Designation: D7515 – 09 (Reapproved 2014)

Standard Test Method for Purity of 1,3-Propanediol (Gas Chromatographic Method)[1]

This standard is issued under the fixed designation D7515; 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 This test method describes the gas chromatographic determination of purity for 1,3-propanediol (PDO). This test method was originally developed to determine the purity of 1,3-propanediol used for the application as the freeze point depressant base fluid in formulated PDO engine coolants. Use of the method for purity of PDO for other applications may be viable.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E300 Practice for Sampling Industrial Chemicals

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 The neat sample is analyzed by a temperature-programmed gas chromatograph, equipped with a capillary column and flame ionization detector (FID), and quantification is performed by direct area normalization.

3.2 Additionally, the use of a reference sample using Ethylene, Propylene or Dipropylene Glycol (EG, PG or DPG) in 1,3-PDO (minimum purity 99.5 %) should be used as a performance check (see Section 8).

NOTE 1—The application of this reference sample is also used to demonstrate the separation of commonly used glycols (EG, PG and DPG) in engine coolants, from PDO. Solutions of EG, PG, or DPG in concentrations of 0.1 to not more than 1 % may be used.

4. Significance and Use

4.1 Knowledge of an approved method is required to establish whether the product meets the requirements of its specifications. The use of glycols in the reference sample is not intended to suggest the presence of glycol (EG, PG and DPG) impurities, but to demonstrate and quantify the separation of commonly used Engine Coolant glycols from PDO.

5. Apparatus

5.1 *Gas Chromatograph(s)*—provided with a sample splitter or on-column injection, flame ionization detector and temperature-programming facilities. The instrument must be suitable for analysis according to the operating instructions given in Table 1. To account for differences among laboratory equipment, the two most common column choices are listed.

NOTE 2—Other column suppliers market alternative stationary phases, therefore, it is permissible to use a different column from an alternative supplier. However, the chromatogram obtained must be identical, with regard to separation of PDO and other glycol components, to those illustrated in Fig. A1.1 and Fig. A1.2.

5.1.1 *Columns*—The analytical column used must completely separate EG, PG or DPG from PDO. Fig. A1.1 and Fig. A1.2 show examples of chormatograms conforming to the requirements.

5.2 *Digital Integration Equipment*—A computer with data collection software.

5.3 *Analytical Balance,* readability 0.1 mg, calibrated. Calibrate and verify at regular intervals.

5.4 *Crimp Top Vials,* 1 mL and 5 mL.

5.5 *Crimper/De-capper,* for capping and de-capping the vials.

5.6 *Micro Syringes,* 5 µL or 10 µL.

5.7 *Bottles,* 100 mL, with screw cap.

[1] This test method is under the jurisdiction of ASTM Committee D15 on Engine Coolants and Related Fluids and is the direct responsibility of Subcommittee D15.07 on Specifications.

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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.

TABLE 1 Typical Operating Parameters for the GC Analysis of PDO

Column[A]	Option A	Option B
Type	Capillary	Capillary
Material	Fused Silica	PEG
Length × I.D.	10 m × 0.1 mm	30 m × 0.25 mm
Stationary Phase	DB-5	ZB-Wax
Film Thickness	0.17 µm	0.25 µm
Detector System		
Type	FID	FID
Sensitivity	The ratio of the signal to the noise level must be at least 2:1 at a concentration of 5 mg/kg glycols in PDO	The ratio of the signal to the noise level must be at last 2:1 at a concentration of 5 mg/kg glycols in PDO
Temperatures		
Column Oven		
Initial	0.5 min at 35°C	0 min at 50°C
Ramp 1	35 to 85°C at 50°C/min	50 to 200°C at 15°C/min
Ramp 2	85 to 325°C at 100°C/min	200 to 250°C at 40°C/min
Ramp 3	2 min at 325°C	17 min at 250°C
Detector	325°C	250°C
Carrier Gas	Helium	Helium
Calibration	This method employs straight area normalization so no calibration is required	This method employs straight area normalization so no calibration is required
Injected Volume	01. µL	0.2 µL
Pressure Program	0.5 min 30 psi 30 to 100 psi at 100 psi/min 8 min at 100 psi Gas saver on at 0.5 min	Pressure: 13.2 psi at 50°C Flow: 1.1 mL/min Velocity: 28 cm/s
Split Ratio	1:250 or appropriate split ratio to allow adequate sensitivity as defined under Detector System	1:18 or appropriate split ratio to allow adequate sensitivity as defined under Detector System (only if split injection technique is used)

[A] The columns are available commercially. Some column suppliers market alternative stationary phases. The chromatogram obtained must be identical, with regard to separation of PDO and other glycol components, to those illustrated in Fig. A1.1 and Fig. A1.2.

