Designation: D2195 – 05

Standard Test Methods for Pentaerythritol[1]

This standard is issued under the fixed designation D2195; 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 testing of pentaerythritol for use in the manufacture of alkyd resins and other synthetic resins.

1.2 The test procedures appear in the following sections:

	Section
Sulfate ash	5 to 10
Moisture	11 to 16
Hydroxyl	17 to 22
Assay (by dibenzal)	23 to 29
Assay (by gas chromatography)	30 to 41
Phthalate ester color	42 to 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 For purposes of determining conformance of an observed or a calculated value using this test method to relevant specifications, test result(s) shall be rounded off "to the nearest unit" in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E29.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 34.

1.6 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)

D1615 Test Methods for Glycerol, Ethylene Glycol, and Pentaerythritol in Alkyd Resins[3]

D1728 Test Method for Phthalate Ester Color of High-Gravity Glycerin[3]

D2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography

E1 Specification for ASTM Liquid-in-Glass Thermometers

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

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals[3]

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E203 Test Method for Water Using Volumetric Karl Fischer Titration

E222 Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation

E260 Practice for Packed Column Gas Chromatography

3. Significance and Use

3.1 These test methods provide a measurement of sulfate, ash, moisture (water), hydroxyl content, assay by dibenzal and gas chromatography, and phthalate ester color of pentaerythritol. The results of these measurements can be used for specification acceptance.

4. Purity of Reagents

4.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that 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.

[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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

[4] *Reagent Chemicals, American Chemical Society Specifications*, 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.

***A Summary of Changes section appears at the end of this standard.**

4.2 Unless otherwise indicated, references to water shall be understood to mean Type IV of reagent water conforming to Specification D1193.

SULFATE ASH

5. Summary of Test Method

5.1 The organic matter is burned off, the residue treated with sulfuric acid, ignited, and the ash weighed.

6. Apparatus

6.1 *Crucible or Dish*—A silica, quartz, or platinum crucible or dish having a capacity of 50 to 60 mL.

6.2 *Bunsen Burner*.

6.3 *Electric Muffle Furnace*, maintained at 600 ± 25°C.

7. Reagents and Materials

7.1 *Sulfuric Acid (1 + 1)*—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 1 volume of water.

8. Procedure

8.1 Preignite the crucible or dish at 600°C, transfer to a desiccator, and when cool, weigh to 0.1 mg. Place approximately 20 g of the sample in the crucible or dish and weigh to 0.1 mg. Heat gently with a gas flame and ignite the specimen, allowing it to burn completely. Cool somewhat, and then moisten the residue with 10 to 20 drops of H_2SO_4 (1 + 1). Cautiously ignite until the carbon is completely consumed. Finally, ignite in the muffle furnace at 600°C (dark red heat) to constant weight, cool, and weigh to 0.1 mg.

9. Calculation

9.1 Calculate the percent of sulfate ash, *A*, to three decimal places as follows:

$$A = (R/S) \times 100 \quad (1)$$

where:

R = residue, g, and
S = sample used, g.

9.2 Duplicate determinations that agree within 0.005 % are acceptable for averaging.

10. Precision and Bias

10.1 *Precision*—The following criteria should be used for judging the acceptability of results at the 95 % confidence level:

10.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same analyst should be considered suspect if they differ by more than 0.008 %, absolute.

10.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by analysts in different laboratories should be considered suspect if they differ by more than 0.008 %, absolute.

NOTE 1—The above precision estimates are based on an interlaboratory study involving seven laboratories using three samples with one analyst performing duplicate runs on each of two days. The average level of the ash content of the samples studied was 0.01 %.

10.2 *Bias*—Bias cannot be determined because there is no available material having an accepted reference value.

MOISTURE

11. Summary of Test Method

11.1 The loss in weight on heating at 105°C for 3 h is determined.

12. Preparation of Sample

12.1 Grind a 25-g portion of the sample in a mortar and pestle, to pass a 40-mesh sieve, and use portions for the subsequent tests.

