



Designation: E439 – 10

Standard Test Methods for Chemical Analysis of Beryllium¹

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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 [0.004 % to 0.04 %]	10-19
Iron by the 1,10-Phenanthroline Photometric Test Method [0.05 % to 0.25 %]	20-29
Manganese by the Periodate Photometric Test Method [0.008 % to 0.04 %]	30-39
Nickel by the Dimethylglyoxime Photometric 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 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.

Current edition approved Jan. 15, 2010. Published February 2010. Originally published in 1971. Last previous edition approved in 2004 as E439 – 04a. DOI: 10.1520/E0439-10.

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

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.

procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus, Reagents, and Photometric Practice

5.1 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 E50. Photometers shall conform to the requirements prescribed in Practice E60.

5.2 Photometric and 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 shall be made to Practices E50. 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.

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 Calculated values shall be rounded to the desired number of places as directed in Practice E29.

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 (PHOTOMETRIC) TEST METHOD

10. Scope

10.1 This test method covers the determination of chromium in concentrations 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. Photometric measurement is made at approximately 540 nm.

12. 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. Photometric measurements should be made within 5 min after developing the color.

14. Interferences

14.1 The elements ordinarily present do not interfere if their concentrations 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 ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) 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 ($\text{K}_2\text{Cr}_2\text{O}_7$) 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 *Phosphoric Acid* (1 + 1)—Mix one volume of concentrated phosphoric acid (H_3PO_4 , sp gr 1.69) with one volume of water.

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 sodium hydroxide (NaOH) in water, and dilute to 100 mL.

15.8 *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.

15.9 *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 pipets, 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 approximately 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 H₃PO₄ (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 *Photometry*:

16.4.1 *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.

16.4.2 *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.

16.5 *Calibration Curve*—Plot the net photometric 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 (Note 2). Add 100 mL of water and, in small increments, add 15 mL of H₂SO₄ (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.

17.1.2 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.

17.1.3 Treat the residue with one drop of H₂SO₄ (1 + 1), three drops or four drops of HNO₃, 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 (K₂S₂O₇). 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 for use as the reference solution.

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

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

18. Calculation

18.1 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.

19. Precision and Bias

19.1 *Precision*—Eight cooperators 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 R₂ corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R₁ corresponds to the Repeatability Index r of Practice E1601.

IRON BY THE 1,10-PHENANTHROLINE PHOTOMETRIC TEST METHOD

20. Scope

20.1 This test method covers the determination of iron in concentrations 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. Photometric measurement is made at approximately 515 nm.

22. 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 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.

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

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

determination. Other elements ordinarily present in beryllium do not interfere if their concentrations 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 ($\text{NH}_2\text{OH} \cdot \text{HCl}$) 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 ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) 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 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 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 $\text{NH}_2\text{OH} \cdot \text{HCl}$ 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 *Photometry*:

26.4.1 *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.

26.4.2 *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.

26.5 *Calibration Curve*—Plot the net photometric 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 ($\text{K}_2\text{S}_2\text{O}_7$). 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 *Photometry*—Take the photometric reading of the test solution as directed in 26.4.

28. Calculation

28.1 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.

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**. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice **E1601**.

MANGANESE BY THE PERIODATE PHOTOMETRIC TEST METHOD

30. Scope

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

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