Designation: E 75 – 76 (Reapproved 2004)

Standard Test Methods for Chemical Analysis of Copper-Nickel and Copper-Nickel-Zinc Alloys[1]

This standard is issued under the fixed designation E 75; 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 procedures for the chemical analysis of copper-nickel and copper-nickel-zinc alloys having chemical compositions within the following limits:[2]

Element	Concentration Range,%
Copper	40 and over
Nickel[A]	10 to 50
Zinc[B]	0 to 40
Lead	0 to 15
Tin	0 to 10
Iron	0.00 to 2
Manganese	0.00 to 2
Cobalt	0.00 to 0.5

[A] Includes cobalt.

[B] In the case of copper-base alloys containing 5 % and over of zinc, the zinc is usually calculated by difference.

Whenever possible the technique and procedures for analysis should be checked against a National Institute of Standards and Technology standard sample having a composition comparable to the material being analyzed.

1.2 The test methods appear in the following order:

	Sections
Cobalt:	
Alpha-Nitroso-Beta-Naphthol Method	26 to 28
Nitroso-R-Salt (Photometric) Method	29 to 37
Copper, or Copper and Lead Simultaneously, by the Electrolytic Method	[2a]
Iron:	
Dichromate Method	38 to 40
Thiocyanate (Photometric) Method	[2a]
Salicylate (Photometric) Method	[2a]
Lead:	
Electrolytic Method	12 to 15
Sulfate Method	[2b]
Manganese:	
Persulfate Method	[2b]
Periodate (Photometric) Method	59 to 66
Nickel by the Dimethylglyoxime Method	[2a]
Tin by the Iodimetric Titration Method	[2b]
Zinc by the Oxide or Ferrocyanide Method	[2a]

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.* For precautions to be observed in these test methods, refer to Practices E 50.

2. Referenced Documents

2.1 *ASTM Standards:* [3]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance With Specifications

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals

E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals

E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

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 and Reagents

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

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[2] For procedures for the chemical analysis of nickel-copper alloys containing 50 % and over of nickel, see ASTM Methods E 76, for Chemical Analysis of Nickel-Copper Alloys, *Annual Book of ASTM Standards*, Vol 03.05.

[2a] Discontinued as of June 30, 1975.

[2b] Discontinued Aug. 27, 1976.

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

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.

5. Photometric Practice

5.1 Photometric practice prescribed in these methods shall conform to Practice E 60.

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 given in 3.4 and 3.5 of Practice E 29.

COPPER, OR COPPER AND LEAD SIMULTANEOUSLY, BY THE ELECTROLYTIC TEST METHOD

(This test method, which consisted of Sections 8-11 of this standard, was discontinued in 1975.)

NOTE 1—Sections 8-11 of this standard were removed as a part of the revision of E75 approved June 30, 1975. Since they are no longer an approved part of this standard, the sections are included here for reference purposes only. Subcommittee E03.05 is in the process of updating these methods.

8. Apparatus

8.1 *Electrodes for Electroanalysis*— Apparatus No. 9.

9. Reagents

9.1 *Sodium Hydroxide Solution* (250 g NaOH/L).
9.2 *Sodium Sulfide Solution* (250 g Na_2S/L).
9.3 *Sodium Sulfide Solution* (20 g Na_2S/L).
9.4 *Sulfamic Acid Solution* (100 g/L).

10. Procedure for Alloys Containing Under 6 % of Lead

NOTE 2—If more than 6 % of lead is present, the copper only shall be determined by this procedure as the anode deposit is not sufficiently adherent for safe handling. The lead shall then be determined on a separate sample as described in the sulfate method, Sections 16 and 17.

10.1 Transfer 2.0000 g of the sample to a 250-mL beaker, cover, and dissolve in 25 mL of HNO_3(1 + 1). When dissolution is complete, boil gently to expel brown fumes. Add 50 mL of hot water and observe the clarity of the solution. If the solution is clear, proceed as described in 10.5. If enough tin is present at this point to form a cloud, proceed as described in 10.2 and 10.3 or 10.2 and 10.4.

10.2 Allow to stand on a steam bath for 1 h or until the precipitate has coagulated. Add paper pulp and filter off the metastannic acid through a fine paper into a 250-mL beaker. Wash several times with hot HNO_3 (1 + 99) and reserve the filtrate and washings.

