



Designation: **E536 – 16 E536 – 23**

Standard Test Methods for Chemical Analysis of Zinc and Zinc Alloys¹

This standard is issued under the fixed designation E536; 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 These test methods cover the chemical analysis of zinc and zinc alloys having chemical compositions within the limits of **Table 1**.

TABLE 1 Scope of Mass Fraction Ranges for Zinc and Zinc Alloys

Element	Composition Range, %
Aluminum	0.005 to 4.5
Cadmium	0.001 to 0.5
Copper	0.001 to 1.3
Iron	0.001 to 0.1
Lead	0.001 to 1.6
Magnesium	0.001 to 0.1
Tin	0.001 to 0.1

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 These test methods appear as follows:

Aluminum by the EDTA Titrimetric Method (0.5 to 4.5 %)	Sections 10 – 17
Aluminum, Cadmium, Copper, Iron, Lead, and Magnesium by the Atomic Absorption Spectrometry Method	18 – 28

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health, safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in Section 6.*

1.5 *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.*

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.05 on Cu, Pb, Zn, Cd, Sn, Be, Precious Metals, their Alloys, and Related Metals.

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2. Referenced Documents

2.1 ASTM Standards:²

- D1193 Specification for Reagent Water
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- ~~E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry~~
- E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
- E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition
- E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1997)³
- E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology **E135**.

4. Significance and Use

4.1 These test methods for the chemical analysis of zinc metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications. It is assumed that all who use these test methods 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 and Reagents

5.1 Apparatus and reagents required for each determination are listed in separate sections of each test method. The apparatus, standard solutions, and reagents shall conform to the requirements prescribed in Practices **E50**. ~~Spectrometers shall conform to the requirements prescribed in Practice **E60**.~~

6. Safety Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices **E50**.

7. Sampling

7.1 For procedures ~~for sampling~~ to sample the material, refer to Practices **E55** and **E88**.

8. Rounding Calculated Values

8.1 ~~Calculated values shall be rounded to the desired number of places.~~ Rounding of test results obtained using this test method shall be performed as directed in Practice **E29**, Rounding Method. ~~Method, unless an alternative rounding method is specified by the customer or applicable material specification.~~

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practice **E173**, unless otherwise noted in the precision section.

ALUMINUM BY THE EDTA TITRIMETRIC METHOD

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

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

10. Scope

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11. Summary of Test Method

11.1 After dissolution of the sample in HCl, the solution is buffered and disodium (ethylenedinitrilo) tetraacetate (EDTA) is added. The excess EDTA is titrated with standard zinc solution. Sodium fluoride is added to decompose the aluminum-EDTA complex, and the released EDTA is titrated with standard zinc solution.

12. Interferences

12.1 The elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1.

13. Apparatus

13.1 *Magnetic Stirrer*, with stirring bar covered with tetrafluoroethylene polymer (TFE-fluorocarbon).

14. Reagents

14.1 *Bromcresol Green Indicator Solution* (0.4 g/L)—Dissolve 0.04 g of bromcresol green in 6 mL of 0.01 *N* sodium hydroxide (NaOH) NaOH solution and dilute to 100 mL.

14.2 *EDTA Solution* (90 g/L)—Dissolve 90.0 g of disodium (ethylenedinitrilo) tetraacetate dihydrate (Ethylenedinitrilo) tetraacetic acid disodium salt dihydrate (EDTA) in about 800 mL of warm water. Cool and dilute to ~~1 L~~ 1 L.

NOTE 1—Although it is not critical that this solution be prepared with a ~~1-L volumetric~~ 1-L volumetric flask, doing so makes it more consistent and easier for the ~~analyst run to run user~~. This compound is commonly referred to as EDTA or EDTA (Disodium salt).

14.3 *Methyl Red Indicator Solution* (0.4 g/L)—Dissolve ~~0.1 g~~ 0.1 g of methyl red in 3.72 mL of 0.1 *N* NaOH solution and dilute to 250 mL with water. Filter if necessary.

14.4 *Sodium Acetate Buffer Solution* (320 g/L)—Dissolve 320 g of sodium acetate trihydrate in about 800 mL of water and filter. Using a pH meter, adjust the pH of the solution to 5.5 ± 0.1 with NaOH solution or acetic acid and dilute to 1 L.

