



Standard Test Methods for Chemical Analysis of Magnesium and Magnesium Alloys¹

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1. Scope

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

Aluminum, %	0.5 to 12
Copper, %	0.005 to 0.1
Iron, %	0.002 to 0.1
Lead, %	0.001 to 0.5
Manganese, %	0.01 to 2.0
Nickel, %	0.0005 to 0.5
Rare earth elements, %	0.2 to 10
Silicon, %	0.01 to 0.8
Thorium, %	0.2 to 25
Tin, %	0.5 to 10
Zinc, %	0.3 to 20
Zirconium, %	0.03 to 1.0
Magnesium, %	remainder

1.2 The analytical procedures appear in the following order:

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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 precautions are given in Section 5.

2. Referenced Documents

2.1 ASTM Standards:

- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance With Specifications³
- E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron⁴
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁴
- E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition⁴
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁴
- E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition⁴

3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended 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.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and certain other reagents used

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² Appears in the gray pages of the *Annual Book of ASTM Standards*, Vol 03.05.

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

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50, except that photometers shall conform to the requirements prescribed in Practice E 60.

4.2 The photometric practice prescribed in these test methods shall conform to Practice E 60.

5. Safety Precautions

5.1 For precautions to be observed in the use of certain reagents in these test methods, reference shall be made to Practices E 50.

5.2 Because of the reactivity of magnesium with mineral acids, it is recommended that concentrated acids should not be added directly to the alloy, especially in the case of finely divided material.

6. Sampling

6.1 Wrought products shall be sampled in accordance with Practice E 55. Cast products shall be sampled in accordance with Practice E 88.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places in accordance with the rounding method of Practice E 29.

ALUMINUM BY THE BENZOATE-OXINATE (GRAVIMETRIC) TEST METHOD

8. Scope

8.1 This test method covers the determination of aluminum in concentrations from 0.5 to 12 %. Since this test method is capable of giving very accurate results, it is recommended for referee analysis.

9. Summary of Test Method

9.1 Aluminum is precipitated first as the benzoate and then as the oxinate. The latter is dried and weighed.

10. Interferences

10.1 No appreciable interference is caused by the ordinary quantities of zinc, manganese, tin, or silicon found in magnesium alloys. Copper will remain largely insoluble in hydrochloric acid, the amount going into solution being too small to cause serious interference. Zirconium and thorium would interfere if present, but are not usually encountered in magnesium-aluminum alloys. Zirconium and aluminum are incompatible. Iron can be removed by precipitation from the ammoniacal tartrate solution with hydrogen sulfide just before the precipitation with 8-quinolinol. Interference due to minor quantities of iron and cerium can be eliminated by the addition of hydroxylamine hydrochloride prior to the precipitation of the aluminum as the benzoate.

11. Apparatus

11.1 *Filtering Crucible*—A 15-mL fritted-glass crucible of medium porosity. Apparatus No. 2.

12. Reagents

12.1 *Ammonium Benzoate Solution* (100 g/L)—Dissolve

100 g of ammonium benzoate in 1 L of warm water and add 1 mg of thymol as a preservative.

12.2 *Ammonium Tartrate Solution* (30 g/L)—Dissolve 30 g of ammonium tartrate in 500 mL of water, add 120 mL of NH_4OH , and dilute to 1 L.

12.3 *Benzoate Wash Solution*—To 100 mL of the ammonium benzoate solution, add 900 mL of warm water and 20 mL of glacial acetic acid.

12.4 *8-Quinolinol (Oxine) Solution* (50 g/L)—Dissolve 50 g of 8-quinolinol in 120 mL of glacial acetic acid and dilute to 1 L. Filter and store in a dark bottle.

13. Procedure

13.1 Weigh, to the nearest 1 mg, a portion of the sample calculated to contain 0.2 to 0.3 g of aluminum and transfer to a 400-mL beaker containing 50 mL of water. Dissolve the sample by adding, in small portions, a total of 10 mL of HCl per gram of sample. When dissolved, cool to room temperature and dilute to 500 mL in a volumetric flask. Any residue of undissolved silica, which might contain some occluded aluminum, should be kept in suspension.

13.2 Pipet a 50.0-mL aliquot into a 400-mL beaker and dilute to 100 mL. Neutralize the solution with NH_4OH (1 + 1) by adding dropwise with stirring until the precipitate that forms as each drop strikes finally redissolves only very slowly; that is, until nearly all of the free acid is neutralized without permanent precipitation of $\text{Al}(\text{OH})_3$. Add 1 mL of glacial acetic acid, about 1 g of NH_4Cl , and 20 mL of ammonium benzoate solution. Heat the mixture to boiling while stirring, keep at gentle boiling for 5 min, and then filter on a medium paper. Wash the precipitate eight to ten times with hot benzoate wash solution, making no effort to transfer all of the precipitate to the filter paper.

13.3 Dissolve the precipitate with five 10-mL portions of hot ammonium tartrate solution, washing with hot water after each portion is added. Collect the solution in the original beaker and dilute to 150 to 200 mL. Heat the solution to 70 to 90°C, add 20 mL of 8-quinolinol solution, and digest for 15 min without boiling. Filter the solution through a tared, fritted-glass crucible, and wash eight times with hot water, transferring all of the precipitate.

13.4 Dry the precipitate for 2 h at 120 to 130°C, cool, and weigh as aluminum oxinate ($\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$).

14. Calculation

14.1 Calculate the percentage of aluminum as follows:

$$\text{Aluminum, \%} = [(A \times 0.0587)/B] \times 100 \quad (1)$$

where:

A = aluminum oxinate, g, and

B = sample in aliquot used, g.

15. Precision and Bias

15.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method is adequate for the contemplated use.

**ALUMINUM BY THE SODIUM HYDROXIDE
(POTENTIOMETRIC) TEST METHOD
(Optional Rapid Method)**

16. Scope

16.1 This test method covers the rapid determination of aluminum in concentrations from 2 to 12 %. For referee analysis, the method described in Sections 8-15 shall be used.

17. Summary of Test Method

17.1 The sample is dissolved in hydrochloric acid, the excess acid is partially neutralized with ammonium hydroxide (1 + 2), and the neutralization is completed with 1 *N* sodium hydroxide solution to a final potentiometric end point. Aluminum is then titrated with 1 *N* sodium hydroxide solution to a final potentiometric end point.

18. Interferences

18.1 Bismuth interferes with the potential changes of the antimony electrode and may be removed, if present, by precipitation with hydrogen sulfide and expulsion of excess hydrogen sulfide by boiling before titration. Copper and silver lower the potentials of the end points but do not interfere with the deflections. The presence of abnormal amounts of dissolved silicic acid and ferric iron cause high results. Ceric cerium, thorium, zirconium, titanium, and tin must be absent. Zinc, cadmium, nickel, and manganese do not interfere.

19. Apparatus

19.1 *Apparatus for Potentiometric Titration*—Apparatus No. 3B. The titration assembly shall consist of an antimony electrode and a saturated calomel electrode with a potassium chloride salt bridge terminating in a porous-glass or porcelain plug. These shall dip into a titration beaker, which shall be provided with a thermometer and a mechanical stirrer and be mounted on a support in such a way that the beaker can be heated.

20. Reagents

20.1 *Bromophenol Blue Indicator Solution* (4 g/L)—Place 0.40 g of bromophenol blue in a mortar, add 8.25 mL of sodium hydroxide solution (5 g NaOH per litre), and mix until solution is complete. Dilute to 100 mL with water and mix.

20.2 *Indicator-Buffer Solution*—Add 8 mL of bromophenol blue indicator solution to 1 L of saturated NH₄Cl solution.

20.3 *Sodium Hydroxide, Standard Solution* (1 *N*)—See Reagent No. 16.

21. Procedure

21.1 Weigh, to the nearest 1 mg, a portion of the sample calculated to contain approximately 0.15 g of aluminum and place it in a 250-mL beaker containing 50 mL of water. Add, in small portions, 7.5 mL of HCl per gram of sample, and then 1 mL in excess.

21.2 When the dissolution is complete, cool to room temperature and add 20 mL of the indicator-buffer solution. Place the beaker in the titration assembly, start the stirrer, and titrate the excess acid with dropwise additions of NH₄OH (1 + 2) until the potentiometer shows a rapid increase in deflection.

Continue titrating with 1 *N* NaOH solution, using two-drop increments, to the first potentiometric break, shown by a maximum deflection at a potential of 150 to 190 mV and occurring very nearly at the color change from yellow to blue.

21.3 Heat the solution to 80°C and, while maintaining the temperature of the solution at this level, titrate again with 1 *N* NaOH solution to a second end point as shown by a maximum deflection occurring at a potential of 275 to 300 mV.

NOTE 1—The reaction upon which this titration is based is believed to be as follows:


22. Calculation

22.1 Calculate the percentage of aluminum as follows:

$$\text{Aluminum, \%} = [(AB \times 0.0108)/C] \times 100 \quad (3)$$

where:

A = NaOH solution required for titration of the sample from the first to the second potentiometric end point, mm,

B = normality of the NaOH solution, and

C = sample used, g.

23. Precision and Bias

23.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method is adequate for the contemplated use.

**COPPER BY THE NEOCUPROINE (PHOTOMETRIC)
TEST METHOD**

24. Scope

24.1 This test method covers the determination of copper in concentrations under 0.05 %.

25. Summary of Test Method

25.1 Cuprous copper is separated from other metals by extraction of the neocuproine complex with chloroform. Photometric measurement is made at approximately 455 nm.

26. Concentration Range

26.1 The recommended concentration range is from 0.005 to 0.05 mg of copper in 50 mL of solution, using a cell depth of 5 cm.