6. Reagents and Materials

6.1 *Purity of Reagents*—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.[3] 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 *Reagents:*

6.2.1 *1,3-Propanediol (PDO),* minimum purity 99.5 % mass (m/m).

6.2.2 *Ethylene Glycol (EG),* minimum purity 99.5 % mass (m/m).

6.2.3 *Propylene Glycol (PG),* minimum purity 99.5 % mass (m/m).

6.2.4 *Dipropylene Glycol (DPG),* minimum purity 99.0 % mass (m/m).

6.3 *Water,* HPLC grade.

[3] *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. Pharmacopeia Convention, Inc. (USPC), Rockville, MD.

7. Sampling, Test Specimens and Test Units

7.1 Follow the relevant instructions for sampling as given in Practice E300.

8. Preparation of Apparatus

8.1 *Gas Chromatograph(s) and Column(s)*—Check the performance of the gas chromatograph and column as follows:

8.2 Using the standard quality reagents (6.2), prepare a 1,3-PDO solution containing approximately 0.1 % of EG, PG and DPG respectively. Determine the exact concentration of the components. This will be the reference sample.

8.2.1 Weigh 0.1 g of each glycol reagent to the nearest 0.1 mg, into a 100-mL vial. Add 99.7 g of 1,3-PDO weighed to the nearest 0.1 mg. Cap the vials and mix thoroughly.

8.2.2 Calculate the exact concentration of each glycol in the reference sample.

8.3 Fill a 1-mL GC autosampler vial with the reference sample (8.2) and close the vial.

8.4 Analyze the reference sample using the parameters given in Table 1. Inject the solution at least twice. Calculate the area %.

9. Report

9.1 Report the purity of the sample to the nearest 0.1 % mass (m/m).

10. Precision and Bias

10.1 The following criteria should be used for judging the acceptability of results (see Note 3):

10.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the " *r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

10.1.1.1 Repeatability limits are listed in Table 2.

10.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

10.1.2.1 Repeatability limits are listed in Table 2.

10.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

10.1.4 Any judgment in accordance with 10.1.1 and 10.1.2 would have an approximate 95 % probability of being correct.

NOTE 3—The precision of this test method is based on an intralaboratory study conducted in 2008. Seven laboratories tested three different materials for PDO concentration.[4] Every "test result" represents an individual determination.[4] The laboratories were asked to report four replicate results for each material in order to estimate the repeatability and reproducibility limits of the standard.[4] Practice E691 was followed for the design and analysis of the repeatability data.

10.2 *Bias*—At the time of this study, the test specimens chosen for analysis were not accepted reference materials suitable for determining the bias for this test method, therefore no statement on bias is being made.

10.3 The precision statement was determined through statistical examination of the results submitted by six laboratories, running one analysis, on three different materials. These three materials were described as the following:

TABLE 2 PDO Concentration (%)

Sample	Average[A] $\bar{x}$	Sample Standard Deviation $S_{\bar{x}}$	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation S_R	Repeatability Limit r	Reproducibility Limit R
PDO Sample 1	99.958	0.039	0.010	0.039	0.027	0.111
PDO Sample 2	99.814	0.047	0.032	0.054	0.090	0.152
PDO Sample 3	99.657	0.199	0.030	0.200	0.085	0.561

[A]The average of the laboratory's calculated averages.

Sample 1: 99.9 % 1,3-propanediol
Sample 2: 99.7 % 1,3-propanediol
Sample 3: 99.6 % 1,3-propanediol

10.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

NOTE 4—An alternative test method was written into a research report to support this test method. Details of the research report are available from ASTM Headquarters. Request RR:D15-1023. The alternative test method does not have precision data for the application of this method in analyzing 1,3-propanediol. Use of this method is optional and individuals using the alternative method should assure themselves that the method is sufficiently precise. Precision data presented is only for the original test method listed.

11. Keywords

11.1 1,3-propanediol; dipropylene glycol; ethylene glycol; gas chromatography; propylene glycol

[4] Details of the intrlaboratory study are available from ASTM Headquarters. Request RR:D15-1022.

ANNEX

A1. EXAMPLE CHROMATOGRAMS

A1.1 *Chromatograms using Option A*:

A1.1.1 Chromatogram of PDO (see Fig. A1.1).

A1.1.2 Chromatogram of PDO, EG, PG and DPG (see Fig. A1.2).

