Designation: E 439 – 98

Standard Test Methods for Chemical Analysis of Beryllium[1]

This standard is issued under the fixed designation E 439; 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 beryllium having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.05 to 0.30
Beryllium	97.5 to 100
Beryllium Oxide	0.3 to 3
Carbon	0.05 to 0.30
Copper	0.005 to 0.10
Chromium	0.005 to 0.10
Iron	0.05 to 0.30
Magnesium	0.02 to 0.15
Nickel	0.005 to 0.10
Silicon	0.02 to 0.15

1.2 The test methods in this standard are contained in the sections indicated below.

	Sections
Chromium by the Diphenylcarbazide Photometric Test Method	9-18
Iron by the 1,10-Phenanthroline Photometric Test Method	19-28
Manganese by the Periodate Photometric Test Method	29-38
Nickel by the Dimethylglyoxime Photometric Test Method	39-48

1.3 *This standard does not purport to address all of the safety problems, 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[4]

E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition[4]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition[4]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[4]

3. Significance and Use

3.1 These test methods for the chemical analysis of beryllium metal are primarily intended as referee methods to test such materials for compliance with compositional specifications. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure unless otherwise specified. The apparatus, standard solutions, and reagents shall conform to the requirements prescribed in Practices E 50. Photometers shall conform to the requirements prescribed in Practice E 60.

4.2 Photometric and spectrophotometric practice prescribed in these test methods shall conform to Practice E 60.

5. Hazards

5.1 For precautions to be observed in these test methods, reference shall be made to Practices E 50. Both beryllium metal and its compounds may be toxic. Care should be exercised to prevent contact of beryllium-containing materials with the skin. The inhalation of any beryllium-containing substance, either as a volatile compound or as finely divided powder, should be especially avoided. Beryllium-containing residues (especially ignited oxide) should be carefully disposed of.

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. However, these test methods do not supersede any sampling requirements specified in a specific ASTM material specification.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

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[1] These test methods are under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.05 on Zinc, Tin, Lead, Cadmium, Beryllium, and Other Metals.

Current edition approved May 10, 1998. Published July 1998. Originally published as E 439 – 71 T. Last previous edition E 439 – 88 (1993)$^{\epsilon 1}$.

[2] *Annual Book of ASTM Standards,* Vol 03.05.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] *Annual Book of ASTM Standards,* Vol 14.02.

8. Interlaboratory Studies

8.1 These test methods have been evaluated in accordance with Practices E 173, unless otherwise noted under the precision section.

CHROMIUM BY THE DIPHENYLCARBAZIDE (PHOTOMETRIC) TEST METHOD

9. Scope

9.1 This test method covers the determination of chromium in concentrations from 0.004 to 0.04 %.

10. Summary of Test Method

10.1 Chromium is oxidized by peroxydisulfate in the presence of silver nitrate, and the chromium diphenylcarbazide complex is then developed. Photometric measurement is made at approximately 540 nm.

11. Concentration Range

11.1 The recommended concentration range is from 0.02 to 0.10 mg of chromium per 250 mL of solution, using a 2-cm cell.

NOTE 1—This test method has been written for cells 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.

12. Stability of Color

12.1 The color of the chromium complex develops almost immediately but starts to fade after about 10 min. Photometric measurements should be made within 5 min after developing the color.

13. Interferences

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

14. Reagents

14.1 *Acetone* (CH_3COCH_3).

14.2 *Ammonium Peroxydisulfate Solution* (100 g/L)—Dissolve 10 g of ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) in water and dilute to 100 mL. Do not use a solution that has stood more than 12 h.

14.3 *Chromium, Standard Solution* (1 mL = 0.005 mg Cr)—Dissolve 0.2830 g of potassium dichromate ($K_2Cr_2O_7$) in water in a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 5 mL to a 100-mL volumetric flask, dilute to volume, and mix.

14.4 *Diphenylcarbazide Solution* (5 g/L)—Dissolve 0.50 g of diphenylcarbazide (1,5-diphenylcarbohydrazide) in 100 mL of acetone. Do not use a solution that has stood for more than 1 h.

14.5 *Phosphoric Acid* (1 + 1)—Mix 1 volume of concentrated phosphoric acid (H_3PO_4, sp gr 1.69) with 1 volume of water.

14.6 *Silver Nitrate Solution* (2.5 g/L)—Dissolve 0.25 g of silver nitrate ($AgNO_3$) in water and dilute to 100 mL.