10.3 Transfer the filter paper and contents to the original beaker and add 15 mL of H_2SO_4 and 15 mL of HNO_3. Heat until all organic matter is decomposed, adding additional HNO_3 as necessary, and finally evaporate to fumes. Transfer the digested solution to a 400-mL beaker and dilute to 250 mL. Add NaOH solution until the solution is alkaline and the tin hydroxide has dissolved. Add 20 mL of Na_2S solution (250 g Na_2S/L), stir thoroughly, and digest on the steam bath for several hours, or until the supernatant liquid is clear. Cool to room temperature, filter through a fine paper, and wash the precipitate with Na_2S solution (20 g Na_2S/L). Dissolve the residue in a few millilitres of HNO_3 (1 + 1), neutralize with NH_4OH, and redissolve any precipitate with a minimum of HNO_3 (1 + 1). Combine with the reserved filtrate (10.2) and continue in accordance with 10.5.

10.4 An alternative method for recovering copper and lead is to return the metastannic acid and paper obtained as described in 10.2 to the original beaker, add 15 to 20 mL of HNO_3 and 10 to 15 mL of $HClO_4$, heat to copious white fumes, and boil to destroy organic matter. Cool, wash the cover glass and sides of the beaker, and add 15 to 25 mL of HBr. Heat to copious white fumes to volatilize the tin. If the solution is not clear, repeat the treatment with HBr. Evaporate the solution to near dryness, cool, and dissolve the residue in a few millilitres of water. Combine with the reserved filtrate (10.2) and continue in accordance with 10.5.

10.5 Add 1 drop of HCl (1 + 99) and 5 mL of sulfamic acid solution and dilute to 150 mL. Insert the electrodes into the solution, cover with a pair of split watch glasses, and electrolyze overnight at a current density of 0.5 A/dm^2 or for a short period at a current density of 4 A/dm^2(Note 3). The more rapid procedure requires the use of gauze cathodes. After the blue color of the copper has disappeared, wash down the cover glasses, electrodes, and sides of the beaker, and continue the electrolysis until deposition of the copper is complete, as indicated by failure to plate on a new surface when the level of the solution is raised. When no copper appears, it can be assumed that all the lead also has been deposited (Note 4). Reserve the electrolyte.

NOTE 3—When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes generally available may be employed.

NOTE 4—If the electrolyte is not to be used for subsequent determinations, remove a few drops of the solution, place on a porcelain spot plate, and treat with saturated H_2S solution. Continue electrolysis until no CuS precipitate is observed.

10.6 When deposition of the copper is complete, with the current still on, lower the beaker slowly, while washing the cathode with water. Remove the cathode, rinse it in water, and dip it in two successive baths of ethanol or methanol. Dry in an oven at 110°C for 3 to 5 min, cool, and weigh the deposit as metallic copper.

10.7 If lead is being determined, remove the anode, rinse thoroughly with water, and dry at 110 to 120°C for 30 min. The deposit is fragile and must be handled carefully. Cool the anode and weigh the deposit.

10.8 Correction must be made for manganese, which is frequently present in these alloys and some of which may codeposit with the lead. Place the anode in a 150-mL beaker and dissolve the deposit in 20 mL of HNO_3 (1 + 1) and 1 mL of H_2O_2 (3 %). Remove the anode and wash with water. Add

5 mL of H_3PO_4 and boil for 5 to 10 min. Determine manganese either photometrically by the periodate method (Sections 31–38) or volumetrically by the persulfate method (Sections 56 to 58).

10.9 *Calculation*—Calculate the percentages of copper and lead as follows:

$$\text{Copper, \%} = (A/B) \times 100$$

$$\text{Lead, \%} = ([(C - 1.58\,D) \times 0.866]/B) \times 100$$

where:

A = grams of copper,
B = grams of sample used,
C = grams of combined deposit of PbO_2 plus MnO_2, and
D = grams of manganese.

11. Precision and Bias

11.1 This method was originally approved for publication before the inclusion of precision and accuracy 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 accuracy of this method is adequate for the contemplated use.

LEAD BY THE ELECTROLYTIC TEST METHOD

12. Apparatus

12.1 *Electrodes for Electroanalysis*— Apparatus No. 9. Use the larger electrode as the anode.