NOTE 2—This test method has been written for cells having a 5-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

27. Stability of Color

27.1 The color develops in an aqueous media within 5 min, and the extracted complex is stable for at least a week.

28. Interferences

28.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.2.

29. Reagents

29.1 *Chloroform*.

29.2 *Copper, Standard Solution* (1 mL = 0.01 mg Cu)—Dissolve 0.2000 g of copper in 15 mL of water and 3 mL of HNO₃. When dissolution is complete, boil out all nitrogen oxide fumes, cool, and dilute to 1 L with water. Pipet 50 mL of this solution into another 1-L flask and dilute to volume with water.

29.3 *Hydrogen Peroxide* (30 %)—Concentrated hydrogen peroxide (H₂O₂).

29.4 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 10 g of hydroxylamine hydrochloride (NH₂OH · HCl) in water and dilute to 100 mL.

29.5 *Neocuproine Solution* (1 g/L)—Dissolve 50 mg of 2,9-dimethyl-1,10-phenanthroline hemihydrate in 50 mL of absolute ethyl alcohol.

29.6 *Sodium Citrate Solution* (100 g/L)—Dissolve 100 g of sodium citrate dihydrate in water and dilute to 1 L.

30. Preparation of Calibration Curve

30.1 *Calibration Solutions*—Transfer 0.5, 1.0, 2.0, 3.0, and 5.0 mL of copper solution (1 mL = 0.01 mg Cu) to 100-mL beakers. Dilute to approximately 40 mL and add HCl until the solution is acid to congo red paper. Proceed in accordance with 30.3.

30.2 *Reference Solution*—Transfer 40 mL of water to a 100-mL beaker and add HCl until the solution is acid to congo red paper. Proceed in accordance with 30.3.

30.3 *Color Development*:

30.3.1 Add 5.0 mL of hydroxylamine hydrochloride solution and stir. Add 5.0 mL of sodium citrate solution and swirl. Neutralize the solution with NH₄OH (1 + 1) until it is definitely alkaline to congo red paper. Add 4.0 mL of the neocuproine solution, stir, and allow to stand for 5 min.

30.3.2 Transfer the solution to a 250-mL separatory funnel and add 20 mL of chloroform. Shake the mixture and allow the layers to separate. Place a glass wool plug that has been washed with chloroform in a small funnel and filter the organic layer, catching the filtrate in a dry 50-mL volumetric flask.

30.3.3 Add another millilitre of the neocuproine solution to the separatory funnel, shake, and re-extract with 20 mL of chloroform. Filter the organic layer into the volumetric flask and dilute to volume with chloroform.

30.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 455 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

30.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of copper per 50 mL of solution.

31. Procedure

31.1 *Test Solution*—Weigh, to the nearest 1 mg, a portion of the sample calculated to contain from 0.005 to 0.05 mg of copper and transfer it to a 100-mL beaker. Add 25 mL of water and dissolve the sample by adding small portions of HCl. (Use 7.5 mL of HCl per gram of sample.) When dissolution is

complete (Note 3), add a few drops of hydrogen peroxide solution, boil to remove excess peroxide, cool, and dilute to approximately 40 mL.

NOTE 3—In case there is insoluble material remaining, filter the solution and treat the residue with HF to eliminate silica. Fuse any remaining residue with potassium bisulfate (KHSO₄) and add the dissolved melt to the original filtrate.

31.2 *Reference Solution*—Transfer 40 mL of water to a 100-mL beaker and add HCl until the solution is acid to congo red paper.

31.3 *Color Development*—Develop the color as described in 30.3.

31.4 *Photometry*—Take the photometric reading of the test solution in accordance with 30.4.

32. Calculation

32.1 Convert the photometric reading of the test solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{Copper, \%} = A/(B \times 10) \quad (4)$$

where:

A = copper found, mg, and

B = sample used, g.

33. Precision and Bias

33.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

COPPER BY THE HYDROBROMIC ACID- PHOSPHORIC ACID (PHOTOMETRIC) TEST METHOD

34. Scope

34.1 This test method covers the determination of copper in concentrations from 0.005 to 0.1 %.

35. Summary of Test Method

35.1 Cupric copper forms a violet-colored complex in strong hydrobromic acid solution. Phosphoric acid is added to minimize interference from iron. Photometric measurement is made at approximately 600 nm.

36. Concentration Range

36.1 The recommended concentration range is from 0.05 to 0.6 mg of copper per 25 mL of solution, using a cell depth of 1 cm.

NOTE 4—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

37. Stability of Color

37.1 The color is stable for at least 2 h.

38. Interferences

38.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1. Molybdenum, vanadium, chromium, cobalt, gold, the platinum metals, and certain elements of the rare earth group would cause interference, if present. Iron or nickel may cause somewhat high results if present in an amount equaling or exceeding the amount of copper. Provision is made in the test method for separation of copper from all elements but the noble metals.

39. Reagents

39.1 *Bromine Water (saturated).*

39.2 *Copper, Standard Solution* (1 mL = 0.02 mg Cu)—Dissolve 0.2000 g of “pure” copper in 15 mL of HBr containing 1 mL of bromine (Br₂) and dilute to 250 mL in a volumetric flask. Dilute 25 mL of this solution to 1 L in a volumetric flask.

39.3 *Hydrobromic Acid-Bromine Solution*—Add 1 drop of bromine to 250 mL of HBr and mix.

40. Preparation of Calibration Curve

40.1 *Calibration Solutions*—Transfer 2.0, 5.0, 10.0, 20.0, and 30.0 mL of copper solution (1 mL = 0.02 mg Cu) to 100-mL beakers.

40.2 *Reference Solution*—Prepare a reagent blank, using the same amounts of all reagents, to be used as a reference solution.

40.3 *Color Development*—Add enough bromine water, dropwise, to produce a yellow color, and then add 3 mL of HBr-Br₂ solution. Evaporate the solution to 3 mL, or slightly less, and cool. Add 3 mL of HBr-Br₂ solution plus 12.5 mL of H₃PO₄ and transfer the solution to a 25-mL, glass-stoppered volumetric flask. Rinse the beaker with small portions of HBr-Br₂ solution and add these washings to the flask. Dilute to volume with the HBr-Br₂ solution.

40.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 600 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

40.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of copper per 25 mL of solution.

41. Procedure

41.1 *Test Solution*—Weigh, to the nearest 1 mg, a portion of the sample of not more than 1 g containing from 0.1 to 1.2 mg of copper, but with no more iron or nickel than copper (Note 5). Transfer to a 100-mL beaker and add 25 mL of water. Treat with HBr-Br₂ solution, adding it in small portions and using a total of 10 mL per gram of sample plus an excess of 3 mL. Warm to dissolve all the metal, adding a little bromine water if necessary. Cool, transfer to a 50-mL volumetric flask, and dilute to volume with water. Pipet a 25-mL aliquot into a 100-mL beaker.

NOTE 5—To remove iron or nickel, transfer 0.5 to 1.0 g of the sample to a 250-mL beaker containing 25 mL of water and treat with small

portions of HCl (2 + 3) until a total of 25 mL per gram of sample has been added. After the reaction subsides, add a few drops of H₂O₂ to facilitate the solution of all the copper. Boil the solution to remove chlorine, dilute to about 50 mL, and add 1 g of finely granulated, low-copper lead. Bring the solution to a boil and continue gentle boiling for 15 min to displace the copper completely. Cool, and decant the solution, washing once with water. (If desired, this solution may be placed in a separatory funnel and used for the determination of nickel by the dimethyl-glyoxime photometric method.) Warm the beaker containing the lead and copper gently to remove moisture; then dissolve the metal in 10 mL of HBr-Br₂ solution and a few drops of liquid bromine. Boil to expel the bromine. Cool, transfer to a 50-mL volumetric flask, and dilute to volume with water. Pipet a 25-mL aliquot into a 100-mL beaker and proceed in accordance with 41.3.

41.2 *Reference Solution*—Prepare a reagent blank, using the same amounts of all reagents, for use as a reference solution.

41.3 *Color Development*—Develop the color as described in 40.3. Filter off any insoluble material on a dry, fritted-glass crucible.

41.4 *Photometry*—Take the photometric reading of the test solution in accordance with 40.4.

42. Calculation

42.1 Convert the photometric reading of the test solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{Copper, \%} = A/(B \times 10) \quad (5)$$

where:

A = copper found in 25 mL of the final solution, mg, and
B = sample represented in 25 mL of the final solution, g.

43. Precision and Bias

43.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

IRON BY THE 1,10-PHENANTHROLINE (PHOTOMETRIC) TEST METHOD

44. Scope

44.1 This test method covers the determination of iron in concentrations under 0.1 %. Larger percentages may be determined by taking an aliquot portion of the sample.

45. Summary of Test Method

45.1 Ferrous iron, in a solution having a pH of about 5, forms an orange-red complex with 1,10-phenanthroline. Photometric measurement is made at approximately 510 nm.

NOTE 6—If desired, a 1 % alcoholic solution of 2,2'-bipyridine may be used for color development. Photometric measurement should be made at approximately 520 nm.

46. Concentration Range

46.1 The recommended concentration ranges are from 0.01

to 0.10 mg and from 0.10 to 0.50 mg of iron in 100 mL of solution, using cell depths of 5 cm and 1 cm respectively.

NOTE 7—This procedure has been written for cells having 5-cm and 1-cm light paths. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

47. Stability of Color

47.1 The color develops within 15 min and is stable for at least 2 h.

48. Interferences

48.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1. Neodymium causes a slight positive interference when present in large amounts. Half a milligram of copper per 100 mL of solution changes the hue of the solution, but interferes only slightly when excess reagent is added. Zinc, nickel, and cadmium form complexes and consume 1,10-phenanthroline but do not interfere if sufficient reagent is used.