NOTE 2—The ~~analyst~~ user is not restricted to using the 0.1 *N* solution of NaOH

14.5 *Sodium Fluoride Solution (Saturated)*—Dissolve 60 g of sodium fluoride (NaF) in 1 L of boiling water. Cool and filter through a coarse paper. Store in a polyethylene bottle.

14.6 *Xylenol Orange Indicator Solution* (10 g/L)—Dissolve 0.250 g of xylenol orange in 25 mL of water. Do not use a solution that has stood more than 1 month.

14.7 *Zinc Standard Solution* (1 mL = 1.00 mg Al)—Dissolve 2.423 g of zinc metal (purity: 99.99 % minimum) in 20 mL of HCl. Dilute to 100 mL. Add 3 drops of methyl red solution and neutralize with NH_4OH . Add HCl until the color changes to red. Transfer to a 1-L volumetric flask, dilute to volume, and mix.

14.8 *Purity of Water*—Unless otherwise indicated, reference to water shall ~~be understood to mean~~ reagent water as defined by Type II of Specification **D1193**.

15. Procedure

15.1 Select and weigh a sample to the nearest 1 mg, ~~in accordance as follows:~~

TABLE 2 Recommended Sample Mass

Aluminum, %	Sample Mass, g	Aliquot, mL	EDTA Addition, mL
0.5 to 1.5	10.0	50	165 to 168
1.5 to 2.5	6.0	50	103 to 106
2.5 to 4.5	5.0	40	72 to 75

with **Table 2**.

Transfer the sample to a 400-mL beaker, and cover.

15.2 Add 100 mL of HCl (1 + 1). Heat until dissolution is complete and boil for ~~2 minutes~~min to ~~3 minutes~~min. If a residue remains, add 1 mL of H₂O₂ and boil the solution for at least ~~5 minutes~~min to destroy excess H₂O₂ and expel free chlorine.

~~NOTE 3—Excess peroxide and free chlorine shall be removed to prevent fading of the indicators.~~

15.2.1 Excess H₂O₂ and free chlorine shall be removed to prevent fading of the indicators.

15.3 Transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix.

15.4 Using a pipet, transfer the aliquot specified in **15.1** to a 500-mL wide-mouth Erlenmeyer flask.

15.5 Add the volume of EDTA solution specified in **15.1** and dilute to 200 mL.

~~NOTE 4—The amount of EDTA added shall be sufficient to complex the zinc and aluminum with some excess. The amount of EDTA required is 5.7 mg for each milligram of zinc and 14.0 mg for each milligram of aluminum.~~

15.5.1 The amount of EDTA added shall be sufficient to complex the zinc and aluminum with some excess. The amount of EDTA required is 5.7 mg for each mg of zinc and 14.0 mg for each mg of aluminum.

15.6 Add five drops or six drops of methyl red solution. Add NH₄OH until the color changes to orange.

15.7 Add 25 mL of sodium acetate buffer solution and boil for ~~3 minutes~~min to ~~5 minutes~~min. Cool in a water bath.

15.8 Add four drops of xylenol orange solution and five drops or six drops of bromcresol green solution.

15.9 Using a TFE-fluorocarbon-covered stirring bar and a magnetic stirrer, stir the solution while adding standard zinc solution from a 50-mL buret to complex the excess EDTA. Add the solution dropwise as the end point is approached. Continue the titration until the color changes from green to red. Refill the buret.

15.10 Add 25 mL of NaF solution and boil for ~~3 minutes to 5 minutes~~, 3 min to 5 min. Cool in a water bath.

15.11 Titrate with standard zinc solution as directed in **15.9** and record the volume to the nearest 0.01 mL.

16. Calculation

16.1 Calculate the percentage of aluminum as follows:

$$\text{Aluminum, \%} = (A/B/C) \times 100 \quad (1)$$

where:

A = standard zinc solution used in **15.11**, mL;

B = aluminum equivalent of the standard zinc solution, g/mL (noted in 14.7); and
C = sample represented in the aliquot taken in 15.1, g.

17. Precision and Bias

17.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the results summarized in Table 3.

17.2 *Bias*—No information concerning the accuracy of this test method is available because certified reference materials suitable for chemical test methods were not available when the interlaboratory test was performed. The analyst user is urged to use an accepted reference material, if available, to determine that the accuracy of results is satisfactory.

17.3 Practice E173 has been replaced by Practice E1601. The reproducibility Index R_2 of Practice E173 corresponds to the Reproducibility Index *R* of Practice E1601. Likewise the Repeatability Index R_1 of Practice E173 corresponds to the Repeatability Index *r* of Practice E1601.

