



Standard Test Method for Polyhydric Alcohols in Alkyd Resins¹

This standard is issued under the fixed designation D 2998; 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.

^{ε1} NOTE—Editorial changes were made throughout in November 1996.

1. Scope

1.1 This test method covers the qualitative and quantitative determination of the polyols in alkyd resins, including resin- and polymer-modified alkyds. Quantities as low as 0.5 % may be detected and measured.

1.2 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *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 a specific hazard statement, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

E 260 Practice for Packed Column Gas Chromatography³

3. Summary of Test Method

3.1 The resin sample is dried, subjected to aminolysis to release the polyols, treated directly to form the trimethylsilyl (TMS) ether derivatives of the polyhydric alcohols which are separated by gas-liquid chromatography. An internal standard is used for quantitative purposes. The description of apparatus and the recommended operating conditions are presented as a guide to a satisfactory analysis as all suitable variations in temperatures, column lengths, substrates, liquid phases, programming rates, etc., have not been determined.

4. Significance and Use

4.1 This test method is designed to identify polyhydric alcohols and to quantify amounts of polyols contained in alkyd resins. Polyols are significant ingredients in alkyd resins and impact on such important physical parameters of alkyd paints as weatherability, flexibility, moisture resistance, and adhesion.

Use of this test method will provide a means whereby the relative applicability of the alkyd resin to the particular end use may be estimated by the buyer and the seller.

5. Apparatus

5.1 *Linear Programmed Temperature Gas Chromatograph*—Any instrument with a thermal conductivity detector and with programming features should be suitable if adaptable to the following recommended operating conditions:

Detector cell temperature, °C	300
Detector cell current, mA	160
Injection port temperature, °C	300
Helium flow at exit, cm ³ /min	80
Programmed temperature details:	
Approximate column heating rate, °C/min	6
Starting column temperature, °C	100
Finishing column temperature, °C	300

NOTE 1—Flame ionization detectors are not recommended for this test as the reaction medium can contaminate the flame jet.

5.2 *Column*—A 16-ft (4.9-m) length of ¼-in. (6.4-mm) outside diameter copper tubing packed with 20 weight percent of silicone grease on 60 to 80-mesh white flux-calcined diatomaceous earth,⁴ and conditioned at 315°C until “bleeding” reaches a minimum.

5.3 *Column and Instrument Performance*—Note the separation of closely adjacent polyol peaks and express as peak resolution *R* as follows:

$$R = 2Y/(A + B) \quad (1)$$

where:

Y = distance between maxima of closely adjacent peaks,

A = base width of first peak *A*, and

B = base width of peak *B*.

NOTE 2—If the peak resolution is equal to or greater than 1.0, the column and instrument are in satisfactory condition.

5.4 *Syringe*, having a fixed needle, 50-μL capacity.

5.5 *Erlenmeyer Flask*, 125-mL, with standard joint and water-cooled condenser to fit.

5.6 *Micro Test Tube* or screw cap vial.

¹ This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ The sole source of supply of the flux-calcined diatomaceous earth, Chromosorb W known to the committee at this time is Celite Corp., P. O. Box 5108, Denver, CO 80217-5108. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

6. Reagents

6.1 *Purity of Reagents*—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.⁵ 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6.3 *Bis(trimethylsilyl)trifluoroacetamide*.

6.4 *1,4-Butanediol*.

6.5 *n-Butylamine*.

6.6 *Hexamethyldisilazane (HMDS)*.

6.7 *Methylene Chloride*.

6.8 *Mixed TMS Reagent*—Mix 20 parts by volume of the bis(trimethylsilyl)trifluoroacetamide with 80 parts of the hexamethyldisilazane and protect from moisture. If stored at 60°C in an oven, the reagent remains active and stable.

7. Hazards

7.1 The reagents and samples used in this test method may, under some conditions, be hazardous. Refer to the manufacturer's Material Safety Data Sheets for specific handling and safety precautions. Safe laboratory handling procedures and all applicable OSHA regulations are to be followed.