14.7 *Sodium Hydroxide Solution* (500 g/L—Dissolve 50 g of sodium hydroxide (NaOH) in water, and dilute to 100 mL.

14.8 *Sulfuric Acid* (1 + 1)—Mix carefully and with stirring 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) into 1 volume of water.

15. Preparation of Calibration Curve

15.1 *Calibration Solutions*:

15.1.1 Using pipets, transfer 5, 10, 15, and 20 mL of chromium solution (1 mL = 0.005 mg Cr) to five 400-mL beakers. Add 1 mL of H_3PO_4(1 + 1) and dilute to approximately 250 mL with water.

15.1.2 Adjust the pH to 0.95 ± 0.05 with NaOH solution or H_2SO_4(1 + 1). Add 10 mL of $AgNO_3$ solution, 10 mL of $(NH_4)_2S_2O_8$ solution, and a few glass beads. Cover the beaker with a ribbed cover glass, and boil for at least 25 min. During this period, add water as required to maintain a volume not less than 150 mL. Cool, and transfer to a 250-mL volumetric flask. Proceed as directed in 15.3.

15.2 *Reference Solution*—Add 1 mL of H_3PO_4(1 + 1) to 250 mL of water in a 400-mL beaker. Proceed as directed in 15.1.2.

15.3 *Color Development*—Add 2.0 mL of diphenylcarbazide solution. Dilute to volume, and mix.

15.3.1 Prepare only that number of solutions which can be measured 5 min after color development.

15.4 *Photometry*:

15.4.1 *Multiple-Cell Photometer*—Measure the cell correction, using absorption cells with a 2-cm light path and a light band centered at approximately 540 nm. Using the test cell, take the photometric readings of the calibration solutions.

15.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 540 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

15.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of chromium per 250 mL of solution.

16. Procedure

16.1 *Test Solution*:

16.1.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 250-mL beaker (Note 3). Add 100 mL of water and, in small increments, add 15 mL of H_2SO_4(1 + 1). When apparent reaction has ceased, warm until all action stops.

NOTE 2—If the chromium content of the sample is between 0.02 and 0.04 %, use a 0.25-g sample.

16.1.2 Filter through an 11-cm fine filter paper into a 400-mL beaker. Wash the paper five or six times with hot water. Reserve the filtrate. Transfer the paper to a platinum crucible, dry, and ignite at 700°C.

16.1.3 Treat the residue with 1 drop of H_2SO_4(1 + 1), 3 or 4 drops of HNO_3, and 3 or 4 mL of HF. Evaporate to complete dryness, and ignite for 3 to 4 min at 900°C. Fuse the residue with about 1 g of potassium pyrosulfate ($K_2S_2O_7$). Cool, leach in 25 mL of water, add this solution to the reserved filtrate (16.1.2), and dilute to 250 mL. Proceed as directed in 15.1.2.

16.2 *Reference Solution*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents with the sample omitted for use as the reference solution.

16.3 *Color Development*—Proceed as directed in 15.3.

16.4 *Photometry*—Take the photometric reading of the test solution as directed in 15.4.

17. Calculation

17.1 Convert the net photometric reading of the test solution to milligrams of chromium by means of the calibration curve. Calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = A/(B \times 10) \quad (1)$$

where:

A = chromium found in 250 mL of the final test solution, mg, and

B = sample represented in 250 mL of the final test solution, g.

18. Precision and Bias

18.1 *Precision*—Eight cooperators from seven laboratories cooperated in testing this test method and obtained the data summarized in Table 1.

18.2 *Bias*—No certified reference materials suitable for testing this test method were available when this interlaboratory testing program was conducted. The user of this standard is encouraged to employ accepted reference materials, if available, to determine the bias of this test method as applied in a specific laboratory.

IRON BY THE 1,10-PHENANTHROLINE PHOTOMETRIC TEST METHOD

19. Scope

19.1 This test method covers the determination of iron in concentrations from 0.05 to 0.25 %.

20. Summary of Test Method

20.1 The iron is reduced with hydroxylamine hydrochloride and converted to the 1,10-phenanthroline complex. Photometric measurement is made at approximately 515 nm.

21. Concentration Range

21.1 The recommended concentration range is from 0.05 to 0.250 mg of iron per 100 mL of solution using a 2-cm cell.

NOTE 3—This test method has been written for cells 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.

