Designation: D 2195 – 05

Standard Test Methods for Pentaerythritol[1]

This standard is issued under the fixed designation D 2195; 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 E 29.

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]

D 1193 Specification for Reagent Water

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)

D 1615 Test Methods for Glycerol, Ethylene Glycol, and Pentaerythritol in Alkyd Resins[3]

D 1728 Test Method for Phthalate Ester Color of High-Gravity Glycerin[3]

D 2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography

E 1 Specification for ASTM Liquid-in-Glass Thermometers

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

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E 203 Test Method for Water Using Volumetric Karl Fischer Titration

E 222 Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation

E 260 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.

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[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 Chemicals 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.

[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.**

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4.2 Unless otherwise indicated, references to water shall be understood to mean Type IV of reagent water conforming to Specification D 1193.

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:

$$A = (R/S) \times 100 \tag{1}$$

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:

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

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 E 222.

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 E 203 and add the required amount of water. Calculate the volume of water to add in millilitres per litre of pyridine, V, as follows:

$$V = 4.0 - 9A \tag{3}$$

where A = water in pyridine, %.

19.5 *Sodium Hydroxide, Standard Solution (0.5 N)*—Prepare and standardize in accordance with Practice E 200. 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:

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

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 D 1615.

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.

NOTE 7—Flame ionization detectors are too sensitive for this test method and the reaction medium can contaminate the flame jet.

32.2 *Column* (Note 2), 1.2-m length, 4.8 mm outside diameter stainless steel, packed with approximately 4 g of 17 % silicone rubber on 60/80 mesh acid-washed, dimethylchlorosilane-treated calcined diatomaceous earth support. The 4.8 to 6.4-mm Swagelok adapters should also be filled with packing and the glass wool plugs kept to a minimum volume in order to minimize the dead volume during injection and thus prevent tailing of the peaks.

NOTE 8—Useful information on column preparation may be found in Test Method D 2593 and Practice E 260.

32.3 *Syringe*, microlitre, 50-µL capacity, with fixed needle. A syringe with a removable needle may be used but the fixed needle type is recommended.

NOTE 9—Immediate cleaning with water followed by a volatile solvent, such as acetone, is necessary to prevent blockage of the needle by salts present in the reaction mixture.

32.4 *Flask*, Morton, 500-mL capacity.

32.5 *Evaporator*, rotating vacuum.

32.6 *Bottle*, 30-mL wide mouth, fitted with screw cap having polytetrafluoroethylene liner (see Note 10). The bottle must be of such a shape it will maintain its upright position in a water bath, and tall enough to allow separation of enough supernatant liquid for sampling.

NOTE 10—The bottle caps from regular supply houses may not be available with polytetrafluoroethylene liners and it may be necessary to order the liners separately. Alternatively, they may be cut from polytetrafluoroethylene sheeting.

32.6.1 *Alternatively*, a 17-mL vial, 28-mm diameter, 60-mm high, fitted with screw cap having a polytetrafluoroethylene liner has been found satisfactory.

32.6.2 *Alternatively*, in place of the screw cap bottle or vial, a 50-mL Erlenmeyer flask may be used.

33. Reagents and Materials

33.1 *Chloroform*.

33.2 *Diatomaceous Earth*, calcined, acid-washed, dimethylchlorosilane-treated, 60 to 80 mesh.

33.3 *Column Packing*—Dissolve 20 g of dimethyl polysiloxane gum in 300 mL of chloroform. Weigh 100 g of the treated solid support (33.4) into a 500-mL Morton flask and wet with about 75 mL of chloroform. Pour the dimethyl polysiloxane gum solution into the flask, attach to the rotating evaporator, apply suction with a water aspirator, and allow the flask to rotate until a free-flowing powder results. A steam bath may be used to facilitate the final drying process. Remove the finished packing and store in a screw-capped bottle.

NOTE 11—Gas-Chrom Z has been used as the solid support. Other solid supports that give equivalent values may be used, such as Gas-Chrom Q and acid based silanized supports.

33.4 *Hexamethyldisilazane* (HMDS).