13. Apparatus

13.1 *Weighing Dish*, aluminum, 70 by 30 mm, with cover.

13.2 *Oven*, gravity convection, maintained at 105 ± 2°C.

14. Procedure

14.1 Dry the aluminum dish at 105° C. Cool in a dessicator and store until ready for use.

14.2 Weigh, to 0.1 mg, a 5-g portion of the ground sample into a tared-aluminum dish, and place in the 105 ± 2°C oven for 3 h. Remove, cover, cool in a desiccator, and weigh.

15. Calculation

15.1 Calculate the percent of moisture content, *M*, as follows:

$$M = [(A - B)/W] \times 100 \quad (2)$$

where:

A = weight of dish + specimen before heating, g,
B = weight of dish + specimen after heating, g, and
W = sample used, g.

15.2 Duplicate determinations that agree within 0.15 % are acceptable for averaging.

16. Precision and Bias

16.1 *Precision*—The following criteria should be used for judging the acceptability of results at the 95 % confidence level:

16.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same analyst should be considered suspect if they differ by more than 0.20 %, absolute.

16.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by analysts in different laboratories should be considered suspect if they differ by more than 0.30 % absolute.

NOTE 2—The above precision estimates are based on an interlaboratory study involving seven laboratories using three samples with one analyst performing duplicate runs on each of two days. The mean level of the moisture content of the samples studied was 0.3 %.

16.2 *Bias*—Bias cannot be determined because there is no available material having an accepted reference value.

HYDROXYL CONTENT

17. Summary of Test Method

17.1 The hydroxyl content is determined in accordance with Test Methods E222.

18. Apparatus

18.1 *Flasks*, Erlenmeyer, 300-mL with standard-taper 24/40 joint.

18.2 *Condenser*, 400-mm, standard-taper 24/40 joint with cooling extending into the joint, drip tip.

18.3 *Hot Plates*, with variable resistance for temperature control.

18.4 *Buret*, calibrated, 100-mL, with a 50 or 75-mL reservoir on top of a lower portion calibrated in 0.1-mL divisions. A TFE-fluorocarbon resin stopcock is suitable for this purpose.

19. Reagents and Materials

19.1 *Acetic Anhydride*.

19.2 *Acetylation Reagents*—Mix 105 mL of acetic anhydride with 1 L of pyridine (see 19.4). The reagent shall be freshly prepared each day, and used and kept in a dark bottle. It should not be used if darker than a pale yellow color.

19.3 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g of phenolphthalein in 100 mL of aqueous pyridine solution (1 + 1).

19.4 *Pyridine*, containing 0.30 to 0.45 % water. Determine the water content of the pyridine using Test Method E203 and add the required amount of water. Calculate the volume of water to add in millilitres per litre of pyridine, *V*, as follows:

$$V = 4.0 - 9A \quad (3)$$

where *A* = water in pyridine, %.

19.5 *Sodium Hydroxide, Standard Solution (0.5 N)*—Prepare and standardize in accordance with Practice E200. Apply temperature corrections to the volumes of titrant so that the normality is for concentration at 20°C.

20. Procedure

20.1 Weigh a 0.30 to 0.33-g portion of the ground sample into a small glass-stoppered weighing bottle. Dry for 3 h at 105°C. Weigh accurately, transfer the portion to a 250-mL Erlenmeyer flask with ground joint, and reweigh the bottle to obtain the specimen weight by difference.

20.2 Pipet 25 mL of the acetylation reagent into the flask using a uniform drainage time for all aliquots. Connect the flask to the condenser (Note 3), sealing the joint with 1 or 2 drops of pyridine, and place on a hot plate; if necessary, swirl the flask to dissolve the specimen. Heat at reflux for 30 min, regulating the heat so that the vapors condense in the condenser.

