



Designation: E 35 – 88 (Reapproved 2002)

Standard Test Methods for Chemical Analysis of Magnesium and Magnesium Alloys¹

This standard is issued under the fixed designation E 35; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 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 0.05
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:

	Section
Aluminum:	
Benzoate-Oxinate (Gravimetric) Method	8-15
Sodium Hydroxide (Potentiometric) Method (Optional Routine Method)	16-23
Copper:	
Neocuproine (Photometric) Method	24-33
Hydrobromic Acid-Phosphoric Acid (Photometric) Method	34-43
Iron by the 1,10-Phenanthroline (Photometric) Method	44-53
Lead by the Dithizone (Photometric) Method	54-63
Magnesium—Analysis for Manganese an- Zinc by Direct Current Plasma Spectroscopy (Proposal)	2
Manganese by the Periodate (Photometric) Method	64-73
Nickel:	
Dimethylglyoxime Extraction (Photometric) Method	74-83
Dimethylglyoxime (Gravimetric) Method	84-91
Rare Earth Elements by the Sebacate- Oxalate (Gravimetric) Method	92-98
Silicon:	
Perchloric Acid (Gravimetric) Method	99-104
Molybdosilicic Acid (Photometric) Method	105-114
Thorium by the Benzoate-Oxalate (Gravimetric) Method	115-121
Tin by the Iodine (Volumetric) Method	122-129

Zinc:	
Ethylenediamine Tetraacetate (Volumetric) Method	130-137
Potassium Ferrocyanide (Volumetric) Method	138-144
Zirconium by the Alizarin Red (Photometric) Method	145-154

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

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.04 on Aluminum and Magnesium.

Current edition approved Jan. 29, 1988. Published March 1988. Originally published as E35 – 42. Last previous edition E35 – 63 (1980).

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.

apparatus, standard solutions, and certain other reagents used 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