33.5 *Mannitol* (internal standard), $C_6H_{14}O_6$, melting point 167 to 169°C. (Eastman white label grade is recommended.)

33.6 *Molecular Sieve 5A*, 1.5 mm pellets.

33.7 *Monopentaerythritol* of known assay. It is important that material relatively high in monopentaerythritol be used (greater than 95 % is suggested).

33.8 *Pyridine*.

33.9 *Dimethyl Polysiloxane Gum* (methyl silicone).

33.10 *Trimethylchlorosilane* (TMCS), reagent grade, or distill technical grade material and use that boiling between 57 and 60°C. This reagent is stable when stored under dry inert atmosphere in a glass bottle fitted with a screw-type cap having a chemically inert liner.

34. Hazards

34.1 Avoid contact of hexamethyldisilazane or trimethylchlorosilane with the skin or inhaling their vapors. Wear suitable rubber gloves and work in a suitable fume hood when handling these reagents.

35. Preparation of the Chromatographic Apparatus

35.1 Assemble the apparatus according to the manufacturer's instructions.

35.2 Make the following instrument settings:

Sample inlet temperature, °C	350
Detector temperature, °C	350
Column temperature (programmed):	
Initial,° C	100
Final, °C	350
ΔT, °C/min	10
Carrier gas	helium
Pressure, psi	50
Flow rate, mL/min	80
Detector current, mA	150 (W-1 filaments)
Recorder range, mV	0 to 1
Chart speed, mm/min	25

36. Column Conditioning

36.1 Attach one end of a freshly packed column to the inlet side of the instrument while the exit end of the column remains unattached. With helium flowing through at 80 mL/min, heat the column from 100 to 350°C at 10°/min. Then maintain at 350°C for 1 h. This procedure will thermally strip the column of volatiles and prevent their buildup in the detector. Cool to 100°C and couple the exit of the column to the detector. Inject two 40-µL aliquots of TMS blank (7 mL of pyridine, 1 mL of HMDS, and 2 mL of TMCS). Reprogram the column at 10°C/min to 350°C and hold for 1 h. This procedure will thermally strip the column of additional volatiles that may have reacted with TMS. Recool to 100°C and the column is ready for specimen analysis. Normally, injection of TMS blanks or specimens onto a column at a temperature hotter than 200°C accelerates column deterioration and leads to extraneous peaks and peak tailing due to stripping of some of the liquid phase and exposure of the solid support.

37. Calibration of the Chromatograph

37.1 Use a material of known high assay monopentaerythritol to determine the instrument response factor (Note 12). Very minor impurities may be present in the mannitol internal standard but are not usually significant. Run a blank on the mannitol using regular test reagents to determine impurities. Recalibrate for each new bottle of mannitol or other reagents used.

NOTE 12—For normal use, a material of 95 % minimum monopentaerythritol is adequate for standardization. When purer material is required for more accurate work, prepare it by reacting about 2 g of the available monopentaerythritol with 5 mL of hexamethyldisilazane, 10 mL of trimethylchlorosilane, and 25 mL of dry pyridine as in the normal sample preparation (this is a threefold excess of reagent). Isolate the trimethylsilyl ethers by extracting the reaction mixture with 40 mL of hexane and enough water to form two phases (about 5 mL). Separate and dry the upper hexane layer over anhydrous sodium sulfate. Decant the hexane into a distillation flask and evaporate to dryness on a steam bath with aid of a stream of dry air. Vacuum distill the silyl ether residue at 6 mm pressure. The pure monopentaerythritol derivative is a colorless liquid at room temperature and has a boiling point of 128°C at 6 mm pressure. Apply a conversion factor of the molecular weight of the parent polyol divided by the molecular weight of its derivative to determine the specimen weight of the free polyol. (For Mono-PE this factor is 0.322.)

37.2 The monopentaerythritol peak temperature will be 200 to 210°C and the mannitol peak temperature 250 to 260°C. Response factors of about 0.86 to 0.91 for the monopentaerythritol to 1.00 for mannitol have been found (Note 13). Repeat the determination of response factors until reproducible results are obtained. Determine the factor (in duplicate) each day that analysis is run.

