Designation: E439 – 17

Standard Test Methods for Chemical Analysis of Beryllium[1]

This standard is issued under the fixed designation E439; 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	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 Spectrophotometric Test Method [0.004 % to 0.04 %]	10 – 19
Iron by the 1,10-Phenanthroline Spectrophotometric Test Method [0.05 % to 0.25 %]	20 – 29
Manganese by the Periodate Spectrophotometric Test Method [0.008 % to 0.04 %]	30 – 39
Nickel by the Dimethylglyoxime Spectrophotometric Test Method [0.001 % to 0.04 %]	40 – 49

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E135.

4. Significance and Use

4.1 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.

5. Apparatus, Reagents, and Spectrophotometric Practice

5.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure unless

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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, Precious Metals, their Alloys, and Related Metals.

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[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

otherwise specified. The apparatus, standard solutions, and reagents shall conform to the requirements prescribed in Practices E50. Spectrophotometers shall conform to the requirements prescribed in Practice E60.

5.2 Spectrophotometric practice prescribed in these test methods shall conform to Practice E60.

6. Hazards

6.1 For precautions to be observed in these test methods, reference is made to Practices E50. Both beryllium metal and its compounds may be toxic. Exercise care 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.

7. Sampling

7.1 Wrought products shall be sampled in accordance with Practice E55. Cast products shall be sampled in accordance with Practice E88. However, these test methods do not supersede any sampling requirements specified in a specific ASTM material specification.

8. Rounding Calculated Values

8.1 Rounding of test results obtained using this test method shall be performed as directed in Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practice E173, unless otherwise noted under the precision section.

CHROMIUM BY THE DIPHENYLCARBAZIDE (SPECTROPHOTOMETRIC) TEST METHOD

10. Scope

10.1 This test method covers the determination of chromium from 0.004 % to 0.04 %.

10.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

11. Summary of Test Method

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

12. Chromium Range

12.1 The recommended concentration range is from 0.02 mg 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.

13. Stability of Color

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

14. Interferences

14.1 The elements ordinarily present do not interfere if their mass fractions are under the maximum limits shown in 1.1.

15. Reagents

15.1 *Acetone* (CH_3COCH_3).

15.2 *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.

15.3 *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.

15.4 *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.

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

15.6 *Sulfuric Acid* (1 + 1)—Mix carefully and with stirring one volume of concentrated H_2SO_4 (sp gr 1.84) into one volume of water.

15.7 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

16. Preparation of Calibration Curve

16.1 *Calibration Solutions:*

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

16.1.2 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 16.3.

16.2 *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 16.1.2.

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

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

16.4 *Spectrophotometry:*

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

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

16.5 *Calibration Curve*—Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of chromium per 250 mL of solution.

17. Procedure

17.1 *Test Solution:*

17.1.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 250-mL beaker. Add 100 mL of water and, in small increments, add 15 mL of H_2SO_4 (1 + 1). When reaction has ceased, warm until all action stops. If the chromium content of the sample is between 0.02 % and 0.04 %, use a 0.25-g sample.

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

17.1.3 Treat the residue with one drop of H_2SO_4 (1 + 1), three drops or four drops of HNO_3, and 3 mL or 4 mL of HF. Evaporate to complete dryness, and ignite for 3 min 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 (17.1.2), and dilute to 250 mL. Proceed as directed in 16.1.2.

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

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

17.4 *Spectophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 16.4.

18. Calculation

18.1 Convert the net spectrophotometric absorbance 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.

19. Precision and Bias

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

TABLE 1 Statistical Information

Test Material	Chromium Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1	0.007	less than 0.001	0.001
2	0.020	0.002	0.003

19.2 *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.

19.3 Practice E173 has been replaced by Practice E1601. The Reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.

IRON BY THE 1,10-PHENANTHROLINE SPECTROPHOTOMETRIC TEST METHOD

20. Scope

20.1 This test method covers the determination of iron from 0.05 % to 0.25 %.

20.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

21. Summary of Test Method

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

22. Iron Range

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

NOTE 2—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.

23. Stability of Color

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

24. Interferences

24.1 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 percentages are under the maximum limits shown in 1.1.

25. Reagents

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

25.2 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 5.0 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 50 mL of water. Prepare fresh as needed.

25.3 *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.

25.4 *1,10-Phenanthroline Solution* (1 g/L)—Dissolve 0.1 g of 1,10-phenanthroline monohydrate in 100 mL of water.

25.5 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

26. Preparation of Calibration Curve

26.1 *Calibration Solutions*—Using pipet, 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 26.3.

26.2 *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 26.3.

26.3 *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.

26.4 *Spectrophotometry:*

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

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

26.5 *Calibration Curve*—Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of iron per 100 mL of solution.

27. Procedure

27.1 *Test Solution:*

27.1.1 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.

27.1.2 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.

27.1.3 Treat the residue with one drop of H_2SO_4 (1 + 1), three drops or four drops of HNO_3, and 3 mL to 4 mL of HF. Evaporate to complete dryness and ignite for 3 min 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 (27.1.2). Dilute to volume and mix. Using a pipet, transfer 50.0 mL to a 100-mL volumetric flask.

27.2 *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.

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

27.4 *Spectrophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 26.4.

28. Calculation

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

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

where:

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

29. Precision and Bias

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

29.2 *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.