13. Procedure for Alloys Containing Under 0.05 % of Tin

13.1 *Solution of Samples Containing Under 0.1 % of Lead*—Transfer 10 g of the sample to a 400-mL beaker, cover, and dissolve in 60 mL of HNO_3 (1 + 1). When dissolution is complete, boil gently to expel brown fumes. Wash down the cover glass and the sides of the beaker and dilute to 250 mL.

13.2 *Solution of Samples Containing 0.1 to 6 % of Lead (see Note 2)*— Transfer 1.000 g of the sample to a 250-mL beaker, cover, and dissolve in 20 mL of HNO_3 (1 + 1). When dissolution is complete, boil gently to expel brown fumes. Wash down the cover glass and the sides of the beaker and dilute to 150 mL.

13.3 Insert the electrodes into the solution, cover with a pair of split watch glasses, and electrolyze for 2 h at a current density of 1.25 to 1.50 A/dm^2. It is preferable to agitate the electrolyte. Electrolysis may take place overnight without agitation and using a lower current density. Wash down the cover glasses, electrodes, and sides of the beaker, and continue the electrolysis until no darkening of the newly exposed surface of the platinum anode can be detected when the current has been continued for 15 min after the level of the liquid was raised.

13.4 When deposition of the lead is complete, without interrupting the current, siphon off the electrolyte, at the same time filling the beaker with water. Remove the anode quickly, rinse thoroughly with water, and dry at 110 to 120°C for 30 min. The deposit is fragile and must be handled carefully. Cool the anode and weigh the deposit.

13.5 Correct for manganese and calculate the percentage of lead in accordance with 10.8 and 10.9.

14. Procedure for Alloys Containing 0.05 % and Over of Tin

14.1 Proceed in accordance with 13.1 or 13.2. Remove tin in accordance with 10.2 and 10.3 or 10.2 and 10.4. Electrolyze and determine lead as directed in 13.3-13.5.

15. Precision and Bias

15.1 This test method was originally approved for publication before the inclusion of precision and accuracy 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 accuracy of this method is adequate for the contemplated use.

LEAD BY THE SULFATE TEST METHOD

(This test method, which consisted of Sections 16 and 17, was discontinued in 1976.)

TIN BY THE IODOMETRIC TITRATION TEST METHOD

(This test method, which consisted of Sections 18 through 20, was discontinued in 1976.)

ZINC BY THE OXIDE OR FERROCYANIDE TEST METHOD

(This test method, which consisted of Sections 21 and 22 of this standard, was discontinued in 1975.)

NICKEL BY THE DIMETHYLGLYOXIME TEST METHOD

(This test method, which consisted of Sections 23 through 25 of this standard, was discontinued in 1975.)

COBALT BY THE ALPHA-NITROSO-BETA-NAPHTHOL TEST METHOD

26. Reagents

26.1 *Alpha-Nitroso-Beta-Naphthol Solution* (70 g/L)—Dissolve 7 g of alpha-nitroso-beta-naphthol in 100 mL of glacial acetic acid and filter the solution. Prepare this reagent as required just before using.

26.2 *Zinc Oxide Suspension*—Transfer 300 mL of water and 50 g of finely powdered ZnO to a 500-mL flask. Stopper the flask and shake the mixture vigorously each time before using.

27. Procedure

27.1 Transfer 5 g of the sample to a 250-mL beaker and dissolve in 40 mL of HNO_3 (1 + 1). When dissolution is complete, boil gently to expel brown fumes. If a precipitate of tin is present, add 50 mL of hot water, heat on the steam bath for 1 h, and filter off the metastannic acid through a fine paper, washing thoroughly with hot HNO_3 (1 + 99).

27.2 Remove the copper and lead in accordance with 10.5.

27.3 Evaporate the electrolyte to a thick syrup, and convert the nitrates to chlorides by two evaporations to dryness with 25-mL portions of HCl. Cool, add 100 mL of HCl (1 + 19), and heat until the salts are dissolved. Transfer to a 500-mL Erlenmeyer flask and dilute to 250 mL.