8. Procedure

8.1 Weigh a specimen of resin containing approximately 2 g of nonvolatile material into the 125-mL flask. Add 3 mL of methylene chloride, mix, and evaporate the solvents in a 60°C bath with a current of air. Repeat the drying twice, dissolving the resin each time in 3 mL of methylene chloride. Check for odor of residual solvent and, if necessary, dissolve and dry a fourth time.

8.2 Weigh accurately about 200 mg of 1,4-butanediol (Note 3) as standard into the flask followed by 10 mL of butylamine added from a pipet. Reflux under the water condenser for 2 h, add 0.5 mL of water to the flask through the condenser, and continue refluxing for 2 additional hours.

NOTE 3—Other polyhydric alcohols may be substituted for the 1,4-butanediol standard if sufficiently pure.

8.3 Place 5 drops of the aminolysis mixture in a micro test tube, add 0.5 mL of the mixed TMS reagent, and mix by shaking. Heat for 30 min at 60°C in an oven. Inject 40 μ L onto the silicone grease column of the chromatograph and follow the operating conditions recommended in 5.1. Hold the temperature at 300°C at the completion of the program until all the volatile components have emerged as shown by the chromatogram.

⁵ *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.

TABLE 1 Relative Retention Time of Trimethylsilyl Ethers

Polyol	Retention Time Relative to 1,4-Butanediol
Ethylene glycol	0.58
Propylene glycol	0.63
2,3-Butanediol	0.73
1,3-Butanediol	0.83
Neopentyl glycol	0.86
1,4-Butanediol	1.00
Diethylene glycol	1.19
Glycerol	1.29
Trimethylol ethane	1.46
Trimethylolpropane	1.63
Triethylene glycol	1.83
Pentaerythritol	1.88

TABLE 2 Precision of Test Method

Polyol	Degrees of Freedom	Repeatability		Reproducibility	
		Standard Deviation	Least Significant Difference	Standard Deviation	Least Significant Difference
Ethylene glycol	6	0.125	0.44	0.472	1.63
Glycerol	12	0.212	0.65	0.731	2.25
Pentaerythritol	12	0.137	0.42	0.298	0.92

9. Identification

9.1 The peaks on the chromatogram for the polyols can be identified by their relative retention times given in Table 1, if the recommended operating conditions are followed. Calibration is always recommended and can be made by applying the procedure to a synthetic mixture of polyols.

10. Calculation

10.1 Relate the height of each polyol peak to the height of the known amount of internal standard. Establish correction factors by dissolving known amounts (0.1 to 0.5 g) of the various polyols and internal standard in butylamine by warming, and proceeding as in 8.3 for derivative formation and chromatographing. For additional information on calibration and standardization, see Section 9 of Practice E 260.

10.2 Calculate the percent polyol *C* as follows:

$$C = (A \times F \times P) / (I \times S \times N) \quad (2)$$

where:

A = height of polyol peak, mm,

F = correction factor,

P = weight of internal standard, g \times 100,

I = height of standard peak, mm,

S = weight of resin specimen, g, and

N = nonvolatile fraction.

NOTE 4—The nonvolatile fraction *N* may be omitted from the calculation if the determination is preferred on a solution basis.

11. Precision

11.1 On the basis of an interlaboratory test of this test method in which one operator in six laboratories analyzed two alkyd resins containing 14.0 and 11.1 % glycerol, 6.8 and 7.2 % pentaerythritol, and 4.2 % ethylene glycol, the within- and between-laboratory standard deviations were found to be as given in Table 2. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at a 95 % confidence level:

11.1.1 *Repeatability*—Results obtained by the same analyst in two successive determinations should be considered suspect if they differ by more than the values given in Table 2.

11.1.2 *Reproducibility*—Two results, each the mean of duplicate measurements, obtained by analysts in different laboratories should be considered suspect if they differ by more

than the values given in the Table 2.

12. Keywords

12.1 alkyd resins; gas chromatography; polyhydric alcohols; polyols

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