49. Reagents

49.1 *Acetate Buffer Solution* (pH 5)—Dissolve 272 g of sodium acetate trihydrate in 500 mL of water. Add 240 mL of glacial acetic acid, cool, and dilute to 1 L.

49.2 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 10 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in water and dilute to 100 mL.

49.3 *Iron, Standard Solution A* (1 mL = 0.100 mg Fe)—Dissolve 0.1000 g of iron wire (primary standard) in 50 mL of water, 25 mL of HCl, and 1 mL of HNO_3 . Dilute with water to 1 L in a volumetric flask.

49.4 *Iron, Standard Solution B* (1 mL = 0.010 mg Fe)—Pipet 100 mL of iron Solution A into a 1-L volumetric flask, add 10 mL of HCl, and dilute to volume.

49.5 *Phenanthroline Solution* (10 g/L)—Dissolve 2.5 g of 1,10-phenanthroline in methyl alcohol and dilute to 250 mL with alcohol.

50. Preparation of Calibration Curves

50.1 Calibration Solutions:

50.1.1 Transfer 1.0, 2.0, 3.0, 4.0, and 5.0 mL of iron Solution A (1 mL = 0.100 mg Fe) to five 100-mL volumetric flasks. Dilute to 50 mL and proceed in accordance with 50.3.

50.1.2 Transfer 1.0, 3.0, 5.0, 8.0, and 10.0-mL portions of iron Solution B (1 mL = 0.010 mg Fe) to five 100-mL volumetric flasks. Dilute to 50 mL and proceed in accordance with 50.3.

50.2 *Reference Solution*—Transfer 50 mL of water to a 100-mL volumetric flask and proceed in accordance with 50.3.

50.3 *Color Development*—Add in order the following solutions, mixing after each addition: 4 mL of hydroxylamine hydrochloride solution, 10 mL of acetate buffer solution, and 10 mL of phenanthroline solution. Dilute to volume and mix. Allow to stand for 15 min.

50.4 Photometry:

50.4.1 Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path and adjust the photometer to the initial setting, using a light band centered at

approximately 510 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions containing 0.01 to 0.10 mg of iron.

50.4.2 Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 510 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions containing from 0.10 to 0.50 mg of iron.

50.5 *Calibration Curves*—Plot the photometric readings of the calibration solutions against milligrams of iron per 100 mL of solution.

51. Procedure

51.1 Test Solution:

51.1.1 If the sample is in rod, bar, or sheet form, remove adventitious iron by immersing the entire sample in HCl (1 + 9) for 5 to 10 s, washing with water, then with acetone, and drying. Transfer a portion of the sample, weighed to the nearest 1 mg and containing from 0.01 to 0.50 mg of iron, to a 100-mL beaker and add 25 mL of water. Add HCl in small portions until 7.5 mL per gram of sample have been added, and then add 0.5 mL in excess. When dissolution is complete, heat the solution for a few minutes and filter if necessary. Reserve the filter paper and precipitate for the recovery of insoluble iron. Evaporate the filtrate to a volume of approximately 25 mL. Cool and reserve.

51.1.2 Transfer the filter paper containing the insoluble iron to a platinum crucible. Dry, char, and ignite the precipitate at 600°C for 1 h. Cool the crucible to room temperature, moisten the residue with a few drops of water, add 2 drops of H_2SO_4 and 1 to 2 mL of HF, evaporate to dryness, and cool. Dissolve the residue with 3 to 5 drops of HCl and a minimum of water. Warm the crucible to hasten the dissolution, if necessary. Combine this solution with the original filtrate reserved from 51.1.1. Transfer the solution containing the total iron to a 100-mL volumetric flask.

51.2 *Reference Solution*—Prepare a reagent blank, using the same amounts of all reagents, for use as a reference solution.

51.3 *Color Development*—Develop the color in accordance with 50.3.

51.4 *Photometry*—Take the photometric reading of the test solution in accordance with 50.4.1 or 50.4.2 as required.

52. Calculation

52.1 Convert the photometric reading of the test solution to milligrams of iron, using the appropriate calibration curve. Calculate the percentage of iron as follows:

$$\text{Iron, \%} = A/(B \times 10) \quad (6)$$

where:

A = iron found in 100 mL of final solution, mg, and

B = sample used, g.

53. Precision and Bias

53.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory

test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

LEAD BY THE DITHIZONE (PHOTOMETRIC) TEST METHOD

54. Scope

54.1 This test method covers the determination of lead in concentrations from 0.001 to 0.5 %.

55. Summary of Test Method

55.1 Lead reacts with diphenylthiocarbazono to form a pink-colored complex in a chloroform solution. The complex is separated from other metals by extraction with chloroform from an aqueous, ammonium citrate-cyanide solution. Photometric measurement is made at approximately 520 nm.

56. Concentration Range

56.1 The recommended concentration range is from 0.002 to 0.015 mg of lead in 10 mL of solution, using a cell depth of 1 cm (Note 4).

57. Stability of Color

57.1 The color is quite stable if the solution is protected against evaporation and decomposition of the chloroform. Because of the nature of the solvent, it is advisable to make the reading promptly.

58. Interferences

58.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1.

NOTE 8—Bismuth, thallium, indium, and stannous tin interfere but are not likely to be present in magnesium alloys. Bismuth can be determined and compensated for through the use of suitable calibration curves if a second reading is made at 420 to 450 nm. Tin may be oxidized to the harmless stannic form by boiling the hydrochloric acid solution with 1 mL of nitric acid; the other constituents should then be reduced by boiling with a slight excess of hydroxylamine hydrochloride. The blank should receive the same treatment.

59. Reagents

59.1 *Ammonium Citrate Solution* (50 g/L)—Dissolve 40 g of citric acid in water, neutralize with NH_4OH , and dilute to 1 L.

59.2 *Dithizone Solution*—Dissolve 0.0025 g of diphenylthiocarbazono in 100 mL of chloroform.

59.3 *Extraction Solution A*—To 435 mL of water, add 30 mL of KCN solution, 30 mL of ammonium citrate solution, and 5 mL of NH_4OH .

59.4 *Extraction Solution B*—To 500 mL of water, add 10 mL of KCN solution and 5 mL of NH_4OH .

59.5 *Lead, Standard Solution* (1 mL = 0.001 mg Pb)—Dissolve 0.1342 g of lead chloride (PbCl_2) in water containing 1 mL of HCl and dilute to 1 L in a volumetric flask. Pipet a 10-mL aliquot of this solution into another 1-L volumetric flask, add 0.5 mL of HCl, and dilute to volume. Prepare fresh as needed.

59.6 *Potassium Cyanide Solution* (50 g/L)—Dissolve 50 g of potassium cyanide (KCN) in water and dilute to 1 L.

60. Preparation of Calibration Curve

60.1 *Calibration Solutions*—Transfer 2.0, 5.0, 10.0, and 15.0 mL of the lead solution (1 mL = 0.001 mg Pb) to 125-mL separatory funnels (Note 9) and add enough water to make a total volume of 15 mL. Add 15 mL of extraction Solution A.

NOTE 9—All glassware used in this determination shall be cleaned thoroughly with HNO_3 and rinsed well with water.

60.2 *Reference Solution*—Add 15 mL of water and 15 mL of extraction Solution A to a 125-mL separatory funnel.

60.3 *Color Development*—From a buret, add dithizone solution in 1-mL increments, introducing just enough so that after shaking and allowing the layers to separate, the lower layer has a noticeable purple to green color which indicates a slight excess of dithizone. From another buret, add chloroform to make a total volume of dithizone solution and chloroform of exactly 10 mL. Shake the mixture well and allow the layers to separate. Draw off the lower chloroform layer into another 125-mL separatory funnel containing 20 mL of extraction Solution B. Discard the aqueous solution in the first funnel. Shake the mixture in the second funnel well, allow the layers to separate, and drain off the lower chloroform layer into a third 125-mL separatory funnel containing 20 mL of extraction Solution B. Shake the mixture and allow the layers to separate thoroughly. Insert a small plug of cotton in the stem of the separatory funnel.

60.4 *Photometry*—Filter a suitable portion of the reference solution through the cotton plug into an absorption cell with a 1-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 520 nm (Note 10). While maintaining this adjustment, take the photometric readings of the calibration solutions.

NOTE 10—The color of the reference solution may be due not only to lead in the reagents but to oxidation products of the dithizone.

60.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of lead per 10 mL of solution.

61. Procedure

61.1 Test Solution:

61.1.1 Weigh, to the nearest 1 mg, a portion of the sample calculated to contain 0.1 to 0.7 mg of lead and transfer to a 250-mL beaker. Add 30 mL of water and dissolve the sample with HCl (1 + 1), using 20 mL per gram of sample. When dissolution is complete, heat to boiling and dilute to 200 mL. Cool the solution, transfer to a 500-mL volumetric flask, and dilute to volume.

61.1.2 Pipet a 10-mL aliquot into a 125-mL separatory funnel. Pipet another 10-mL aliquot into a small beaker and titrate with NH_4OH (1 + 9) until alkaline to methyl red. To the aliquot in the separatory funnel, add 15 mL of extraction Solution A and as much NH_4OH (1 + 9) as was found necessary to neutralize the free acid in the duplicate aliquot (Note 11). Proceed in accordance with 61.3.

NOTE 11—If the lead content is low, so that the aliquot taken contains appreciable aluminum, additional ammonium citrate may be required to

prevent the precipitation of aluminum hydroxide. Since citrate hinders the extraction of lead, as little as possible should be used.