27.4 Heat to 60 to 80°C, swirl vigorously, and add ZnO suspension in small increments until an excess of ZnO is present. The presence of excess ZnO is indicated by a milky turbidity in the supernatant liquid and white particles on the bottom of the flask on standing. Heat on a steam bath for 15 min and filter through a medium paper into a 600-mL beaker. Wash the residue with hot water and discard it. Add 20 mL of HCl to the filtrate and adjust the volume to 400 mL.

27.5 Heat the solution to 60°C, add 15 mL of alpha-nitroso-beta-naphthol solution, and stir vigorously for 1 min. Cool to room temperature, and stir occasionally for 1 h. Filter through a medium, ashless paper, wash thoroughly with hot HCl (1 + 19), and finally with hot water.

27.6 Ignite the precipitate in a 30-mL, tall-form porcelain crucible. Allow the crucible to cool, add 1 to 2 g of $Na_2S_2O_7$, and heat on a hot plate until dense white fumes appear. Fuse until the oxides are dissolved, allow to cool, tap gently to detach the melt, and transfer it to a 400-mL beaker. Rinse the crucible thoroughly with hot water, and add the rinsings to the beaker. Heat gently until the melt dissolves, add 10 mL of HCl, and dilute to 200 mL. Reprecipitate, filter, and wash as described in 27.5.

27.7 Ignite the reprecipitated cobalt in a tared porcelain crucible at 750 to 850°C to constant weight. Cool in a desiccator and weigh as Co_3O_4.

27.8 *Blank*—Make a blank determination, following the same procedure and using the same amounts of all reagents.

27.9 *Calculation*—Calculate the percentage of cobalt as follows:

$$\text{Cobalt, \%} = ([(A - B) \times 0.734]/C) \times 100$$

where:

A = grams of Co_3O_4 in sample,
B = correction for blank, g, and
C = grams of sample used.

28. Precision and Bias

28.1 This test method was originally approved for publication before the inclusion of precision and accuracy 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 accuracy of this test method is adequate for the contemplated use.

COBALT BY THE NITROSO-R-SALT (PHOTOMETRIC) TEST METHOD

29. Summary of Test Method

29.1 Cobalt, in a hot solution buffered with sodium acetate, forms an orange-colored complex with nitroso-R-salt. The addition of a controlled amount of nitric acid destroys interfering complexes and stabilizes the cobalt complex. Photometric measurement is made at approximately 520 nm.

30. Concentration Range

30.1 The recommended concentration range is from 0.005 to 0.10 mg of cobalt in 50 mL of solution, using a cell depth of 2 cm.[4]

31. Stability of Color

31.1 The color is stable for more than 2 h.

32. Interfering Elements

32.1 Provision is made in the procedure for preventing, or compensating for, interference from metals present in the maximum limits given in 1.1.

33. Apparatus

33.1 *Electrodes for Electroanalysis*—Apparatus No. 9.

34. Reagents

34.1 *Cobalt Standard Solution* (1 mL = 0.01 mg Co)—*Dissolve 0.1000 g of pure cobalt metal (Note 5) in about 10 mL of HNO_3 (1 + 1). Boil to expel brown fumes. Cool and dilute to 1 L in a volumetric flask and mix. Dilute 100 mL of this solution to 1 L in a volumetric flask and mix.*

NOTE 5—Alternatively, the solution may be prepared as follows: Dissolve 0.4770 g of $CoSO_4 \cdot 7H_2O$ in about 75 mL of water, add 2 mL of H_2SO_4, dilute to 1 L in a volumetric flask, and mix. Standardize the solution as follows: Transfer a 100-mL aliquot to a 400-mL beaker, add 10 mL of HCl, and dilute to 200 mL. Proceed in accordance with 27.5 and 27.7. For use, dilute 100 mL of this standardized solution to 1 L in a volumetric flask and mix.

34.2 *Nitroso-R-Salt Solution* (7.5 g/L)—Dissolve 0.75 g of nitroso-R-salt in water and dilute to 100 mL.

34.3 *Sodium Acetate Solution* (500 g/L)—Dissolve 500 g of $NaC_2H_3O_2 \cdot 3H_2O$ in about 600 mL of water and dilute to 1 L.

35. Preparation of Calibration Curve

35.1 Transfer 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0-mL aliquots of standard cobalt solution to 50-mL volumetric flasks and dilute to 10 mL. Add 10 mL of water to an additional 50-mL volumetric flask and carry through as a reagent blank.