NOTE 3—If the surrounding atmosphere is humid, connect the condenser to a drying trap containing a mixture of No. 2 mesh calcium chloride and indicating anhydrous calcium sulfate.

20.3 Allow the flask to cool somewhat, then rinse the condenser with 25 mL of water. Remove the condenser and rinse the joint of the condenser and the flask with water, collecting the rinsing in the flask.

20.4 Cool the flask in an ice-water bath so that the contents are below 20°C, add 0.5 to 1.0 mL of phenolphthalein indicator solution, and titrate slowly with the 0.5 *N* NaOH solution to the first permanent, faint pink end point. The solution must be swirled or magnetically stirred during the titration, and the solution must be vigorously swirled as the end point is approached. Read the volume of the titrant to 0.02 mL (Note 4). Record the temperature of the 0.5 *N* NaOH solution.

NOTE 4—If the volume of 0.5 *N* NaOH solution required for the specimen is less than 80 % of that required for the blank, the specimen was too large and the analysis must be repeated with a smaller specimen weight.

20.5 Perform a blank determination in parallel by the same procedure, omitting only the addition of the specimen.

21. Calculation

21.1 Calculate the percent of hydroxyl content, *H*, as follows:

$$H = [(B - V)\,N \times 17.01] / [S \times 1000] \times 100 \quad (4)$$

where:

V = NaOH solution required for titration of the specimen, mL,
B = NaOH solution required for titration of the reagent blank, mL,
N = normality of the NaOH solution used, and
S = specimen used, g.

21.2 Duplicate determinations that agree within 0.3 % are acceptable for averaging.

22. Precision and Bias

22.1 *Precision*—The following criteria should be used for judging the acceptability of results at the 95 % confidence level:

22.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same analyst should be considered suspect if they differ by more than 0.8 %, absolute.

22.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by analysts in different laboratories should be considered suspect if they differ by more than 1.2 %, absolute.

NOTE 5—The above precision estimates are based on an interlaboratory study involving seven laboratories using three samples with one analyst performing duplicate runs on each of two days. The mean level of the hydroxyl value of the samples studied was 48%.

22.2 *Bias*—Bias cannot be determined because there is no available material having an accepted reference value.

ASSAY (BY DIBENZAL)

23. Scope and Application

23.1 This test method covers the determination of the monopentaerythritol content of pentaerythritol (PE) by the dibenzal method. It is applicable to material containing 75 % or more monopentaerythritol. Normal amounts of dipentaerythritol do not interfere. Tripentaerythritol, etc, interferes due to its insolubility in the reaction mixture. Refer to Test Methods D1615.

24. Summary of Test Method

24.1 A weighed specimen is dissolved in water, a methanol solution of benzaldehyde is added, followed by hydrochloric acid, and the mixture cooled to 0°C. The pentaerythritol-dibenzal precipitate is filtered, dried, and weighed. A solubility correction factor is added to the weight of precipitate found.

25. Apparatus

25.1 *Crucibles*, filtering, fritted-glass, medium-porosity.

25.2 *Stirring Rods*, about 70 mm long, preferably having one flat end.

25.3 *Vacuum Pump or Water Aspirator*— It is convenient to have at least two outlets, in order to make duplicate filtrations simultaneously.

26. Reagents and Materials

26.1 *Benzaldehyde*, N.F. grade, 98 % minimum purity. This material is easily oxidized by air. If it is to be used over a long period, transfer the contents of a 0.5-kg bottle to a number of 22-mL capacity screw-cap vials.

26.2 *Benzaldehyde-Methanol Reagent*—Add 20 mL of benzaldehyde to 100 mL of methanol. Prepare fresh for each series of determinations.

26.3 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

26.4 *Methanol*.

26.5 *Methanol-Water Wash Solution (1+1)*—Mix equal volumes of methanol and water and cool to 20 to 25°C.

27. Procedure

27.1 Weigh approximately a 0.5-g portion of the ground sample into a small glass-stoppered weighing bottle. Dry for 3 h at 105°C.