37.3 Calculate the response factor, F, as follows:

$$F = [(W_c \times P / 100) / W_s] \times (A_s / A_c) \times (S_s / S_c) \quad (6)$$

where:

W_c = weight of purest monopentaerythritol available, mg,
P = monopentaerythritol, weight %,
W_s = weight of internal standard, mg,
A_s = peak area for internal standard, mm ^{2},
A_c = peak area for monopentaerythritol, mm^2,
S_s = sensitivity setting for internal standard, usually 2, and
S_c = sensitivity setting for monopentaerythritol, usually 2.

NOTE 13—Lack of reproducible response factors or improperly shaped peaks are indications of improper column condition, inadequate temperature control at the injection port, poor temperature programming reproducibility, or a combination of these factors. Each TMS series should start with a conditioning blank run to 350°C.

38. Procedure

38.1 Weigh, to 0.1 mg, about 120 to 150 mg of sample and 120 to 150 mg of mannitol into a 30-mL screw cap bottle (or 17-mL vial) having a polytetrafluoroethylene cap liner. Pipet 7 mL of dry pyridine and 1 mL of hexamethyldisilazane into the bottle (or vial) and close it with the screw cap. An open vial may be used, but close attention is necessary to avoid overheating and loss of specimen or reagents. (Alternatively, as noted in 32.6.2, a 50-mL Erlenmeyer flask may be used. When using the flask, add the same amount of samples and reagents as when using the screw cap bottle. Place the flask on a hot plate in a hood and heat just under boiling for 10 min. With proper heating, the vapor ring should be maintained about 13 mm from the top of the flask neck.)

38.2 Place the bottle in a bath of boiling water in a hood and heat for 15 min with intermittent gentle swirling. The water in the bath should be at about the same level as the liquid in the bottle and should not reach the bottle cap. After heating, allow the bottle and contents to cool to room temperature and wipe the outside of the bottle dry. It is extremely important that the final solution be clear and free of solid particles.

38.3 Pipet 2 mL of trimethylchlorosilane into the bottle or flask and swirl for 2 or 3 min. Then warm the solution in a hot water bath maintained at 70 to 80°C for 5 min (Note 14). As before, the water in the bath should be at about the same level as the liquid in the bottle. Immediately remove the bottle from the bath and swirl for 1 min. Adequate agitation is important to assure a suitable reaction. Dry and allow to cool to room temperature. This preparation is stable and can be stored for at least 24 h at room temperature in the screw-capped bottles.

NOTE 14—For specimens that contain appreciable amounts of such impurities as di- or tripentaerythritol, a 5-min reaction time may not be sufficient. A longer reaction time, up to about 15 min, has been found satisfactory and may be used as necessary.

38.4 At 350°C, the life of even commercially available silicone rubber septa is short. Replace the septa (on both channels even if the other one is not used) every day. The syringe barrel should be tight (no back-flush) and injection should be rapid. For most operators, slow withdrawal of the needle appears best for preventing injection losses; however, some operators prefer rapid withdrawal.

38.5 With the chromatograph in operation and the column at 100°C, inject about 15 µL of the supernatant liquid (Note 15) and obtain the chromatogram, programming at about 10°C/min until a temperature of 350°C is reached. Use sensitivity setting (2×) or attenuate the sensitivity setting as necessary for full scale major peaks.

NOTE 15—Never inject anything but *clear* supernatant liquid onto the column. If the NH_4Cl precipitate has not settled, heat the solution until it does or centrifuge it.

38.6 Repeat the procedure using only 120 to 150 mg of mannitol to identify peaks due to impurities in the reagents.

38.7 After each run, cool the column to 100°C for the next specimen.

38.8 Measure to 1 mm^2, by triangulation or other suitable methods, the peak areas for the mannitol (internal standard) and monopentaerythritol.

39. Calculation

39.1 Calculate the percent of monopentaerythritol, M, content as follows:

$$M = \frac{S_c \times A_c \times W_s \times F \times 100}{S_s \times A_s \times \text{mg of specimen}} \quad (7)$$

where:

S_c = sensitivity setting for monopentaerythritol, usually 2,
S_s = sensitivity setting for internal standard, usually 2,
A_c = peak area for monopentaerythritol, mm^2,
A_s = peak area for internal standard, mm^2,
F = appropriate response factor for the monopentaerythritol (see 37.2), and
W_s = weight of internal standard, mg.