22. Stability of Color

22.1 The color develops within 10 min and is stable for at least 2 h.

23. Interferences

23.1 Nickel forms a complex with and consumes 1,10-phenanthroline. However, an amount of nickel equivalent to four times the amount of iron does not affect the iron determination. Other elements ordinarily present in beryllium do not interfere if their concentrations are under the maximum limits shown in 1.1.

TABLE 1 Statistical Information

Test Material	Chromium Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.007	less than 0.001	0.001
2	0.020	0.002	0.003

24. Reagents

24.1 *Ammonium Acetate Solution* (230/L)—Dissolve 115 g of ammonium acetate in water and dilute to 500 mL.

24.2 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Reagent No. 131.

24.3 *Iron, Standard Solution* (1 mL = 0.01 mg Fe)—Dissolve 0.7020 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) in 10 mL of water, and add 1 mL of H_2SO_4(1 + 1). Transfer to a 100-mL volumetric flask, dilute to volume, and mix.

24.4 *1,10-Phenanthroline Solution* (1 g/L)—Dissolve 0.1 g of 1,10-phenanthroline monohydrate in 100 mL of water.

25. Preparation of Calibration Curve

25.1 *Calibration Solutions*—Using pipets, transfer 5, 10, 15, 20, and 25 mL of iron solution (1 mL = 0.01 mg Fe) to 100-mL volumetric flasks. Add 1 mL of H_2SO_4 (1 + 1) and dilute to 50 mL. Proceed as directed in 25.3.

25.2 *Reference Solution*—Transfer 50 mL of water and 1 mL of H_2SO_4(1 + 1) to a 100-mL volumetric flask. Proceed as directed in 25.3.

25.3 *Color Development*—Add 3 mL of $NH_2OH \cdot HCl$ solution, and 20 mL of ammonium acetate solution, and mix. Add 10 mL of 1,10-phenanthroline solution, and mix. Check the pH of the solution with indicator paper and, if required, add ammonium acetate solution to adjust the pH to between 4.0 and 4.5. Dilute to volume, and mix.

25.4 *Photometry*:

25.4.1 *Multiple-Cell Photometer*—Determine the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 515 nm. Using the test cell, take the photometric readings of the calibration solutions.

25.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 515 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

25.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of iron per 100 mL of solution.

26. Procedure

26.1 *Test Solution*:

26.1.1 Transfer a 1.0-g sample, weighed to the nearest 1 mg to a 250-mL beaker. Add 100 mL of water and, in small increments, add 25 mL of H_2SO_4(1 + 1). When the apparent reaction has ceased, warm until all action stops.

26.1.2 Filter using an 11-cm fine paper into a 500-mL volumetric flask. Wash the paper five or six times with hot water. Transfer the paper to a platinum crucible and ignite at 700°C. Reserve the filtrate.

26.1.3 Treat the residue with 1 drop of H_2SO_4(1 + 1), 3 or 4 drops of HNO_3, and 3 to 4 mL of HF. Evaporate to complete

dryness and ignite for 3 to 4 min at 900°C. Fuse the residue with 1 g of potassium pyrosulfate ($K_2S_2O_7$). Cool, leach in 25 mL of water, and add this solution to the reserved filtrate (26.1.2). Dilute to volume and mix. Transfer 50.0 mL to a 100-mL volumetric flask.

26.2 *Reference Solution*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents with the sample omitted, for use as the reference solution.

26.3 *Color Development*—Proceed as directed in 25.3.

26.4 *Photometry*—Take the photometric reading of the test solution as directed in 25.4.

27. Calculation

27.1 Convert the net photometric reading of the test solution to milligrams of iron by means of the calibration curve. Calculate the percentage of iron as follows:

$$\text{Iron, \%} = A/(B \times 10) \quad (2)$$

where:

A = iron found in 100 mL of final test solution, mg, and
B = sample represented in 100 mL of final test solution, g.

28. Precision and Bias

28.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 2.

28.2 *Bias*—No certified reference materials suitable for testing this test method were available when this interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the bias of this test method as applied in a specific laboratory.

MANGANESE BY THE PERIODATE PHOTOMETRIC TEST METHOD

29. Scope

29.1 This test method covers the determination of manganese in beryllium metal in concentrations from 0.008 to 0.04 %.

30. Summary of Test Method

30.1 Manganese is oxidized to permanganate with potassium periodate in a nitric-sulfuric-phosphoric acid medium. Photometric measurement is made at approximately 525 nm.