27.2 Weigh accurately, transfer the portion to a 125-mL Erlenmeyer flask, and reweigh the bottle to obtain the specimen weight by difference.

27.3 Add 5.0 mL of water, insert a stopper loosely, and heat to incipient boiling on a hot plate with swirling, until the specimen is dissolved.

27.4 To the hot solution, preferably in a hood, add 15 mL of benzaldehyde-methanol reagent and 12 mL of HCl. The solution should be clear at this point. Insert the stopper loosely, and allow the flask to stand for 15 min at room temperature. Swirl the flask occasionally to prevent the precipitate from adhering to the bottom of the flask. Place the flask in an ice bath at 0 to 2°C for 1 h or more. Also, place 25 mL of 1+1 methanol-water wash solution in the ice bath, for later use.

27.5 Remove the flask from the ice bath and immediately filter the reaction mixture with suction through a weighed, fritted glass crucible. Complete the transfer of the precipitate with 25 mL of the cold (0 to 2°C) 1+1 methanol-water wash solution.

27.6 Wash the precipitate with a total of 100 mL of 1+1 methanol-water wash solution at 20 to 25°C, in several portions, as follows. Disconnect the vacuum line, pour a 10-mL portion of the methanol-water wash solution from a graduate into the crucible, and stir the precipitate to form a homogeneous slurry. Connect the vacuum line and draw the wash solution through the crucible. Repeat this washing operation six times. With the last 30 mL of methanol-water wash solution, rinse the interior walls of the crucible, and rinse and remove the stirring rod.

27.7 Aspirate thoroughly and dry the precipitate at 105 ± 2°C for 2 h. Cool in a desiccator and weigh.

28. Calculation

28.1 Calculate the percent of pentaerythritol, *E*, as follows:

$$E = [(P + 0.0269) \times 43.59] / S \quad (5)$$

where:

S	=	sample used, g,
P	=	precipitate, g,
0.0269	=	solubility correction factor, and
43.59	=	(mol weight PE / mol weight PE-dibenzal) × 100.

28.2 Duplicate determinations that agree within 0.3 % are acceptable for averaging.

29. Precision and Bias

29.1 *Precision*—The following criteria should be used for judging the acceptability of results at the 95 % confidence level:

29.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same analyst should be considered suspect if they differ by more than 1.2 %, absolute.

29.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by analysts in different laboratories should be considered suspect if they differ by more than 3.3 %, absolute.

NOTE 6—The above precision estimates are based on an interlaboratory study involving seven laboratories using three samples with one analyst performing duplicate runs on each of two days. The average level of the monopentaerythritol content of the samples studied was 88 %.

29.2 *Bias*—Bias cannot be determined because there is no available material having an accepted reference value.

ASSAY (BY GAS CHROMATOGRAPHY)

30. Summary of Test Method

30.1 A solution of material in pyridine and containing mannitol as an internal standard is etherified with trimethylchlorosilane using hexamethyldisilazane as a promoter. A portion of the etherified solution is injected onto a gas chromatography column consisting of 17 % dimethyl polysiloxane gum on an acid-washed and dimethylchlorosilane-treated calcined diatomaceous earth support. The column is initially at 100°C and is gradually heated to 350°C to obtain the chromatogram. Programming to 350°C is necessary in order that all impurities possibly present in commercial pentaerythritol are removed in a reasonable length of time.

30.2 The monopentaerythritol content is calculated from the ratio of the peak areas of the internal standard and the monopentaerythritol.

31. Significance and Use

31.1 This test method is useful for determining the amount of monopentaerythritol in commercial grades of pentaerythritol by physical means.

31.2 The test results are calculated using an internal standard method.

32. Apparatus

32.1 *Programmed Temperature Gas Chromatograph* with thermal conductivity detectors (see Note 7) and capable of operating efficiently at temperatures up to 350°C.