A1.2 *Chromatograms Using Option B*:

A1.2.1 Chromatogram of PDO (see Fig. A1.3).

A1.2.2 Chromatogram of PDO, EG, PG and DPG (see Fig. A1.4).

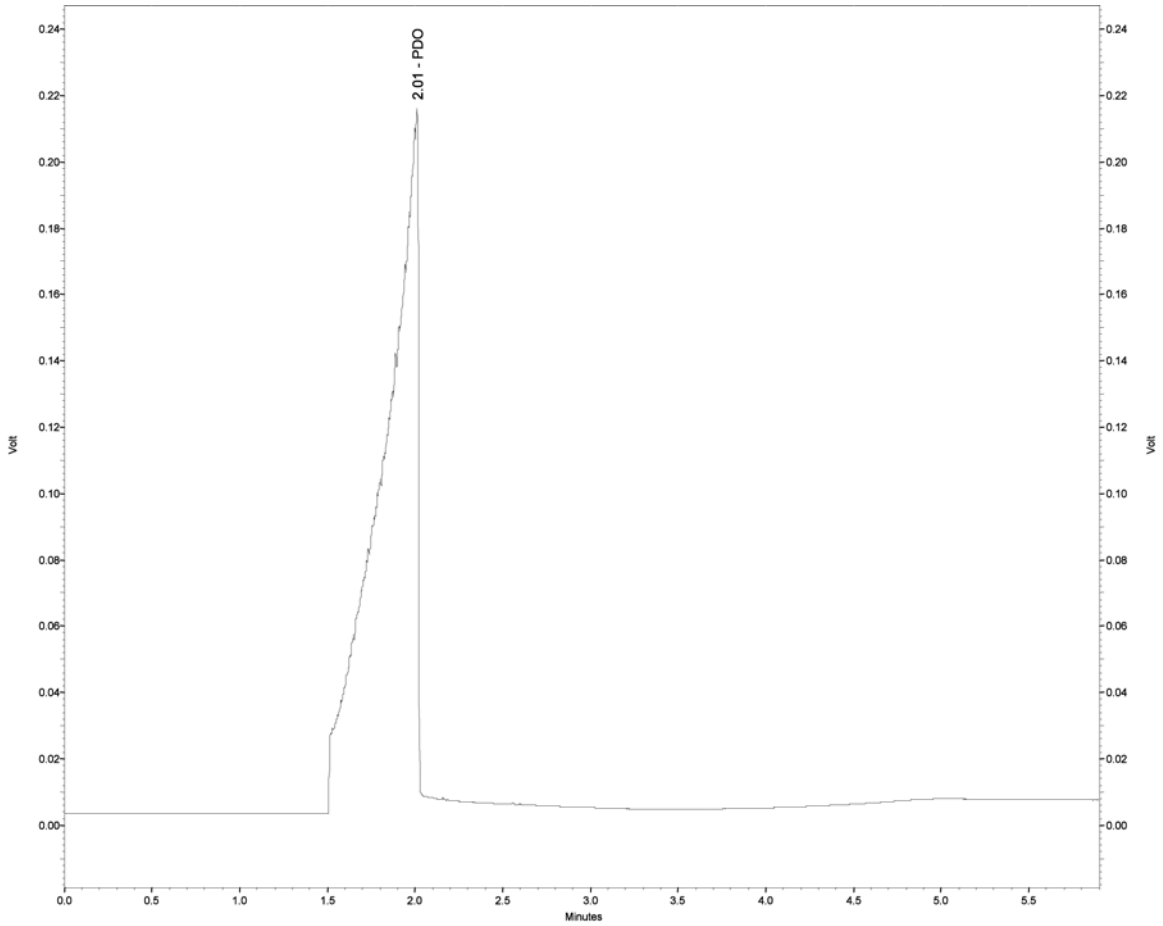

FIG. A1.1 Chromatogram of PDO

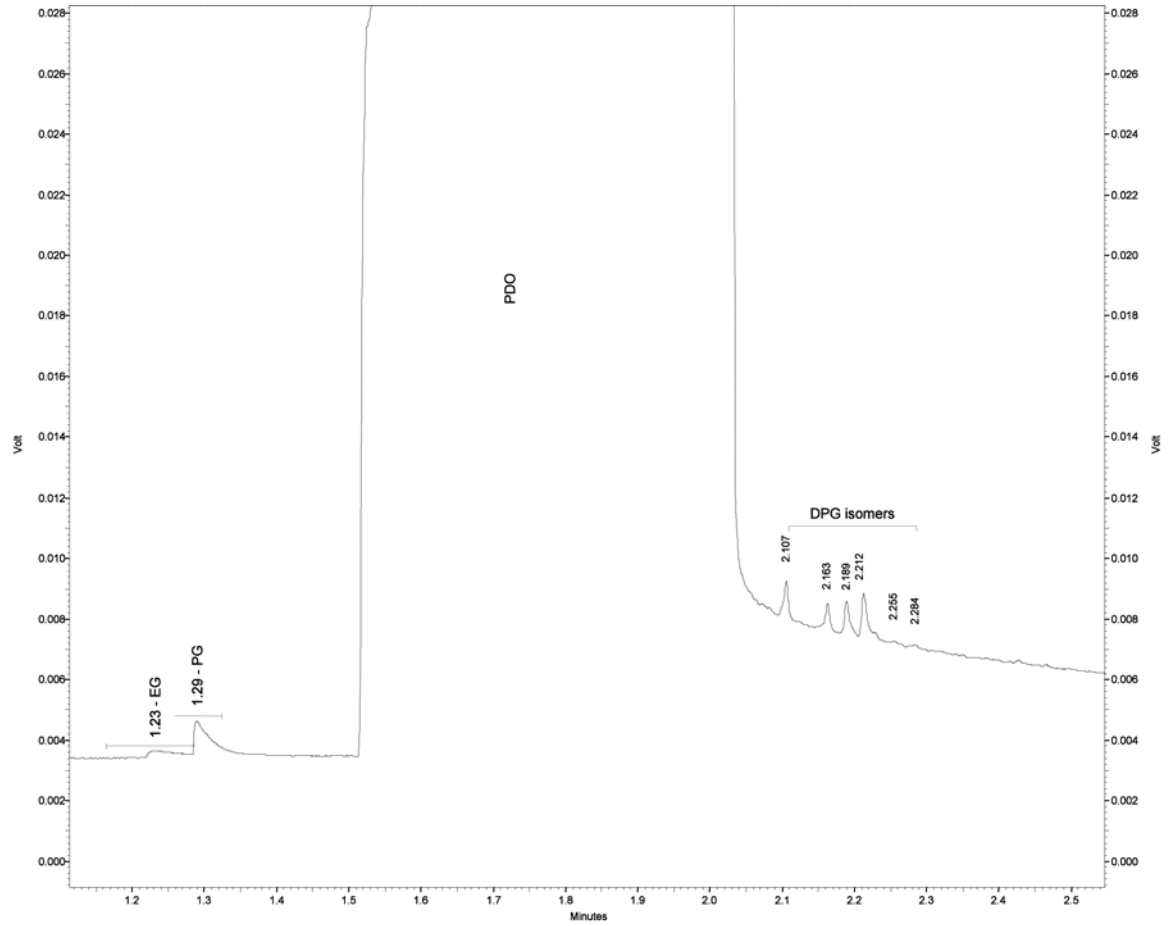

FIG. A1.2 Chromatogram of PDO, EG, PG and DPG