ALUMINUM, CADMIUM, COPPER, IRON, LEAD, AND MAGNESIUM BY THE ATOMIC ABSORPTION METHOD—SPECTROMETRY METHOD

18. Scope

18.1 This test method covers the determination of aluminum in compositions from 0.002 % to 0.5 %, cadmium from 0.001 % to 0.5 %, copper from 0.001 % to 1.3 %, iron from 0.003 % to 0.1 %, lead from 0.002 % to 1.6 %, and magnesium from 0.001 % to 0.1 %.

18. Scope

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19. Summary of Test Method

19.1 An HCl solution of the sample is aspirated into the flame of an atomic absorption spectrometer. The absorption of the resonance line energy from the spectrum of each element is measured and compared with that of calibration solutions of the same element. The wavelengths of the spectral lines and other method parameters are tabulated in 22.1 for each element.

20. Composition Range

20.1 The composition range for each element shall be determined experimentally, because the optimum range will depend upon the individual instrument. If the optimum composition range and instrument parameters have been determined, proceed in accordance with Section 26; otherwise, determine the composition range in accordance with Section 22.

Note 5—The composition range will depend on the instrument. Section 24.1 lists the typical calibration composition ranges that most often will be acceptable, however this can be determined by using the criteria in Section 22. The analyst may find that different calibration composition ranges are required and must be adjusted accordingly to suit their instrument.

20.2 The composition range will depend on the instrument. Section 24.1 lists the typical calibration composition ranges that most often will be acceptable, however this can be determined by using the criteria in Section 22. The user may find that different calibration composition ranges are required and must be adjusted accordingly to suit their instrument.

TABLE 3 Statistical Information

Test Specimen	Aluminum Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
G-3	0.3998	0.0190	0.0254
H-2	4.04	0.052	0.074

21. Interferences

21.1 The elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1.

22. Apparatus

22.1 *Flame Atomic Absorption Spectrometer*, equipped with a premix burner, with facilities for using the oxidizer-fuel combinations listed in [Table 4](#). Use hollow-cathode lamps operated in accordance with manufacturer's recommendations as sources for the ~~spectral lines—wavelengths~~. The instrument may be considered suitable for this test method if a composition range can be found for which the minimum response, calibration variability, and reference variability tabulated in [Table 4](#) can be met.

22.1.1 Prepare the dilute standard solution, reference, and calibration solutions in accordance with Section 24. Refer to [Table 5](#), for suggested initial compositions.

22.1.2 Prepare the instrument for use in accordance with [26.1](#). Measure the instrument response while aspirating the reference solution, the lowest, and the two highest calibration solutions, performing the measurements in accordance with [26.2.2](#) and [26.2.3](#).

22.1.3 *Minimum Response*—Calculate the difference between the readings of the two highest of the five equally spaced calibration solutions. This difference shall be equal to or greater than the number of ~~scale response~~ units specified in [Table 4](#). For purposes of this test method, the ~~scale response~~ unit is defined as one in the least significant digit of the ~~scale response~~ reading of the most concentrated calibration solution.

22.1.4 *Curve Linearity*—Calculate the difference between the ~~scale readings~~ response units of the reference solution and the lowest of the five equally spaced calibration solutions. If necessary, convert this difference and the difference calculated in [22.1.3](#) to absorbance units. Divide the difference for the highest interval by that for the lowest interval. This ratio shall be equal to or greater than 0.70.

22.1.5 If the instrument meets or surpasses the minimum response and curve linearity criteria, the initial composition range may be considered suitable. In this case, proceed in accordance with [22.1.7](#); otherwise, proceed as follows:

22.1.6 If the minimum response is not achieved, prepare another dilute ~~standard~~ solution to provide a higher composition range, and repeat [22.1.1](#) – [22.1.4](#). If the calibration curve does not meet the linearity criterion, prepare another dilute ~~standard~~ solution to provide a lower composition range, and repeat [22.1.1](#) – [22.1.4](#). If a composition range cannot be found for which both criteria can be met, do not use this test method until the performance of the ~~apparatus~~ instrument satisfies the requirements.