31. Concentration Range

31.1 The recommended concentration range is from 0.02 to 0.10 mg of manganese per 50 mL of solution using a 5-cm cell.

NOTE 4—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.

TABLE 2 Statistical Information

Test Material	Iron Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.134	0.006	0.013
2	0.095	0.006	0.015

32. Stability of Color

32.1 The permanganate color is stable for at least 24 h in the absence of reducing agents.

33. Interferences

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

34. Reagents

34.1 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

34.2 *Manganese, Standard Solution* (1 mL = 0.005 mg Mn—Dissolve 0.1000 g of manganese (purity: 99.5 % min) in 10 mL of HNO_3(1 + 1). Boil gently to expel oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 50 mL to a 1-L volumetric flask, dilute to volume, and mix.

34.3 *Potassium Periodate* (KIO_4).

34.4 *Sodium Nitrite* ($NaNO_2$).

35. Preparation of Calibration Curve

35.1 *Calibration Solutions*:

35.1.1 Using pipets, transfer 4, 8, 10, 15, and 20 mL of manganese solution (1 mL = 0.005 mg Mn) to 150-mL beakers. Adjust the volume of the solution to 20 mL.

35.1.2 Add 18 mL of HNO_3, 6 mL of H_2SO_4(1 + 1), and 5 mL of H_3PO_4. Cover the beakers and heat the solution to boiling. Remove from the hot plate. Proceed as directed in 35.4.

35.2 *Reference Solution*—Distilled water.

35.3 *Reagent Blank Solution*—Transfer 20 mL of water to a 150-mL beaker. Proceed as directed in 35.1.2.

35.4 *Color Development*—Add 0.5 g of KIO_4, return to the hot plate, and boil until the KIO_4 dissolves. Then place the beaker on a steam bath at not less than 90°C for 15 min for full color development. Cool, transfer to a 50-mL volumetric flask, dilute to volume (Note 6), and mix.

35.5 *Background Color Solution*—To the remainder of the calibration and reagent blank solutions, after obtaining the photometric readings, add a few grains of $NaNO_2$ and mix the solution thoroughly, until the permanganate is reduced.

NOTE 5—Photometric readings should be made immediately, because reoxidation of manganese occurs on standing.

35.6 *Photometry*:

35.6.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 5-cm light path and a light band centered at approximately 525 nm. Using the test cell, take the photometric readings of the calibration, reagent blank, and background color solutions.

35.6.2 *Single-Cell Photometer*—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 525 nm. While maintaining this adjustment, take the photometric readings of the calibration, reagent blank, and background color solutions.

35.7 *Calibration Curve*—Correct the photometric readings of the calibration solutions for the cell correction, reagent

blank, and background color photometric readings. Plot the net photometric readings of the calibration solutions against milligrams of manganese per 50 mL of solution.

36. Procedure

36.1 *Test Solution*:

36.1.1 Transfer a 5.0-g sample weighed to the nearest 1 mg to a 400-mL beaker. Add 100 mL of water and, in small increments, add 120 mL of H_2SO_4(1 + 1). During dissolution cool the beaker in a running water bath. When apparent reaction has ceased, warm until all action stops.

36.1.2 Filter using an 11-cm fine paper into a 400-mL beaker. Wash the paper five or six times with hot water. *Reserve the filtrate.* Transfer the paper to a platinum crucible, ignite at 700°C, and cool.

36.1.3 Add 1 drop of H_2SO_4(1 + 1), 3 or 4 drops of HNO_3, and 3 to 4 mL of HF. Evaporate to complete dryness, and then ignite at 900°C for 3 to 4 min. Fuse the residue with 1 g of $K_2S_2O_7$, cool, and leach in 25 mL of water. Add this solution to the reserved filtrate (36.1.2).

36.1.4 Transfer the solution to a 500-mL volumetric flask, dilute to volume, and mix.

36.1.5 Using a pipet, transfer 25 mL to a 150-mL beaker, and add 18 mL of HNO_3 and 5 mL of H_3PO_4. Cover the beaker and heat the solution to boiling. Remove from the hot plate. Proceed as directed in 36.4.

36.2 *Reference Solution*—Proceed as directed in 35.2.

36.3 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents with the sample omitted.

36.4 *Color Development*—Proceed as directed in 35.4.

36.5 *Background Color Solution*—Proceed as directed in 35.5.

36.6 *Photometry*—Take the photometric readings of the test, reagent blank, and background color solutions as directed in 35.6.

