



Designation: **E536—08 E536 – 15**

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 following ~~limits:~~limits of [Table 1](#).

Element	Concentration 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

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

Element	Concentration 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:

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

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

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
- E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
- ~~E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry~~
- 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 1998)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, Reagents, and Photometric Practice~~ 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**. ~~Photometers 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 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 as directed in Practice **E29**, Rounding Method.

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

10. Scope

- 10.1 This test method covers the determination of aluminum in concentrations from 0.5 % to 4.5 %.

11. Summary of Test Method

11.1 After dissolution of the sample in ~~hydrochloric acid, 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 concentrations are under the maximum limits shown in **1.1**.

13. Apparatus

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

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.

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) solution and dilute to 100 mL.

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

NOTE 1—Although it is not critical that this solution be prepared with a 1 L volumetric, doing so makes it more consistent and easier for the analyst run to run.

14.3 *Methyl Red Indicator Solution* (0.4 g/L)—Dissolve 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 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 % min) in 20 mL of hydrochloric acid (HCl). Dilute to 100 mL. Add 3 drops of methyl red solution and neutralize with ammonium hydroxide (NH₄OH). 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 with **Table 2** the following:

Aluminum, %	Sample Weight, 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

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 to 3 min. If a residue remains, add 1 mL of hydrogen peroxide (H₂O₂) and boil the solution for at least 5 min to destroy excess H₂O₂ and expel free chlorine.

NOTE 3—Excess peroxide and free chlorine must 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 must 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.

15.6 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 to 5 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 min. Cool in a water bath.

TABLE 2 Recommended Sample Weight

Aluminum, %	Sample Weight, 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

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:

$$\text{Aluminum, \%} = (AB/C) \times 100 \tag{1}$$

where:

- A = standard zinc solution used in 15.11, mL;
- B = aluminum equivalent of the standard zinc solution, g/mL; and
- B = aluminum equivalent of the standard zinc solution, g/mL (noted in 14.7); and
- C = sample represented in the aliquot taken, g.
- 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 43.

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 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 , 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

18. Scope

18.1 This test method covers the determination of aluminum in concentrations 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 %.

19. Summary of Test Method

19.1 ~~A hydrochloric acid~~ An HCl solution of the sample is aspirated into the flame of an atomic absorption spectrophotometer. 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. ~~Concentration-Calibration Composition Range~~

20.1 The ~~concentration-calibration composition range~~ for each element must be determined experimentally, because the optimum range will depend upon the individual instrument. If the optimum ~~concentration-calibration~~ range and instrument parameters have been determined, proceed in accordance with ~~in~~ Section 26; otherwise, determine the ~~concentration-calibration~~ range in accordance with ~~in~~ 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 adjust accordingly to suit their instrument.

21. Interferences

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

22. Apparatus

22.1 *Atomic Absorption Spectrophotometer, Spectrometer*, equipped with a premix burner, with facilities for using the oxidizer-fuel combinations listed in Table 4the following table. Use hollow-cathode lamps operated in accordance with manufacturer’s recommendations as sources for the spectral lines. The instrument may be considered suitable for this test method

TABLE 43 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

TABLE 4 Minimum Response, Calibration, and Reference Variability

Element	Spectral Line, 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

if a concentration composition range can be found for which the minimum response, calibration variability, and reference variability tabulated in the [Table 4](#) following table can be met:

Element	Spectral Line, 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

22.1.1 Prepare the dilute standard solution, reference, and calibration solutions in accordance with Section 24. Refer to the [Table 5](#) table in 24.1 for suggested initial concentrations.

22.1.2 Prepare the instrument for use in accordance with in 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 must be equal to or greater than the number of scale units specified in the [Table 4](#) table in 22.1. For purposes of this test method, the scale unit is defined as one in the least significant digit of the scale reading of the most concentrated calibration solution.

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

22.1.4 *Curve Linearity*—Calculate the difference between the scale readings 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 must 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 concentration 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 concentration 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 concentration range, and repeat 22.1.1 – 22.1.4. If a concentration range cannot be found for which both criteria can be met, do not use this test method until the performance of the apparatus satisfies the requirements.

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

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

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

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

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

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,

V_o = reference variability relative to \bar{c} ;

V_o = reference variability relative to \bar{c} ;

\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 22.1.4 Table 4, the stability of the instrument must be improved before this test method may be used.

23. Reagents

23.1 *Aluminum, Standard Solution* (1 mL = 1.00 mg Al)—Transfer 1 g of aluminum (purity: 99.95 % ~~min~~ 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 mg Cd)—Transfer 1 g of cadmium (purity: 99.95 % ~~min~~ 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 mg Cu)—Transfer 1 g of copper (purity: 99.95 % ~~min~~ 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 mg Fe)—Transfer 1 g of iron (purity: 99.95 % ~~min~~ 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.

23.5 *Lead, Standard Solution* (1 mL = 1 mg Pb)—Transfer 1 g of lead (purity: 99.95 % ~~min~~ minimum) to a 250-mL beaker, cover, and add 50 mL of HNO₃ (1 + 1). Boil gently to complete dissolution and to remove oxides of nitrogen. Cool and transfer to a 1-L volumetric flask. Add 50 mL of HNO₃, dilute to volume, and mix. Store in a polyethylene bottle.

23.6 *Magnesium, Standard Solution* (1 mL = 0.1 mg Mg)—Transfer 0.1 g of magnesium (purity: 99.95 % ~~min~~ minimum) to a 250-mL beaker, cover, and add 25 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.