



Designation: E 536 – 04

## Standard Test Methods for Chemical Analysis of Zinc and Zinc Alloys<sup>1</sup>

This standard is issued under the fixed designation E 536; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

### 1. Scope

1.1 These test methods cover the chemical analysis of zinc and zinc alloys having chemical compositions within the following limits:

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 These test methods appear as follows:

	Sections
Aluminum by the EDTA Titrimetric Method (0.5 to 4.5 %)	9-16
Aluminum, Cadmium, Copper, Iron, Lead, and Magnesium by the Atomic Absorption Method	17-27

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 precautionary statements are given in Section 6.

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals
- E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

<sup>1</sup> These test methods are 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 Cu, Pb, Zn, Cd, Sn, Be, their Alloys and Related Materials.

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<sup>2</sup> 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.

- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals
- E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals
- E 1601 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 E 135.

### 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

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 E 50. Photometers shall conform to the requirements prescribed in Practice E 60.

### 6. Safety Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E 50.

### 7. Sampling

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

### 8. Rounding Calculated Values

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

## 9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the precision section.

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

## 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, 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.

### 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 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.

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  $5.5 \pm 0.1$  with NaOH solution or acetic acid and dilute to 1 L.

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 HCl. Dilute to 100 mL. Add 3 drops of methyl red solution and neutralize with  $\text{NH}_4\text{OH}$ . Add HCl until the color changes to red. Transfer to a 1-L volumetric flask, dilute to volume, and mix.

### 15. Procedure

15.1 Select and weigh a sample to the nearest 1 mg, in accordance with the following:

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 to 3 min. If a residue remains, add 1 mL of  $\text{H}_2\text{O}_2$  and boil the solution for at least 5 min to destroy excess  $\text{H}_2\text{O}_2$  and expel free chlorine.

NOTE 1—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 2—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 5 or 6 drops of methyl red solution. Add  $\text{NH}_4\text{OH}$  until the color changes to orange.

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

15.8 Add 4 drops of xylenol orange solution and 5 or 6 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 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:

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

where:

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

*B* = aluminum equivalent of the standard zinc solution, g/mL, and

*C* = sample represented in the aliquot taken, g.

### 17. Precision and Bias

17.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the results summarized in Table 1.

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

**TABLE 1 Statistical Information**

Test Specimen	Aluminum Found, %	Repeatability ( $R_1$ , E 173)	Reproducibility ( $R_2$ , E 173)
G-3	0.3998	0.0190	0.0254
H-2	4.04	0.052	0.074

Element	Concentration, %	Flame	Wavelength, nm	Repeatability, %	Reproducibility, %
Aluminum	309.2	$N_2O-C_2H_2$	"A"	9	3.5
			"B"	25	1.0
Cadmium	228.8	Air- $C_2H_2$	...	50	0.8
Copper	324.7	Air- $C_2H_2$	"A"	15	2.0
			"B"	50	0.8
Iron	248.3	Air- $C_2H_2$	"A"	15	2.0
			"B"	25	1.0
Lead	217.0	Air- $C_2H_2$	"A"	10	2.0
			"B"	30	1.0
Magnesium	285.2	$N_2O-C_2H_2$	...	20	1.5

an accepted reference material, if available, to determine that the accuracy of results is satisfactory.

17.3 Practice E 173 has been replaced by Practice E 1601. The reproducibility Index  $R_2$ , corresponds to the Reproducibility Index R of Practice E 1601. Likewise the Repeatability Index  $R_1$  of Practice E 173 corresponds to the Repeatability Index r of Practice E 1601.

### 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 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 Range

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

#### 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*, equipped with a premix burner, with facilities for using the oxidizer-fuel combinations listed in the 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 if a concentration range can be found for which the minimum response, calibration variability, and reference variability tabulated in the following table can be met:

Element	Spectral Line, nm	Oxidizer-Fuel	Standard Solution	Minimum Response, Units	Calibration Variability, %	Reference Variability, %
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22.1.1 Prepare the dilute standard solution, reference, and calibration solutions in accordance with Section 24. Refer to the 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 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.

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:

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

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