35.2 Add to each flask, in the order given, 5 mL of sodium acetate solution and 2.0 mL of nitroso-R-salt solution, mixing between additions (Note 6). Add a glass bead, heat to boiling, and maintain just under the boiling temperature for 1 to 2 min. Add 5.0 mL of HNO_3 (1 + 2) and boil gently for 1 to 2 min. Cool to room temperature, dilute to the mark, and mix.

NOTE 6—The pH of the solutions at this point should be about 5.5.

35.3 Transfer a suitable portion of each solution to an absorption cell and measure the transmittance or absorbance against the blank at approximately 520 nm.

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[4] This procedure has been written for a cell having a 2-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

35.4 Plot the values obtained against milligrams of cobalt per 50 mL of solution.

36. Procedure

36.1 If the electrolyte, or an aliquot of it, reserved in accordance with 10.5 is available, proceed as directed in 36.2. If the electrolyte is not available, transfer 2.00 g of the sample to a 250-mL beaker. Dissolve the sample and remove copper, lead, and tin in accordance with 10.1-10.5. Carry a blank through all steps of the procedure.

36.2 Transfer the electrolyte or aliquot of it, reserved in accordance with 10.5 or obtained in accordance with 36.1, to a 200-mL volumetric flask, dilute to the mark, and mix. Transfer two equal aliquots (not exceeding 5.0 mL) containing under 0.10 mg of cobalt (preferably about 0.075 mg) to 50-mL volumetric flasks and dilute to 10 mL. Proceed in accordance with 35.2, except to omit the addition of nitroso-R-salt to one of the aliquots. Treat similar aliquots of the blank solution in the same way.

36.3 Transfer a suitable portion of each solution to an absorption cell and measure the transmittance or absorbance, at approximately 520 nm, of the solutions containing the cobalt complex against the corresponding solutions in which the cobalt complex was not developed.

36.4 Using the value obtained, read from the calibration curve the number of milligrams of cobalt present in 50 mL of the final solution.

36.5 *Calculation*—Calculate the percentage of cobalt as follows:

$$\text{Cobalt, \%} = (A - B)/(C \times 10)$$

where:

A = milligrams of cobalt found in 50 mL of the final solution,

B = correction for the reagent blank, in milligrams of cobalt, and

C = grams of sample represented in 50 mL of the final solution.

37. Precision and Bias

37.1 This test method was originally approved for publication before the inclusion of precision and accuracy 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 accuracy of this test method is adequate for the contemplated use.

IRON BY THE DICHROMATE TEST METHOD

38. Reagents

38.1 *Ammonium Chloride Wash Solution*—Dissolve 20 g of NH_4Cl in 1 L of water made slightly alkaline with a few drops of NH_4OH.

38.2 *Mercuric Chloride Solution*—(*Saturated*)—Add 60 to 100 g of $HgCl_2$ to 400 mL of hot water, shake, and cool to room temperature. More water may be added from time to time as long as crystals remain undissolved.

38.3 *Potassium Dichromate Standard Solution* (0.05 *N*)—Reagent No. 10.

38.4 *Sodium Diphenylamine Sulfonate Indicator Solution* (2 g/L).

38.5 *Stannous Chloride Solution* (42 g $SnCl_2$*/L*)—Dissolve 12.5 g of $SnCl_2 \cdot 2H_2O$ in 25 mL of HCl, and dilute to 250 mL. Keep the solution in a well-stoppered bottle.

39. Procedure

39.1 If the iron content is under 0.25 %, transfer 5.0 g of the sample, from which adventitious iron has been removed, to a 400-mL beaker and dissolve in 50 mL of HNO_3 (1 + 1). If the iron content is 0.25 % or over, transfer 1.00 to 2.00 g of the sample, from which adventitious iron has been removed, to a 250-mL beaker and dissolve in 25 mL of HNO_3 (1 + 1). When dissolution is complete, boil gently to expel brown fumes. Add 50 mL of hot water and observe the clarity of the solution. If the solution is clear, proceed, as directed in 39.2. If enough tin is present to form a cloud, proceed in accordance with 10.2 and 10.3 or 10.3 and 10.4 to remove the tin and recover the iron in the metastannic acid precipitate before continuing in accordance with 39.2 of this section.

