Designation: D7515 – 19 (Reapproved 2023)

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.

1.2.1 *Exception*—Inch-pound units (psi) are used in Table 1, Pressure Program, Options A and B.

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

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1123 Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method

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

E2409 Test Method for Glycol Impurities in Mono-, Di-, Tri- and Tetraethylene Glycol and in Mono- and Dipropylene Glycol (Gas Chromatographic Method)

3. Summary of Test Method

3.1 The 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.

[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 D15.04 on Chemical Properties.

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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	Option C[B]
Type	Capillary	Capillary	Capillary
Material	Fused Silica	PEG	PEG
Length × I.D.	10 m × 0.1 mm	30 m × 0.25 mm	30 m × 0.32 mm
Stationary Phase	DB-5	ZB-Wax	ZB-Wax
Film Thickness	0.17 µm	0.25 µm	1 µm
Detector System			
Type	FID	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 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 least 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	0 min at 100 °C retention time 0.5 min
Ramp 1	35 °C to 85 °C at 50 °C/min	50 °C to 200 °C at 15 °C/min	100 °C to 180 °C at 15 °C/min; 5.83 min
Ramp 2	85 °C to 325 °C at 100 °C/min	200 °C to 250 °C at 40 °C/min	180 °C to 225 °C at 30 °C/min; 0 min
Ramp 3	2 min at 325 °C	17 min at 250 °C	Hold 3.7 min at 225 °C
Detector	325 °C	250 °C	250 °C
Carrier Gas	Helium	Helium	Helium or Nitrogen
Calibration	This method employs straight area normalization so no calibration is required	This method employs straight area normalization so no calibration is required	Calibration
Injected Volume	01. µL	0.2 µL	1.0 µL
Pressure Program	0.5 min at 30 psi 30 psi 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	Constant flow at 5 mL/min
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)	Inlet temperature 235 °C Split flow 300 mL/min Split ratio 60

[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.
[B] Option C instrument method is for reference only; due to instrument operational variations, temperature ramp, gas flow, and split flow/ratio may need adjustment to achieve separation of analyzed glycols.

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.

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 or Methanol,* HPLC grade.

6.4 *Internal Reference Sample*.

7. Sampling, Test Specimens and Test Units

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

[3] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

8. Preparation of Apparatus

8.1 *Method 1 (Neat):*

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

8.1.2 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.

8.1.2.1 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.

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

8.1.3 Fill a 1 mL GC autosampler vial with the reference sample (8.1.2) and close the vial.

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

8.2 *Method 2 (Calibration):*

8.2.1 Dilutions in this method require HPLC Grade Methanol (using water for dilutions may harm GC column).

8.2.2 To make Stock Standard Solution, weigh 1 g of each: 1,3 Propanediol, Ethylene Glycol, Propylene Glycol, Dipropylene Glycol and Internal Reference Sample to the nearest 0.1 mg into a 100 mL volumetric flask; dilute to mark.

8.2.3 Calculate the exact concentration of each component in stock standard solution.

8.2.4 To make Internal Reference Standard, weigh 5 g of Reference Sample into 500 mL volumetric flask; dilute to volumetric mark. Calculate concentration of reference standard solution.

8.2.5 Prepare calibration standards by pipetting 0.1 mL, 1.0 mL, 5.0 mL, and 10 mL stock standard solution into separate 100 mL volumetric flasks; dilute to volumetric mark.

8.2.6 Calculate the concentration of each glycol in the 0.1 mL, 1.0 mL, 5.0 mL, and 10 mL standard solutions; enter the calculated concentration as % Mass into the instrument's data processing software.

8.2.7 Prepare a blank 1 mL GC auto sample vial using HPLC grade methanol.

8.2.8 Prepare a 1 mL GC auto sample vial of each dilution of the standard stock solution.

8.2.9 In accordance with GC instrument calibration method, calibrate instrument using calibration standards.

8.2.10 Prepare verification standards by pipetting 3.0 mL and 7.0 mL of stock standard solution into separate 100 mL volumetric flasks. Dilute to volumetric mark.

8.2.10.1 Verification standards are run as unknown samples to verify the calibration slope of the GC instrument.

8.3 *Sample Preparation:*

8.3.1 Weigh 0.1 g 1,3 PDO sample to the nearest 0.1 mg in a 100 mL volumetric flask, record weight; add 5.0 mL of internal reference standard solution into flask and dilute to volumetric mark.