37. Calculations

37.1 Convert the photometric reading of the test solution to milligrams of manganese, and the photometric readings of the reagent blank and background color solutions to the equivalent milligrams of manganese by means of the calibration curve. Calculate the percent manganese as follows:

$$\text{Manganese, \%} = [(A - B) - (C - D)]/(E \times 10) \quad (3)$$

where:

- A = manganese found in 50 mL of final test solution, mg,
- B = manganese equivalent found in the background color solution after reducing the permanganate in the final test solution, mg,
- C = manganese equivalent found in 50 mL of the reagent blank solution, mg,
- D = manganese equivalent found in the background color solution after reducing the permanganate in the final reagent blank solution, mg, and,
- E = sample represented in 50 mL of the final test solution, g.

38. Precision and Bias

38.1 *Precision*—Seven laboratories cooperated in testing this test method and obtained the data summarized in Table 3. Since insufficient data were available to evaluate the test method in accordance with Practices E 173, standard deviation and coefficient of variation were calculated.

38.2 *Bias*—No certified reference materials suitable for testing this test method were available when this interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the bias of this test method as applied in a specific laboratory.

NICKEL BY THE DIMETHYLGLYOXIME (PHOTOMETRIC TEST METHOD)

39. Scope

39.1 This test method covers the determination of nickel in concentrations from 0.001 to 0.04 %.

40. Summary of Test Method

40.1 Nickel is precipitated from an ammoniacal solution with 1,2,3-benzotrazole using cadmium as a carrier. After filtration, the paper and residue are wet ashed with nitric and perchloric acids. The nickel is oxidized by potassium peroxydisulfate in an alkaline medium, and the nickel dimethylglyoxime color is developed. Photometric measurement is made at approximately 465 nm.

41. Concentration Range

41.1 The recommended concentration range is from 0.005 to 0.04 mg of nickel per 50 mL of solution using a 5-cm cell.

NOTE 6—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.

42. Stability of Color

42.1 The color develops within 30 min and is stable for at least 24 h.

43. Interferences

43.1 Although copper forms a complex with dimethylglyoxime, an amount of copper equal to that of nickel causes a positive error of only 2 %. Other elements ordinarily present do not interfere, if their concentrations are under the limits shown in 1.1.

44. Reagents

44.1 *1,2,3-Benzotrazole Solution* (20 g/L)—Dissolve 2 g of 1,2,3-benzotrazole (benzotriazole) in hot water, filter, cool, and dilute to 100 mL. Prepare fresh as needed.

44.2 *1,2,3-Benzotrazole Wash Solution*—Dissolve 2 g of 1,2,3-benzotrazole and 10 g of tartaric acid in 500 mL of water. Adjust the pH to 8.5 with NH_4OH and dilute to 1 L. Do not use a solution that has stood more than 12 h.

TABLE 3 Statistical Information

Test Material	Manganese Found, %	Standard Deviation, %	Coefficient of Variation, %
1	0.0086	0.0007	8.1
2	0.0081	0.0009	10.5

44.3 *Cadmium Solution* (4 g/L)—Dissolve 4 g of cadmium metal (purity: 99.9 % min, 10 ppm max) in 20 mL of HNO_3(1 + 1). Boil to expel oxides of nitrogen, cool, and dilute to 1 L.

44.4 *Citric Acid Solution* (50 g/L)—Dissolve 5 g of citric acid in water, and dilute to 100 mL. Do not use a solution that has stood more than 12 h.

44.5 *Nickel, Standard Solution* (1 mL = 0.002 mg Ni)—Dissolve 0.1000 g of nickel (purity: 99.9 % min) in 20 mL of HNO_3(1 + 1). Gently boil to expel oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 1-L volumetric flask, dilute to volume, and mix.

44.6 *Potassium Peroxydisulfate Solution* (50 g/L)—Dissolve 5 g of potassium peroxydisulfate ($K_2S_2O_8$) in water, and dilute to 100 mL. Prepare fresh as needed.

44.7 *Sodium Dimethylglyoximate Solution* (30 g/L)—Dissolve 3 g of sodium dimethylglyoximate in water, and dilute to 100 mL. Do not use a solution that has stood for more than 12 h.

44.8 *Sodium Hydroxide Solution* (400 g/L)—Dissolve 40 g of sodium hydroxide (NaOH) in water, and dilute to 100 mL. Store in polyethylene bottle.

44.9 *Tartaric Acid Solution* (500 g/L)—Dissolve 50 g of tartaric acid in water, and dilute to 100 mL.