22.1.7 *Instrument Stability*—Calculate the calibration variability and reference variability as follows:

TABLE 4 Minimum Response, Calibration, and Reference Variability

Element	Spectral Line, nm	Oxidizer-Fuel	Standard Solution	Minimum Response, Units	Calibration Variability, %	Reference Variability, %
Element	Wavelength, nm	Oxidizer-Fuel	Standard Solution	Minimum Response, Units	Calibration Variability, %	Reference Variability, %
Aluminum	309.2	N ₂ O– C ₂ H ₂	"A"	9	3.5	2.0
			"B"	25	1.0	0.5
Cadmium	228.8	Air– C ₂ H ₂	...	50	0.8	0.4
Copper	324.7	Air– C ₂ H ₂	"A"	15	2.0	0.8
			"B"	50	0.8	0.4
Iron	248.3	Air– C ₂ H ₂	"A"	15	2.0	1.0
			"B"	25	1.0	0.5
Lead	217.0	Air– C ₂ H ₂	"A"	10	2.0	1.5
			"B"	30	1.0	0.4
Magnesium	285.2	N ₂ O– C ₂ H ₂	...	20	1.5	0.8

TABLE 5 Dilute Standard Solutions

Dilute Standard Solution	Composition Range, %	Volume, mL	Concentration of Dilute Standard Solution, mg/mL
Aluminum "A"	0.004 to 0.020	5	0.05
Aluminum "B"	0.020 to 0.50	20	0.20
Cadmium	0.001 to 0.50	2	0.020
Copper "A"	0.001 to 0.005	2	0.020
Copper "B"	0.005 to 2.5	10	0.10
Iron "A"	0.001 to 0.005	2	0.020
Iron "B"	0.005 to 0.10	10	0.10
Lead "A"	0.001 to 0.005	2	0.020
Lead "B"	0.005 to 2.5	10	0.10
Magnesium	0.001 to 0.10	4	0.004

$$V_c = \frac{100}{\bar{c}} \left(\frac{\sum (c - \bar{c})^2}{n - 1} \right)^{\frac{1}{2}} \quad (2)$$

$$V_o = \frac{100}{\bar{c}} \left(\frac{\sum (o - \bar{o})^2}{n - 1} \right)^{\frac{1}{2}} \quad (3)$$

where:

V_c = calibration variability,

\bar{c} = average absorbance value for the highest calibration solution,

C = individual absorbance readings on the highest calibration solution,

$\sum (c - \bar{c})^2$ = sum of the squares of the n differences between the absorbance readings on the highest calibration solution and their average,

$\frac{V_o}{\bar{c}}$ = reference variability relative to \bar{c} ,

$\frac{V_o}{\bar{o}}$ = reference variability,

\bar{o} = average absorbance value for the reference solution,

o = individual absorbance readings on the reference solution,

$\sum (o - \bar{o})^2$ = sum of the squares of the n differences between the absorbance readings on the reference solution and their average, and

n = number of readings taken on each solution.

22.1.8 If the variability of the readings of the highest calibration and the reference solutions are not equal to or smaller than the values specified in **Table 4**, the stability of the instrument shall be improved before this test method may be used.

23. Reagents

23.1 *Aluminum, Standard Solution* (1 mL = 1.00 mg Al)—Transfer ±1.0000 g of aluminum (purity: 99.95 % minimum) to a 250-mL beaker, cover, and add 50 mL of HCl (1 + 1). After the reaction has subsided, add 1 mL of H₂O₂ and boil to complete dissolution. Cool and transfer to a 1-L volumetric flask. Add 50 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle.

23.2 *Cadmium, Standard Solution* (1 mL = 1.00 mg Cd)—Transfer ±1.0000 g of cadmium (purity: 99.95 % minimum) to a 250-mL beaker, cover, and add 25 mL of HNO₃ (1 + 1) and 5 mL of HCl. Boil gently to complete dissolution and to remove oxides of nitrogen. Cool and transfer to a 1-L volumetric flask. Add 50 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle.

23.3 *Copper, Standard Solution* (1 mL = 1.00 mg Cu)—Transfer ±1.0000 g of copper (purity: 99.95 % minimum) to a 250-mL beaker, cover, and add 25 mL of HNO₃ (1 + 1) and 5 mL of HCl. Boil gently to complete dissolution and to remove the oxides of nitrogen. Cool and transfer to a 1-L volumetric flask. Add 50 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle.

23.4 *Iron, Standard Solution* (1 mL = 1.00 mg Fe)—Transfer ±1.0000 g of iron (purity: 99.95 % minimum) to a 250-mL beaker, cover, and add 50 mL of HCl (1 + 1). Boil gently to complete dissolution. Cool and transfer to a 1-L volumetric flask. Add 50 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle.