Designation: E439 – 23

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 as follows.

	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 concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental 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 1997)[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

[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 and standard solutions 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.

5.3 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6. Hazards

6.1 For precautions to be observed in these test methods, refer to Practices E50.

6.2 Processing beryllium and beryllium-containing materials poses a health risk if safe-handling practices are not followed. Inhalation of airborne beryllium may cause a serious lung disorder in some individuals. Occupational safety and health regulatory agencies have set mandatory limits on occupational respiratory exposures. Read and follow the guidance in the SDS before working with these materials.

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 practices 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 in 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 %.

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 Concentration 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 *Potassium Pyrosulfate* ($K_2S_2O_7$).

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

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

15.8 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Type I or Type II of Specification D1193. Type III or Type IV may be used if they effect no measurable change in the blank or sample.

16. Preparation of Calibration Curve

16.1 *Calibration Solutions:*

16.1.1 Using a pipet, transfer (5, 10, 15, and 20) mL of chromium standard 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.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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.

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 of Practice E173 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability Index R_1 of Practice E173 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 %.

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 Concentration 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.

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

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 mass fractions 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 *Potassium Pyrosulfate* ($K_2S_2O_7$).

25.6 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Type I or Type II of Specification D1193. Type III or Type IV may be used if they effect no measurable change in the blank or sample.

26. Preparation of Calibration Curve

26.1 *Calibration Solutions*—Using a pipet, transfer (5, 10, 15, 20, and 25) mL of iron standard 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 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 times 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.

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:

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

where:

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

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,

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

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 of Practice E173 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability Index R_1 of Practice E173 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 %.

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 Concentration 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 mass fractions are under the limits shown in 1.1.

35. Reagents

35.1 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Type I or Type II of Specification D1193. Type III or Type IV may be used if they effect no measurable change in the blank or sample.

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 *Potassium Pyrosulfate* ($K_2S_2O_7$).

35.5 *Sodium Nitrite* ($NaNO_2$).

36. Preparation of Calibration Curve

36.1 *Calibration Solutions:*

36.1.1 Using a pipet, transfer (4, 8, 10, 15, and 20) mL of manganese standard 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 heat. 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, 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 absorbance 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.