61.2 *Reference Solution*—Carry a reagent blank through all of the steps of the procedure, starting with the same quantity of HCl (1 + 1) and evaporating most of it before diluting. Proceed in accordance with 61.3.

61.3 *Color Development*—Develop the color in accordance with 60.3.

61.4 *Photometry*—Take the photometric reading of the test solution in accordance with 60.4.

62. Calculation

62.1 Convert the photometric reading of the test solution to milligrams of lead by means of the calibration curve. Calculate the percentage of lead as follows:

$$\text{Lead, \%} = A/(B \times 10) \quad (7)$$

where:

A = lead found in 10 mL of final solution, mg, and

B = sample represented in 10 mL of final solution, g.

63. Precision and Bias

63.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

MANGANESE BY THE PERIODATE (PHOTOMETRIC) TEST METHOD

64. Scope

64.1 This test method covers the determination of manganese in concentrations under 2.0 %.

65. Summary of Test Method

65.1 Manganese in an acid solution is oxidized to permanganate by potassium periodate. Photometric measurement is made at approximately 545 nm.

66. Concentration Range

66.1 The recommended concentration range is from 0.10 to 1.5 mg of manganese in 100 mL of solution, using a cell depth of 1 cm (Note 4).

67. Stability of Color

67.1 The color develops within 15 min and is stable for several weeks providing excess periodate is present.

68. Interferences

68.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1. At least ten times as much cerium as manganese can be present without causing interference.

69. Reagents

69.1 *Manganese, Standard Solution* (1 mL = 0.10 mg

Mn)—Reagent No. 24.

69.2 *Potassium Periodate* (KIO₄).

70. Preparation of Calibration Curve

70.1 *Calibration Solutions*—Transfer 1.0, 5.0, 10.0, and 15.0 mL of the manganese solution (1 mL = 0.10 mg Mn) to 250-mL beakers and dilute to approximately 40 mL. Add 15 mL of H₂SO₄ (1 + 4) and 25 mL of HNO₃.

70.2 *Reference Solution*—Prepare a blank containing 40 mL of water, 15 mL of H₂SO₄ (1 + 4), and 25 mL of HNO₃ for use as a reference solution.

70.3 *Color Development*—Heat the solution to boiling, cool slightly, and carefully introduce 0.5 g of KIO₄. Boil for 3 min and then digest just below boiling for 15 min to develop the full intensity of color. Cool, dilute to 100 mL in a volumetric flask.

70.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 545 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

70.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of manganese per 100 mL of solution.

71. Procedure

71.1 *Test Solutions*:

71.1.1 For alloys with manganese content under 0.15 %, transfer 1.0 g of the sample, weighed to the nearest 1 mg, to a 250-mL beaker. Add 15 mL of water and 25 mL of H₂SO₄ (1 + 4) to dissolve the sample. When the action ceases, add 5 mL of HNO₃ and boil to dissolve any dark residue. If the solution is turbid, filter through a fine paper. Add 20 mL of HNO₃ and proceed in accordance with 70.3.

71.1.2 For alloys with a manganese content over 0.15 %, transfer to a 250-mL beaker, a portion of the sample weighed to the nearest 1 mg and calculated to contain 10 to 20 mg of manganese, and add 15 mL of water. Add 25 mL of H₂SO₄ (1 + 4) per gram of sample. When the action ceases, add 5 mL of HNO₃ and boil to dissolve any dark residue. If the solution appears turbid, filter through a fine paper. Transfer the solution to a 500-mL volumetric flask, dilute to volume, and mix. Pipet an aliquot containing 0.2 to 1.5 mg of manganese into a 250-mL beaker. Add 15 mL of H₂SO₄ (1 + 4) and 25 mL of HNO₃. Proceed in accordance with 70.3.

71.2 *Reference Solution*—Prepare a reference solution as described in 70.2, and proceed in accordance with 70.3.

71.3 *Photometry*—Take the photometric reading in accordance with 70.4.

72. Calculation

72.1 Convert the photometric reading of the sample solution to milligrams of manganese by means of the calibration curve. Calculate the percentage of manganese as follows:

$$\text{Manganese, \%} = A/(B \times 10) \quad (8)$$

where:

A = manganese found in 100 mL of final solution, mg, and

B = sample represented in 100 mL of final solution, g.

73. Precision and Bias

73.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

NICKEL BY THE DIMETHYLGLYOXIME EXTRACTION (PHOTOMETRIC) TEST METHOD

74. Scope

74.1 This test method covers the determination of nickel in concentrations from 0.0005 to 0.005 %. Larger percentages may be determined by taking an aliquot portion of the sample.

75. Summary of Test Method

75.1 Nickel is separated from other metals by extraction of the dimethylglyoxime complex with chloroform. The nickel is re-extracted with acid, oxidized with bromine, and determined photometrically as nickelic dimethylglyoxime at approximately 530 nm.

76. Concentration Range

76.1 The recommended concentration range is from 0.005 to 0.050 mg of nickel in 100 mL of solution, using a cell depth of 5 cm (Note 2).

77. Stability of Color

77.1 The color intensity increases slowly on standing. Readings should be made exactly 10 min after mixing.

78. Interferences

78.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1.

79. Reagents and Materials

79.1 *Bromine Water* (saturated).

79.2 *Chloroform* (CHCl_3).

79.3 *Dimethylglyoxime Solution* (10 g/L in alcohol)—Reagent No. 104.

79.4 *Hydroxylamine Hydrochloride Solution* (50 g/L)—Dissolve 5 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in water and dilute to 100 mL. Prepare fresh as needed.

79.5 *Nickel, Standard Solution* (1 mL = 0.005 mg Ni)—Dissolve 0.1000 g of nickel in 10 mL of water and 5 mL of HNO_3 in a 150-mL beaker. When dissolution is complete, boil to remove the lower oxides of nitrogen. Cool to room temperature, transfer to a 1-L volumetric flask, and dilute to volume. Pipet 25.0 mL of this solution into a 500-mL volumetric flask and dilute to volume. Optionally, the original solution may be prepared from a nickel salt and standardized gravimetrically.

79.6 *Sodium Citrate Solution* (100 g/L)—Dissolve 100 g of sodium citrate dihydrate in water, dilute to 1 L, and mix.

80. Preparation of Calibration Curve

80.1 Calibration Solutions:

80.1.1 Transfer 1.0, 2.0, 5.0, 7.0, and 10.0 mL of the nickel solution (1 mL = 0.005 mg Ni) to 200-mL separatory funnels containing 50 mL of water. Add 2 mL of HNO_3 and 10 mL of sodium citrate to each funnel.

80.1.2 Neutralize each solution to litmus by the dropwise addition of NH_4OH and add a few drops in excess. Introduce 3 mL of dimethylglyoxime solution, mix, and allow to stand for 5 min. Extract with three 10-mL portions of CHCl_3 and combine the CHCl_3 layers in a clean separatory funnel. Wash the combined extracts with a 25-mL portion of NH_4OH (2 + 98) and draw off the CHCl_3 layer into another clean separatory funnel. Extract the ammoniacal wash layer with a 5-mL portion of CHCl_3 , and add this to the main extract. Extract the combined CHCl_3 solution for 1 min successively with a 25-mL and a 15-mL portion of HCl (1 + 19). After the second extraction, draw off the CHCl_3 layer, separating it as completely as possible, and discard. Draw off both acid layers into a 100-mL volumetric flask. Proceed in accordance with 80.3.

80.2 *Reference Solution*—To a 200-mL separatory funnel, add 50 mL of water, 2 mL of HNO_3 , and 10 mL of sodium citrate solution, and proceed in accordance with 80.1.2.

80.3 *Color Development*—To the combined acid extracts add 5 drops of saturated bromine water. Add NH_4OH (1 + 1) dropwise until the bromine color is destroyed, and then 3 or 4 drops in excess. Add 0.5 mL of dimethylglyoxime solution, dilute to 100 mL, and mix. Allow the solution to stand exactly 10 min.

80.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 5.0-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 530 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

80.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of nickel per 100 mL of solution.

81. Procedure

81.1 Test Solution:

81.1.1 Transfer 1 g of the sample, weighed to the nearest 1 mg, to a 250-mL beaker. Add 25 mL of water and dissolve the sample by gradually adding 10 mL of HCl and 2 mL of HNO_3 . When dissolution is complete, cool to room temperature. If the sample contains 0.005 % nickel or less, transfer the solution to a 200-mL separatory funnel using as little water as possible so that the total volume does not exceed 60 mL. If the sample contains over 0.005 % nickel, transfer the solution to a volumetric flask and dilute to volume. Pipet an aliquot calculated to contain 0.005 to 0.050 mg of nickel into a 200-mL separatory funnel and dilute to approximately 60 mL with water.

81.1.2 To the solution in the separatory funnel, add 10 mL of sodium citrate solution (more, if the aluminum is unusually high). If manganese is also present, add 5 mL of hydroxylamine hydrochloride solution. Proceed in accordance with 80.1.2.

81.2 *Reference Solution*—To a 200-mL separatory funnel, add 50 mL of water, 2 mL of HNO₃, and the amounts of sodium citrate solution and hydroxylamine hydrochloride solution used for the sample. Proceed in accordance with 80.1.2.

81.3 *Color Development*—Develop the color of the test solution in accordance with 80.3.

81.4 *Photometry*—Take the photometric reading of the test solution in accordance with 80.4.

82. Calculation

82.1 Using the calibration curve, convert the photometric reading of the test solution to milligrams of nickel. Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = A/(B \times 10) \quad (9)$$

where:

A = nickel found in 100 mL of final solution, mg, and

B = sample represented in 100 mL of final solution, g.