40. Report

40.1 Report the following information:

40.1.1 Monopentaerythritol content to the nearest 0.1 %.

41. Precision and Bias

41.1 *Precision*—The precision statements are based upon an interlaboratory study in which one operator in 13 laboratories analyzed two samples of technical pentaerythritol containing approximately 84 and 89 % monopentaerythritol, respectively, in duplicate on two successive days. Results were analyzed in accordance with Practice E 180. The within laboratory standard deviation of results, each the mean of duplicates, was found to be 0.56 % absolute at 21 df. The between-laboratories standard deviation, each the mean of duplicates, appeared to vary with the monopentaerythritol content and has been estimated for the two different levels to be as shown in Table 1. Based on these standard deviations, the following criteria should be used in judging the acceptability of results at the 95 % confidence level:

41.1.1 *Repeatability*—Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 1.7 % absolute.

41.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than the values listed in Table 1.

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

PHTHALATE ESTER COLOR

42. Summary of Test Method

42.1 The ester is prepared by reacting pentaerythritol (PE) with phthalic anhydride under controlled conditions. The resulting ester color is measured while warm by use of a spectrophotometer calibrated with platinum-cobalt standards. This method is similar to that in Test Method D 1728.

43. Apparatus

43.1 *Oil or Wax Bath* with stirrer and heating coil, thermostatically controlled, maintained at 225 ± 1°C.

NOTE 16—An insulated metal bath of 18 to 23-L capacity, equipped with heating elements of 625 to 700-W capacity heat input, is satisfactory for preparing five to six esters simultaneously without an excessive temperature drop.

43.2 *Test Tubes*, borosilicate glass, 22 by 175 mm.

43.3 *Clamps and Supports*, for use with 22 by 175-mm test tubes.

43.4 *Thermometer*, ASTM Solvents Distillation Thermometer having a range from 95 to 255°C, 100-mm immersion, and conforming to the requirements for Thermometer 42C as prescribed in Specification E 1.

43.5 *Timer*, 60-min.

43.6 *Spectrophotometer or Filter Photometer*, capable of measuring the absorbance or transmittance of a sample at a wave-length of 450 nm. A spectrophotometer employing essentially monochromatic light of a half-band width at 450 nm of not more than 2.0 nm should be used for referee work.

43.7 *Rectangular Cuvettes or Optical Cells*, suitable for the instrument to be used for color measurement. The optical light path of the cuvette should be not less than 10 mm nor greater than 20 mm. The cuvettes used for calibration and for measurement must be matched optically, and light paths must not differ by more than 0.1 mm.

44. Reagents and Materials

44.1 *Cobalt Chloride* ($CoCl_2 \cdot 6H_2O$).

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

44.3 *Phthalic Anhydride* ($C_8H_4O_3$)—Solidification point 131°C min; melt color 15 platinum-cobalt, max, heat stability color 25, max.

NOTE 17—As a check on the heat stability of the phthalic anhydride, a specimen of the phthalic anhydride should be held at 225°C for 45 min. The original melt color and the heat stability color should be measured, using a 50-mL long-form Nessler tube, and compared against the platinum-cobalt standards described in Test Method D 1209. Material of the specified quality should be procured by selection or by direct correspondence with the manufacturers.

44.4 *Potassium Chloroplatinate* (K_2PtCl_6).

45. Preparation of Standards

45.1 *Platinum-Cobalt Stock Solution*— Dissolve 1.245 g of K_2PtCl_6 and 1.000 g of $CoCl_2 \cdot 6H_2O$ in water. Add 25 mL of HCl and dilute to 250 mL with water. This stock solution has a platinum-cobalt color of 2000.

45.2 *Platinum-Cobalt Standards*—From the stock solution, prepare color standards as given in Table 2 by diluting the required volumes to 20 mL with water.