29.3 Practice E173 has been replaced by Practice E1601. The Reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.

MANGANESE BY THE PERIODATE SPECTROPHOTOMETRIC TEST METHOD

30. Scope

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

30.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

TABLE 2 Statistical Information

Test Material	Iron Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1	0.134	0.006	0.013
2	0.095	0.006	0.015

Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

31. Summary of Test Method

31.1 Manganese is oxidized to permanganate with potassium periodate in a HNO_3-H_2SO_4-H_3PO_4 acid medium. Spectrophotometric measurement is made at 525 nm.

32. Manganese Range

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

NOTE 3—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.

33. Stability of Color

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

34. Interferences

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

35. Reagents

35.1 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

35.2 *Manganese, Standard Solution* (1 mL = 0.005 mg Mn)—Dissolve 0.1000 g of manganese (purity: 99.5 % minimum) 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.

35.3 *Potassium Periodate* (KIO_4).

35.4 *Sodium Nitrite* ($NaNO_2$).

36. Preparation of Calibration Curve

36.1 *Calibration Solutions:*

36.1.1 Using pipet, 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.

36.1.2 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 36.4.

36.2 *Reference Solution*—Distilled water.

36.3 *Reagent Blank Solution*—Transfer 20 mL of water to a 150-mL beaker. Proceed as directed in 36.1.2.

36.4 *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, and mix. Spectrophotometric readings should be made immediately, because reoxidation of manganese occurs on standing.

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

36.6 *Spectrophotometry:*

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

36.6.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path, and adjust the spectrophotometer to the initial setting, using a light band centered at 525 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration, reagent blank, and background color solutions.

36.7 *Calibration Curve*—Correct the spectrophotometric absorbance readings of the calibration solutions for the cell correction, reagent blank, and background color spectrophotometric readings. Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of manganese per 50 mL of solution.

37. Procedure

37.1 *Test Solution:*

37.1.1 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 reaction has ceased, warm until all action stops.

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

37.1.3 Add one drop of H_2SO_4 (1 + 1), three drops or four drops of HNO_3, and 3 mL to 4 mL of HF. Evaporate to complete dryness, and then ignite at 900 °C for 3 min 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 (37.1.2).

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

37.1.5 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 37.4.

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

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

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

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

37.6 *Spectrophotometry*—Take the spectrophotometric absorbance readings of the test, reagent blank, and background color solutions as directed in 36.6.

38. Calculations

38.1 Convert the spectrophotometric absorbance reading of the test solution to milligrams of manganese, and the spectrophotometric absorbance 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.

39. Precision and Bias

39.1 *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 Practice E173, standard deviation and coefficient of variation were calculated.

39.2 *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.

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

NICKEL BY THE DIMETHYLGLYOXIME (SPECTROPHOTOMETRIC TEST METHOD)

40. Scope

40.1 This test method covers the determination of nickel from 0.001 % to 0.04 %.

40.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

41. Summary of Test Method

41.1 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 HNO_3 and $HClO_4$. The nickel is oxidized by potassium peroxydisulfate in an alkaline medium, and the nickel dimethylglyoxime color is developed. Spectrophotometric measurement is made at 465 nm.

42. Nickel Range

42.1 The recommended concentration range is from 0.005 mg to 0.04 mg of nickel 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.

43. Stability of Color

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

44. Interferences

44.1 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 percentages are under the limits shown in 1.1.

45. Reagents

45.1 *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.

45.2 *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.

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

45.4 *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.

45.5 *Nickel, Standard Solution* (1 mL = 0.002 mg Ni)—Dissolve 0.1000 g of nickel (purity: 99.9 % minimum) 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.

45.6 *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.

45.7 *Sodium Dimethylglyoximate Solution* (30g/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.

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

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

45.10 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

46. Preparation of Calibration Curve

46.1 *Calibration Solutions*—Using pipet, 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 46.3.

46.2 *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 46.3.

46.3 *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.

46.4 *Spectrophotometry:*

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

46.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path, and adjust the spectrophotometer to the initial setting, using a light band centered at 465 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

46.5 *Calibration Curve*—Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of nickel per 50 mL of solution.

47. Procedure

47.1 *Test Solution:*

47.1.1 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.

47.1.2 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 5—Some brands of filter paper and, particularly, filter pulp, contain significant and varying amounts of nickel.

47.1.3 Treat the residue with one drop of H_2SO_4 (1 + 1), three drops or four drops of HNO_3, and 3 mL to 4 mL of HF. Evaporate to complete dryness, and ignite for 3 min 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 (47.1.2). If the solution contains more than 0.04 mg of nickel, transfer to a 250-mL volumetric flask, dilute to volume, and mix.

47.1.4 Transfer the solution, or an aliquot of the solution containing between 0.005 mg 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.

47.1.5 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 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.

47.1.6 Filter using an 11-cm medium paper (Note 5) and wash twice with 1,2,3-benzotrazole wash solution.

47.1.7 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.

47.1.8 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.

47.2 *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.

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

47.4 *Spectrophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 46.4.

48. Calculation

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

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

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.

49. Precision and Bias

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

49.2 *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.

TABLE 4 Statistical Information

Test Material	Nickel Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1	0.019	0.003	0.003
2	0.014	0.003	0.005

49.3 Practice E173 has been replaced by Practice E1601. The Reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.

50. Keywords

50.1 beryllium; chromium; iron; manganese; nickel; spectrophotometry

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