83. Precision and Bias

83.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

NICKEL BY THE DIMETHYLGLYOXIME (GRAVIMETRIC) TEST METHOD

84. Scope

84.1 This test method covers the determination of nickel in concentrations from 0.005 to 0.5 %.

85. Summary of Test Method

85.1 Nickel is precipitated, dried, and weighed as the dimethylglyoxime salt.

86. Interferences

86.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1. If tin is present, dissolve the sample by adding a small excess of hydrochloric acid. Copper, tin, and the other members of the hydrogen sulfide group can be removed by precipitation with hydrogen sulfide. The interference of appreciable amounts of cobalt and zinc can be removed by adding excess reagent. Silicon, if present, should be removed as described in the procedure.

87. Apparatus

87.1 *Filtering Crucible*—A 15-mL fritted-glass crucible of medium porosity. Apparatus No. 2.

88. Reagents

88.1 *Ammonium Chloride Solution* (saturated).

88.2 *Dimethylglyoxime, Alcoholic Solution* (10 g/L)—Reagent No. 104.

88.3 *Tartaric Acid*.

89. Procedure

89.1 Weigh, to the nearest 1 mg, a portion of the sample containing from 0.005 to 0.02 g of nickel and transfer to a 400-mL beaker. Add 50 mL of water, and dissolve by adding successive small portions of HNO₃. Dilute to about 200 mL. Add 30 mL of saturated NH₄Cl solution and 5 g of tartaric acid. Neutralize the solution to litmus with NH₄OH (1 + 4). If a precipitate forms, acidify the solution and add more NH₄Cl solution or tartaric acid, whichever is needed. Neutralize again with NH₄OH (1 + 4).

89.2 Make slightly acid with HCl (1 + 2), warm to 70°C, and add 25 mL of the alcoholic solution of dimethylglyoxime. Neutralize to litmus with NH₄OH (1 + 4), and add 2 or 3 mL in excess. Digest on a steam bath for at least 1 h, and allow to stand overnight if the precipitate is small. Filter on a tared fritted-glass crucible and wash with cold water.

89.3 In case the alloy contains more than 0.1 % silicon, dissolve the washed nickel dimethylglyoxime precipitate in HCl (1 + 3) and return to the original beaker. Add 5 mL of H₂SO₄ (1 + 1) and evaporate to dense white fumes. Add 2 mL of HNO₃ and take up with water. Boil until the salts are dissolved, filter through a fine paper, and wash the residue with hot water. Warm the filtrate to 70°C, add 25 mL of the alcoholic solution of dimethylglyoxime, and proceed with the neutralization and precipitation in accordance with 89.2.

89.4 Dry the precipitate at 150°C to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

90. Calculation

90.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = [(A \times 0.2032)/B] \times 100 \quad (10)$$

where:

A = nickel dimethylglyoxime, g, and

B = sample used, g.

91. Precision and Bias

91.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

RARE EARTH ELEMENTS BY THE SEBACATE- OXALATE (GRAVIMETRIC) TEST METHOD

92. Scope

92.1 This test method covers the determination of from 0.2 to 10 % of rare earth elements.

93. Summary of Test Method

93.1 Rare earth elements are precipitated with ammonium sebacate and the sebacates are ignited. The oxides formed are redissolved, precipitated as oxalates, ignited, and weighed as oxides.

94. Interferences

94.1 Yttrium and scandium, if present, will be included with

the rare earth elements. Combinations of thorium and rare earth elements are not ordinarily present in magnesium alloys but may occur. If so, thorium may be precipitated by benzoic acid prior to the precipitation of the rare earth elements.

95. Reagents

95.1 *Ammonium Hydroxide Wash Solution* (1 + 49)—Mix 1 volume of NH_4OH with 49 volumes of water.

95.2 *Ammonium Sebacate Solution* (50 g/L)—Dissolve 50 g of sebacic acid in 400 mL of NH_4OH and 300 mL of water. Filter, dilute to 1 L with water, and mix. Store in a polyethylene bottle.

95.3 *Bromophenol Blue Indicator Solution* (4 g/L)—Place 0.40 g of bromophenol blue in a mortar, add 8.25 mL of sodium hydroxide solution (5 g NaOH/L), and mix until solution is complete. Dilute to 100 mL with water and mix.

95.4 *Hydrogen Peroxide* (30 %)—Concentrated hydrogen peroxide (H_2O_2).

95.5 *Nitric Acid-Hydrogen Peroxide Solution*—Dilute 30 mL of H_2O_2 (30 %) with 150 mL of water and 30 mL of HNO_3 .

95.6 *Oxalic Acid Solution (saturated)*—Dissolve 150 g of oxalic acid dihydrate in 1 L of warm water. Allow to cool and filter off any insoluble material.

95.7 *Oxalic Acid Wash Solution*—Dilute 70 mL of saturated oxalic acid solution to 500 mL with water.

95.8 *Potassium Pyrosulfate*—($\text{K}_2\text{S}_2\text{O}_7$).

96. Procedure

96.1 Weigh, to the nearest 1 mg, a portion of the sample containing from 10 to 100 mg of rare earth elements. Transfer to a 400-mL beaker containing 50 mL of water and add HCl a little at a time until dissolution of the metal is complete (7.5 mL of HCl will dissolve 1 g of sample). Heat the solution to boiling on a hot plate, cool, and filter if necessary (Note 12). Dilute to about 100 mL.

NOTE 12—The residue, if any, will be mainly zirconium and in most cases can be ignored. For very exact work, however, traces of rare earth elements may be recovered by igniting the paper and residue, fusing with 0.5 g of $\text{K}_2\text{S}_2\text{O}_7$, dissolving in water plus HCl , filtering, and combining with the main filtrate.

96.2 Add 3 drops of bromophenol blue indicator solution and adjust the acidity to the blue color with NH_4OH (1 + 4). Heat the mixture to boiling, remove from the heat, and allow to stand for 5 min with occasional stirring. Filter on a medium paper and wash the precipitate thoroughly with hot water. The volume of filtrate at this point should be no greater than 250 mL. Reserve this filtrate containing most of the rare earth elements. Dissolve the zirconium hydroxide precipitate, and any rare earths that may have been occluded, into the original beaker with 10 mL of HNO_3 - H_2O_2 solution, and wash the paper with hot water. Evaporate the solution to approximately 25 mL and reserve.

96.3 To the filtrate containing most of the rare earths, add 10 g of NH_4Cl , and adjust the pH of the solution between 7.5 and 8.5 with NH_4OH (1 + 4). If zinc is present, the pH should be raised to 8.5 to 9.5. (Indicator paper may be used to test the pH.) Warm on a hot plate, remove from the heat, and, while stirring, add 20 mL of ammonium sebacate solution. Allow to stand for 15 min with occasional stirring. Filter the mixture on

a medium paper, police the beaker, and wash it thoroughly with hot NH_4OH wash solution. If zinc is present, wash the precipitate once more with 20 mL of NH_4OH (1 + 1). Transfer the precipitate and paper to a clean, tared porcelain crucible. Dry, burn off the paper, and ignite at a temperature above 500°C.

96.4 Remove the crucible from the furnace, allow it to cool, and carefully wash the contents into the beaker containing the zirconium reserved from 96.2. Heat until dissolution of the rare earth oxides is complete. An additional amount of H_2O_2 may be needed at this point. Remove from the hot plate, wash down the sides of the beaker, and dilute the solution to approximately 125 mL. While stirring, slowly add 25 mL of saturated oxalic acid solution. Place the beaker on a steam bath for half an hour or until small bubbles begin to form quite vigorously in the solution. Remove from the heat and allow the mixture to stand overnight. Filter the precipitated rare earth oxalates on a fine paper. Police the beaker and wash thoroughly with oxalic acid wash solution.

96.5 Place the filter paper and precipitate in the original crucible, dry, burn off the paper, and ignite the residue at 950°C to constant weight, cooling each time in a desiccator charged with anhydrous magnesium perchlorate ($\text{Mn}(\text{ClO}_4)_2$).

97. Calculation

97.1 Calculate the percentage of rare earth oxides as follows:

$$\text{Rare earth oxides, \%} = (A/B) \times 100 \quad (\text{Note 13}) \quad (11)$$

where:

A = rare earth oxides, g, and

B = sample used, g.

NOTE 13—If it is desired to calculate the rare earth oxides as metals, the following factors should be used: cerium 0.8141, praseodymium 0.8277, neodymium 0.8574, lanthanum 0.8527, mischmetal 0.829, and didymium 0.853. The factors for mischmetal and didymium were calculated from analyses of commercial mischmetal and a didymium salt. These factors may vary slightly with each new batch of mischmetal and didymium salt used, as the proportions of individual rare earth elements vary.

98. Precision and Bias

98.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

SILICON BY THE PERCHLORIC ACID (GRAVIMETRIC) TEST METHOD

99. Scope

99.1 This test method covers the determination of silicon in concentrations over 0.1 %.

100. Summary of Test Method

100.1 The sample is dissolved in nitric acid and the silica is dehydrated with perchloric acid. The dehydrated silica is ignited, weighed, and volatilized with hydrofluoric acid. The

residue is ignited and weighed. The loss in weight represents silica (SiO₂).

101. Interferences

101.1 The metals ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in 1.1.

102. Procedure

102.1 Weigh, to the nearest 1 mg, a portion of the sample calculated to contain 0.010 g to 0.075 g of silicon, transfer it to a 400-mL beaker, and add 50 mL of water. Cautiously add HNO₃ in small portions until the sample is dissolved. When dissolution is complete, warm the solution to dissolve any dark residue, cool, and add 10 mL of HClO₄ for each gram of alloy present. Evaporate to dense white fumes of HClO₄ and then continue the heating for an additional 15 min.