39.2 Dilute the solution from 150 to 200 mL and add 5 g of NH_4Cl. Add NH_4OH (1 + 1) until the basic salts of copper and nickel are dissolved and the solution is deep blue in color; then boil gently for a few minutes. Allow the precipitate to settle for a few minutes, and filter while hot, using a medium paper. Wash the beaker and precipitate, first with hot NH_4Cl wash solution, and finally with hot water to remove most of the soluble salts. Place the original beaker under the funnel and dissolve the precipitate through the paper with 20 mL of hot HCl (1 + 1) to which has been added 5 mL of H_2O_2 (3 %). Add the HCl in several portions, washing alternately with hot water. Finally, wash thoroughly with hot water.

39.3 Reprecipitate the iron, wash, and dissolve as described in 39.2.

39.4 Evaporate the solution from 10 to 12 mL and wash down the sides of the beaker. Heat to boiling and add $SnCl_2$ solution dropwise, while swirling the beaker over a white background, until the yellow color of the $FeCl_3$ disappears. The sample must be kept near boiling for the entire period of reduction. Add 2 drops of $SnCl_2$ solution in excess but no more.

39.5 Dilute the reduced solution to 50 mL and cool to room temperature. While stirring, add at one stroke 10 mL of a saturated solution of $HgCl_2$. The resultant precipitate should be pure white in color, and in amount should be preferably not more than enough to give a pearly opalescence. If the precipitate is gray or dark, too large an excess of $SnCl_2$ has been used and it will be necessary to discard the solution and start anew. To the properly reduced solution, add 10 mL of H_3PO_4 (1 + 3) and 4 drops of sodium diphenylamine sulfonate indicator solution.

39.6 While stirring constantly, titrate slowly with $K_2Cr_2O_7$ solution until the color of the solution changes from green to a gray-green. Continue the titration dropwise until the first tinge of purple or violet-blue appears.

39.7 *Blank*—Make a blank determination, following the same procedure and using the same amounts of all reagents.

NOTE 7—Ferric iron must be present in the solution in order to obtain the purple or violet-blue end point color. If the color fails to form, the blank is less than the equivalent of 1 drop of 0.02 *N* $FeSO_4$ solution as this contains sufficient iron to yield an end point.

39.8 *Calculation*—Calculate the percentage of iron as follows:

$$\text{Iron, \%} = ([(A - B)C \times 0.0559]/D) \times 100$$

where:

A = millilitres of $K_2Cr_2O_7$ solution required to titrate the sample,
B = millilitres of $K_2Cr_2O_7$ solution required to titrate the blank,
C = normality of the $K_2Cr_2O_7$ solution, and
D = grams of sample used.

40. Precision and Bias

40.1 This test method was originally approved for publication before the inclusion of precision and accuracy 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 accuracy of this test method is adequate for the contemplated use.

IRON BY THE THIOCYANATE (PHOTOMETRIC) TEST METHOD

(This test method, which consisted of Sections 41 through 48 of this standard, was discontinued in 1975.)

IRON BY THE SALICYLATE (PHOTOMETRIC) TEST METHOD

(This test method, which consisted of Sections 49 through 55 of this standard, was discontinued in 1975.)

MANGANESE BY THE PERSULFATE TEST METHOD

(This test method, which consisted of Sections 56 through 58, was discontinued in 1976.)

MANGANESE BY THE PERIODATE (PHOTOMETRIC) TEST METHOD

59. Summary of Test Method

59.1 Manganese in an acid solution is oxidized to permanganate by heating with potassium periodate. Photometric measurement is made at approximately 520 nm.

60. Concentration Range

60.1 The recommended concentration range is from 0.06 to 1.25 mg of manganese in 100 mL of solution, using a cell depth of 2 cm.[4]

61. Stability of Color

61.1 The permanganate color is stable indefinitely if reducing agents are absent.

62. Interfering Elements

62.1 Provision is made in the procedure for preventing, or compensating for, interference from metals present in the maximum limits given in 1.1.

63. Reagents

63.1 *Hydrobromic Acid-Bromine Mixture*—Dilute 10 mL of bromine to 100 mL with HBr.