46. Calibration of Photometer

46.1 Calibrate the photometer against the platinum-cobalt standards in cuvettes at a wavelength of 450 nm. Prepare a calibration curve of absorbance or transmittance values versus the platinum-cobalt standards.

47. Procedure

47.1 Bring the bath to 225 ± 1°C and maintain the temperature within the specified range.

47.2 Weigh 20.0 g of phthalic anhydride into a clean, dry 22 by 175-mm test tube. Clamp the test tube in the bath (with the lip of the tube 20 ± 5 mm above the level of the bath liquid). When the crystals have melted, add, from a weighing scoop,

TABLE 1 Reproducibility

	Mean monopentaerythritol content, %	
	88.82	83.74
Degrees of freedom	9	10
Standard deviation, % absolute	0.62	1.36
Maximum acceptable range between laboratory means, % absolute	2.0	4.3

TABLE 2 Platinum-Cobalt Color Standards

Color Standard Number	Stock Solution, mL	Color Standard Number	Stock Solution, mL
200	2	1200	12
400	4	1400	14
600	6	1800	18
1000	10	2000	20

20.0 g of the pentaerythritol sample, in small portions, while stirring with a stirring rod. Set the timer for 45 min.

47.3 When the crystals have dissolved, remove the stirring rod and immediately cap the tube tightly with aluminum foil. Water formed in the reaction should reflux in the vapor space and thus wash down sublimed phthalic anhydride crystals.

47.4 After placing several specimens in the bath at one time, the bath temperature should not drop more than 5°C, and the time required for the temperature of the bath to return to 225 ± 1°C should not exceed 5 min.

47.5 Remove the test tube from the bath at the end of 45 min. If appreciable phthalic anhydride crystals have collected on the inside of the test tube, rerun the esterification. If only a few crystals are present, pour a portion of the ester melt into a waste receptacle to clear the lip and side of the test tube of any crystals that may interfere with the procedure described in 47.6.

47.6 Preheat the cuvette or optical cell at 100°C. Pour the ester melt carefully into the cell or rectangular cuvette in which the measurement is to be made. If air has been entrained, heat the melt at 100 to 150°C so that the bubbles may rise clear of the optical light path. Do not attempt to determine the color of any ester that appears to contain any suspended matter or haze. Discard such an ester and prepare another. To obtain reproducible results, it is mandatory that all esters be perfectly clear.

47.7 While still warm, measure the absorbance or transmittance of the ester at 450 nm and read the platinum-cobalt color from the previously prepared calibration curve.

47.8 The cells may crack if allowed to cool. To clean the cells, stand them upside down on a wire gauze, suspended by bending the corners, about 25 mm from the bottom of a beaker. Immediately place them in an oven at 125°C for a few hours to melt the bulk of the ester. Complete the cleaning by placing the cells on a gauze in a beaker, add acetone or methyl ethyl ketone to a depth just below the gauze, cover the beaker with a watch glass, and place on a steam bath.

48. Report

48.1 Report the color of the ester as the platinum-cobalt color value read from the instrument calibration curve.

48.1.1 Duplicate runs that agree within 70 platinum-cobalt units are acceptable for averaging.

49. Precision and Bias

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

49.1.1 *Repeatability*—The usual difference between two results, each the mean of duplicate determinations, obtained by the same analyst on different days approximates 20 platinum-cobalt units. Two such values should be considered suspect if they differ by more than 60 units.

49.1.2 *Reproducibility*—The usual difference between two results, each the mean of duplicate determinations obtained by analysts in different laboratories, approximates 50 platinum-cobalt units. Two such values should be considered suspect if they differ by more than 150 units.

NOTE 18—The above precision estimates are based on an interlaboratory study on three samples, each from a different supplier, covering a color range of 400 to 700 platinum-cobalt units. One analyst in each of seven laboratories performed duplicate determinations and repeated these determinations one day later for a total of 84 determinations.

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

50. Keywords

50.1 pentaerythritol test methods

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D 2195 – 00) that my impact the use of this standard.

(1) Added reference to Practice E 29 in 1.4 of the Scope section.

(2) Added Practice E 29 to list of Referenced Documents.

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