45. Preparation of Calibration Curve

45.1 *Calibration Solutions*—Using pipets, transfer 2, 5, 10, 15, and 20 mL of nickel solution (1 mL = 0.002 mg Ni) to 100-mL beakers. Add 3 mL of citric acid solution and 1 mL of HCl. Dilute to 30 mL. Proceed as directed in 45.3.

45.2 *Reference Solution*—Transfer 3 mL of citric acid solution and 1 mL of HCl to a 100-mL beaker. Dilute to 30 mL. Proceed as directed in 45.3.

45.3 *Color Development*—Using a pH meter, adjust the pH of the solution to 8.5 with NH_4OH (1 + 1). Add NaOH solution dropwise until a pH of 10.5 ± 0.1 is attained. Add 3 mL of $K_2S_2O_8$ solution and 1.0 mL of dimethylglyoximate solution. Transfer to a 50-mL volumetric flask, dilute to volume, and mix. Allow to stand 30 min.

45.4 *Photometry*:

45.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 5-cm light path and a light band centered at approximately 465 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

45.4.2 *Single-Cell Photometer*—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 465 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

45.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of nickel per 50 mL of solution.

46. Procedure

46.1 *Test Solution*:

46.1.1 Transfer a 1.0-g sample, weighed to the nearest 1 mg, to a 250-mL beaker. Add 100 mL of water and, in small increments, add 25 mL of H_2SO_4(1 + 1). When apparent reaction has ceased, warm until all action stops.

46.1.2 Filter through an 11-cm fine filter paper into a 400-mL beaker. Wash the paper five or six times with hot water. Reserve the filtrate. Transfer the paper to a platinum crucible, dry, and ignite at 700°C.

NOTE 7—Some brands of filter paper and, particularly, filter pulp, contain significant and varying amounts of nickel.

46.1.3 Treat the residue with 1 drop of H_2SO_4(1 + 1), 3 or 4 drops of HNO_3, and 3 to 4 mL of HF. Evaporate to complete dryness, and ignite for 3 to 4 min at 900°C. Fuse the residue with 1 g of $K_2S_2O_7$. Cool, dissolve in 25 mL of water, and add this solution to the reserved filtrate (46.1.2). If the solution contains more than 0.04 mg of nickel, transfer to a 250-mL volumetric flask, dilute to volume, and mix.

46.1.4 Transfer the solution, or an aliquot of the solution containing between 0.005 and 0.04 mg of nickel, to a 600-mL beaker. For each 0.1 g of beryllium, add 3 mL of tartaric acid solution, and dilute to 400 mL.

46.1.5 Add 15 mL of cadmium solution. Using a pH meter, adjust the pH to 8.5 ± 0.1 with NH_4OH (1 + 1). Add 60 mL of 1,2,3-benzotrazole solution and a small amount of filter pulp. Warm the solution at approximately 90°C for 1 h stirring occasionally to aid the coagulation of the precipitate. Allow to stand at room temperature for at least 3 h preferably overnight.

46.1.6 Filter using an 11-cm medium paper (Note 7) and wash twice with 1,2,3-benzotrazole wash solution.

46.1.7 Transfer the paper to the 600-mL beaker. Add 30 mL of HNO_3 and 10 mL of $HClO_4$. Evaporate to fumes of $HClO_4$ and finally to dryness. Cool to room temperature.

46.1.8 Add 1 mL of HCl and 3 mL of citric acid solution. Transfer the solution to a 100-mL beaker, and dilute to 30 mL.

46.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents, with the sample omitted, for use as a reference solution.

46.3 *Color Development*—Proceed as directed in 45.3.

46.4 *Photometry*—Take the photometric reading of the test solution as directed in 45.4.

47. Calculation

47.1 Convert the net photometric reading of the test solution to milligrams of nickel by means of the calibration curve. Calculate the percentage of nickel as follows:

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

where:

A = nickel found in 50 mL of the final test solution, mg, and,

B = sample represented in 50 mL of the final test solution, g.

48. Precision and Bias

48.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 4.

48.2 *Bias*—No certified reference materials suitable for testing this test method were available when this interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials,

TABLE 4 Statistical Information

Test Material	Nickel Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.019	0.003	0.003
2	0.014	0.003	0.005

if available, to determine the bias of this test method as applied in a specific laboratory.

49. Keywords

49.1 beryllium; chromium; iron; manganese; nickel