63.2 *Manganese Standard Solution* (1 mL = 0.125 mg Mn)—Dissolve 0.3596 g of $KMnO_4$ in about 100 mL of water. Add 20 mL of H_2SO_4 (1 + 1) and transfer to a 1-L volumetric flask. Add H_2O_2 (3 %) in small increments until the pink color of the permanganate is discharged. Boil the solution gently for about 10 min to destroy excess H_2O_2. Cool, dilute to the mark, and mix.

63.3 *Nitric-Phosphoric Acid Mixture*—Mix 400 mL of water, 200 mL of HNO_3, and 500 mL of H_3PO_4.

63.4 *Potassium Periodate Solution* (75 g KIO_4/L)—Dissolve 1.0 g of urea in 100 mL of HNO_3 (1 + 3). To this solution add 7.5 g of KIO_4 and dissolve by shaking in a glass-stoppered bottle.

64. Preparation of Calibration Curve

64.1 Transfer 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0-mL aliquots of standard manganese solution to 100-mL volumetric flasks. Carry through an additional 100-mL volumetric flask for a reagent blank. Add to each flask 5 mL of H_3PO_4 and dilute to about 50 mL.

64.2 Add 2 mL of KIO_4 solution and a chip of silicon carbide. Heat to boiling and boil gently for about 2 min. Digest at slightly below boiling temperature for an additional 10 min. Cool to room temperature, dilute to the mark, and mix.

64.3 Transfer a suitable portion of each solution to an absorption cell and measure the transmittance or absorbance against the blank at approximately 520 nm.

64.4 Plot the values obtained against milligrams of manganese per 100 mL of solution.

65. Procedure

65.1 If the tin content of the sample is such that there will be 50 mg or under of tin in the portion used, transfer 0.5 to 2.00 g of the sample, containing 0.12 to 12.5 mg of manganese, to a 150-mL beaker and dissolve in 25 mL of HNO_3-H_3PO_4 mixture (Note 8). Carry a blank through all steps of the procedure. When dissolution of the sample is complete, boil gently to expel brown fumes. Cool, transfer to a 100-mL volumetric flask, dilute to the mark, and mix. Continue in accordance with 65.3.

NOTE 8—The H_3PO_4 contained in 25 mL of dissolving solution is sufficient to hold about 50 mg of tin in solution, provided the sample is not subjected to excessive boiling nor prolonged digestion. For larger amounts of tin, proceed as directed in 65.2.

65.2 If the tin content of the sample is such that there will be over 50 mg of tin in the portion used, transfer 0.5 to 2.00 g of the sample, containing 0.12 to 12.5 mg of manganese, to a 300-mL Erlenmeyer flask and dissolve in 15 to 25 mL of HBr-Br_2 mixture. Carry a blank through all steps of the procedure. Add 10 mL of $HClO_4$ and 5 mL of H_3PO_4, and heat to dense white fumes to volatilize the tin. Cool and add 50 mL of water and 5 mL of HNO_3. Cool, transfer to a 100-mL volumetric flask, dilute to the mark, and mix. Continue in accordance with 65.3.

65.3 Transfer two equal aliquots containing under 1.25 mg of manganese (preferably about 0.75 mg) to 100-mL volumetric flasks. Add sufficient H_3PO_4 to bring the total content to 5 mL (assuming that the content of H_3PO_4 in the original sample solution was 10 mL) and dilute to about 50 mL. Treat similar aliquots of the blank solution in the same way.

65.4 Proceed as directed in 64.2, except to omit the addition of KIO_4 to one of the aliquots in each pair.

65.5 Transfer a suitable portion of each solution to an absorption cell and measure the transmittance or absorbance of the solutions in which the permanganic acid color was developed against the corresponding solutions in which the color was not developed.

65.6 Using the value obtained, read from the calibration curve the number of milligrams of manganese present in 100 mL of the final solution.

65.7 *Calculation*—Calculate the percentage of manganese as follows:

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

where:

A = milligrams of manganese found in 100 mL of the final solution,

B = correction for the reagent blank, mg, of manganese, and

C = grams of sample represented in 100 mL of the final solution.

66. Precision and Bias

66.1 This test method was originally approved for publication before the inclusion of precision and accuracy 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 accuracy of this test method is adequate for the contemplated use.