102.2 Cool, add 75 mL of water, and warm to dissolve the metallic salts. Filter on a fine, low-ash paper containing paper pulp, and wash the precipitate once with hot water and then five times with H₂SO₄ (1 + 4), using a total of 75 mL of the H₂SO₄ solution. Finally, wash the precipitate several times with hot water, using a total of about 250 mL. It is imperative that the HClO₄ be completely removed prior to drying the precipitate, otherwise a sudden deflagration may occur. Place the filter paper in a platinum crucible, dry and char the paper at a low temperature, and then ignite at 1000°C or above for 1½ h. Cool in a desiccator and weigh.

102.3 To the residue add a few drops of H₂SO₄ (1 + 1) and about 5 mL of HF. Evaporate carefully to dryness on a hot plate, ignite at 1000°C or above, cool in a desiccator, and weigh. Repeat the treatment with HF and ignite to constant weight. The loss in weight represents SiO₂.

102.4 Make a blank determination, following the same procedure and using the same amounts of all reagents.

103. Calculation

103.1 Calculate the percentage of silicon as follows:

$$\text{Silicon, \%} = [(A - B) \times 0.4675] / C \times 100 \quad (12)$$

where:

A = SiO₂, g,

B = correction for blank, in g, and

C = sample used, g.

104. Precision and Bias

104.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

SILICON BY THE MOLYBDOSILICIC ACID (PHOTOMETRIC) TEST METHOD

105. Scope

105.1 This test method covers the determination of silicon in concentrations under 0.1 %.

106. Summary of Test Method

106.1 Silicic acid in a true (not colloidal) solution reacts with molybdate to form a soluble yellow-colored molybdosilicic acid. Photometric measurement is made at approximately 420 nm.

107. Concentration Range

107.1 The recommended concentration range is from 0.1 to 0.5 mg of silicon in 100 mL of solution, using a cell depth of 5 cm (Note 2).

108. Stability of Color

108.1 The color is stable for about 1 h.

109. Interferences

109.1 The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limit shown in 1.1. Phosphates cause a yellow color that interferes.

NOTE 14—It appears from the literature that a given weight of phosphorus yields slightly less than half as much color as the same weight of silicon. The possible interferences from elements such as tin, arsenic, or cerium have not been investigated.

110. Reagents

110.1 *Ammonium Molybdate Solution* (80 g/L)—Dissolve 40 g of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) in 500 mL of water.

110.2 *Boric Acid Solution (saturated)*.

110.3 *Silicon, Standard Solution* (1 mL = 0.05 mg Si)—Fuse 0.1070 g of SiO₂ with 1.0 g of Na₂CO₃ in a platinum crucible. Cool the melt, dissolve completely in water, and dilute to 1 L in a volumetric flask. The solution should be stored in a polyethylene bottle, or prepared fresh as needed.

111. Preparation of Calibration Curve

111.1 *Calibration Solutions*—Transfer 2.0, 5.0, and 10.0 mL of the silicon solution (1 mL = 0.05 mg Si) to 100-mL volumetric flasks. To each flask add 40 mL of water, 1.0 mL of H₂SO₄ (1 + 4), and 10 g of MgSO₄·7H₂O. Swirl the flask to dissolve the MgSO₄.

111.2 *Reference Solution*—Prepare an additional 100-mL volumetric flask containing 40 mL of water, 1.0 mL of H₂SO₄ (1 + 4), and 10 g of MgSO₄·7H₂O for use as a reference solution. Swirl the flask to dissolve the MgSO₄.

111.3 *Color Development*—To each flask add 5.0 mL of ammonium molybdate solution, dilute to 100 mL, and mix.

NOTE 15—The yellow color ordinarily develops within 5 min and should be read within 1 h after addition of molybdate, since fading takes place after a longer time.

111.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 420 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

111.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of silicon per 100 mL of solution.

112. Procedure

112.1 Test Solutions:

112.1.1 *Soluble Silicon*—Transfer to a 150-mL beaker, a portion of the sample weighed to the nearest 1 mg and calculated to contain less than 0.5 mg of silicon and not more than 2 g of magnesium. Add 25 mL of water and 5 mL of the boric acid solution. Add in small quantities, 11.7 mL of freshly prepared H_2SO_4 (1 + 4) per gram of sample, meanwhile keeping the beaker in a cold water bath to prevent loss of silicon as the hydride. Add 1.0 mL of H_2SO_4 (1 + 4) in excess. When the sample is dissolved, introduce 0.1 g of potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) to oxidize ferrous iron or other reducing agents. Allow to stand for at least 10 min, dilute to about 60 mL, and filter through a fine, low-ash paper, catching the filtrate in a 100-mL volumetric flask. Wash the beaker and paper with enough water to dilute the filtrate to approximately 90 mL. Reserve the paper. Continue in accordance with 112.3.

112.1.2 *Insoluble Silicon*—Place the reserved paper in a clean platinum crucible and ignite at approximately 500°C. Add 0.1 g of Na_2CO_3 and fuse at approximately 900°C. Dissolve the residue in water with enough freshly prepared H_2SO_4 (1 + 4) to neutralize the Na_2CO_3 , plus 1.0 mL in excess, and filter through a fine low-ash paper into another 100-mL volumetric flask. Rinse the beaker and paper with enough water to dilute the filtrate to approximately 90 mL. Proceed in accordance with 112.3.

112.2 *Reference Solutions*—Prepare two reagent blanks, one for the soluble silicon portion and the other for the insoluble silicon portion for use as reference solutions. These blanks should contain all of the reagents, including the filter paper, except that only 1 mL of H_2SO_4 (1 + 4) shall be used per 100 mL of solution, since the color is affected by the acidity.

112.3 *Color Development*—To each flask add 5.0 mL of ammonium molybdate solution. If a green color develops due to the presence of reducing agents, add 0.1 g of $\text{K}_2\text{S}_2\text{O}_8$. Dilute to volume and mix.

112.4 *Photometry*—Take the photometric readings of the test solutions in accordance with 111.4.

113. Calculation

113.1 Convert the photometric readings of the test solutions to milligrams of silicon by means of the calibration curve. Add together the amounts found in the soluble and insoluble silicon portions. Calculate the percentage of silicon as follows:

$$\text{Silicon, \%} = A/(B \times 10) \quad (13)$$

where:

A = total silicon found, mg, and

B = sample used, g.

114. Precision and Bias

114.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

THORIUM BY THE BENZOATE-OXALATE (GRAVIMETRIC) TEST METHOD

115. Scope

115.1 This test method covers the determination of thorium in concentrations from 0.2 to 25 %.

116. Summary of Test Method

116.1 Thorium, along with zirconium if present, is precipitated as the benzoate. The combined benzoate precipitate is dissolved and thorium is precipitated as the oxalate, ignited to the oxide, and weighed.

117. Interferences

117.1 Provision is made in the test method to take care of all elements ordinarily present in magnesium-thorium alloys.

118. Reagents

118.1 *Benzoic Acid Solution* (20 g/L)—Dissolve 2 g of benzoic acid in hot water and dilute to 100 mL.

118.2 *Benzoic Acid Wash Solution* (2.5 g/L)—Dissolve 2.5 g of benzoic acid in hot water and dilute to 1 L.

118.3 *Bromophenol Blue Indicator Solution* (4 g/L)—Place 0.40 g of bromophenol blue in a mortar, add 8.25 mL of NaOH solution (5 g/L), and mix until solution is complete. Dilute to 100 mL with water.

118.4 *Hydroxylamine Hydrochloride*—($\text{NH}_2\text{OH} \cdot \text{HCl}$).

118.5 *Oxalic Acid Solution (saturated)*—Dissolve 150 g of oxalic acid dihydrate in 1 L of warm water. Allow to cool, and filter off any insoluble material.

118.6 *Oxalic Acid-Hydrochloric Acid Wash Solution*—Dilute 70 mL of saturated oxalic acid solution to 500 mL with water and add 5 mL of HCl.

119. Procedure

119.1 Weigh, to the nearest 1 mg, a portion of the sample containing from 10 to 100 mg of thorium and transfer to a 400-mL beaker. Add 50 mL of water, and dissolve the metal by adding HCl a little at a time until dissolution is complete (7.5 mL of HCl dissolves 1 g of sample). Heat the solution to boiling, cool, filter through a fine paper, and wash with water. Dilute the solution to 100 mL.

119.2 If rare earth elements are present, add 1 g of hydroxylamine hydrochloride to reduce any ceric cerium. Add 3 drops of bromophenol blue indicator and adjust the acidity with either NH_4OH (1 + 4) or HCl (1 + 4) until the solution is just basic to bromophenol blue. Add 10 g of NH_4Cl and heat to boiling. Add 100 mL of hot benzoic acid solution, while stirring, and continue to heat for 10 min. Allow to stand until the precipitate settles, and then filter on a rapid, hardened paper. Police the beaker and wash thoroughly with hot benzoic acid wash solution.

119.3 Punch a hole in the filter paper and wash the benzoate precipitate back into the original beaker with 50 mL of hot water. Wash the filter paper with 10 mL of HCl (1 + 4) and 50 mL of hot water. Heat to boiling. Remove from the hot plate and add 25 mL of saturated oxalic acid solution while stirring. Allow the mixture to stand overnight and then filter on a fine paper. Police and wash the beaker thoroughly with oxalic acid-hydrochloric acid wash solution.

119.4 Transfer the precipitate and paper to a clean, tared, porcelain crucible. Dry, burn off the paper, and finally ignite at 950°C to constant weight, cooling each time in a desiccator charged with anhydrous magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$).

120. Calculation

120.1 Calculate the percentage of thorium as follows:

$$\text{Thorium, \%} = [(A \times 0.8788)/B] \times 100 \quad (14)$$

where:

A = thorium oxide (ThO_2), g, and

B = sample used, g.