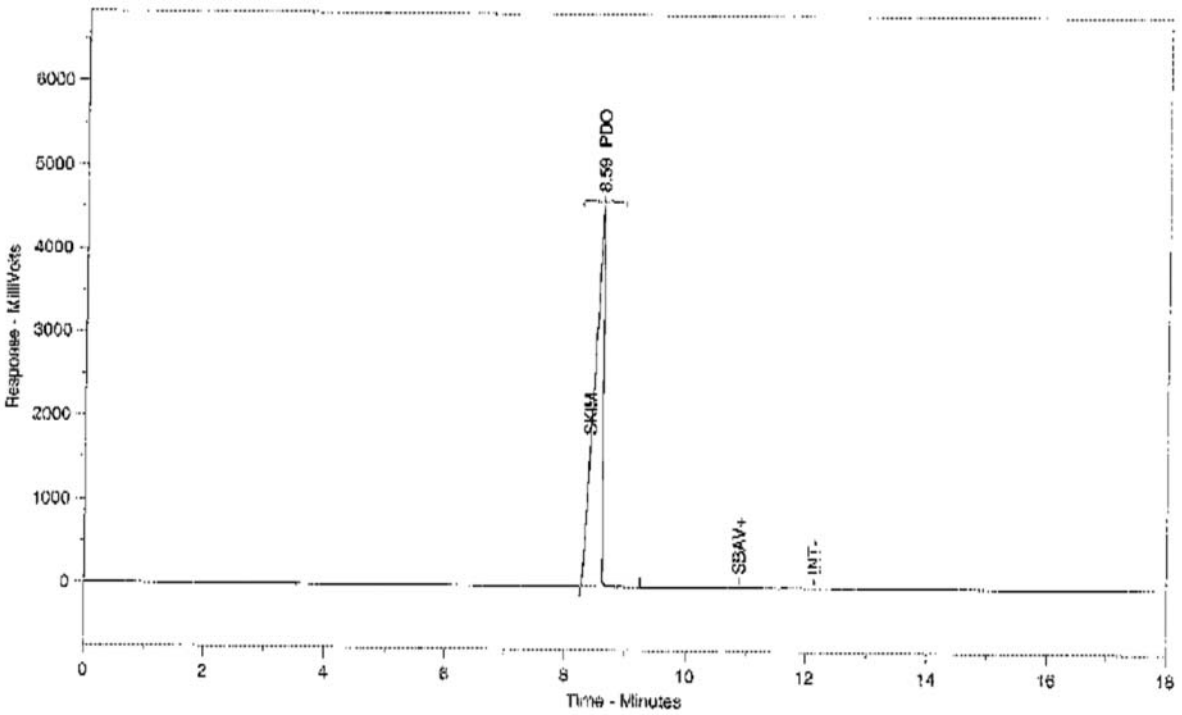

FIG. A1.3 Chromatogram of PDO

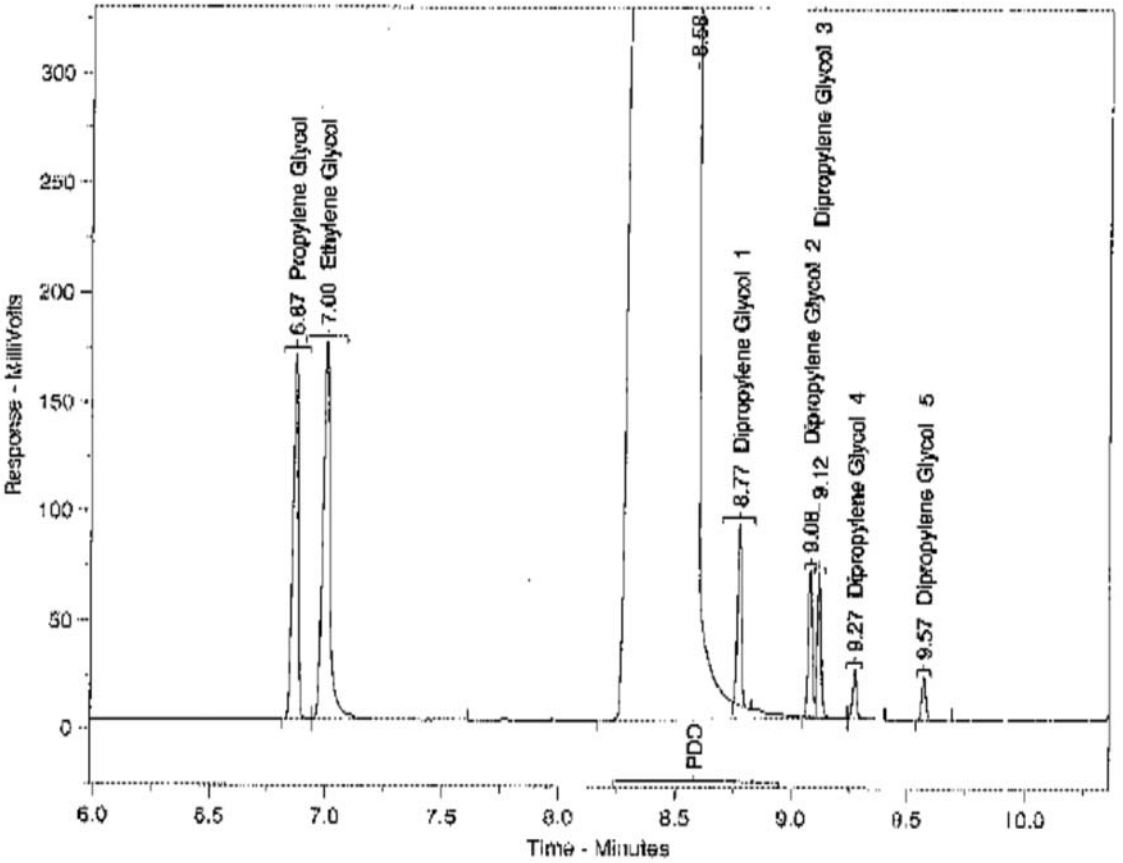

FIG. A1.4 Chromatogram of PDO, EG, PG and DPG