.097	0.319
	Gal-7	4	6.93	0.384	0.582
Cadmium	Gal-5	4	0.00020	ND ^A	ND ^A
	Gal-6	4	0.00008	ND ^A	ND ^A
	Gal-7	4	0.0109	0.00067	0.00082
Cerium	Gal-5	4	0.0235	0.0015	0.0026
	Gal-6	4	0.0399	0.0022	0.0031
	Gal-7	4	0.0306	0.0021	0.0020
Iron	Gal-5	4	0.0040	0.00054	0.00076
	Gal-6	4	0.0274	0.0057	0.0114
	Gal-7	4	0.0291	0.0047	0.0074
Lanthanum	Gal-5	4	0.0299	0.0018	0.0044
	Gal-6	4	0.0664	0.0039	0.0050
	Gal-7	4	0.0339	0.0026	0.0072
Lead	Gal-5	3	0.0047	0.00095	0.00090
	Gal-6	3	0.0013	0.0013	0.0012
	Gal-7	3	0.0062	0.00089	0.0011

^A Not determinable. The data was not suitable for R_1 and R_2 calculations.

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