121. Precision and Bias

121.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

TIN BY THE IODINE (VOLUMETRIC) TEST METHOD

122. Scope

122.1 This test method covers the determination of tin in concentrations over 0.5 %.

NOTE 16—Tin in lower concentrations may be determined by this procedure using a 0.01 N iodine solution.

123. Summary of Test Method

123.1 The sample is dissolved in hydrochloric acid in an inert atmosphere and the stannous tin is titrated with a standard iodine solution to the starch-iodide end point.

124. Interferences

124.1 Any element that, after dissolving, will be present in a reduced form which is oxidizable by iodine will interfere. Such elements are not likely to be present in the usual magnesium alloys.

125. Apparatus

125.1 *Apparatus for the Reduction of Tin*—Apparatus No. 7A.

126. Reagents

126.1 *Iodine Standard Solution* (1 mL = 0.006 g Sn; 0.1 N)—Reagent No. 7. Standardize against weighed amounts of tin and tin-free magnesium in accordance with Section 127.

126.2 *Magnesium Metal* (tin-free).

126.3 *Sodium Bicarbonate Solution (saturated)*.

126.4 *Starch Solution* (10 g/L)—Reagent No. 124.

127. Procedure

127.1 Weigh, to the nearest 1 mg, a portion of the sample containing from 0.025 to 0.10 g of tin, transfer to a reduction flask, and add 20 mL of water. Add HCl in small increments until a total of 100 mL has been added. If the metal is finely

divided or the sample weight is large, place the flask and contents in an ice bath during the dissolution.

127.2 After the sample has dissolved, cool and cautiously add 1.0 g of tin-free magnesium metal. Stopper as shown (Apparatus No. 7A, Fig. 6), and dip the outlet tube into saturated NaHCO_3 solution.

127.3 After the magnesium metal disappears, heat on a hot plate until the solution becomes clear (except for silica particles). Allow to cool. The NaHCO_3 solution will draw back sufficiently to maintain an atmosphere of CO_2 in the flask.

127.4 When the solution is cold, remove the head quickly and rinse down the sides of the flask with water through which CO_2 has been bubbled. Add a couple of marble chips, 2 or 3 mL of starch solution, and close with a one-hole rubber stopper. Titrate at once, through the stopper, with 0.1 N iodine solution to the first persistent blue color.

127.5 Make a blank determination following the same procedure and using the same amounts of all reagents.

128. Calculation

128.1 Calculate the percentage of tin as follows:

$$\text{Tin, \%} = [(A - B)C/D] \times 100 \quad (15)$$

where:

A = iodine solution required for titration of the sample, mL,

B = iodine solution required for titration of the blank, mL,

C = tin equivalent of the iodine solution, g/mL, and

D = sample used, g.

129. Precision and Bias

129.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

ZINC BY THE ETHYLENEDIAMINE TETRAACETATE (VOLUMETRIC) TEST METHOD

130. Scope

130.1 This test method covers the determination of zinc in magnesium-base alloys in the range from 0.3 to 20 %.

131. Summary of Test Method

131.1 The zinc thiocyanate complex is extracted with methyl isobutyl ketone to effect a separation from magnesium. The zinc is then removed from the organic extract as the ammonia complex. Zinc and other bivalent metals are complexed with potassium cyanide. Finally, the zinc is selectively released from the cyanide complex and titrated with standard sodium ethylenediamine tetraacetate solution.

132. Interferences

132.1 None of the metals ordinarily present in magnesium base alloys interfere with this test method. This test method also affords a separation of zinc from cadmium in the event that they are encountered together.

133. Apparatus

133.1 *Separatory Funnels*, 500-mL, conical.

133.2 *Magnetic Stirrer*, with a tetrafluoroethylene (TFE-fluorocarbon)-covered magnetic stirring bar.

134. Reagents

134.1 *Ammonium Thiocyanate Solution* (500 g/L)—Dissolve 500 g of ammonium thiocyanate (NH_4CNS) in water and dilute to 1 L.

134.2 *Ammonium Thiocyanate-Hydrochloric Acid Wash Solution*—Add 100 mL of NH_4CNS solution to approximately 700 mL of water and mix. Add 8.3 mL of HCl, 3.3 mL of HNO_3 , and dilute to 1 L with water.

134.3 *Buffer Solution*—Dissolve 65.5 g of NH_4Cl in water, add 570 mL of NH_4OH , and dilute to 1 L with water.

134.4 *Buffer Solution, Dilute*—Dilute 400 mL of the buffer solution to 1 L with water.

134.5 *Formaldehyde* (37 %).

134.6 *Indicator Solution*—Dissolve 0.4 g of eriochrome black-T (1-(1-hydroxy-2-naphthyl-azo)-6-nitro-2-naphthol-4-sulfonic acid, sodium salt) in a mixture of 20 mL of ethyl alcohol and 30 mL of triethanolamine. This solution is stable for at least 3 months when kept in a tightly closed polyethylene dropping bottle.

134.7 *Methyl Isobutyl Ketone*.

134.8 *Potassium Cyanide Solution* (50 g/L)—Dissolve 5 g of potassium cyanide (KCN) in water containing 3 mL of NH_4OH and dilute to 100 mL (**Caution**, see Note 17).

NOTE 17—**Caution:** The preparation, storage, and use of KCN solutions requires care and attention. Avoid inhalation of fumes and exposure of skin to the chemical or its solutions. Work in a well-ventilated hood.

134.9 *Sodium Ethylenediamine Tetraacetate (EDTA), Standard Solution* (0.01 M)—Dissolve 4.0 g of disodium ethylenediamine tetraacetate dihydrate in water. Add to this solution 0.1 g of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and dilute to volume in a 1-L volumetric flask. Standardize this solution against a standard zinc solution in accordance with 135.3 and 135.4.

134.10 *Zinc, Standard Solution* (1 mL = 1.00 mg Zn)—Dissolve 1.000 g of pure zinc in 50 mL of water and 22.6 mL of HCl. Dilute to volume in a 1-L volumetric flask.

135. Procedure

135.1 For alloys with a zinc content under 1.0 %, transfer a sample, weighed to the nearest 1 mg and containing preferably from 4 to 10 mg of zinc (but in no case more than 1.5 g), to a 250-mL beaker. Add 25 mL of water and dissolve the alloy by the addition of 7.5 mL of HCl per gram of sample. Cool and continue in accordance with 135.3.

135.2 For alloys with a zinc content over 1 %, transfer a portion of the sample, weighed to the nearest 1 mg and containing from 40 to 100 mg of zinc, to a 250-mL beaker. Add 25 mL of water and dissolve the sample by the addition of 7.5 mL of HCl per gram of sample. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix. Continue in accordance with 135.3.

135.3 Transfer the solution from either 135.1, or an aliquot portion of the solution from 135.2 containing from 4 to 10 mg of zinc, to a 500-mL separatory funnel. Add 2.5 mL of HCl, 1.0

mL of HNO_3 , dilute to 300 mL, and mix. Add 30 mL of NH_4CNS solution and mix. Add 50 mL of methyl isobutyl ketone and shake well. Allow the layers to separate, and draw off and discard the lower aqueous layer. To the solvent extract, add 100 mL of $\text{NH}_4\text{CNS-HCl}$ wash solution. Shake, allow the layers to separate, and draw off and discard the lower aqueous layer. To the organic layer add 40 mL of the buffer solution (134.3). Cautiously shake, allow the layers to separate, and draw off the lower ammoniacal layer into a 500-mL Erlenmeyer flask. Add 25 mL of the dilute buffer solution (134.4) to the solvent extract and shake. Allow the layers to separate, and draw off and add the lower ammoniacal layer to the Erlenmeyer flask. Discard the organic layer.

135.4 Dilute to approximately 300 mL with water, add 10 mL of KCN solution, a few drops of indicator solution, and a TFE-fluorocarbon-covered stirring bar. Place the flask on a magnetic stirrer and stir at a fairly fast rate. To the blue solution, add 3 mL of formaldehyde and titrate from winered to pure blue with 0.01 M EDTA solution.

136. Calculation

136.1 Calculate the percentage of zinc as follows:

$$\text{Zinc, \%} = AB/(C \times 10) \quad (16)$$

where:

A = standard EDTA solution used, mL,

B = equivalent of the standard EDTA solution in milligrams of zinc per millilitre, and

C = sample in the aliquot used, g.

137. Precision and Bias

137.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

ZINC BY THE POTASSIUM FERROCYANIDE (VOLUMETRIC) TEST METHOD

138. Scope

138.1 This test method covers the determination of zinc in concentrations over 0.5 %.

139. Summary of Test Method

139.1 Zinc is precipitated as the sulfide from a tartaric acid solution buffered with formic acid and ammonium formate. The sulfide is dissolved and the zinc determined by titration with a standard solution of potassium ferrocyanide.

140. Interferences

140.1 Interferences due to copper, iron, manganese, and nickel are eliminated by the separations outlined in the procedure. Interference will be encountered if zirconium is present. This can be overcome by adding citric acid to complex the zirconium. If citric acid is used, no tartaric acid need be added.

141. Reagents

141.1 *Diphenylbenzidine Solution*—Dissolve 0.5 g of diphenylbenzidine in 50 mL of H_2SO_4 . Prepare fresh as needed.

141.2 *Formic Acid Mixture*—Reagent No. 108.

141.3 *Formic Acid Mixture Wash Solution*—Reagent No. 109.

141.4 *Hydrogen Sulfide Wash Solution*—Saturate HCl (3 + 97) with H_2S .

141.5 *Methyl Red Indicator*—Reagent No. 119.

141.6 *Potassium Ferrocyanide, Standard Solution* (1 mL = 0.005 g Zn)—See Reagent No. 11.

141.7 *Tartaric Acid Solution* (50 g/L)—Dissolve 50 g of tartaric acid in water and dilute to 1 L.

142. Procedure

142.1 Weigh, to the nearest 1 mg, a portion of the sample calculated to contain 0.05 to 0.1 g of zinc, transfer it to a 400-mL beaker, and add 25 mL of water. Dissolve by adding small portions of HCl, adding a total of 7.5 mL of HCl for each gram of sample plus a 10-mL excess. If copper remains undissolved, separate it by decantation, dissolve in 1 mL of HNO_3 and 0.5 mL of H_2SO_4 , evaporate to white fumes, cool, take up in water, and add it to the main solution. Dilute the solution to 200 mL and pass in a rapid stream of H_2S for 3 min. Filter, with the aid of a little paper pulp, on a fine paper and wash the precipitate with H_2S wash solution.

142.2 Boil the filtrate for 10 min to expel H_2S , cool, and add 50 mL of tartaric acid solution. Dilute to 300 mL and neutralize to methyl red with NH_4OH (1 + 1). Add 25 mL of formic acid mixture, heat to boiling, and pass in H_2S rapidly (at least 8 bubbles per second) for 15 min. Allow to settle for a short time, filter through a fine paper containing a little paper pulp, and wash twice with formic acid mixture wash solution.

142.3 Dissolve the precipitate from the paper with 20 mL of hot HCl (1 + 4) and wash with hot water. Dilute the solution to 150 mL, boil to expel H_2S , and cool. Make just neutral to litmus with NH_4OH (1 + 1), add 10 g of NH_4Cl and 15 mL of H_2SO_4 (1 + 4), and cool to room temperature. The volume should now be about 200 mL.

142.4 Add a small crystal of potassium ferricyanide, 5 or 6 drops of diphenylbenzidine solution, and allow to stand until a bluish-purple color develops. Titrate slowly with $\text{K}_4\text{Fe}(\text{CN})_6$ solution (1 mL = 0.005 g Zn), using a mechanical stirrer. Near the end point the solution becomes a bright purple, which changes at the end point to a light pea-green color that persists for several minutes.

143. Calculation

143.1 Calculate the percentage of zinc as follows:

$$\text{Zinc, \%} = (AB/C) \times 100 \quad (17)$$

where:

A = $\text{K}_4\text{Fe}(\text{CN})_6$ solution required for titration of the sample, mL,

B = zinc equivalent of the $\text{K}_4\text{Fe}(\text{CN})_6$ solution, g/mL, and

C = sample used, g.

144. Precision and Bias

144.1 This test method was originally approved for publi-

cation before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

ZIRCONIUM BY THE ALIZARIN RED (PHOTOMETRIC) TEST METHOD

145. Scope

145.1 This test method covers the determination of acid-soluble and acid-insoluble zirconium in concentrations from 0.03 to 1.0 %.

146. Summary of Test Method

146.1 The acid-soluble and acid-insoluble zirconium are separated by dissolving the alloy in dilute hydrochloric acid. The insoluble fraction is brought into solution by fusion with potassium pyrosulfate. Zirconium in each solution is determined photometrically through the formation of a colored complex with alizarin red-S at a pH of 0.6 to 0.7. Photometric measurement is made at approximately 510 nm.

147. Concentration Range

147.1 The recommended concentration range is from 0.05 to 0.25 mg of zirconium in 100 mL of solution, using a cell depth of 5 cm.

NOTE 18—This procedure has been written for cells having a 5-cm light path. It has been found necessary to use these deep cells in order to avoid interference in the analysis of samples containing appreciable amounts of thorium. In the absence of unfavorable thorium to zirconium ratios, smaller cell depths can be used, in this case using 5 mL of 0.10 % dye solution and adjusting the sample aliquot to accommodate the larger range of zirconium concentration.

148. Stability of Color

148.1 The color intensity increases rapidly for 15 min and very slowly thereafter.

149. Interferences

149.1 Rare earths, zinc, aluminum, manganese, copper, iron, nickel, and lead, in concentrations likely to be found in magnesium alloys, do not interfere with this test method. Thorium does not interfere at pH values of 0.6 to 0.7, but may cause interference at a higher pH. Hafnium is included as zirconium in this test method.

NOTE 19—Sulfate and phosphate retard the rate of color development, but in concentrations of less than 0.08 g/100 mL the color intensity is at a maximum after 1 h; in greater concentrations full color intensity does not develop. Fluoride in concentrations greater than 0.01 mg/100 mL interferes quantitatively by reacting with zirconium. Very high neodymium concentrations could interfere at 510 nm, but the interference would be less at 500 nm.

150. Reagents

150.1 *Alizarin Red-S Solution* (0.5 g/L)—Dissolve 0.125 g of alizarin red-S in water and dilute to 250 mL.

150.2 *Ferric Chloride Solution* (1 mL = 2.5 mg iron)—Dissolve 0.25 g of iron wire in 10 mL of HCl and 2 mL of HNO_3 . Boil off the fumes and dilute to 100 mL.

150.3 *Potassium Pyrosulfate* ($K_2S_2O_7$).

150.4 *Zirconium, Standard Solution* (1 mL = 0.05 mg Zr)—Dissolve 0.177 g of zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) in about 100 mL of water, add 100 mL of HCl, and dilute to 1000 mL in a volumetric flask. One millilitre contains approximately 0.05 mg of zirconium and 0.1 mL of HCl. Standardize by analyzing 200 mL gravimetrically by the phosphate method (see Section 144 of Methods E 30).

151. Preparation of Calibration Curve

151.1 *Calibration Solutions*—Transfer 1.0, 2.0, 3.0, 4.0, and 5.0 mL of zirconium solution (1 mL = 0.05 mg Zr) to 100-mL volumetric flasks. Add sufficient HCl to give a total of 2.8 mL of HCl in each flask and dilute to about 90 mL.

151.2 *Reference Solution*—Transfer 2.8 mL of HCl to a 100-mL flask and dilute to about 90 mL.

151.3 *Color Development*—Add 5 mL of alizarin red-S solution to each flask, dilute to the mark, and mix. Allow to stand for 15 min.

151.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 510 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

151.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of zirconium per 100 mL of solution.

152. Procedure

152.1 *Test Solution*:

152.1.1 *Rod, Sheet, or Bar*—Transfer 1.5 g of the sample, weighed to the nearest 1 mg, to a 400-mL beaker. Dissolve by adding 125 mL of HCl (1 + 4). The acid should be added all at one time to prevent the possibility of some of the zirconium hydrolyzing because of a deficiency of acid. Filter through a fine paper into a 500-mL volumetric flask. Wash four to five times with hot water. Cool, dilute to volume, and mix. This represents the acid-soluble zirconium. Proceed in accordance with 152.1.4.

152.1.2 *Drillings, Millings, or Pellets*—Transfer 1.5 g of the sample, weighed to the nearest 1 mg, to a 400-mL beaker. Add 50 mL of water and dissolve the sample by adding HCl in 3-mL increments until a total of 25 mL has been added. The increments of acid should be added rapidly and continuously without allowing the reaction to become too vigorous (Note 20). Heat the solutions to 95°C. Remove immediately from the heat, cool, and filter through a fine paper into a 500-mL volumetric flask. Wash 4 to 5 times with hot water, cool, dilute to volume, and mix. This represents the acid-soluble zirconium. Proceed in accordance with 152.1.4.

NOTE 20—The procedure given in 152.1.1 is that recommended for dissolving magnesium-zirconium alloys. The more vigorous treatment of

152.1.2 is necessary with an alloy that is finely divided because zirconium will hydrolyze to some extent as the alloy dissolves. This can be seen as a white turbidity in the solution which should disappear upon heating.

152.1.3 Place the paper containing the insoluble residue in a porcelain crucible and char slowly. Heat at 950°C for 30 min, cool slightly, add about 1 g of $K_2S_2O_7$, and fuse. Cool and dissolve the melt in 100 mL of water containing 1 mL of HCl and 1 mL of $FeCl_3$ solution. Add NH_4OH until all the iron and zirconium are precipitated. Filter through a medium paper and wash the precipitate with hot water. Dissolve the hydroxide from the filter paper with 15 mL of hot HCl (1 + 1). Transfer the solution to a 250-mL volumetric flask, dilute to volume, and mix. This represents the acid-insoluble zirconium. Proceed in accordance with 152.1.4.

152.1.4 From each flask, transfer an aliquot containing from 0.05 to 0.25 mg of zirconium to a 100-mL volumetric flask. Calculate the amount of acid present (a 10-mL aliquot will contain about 0.3 mL), and add sufficient acid to give a total of 2.8 mL of HCl. Dilute to about 90 mL.

152.2 *Reference Solution*—Carry along a reagent blank containing the same amount of all reagents for use as a reference solution.

152.3 *Color Development*—Develop the color in accordance with 151.3.

152.4 *Photometry*—Take the photometric readings of the test solutions in accordance with 151.4.

153. Calculation

153.1 Convert the photometric readings of the test solutions to milligrams of zirconium by means of the calibration curve.

153.2 Calculate the percentage of zirconium in each fraction as follows:

$$\text{Zirconium, \%} = A/(B \times 10) \quad (18)$$

where:

A = zirconium found in 100 mL of each final solution, mg, and

B = sample represented in 100 mL of the same solution, g.


153.3 Report result as a percentage of acid-soluble or acid-insoluble zirconium.

154. Precision and Bias

154.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data for this test method are no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method are adequate for the contemplated use.

155. Keywords

155.1 analysis; chemical; chemical analysis; magnesium and magnesium alloys

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