8.3.2 If applicable, record weight of sample into instrument method sequence to determine concentration of 1,3 PDO and any contaminants.

8.3.3 Prepare a 1 mL GC sample vial of sample; inject solution; run sequence.

9. Report

9.1 *Method 1 (Neat):*

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

9.2 *Method 2 (Calibration):*

9.2.1 Determine percent water per Test Methods D1123.

9.2.2 Calculate the purity of the sample (see Test Method E2409) by means of Eq 1:

$$\text{Glycol of Interest Purity, \% Mass (m/m)} = 100 - O - W \quad (1)$$

where:

O = Other glycols, and
W = Water content of sample.

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.

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.

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:

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 intralaboratory study are available from ASTM International Headquarters and may be obtained by requesting Research Report RR:D15-1022. Contact ASTM Customer Service at service@astm.org.

ANNEX

(Mandatory Information)

A1. EXAMPLE CHROMATOGRAMS

A1.1 *Chromatograms using Option A*:

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

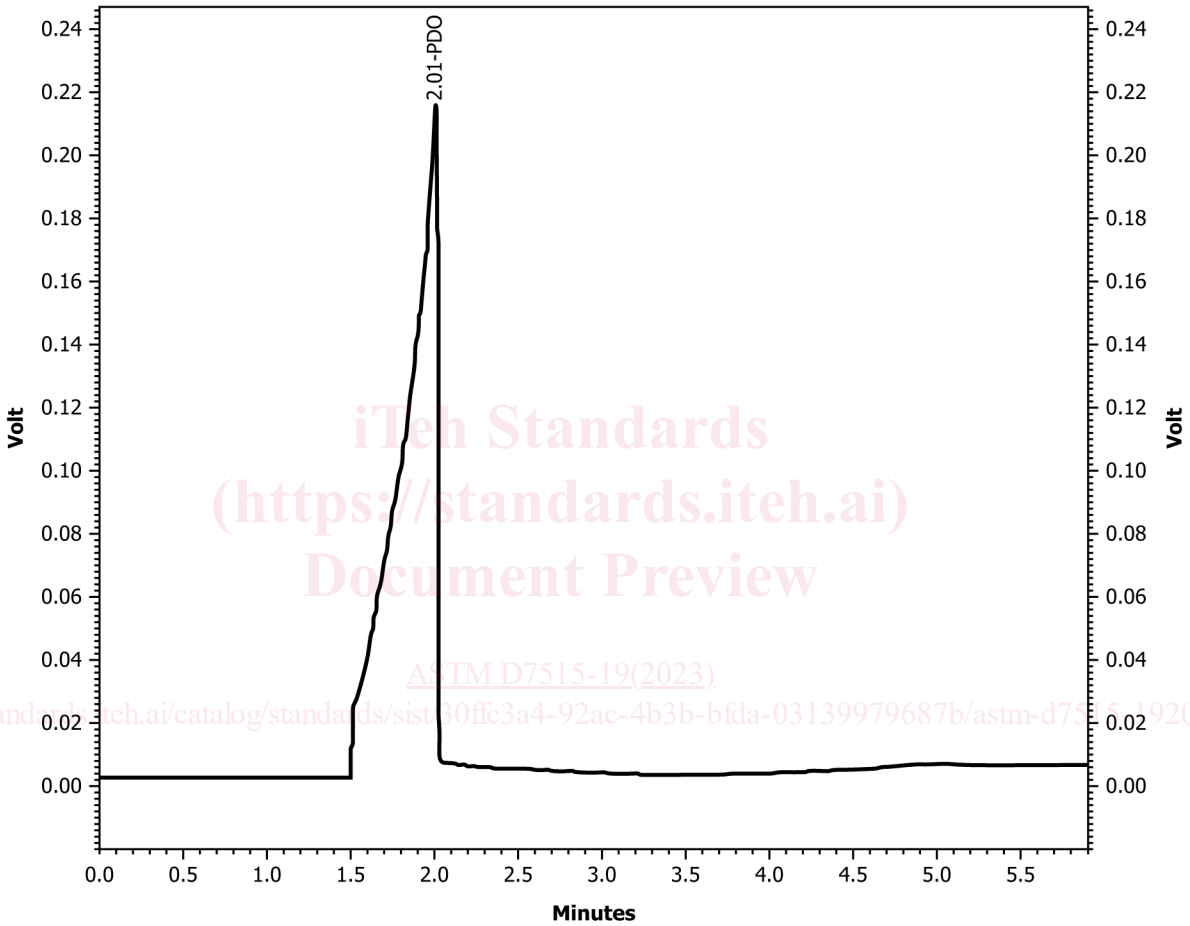

FIG. A1.1 Chromatogram of PDO

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

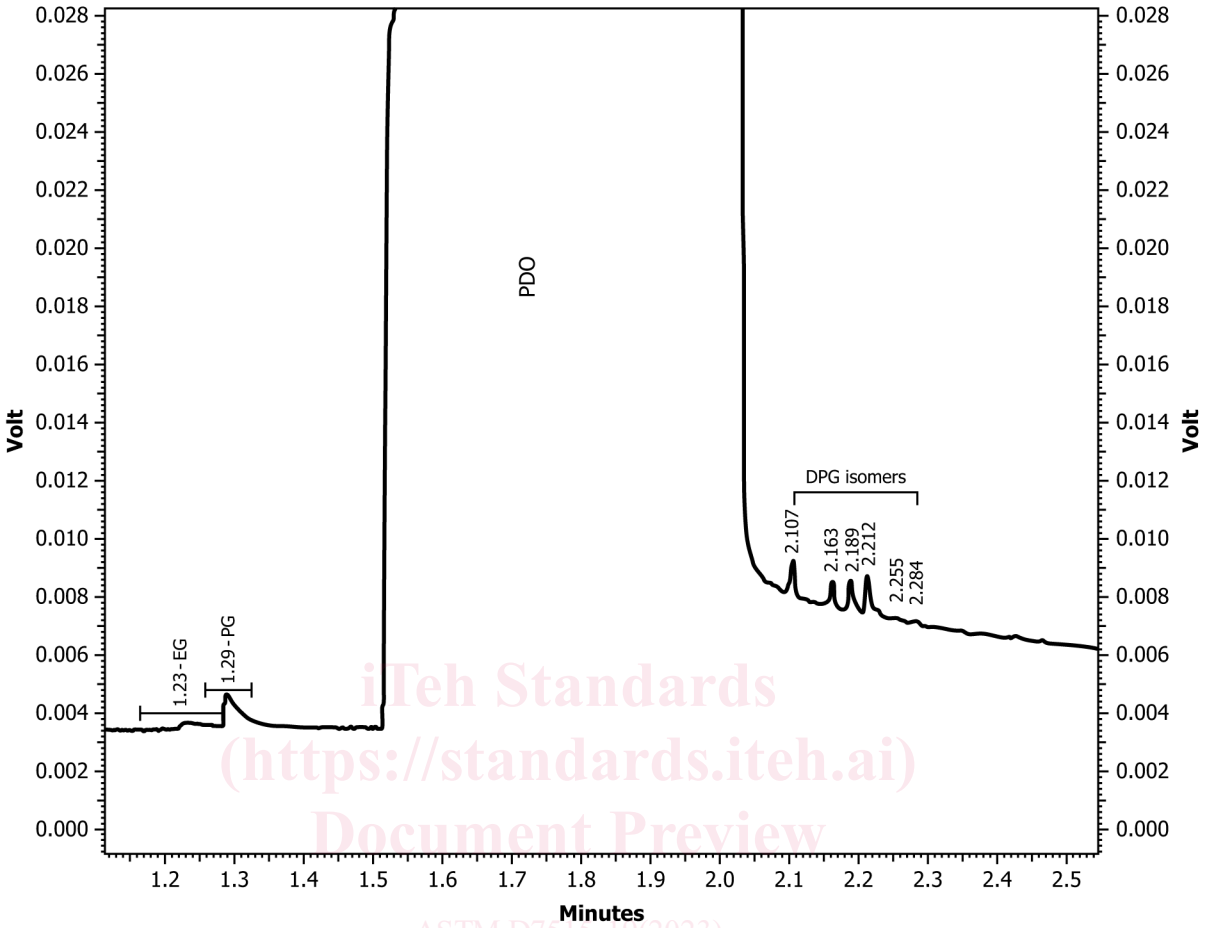

FIG. A1.2 Chromatogram of PDO, EG, PG and DPG

A1.2 *Chromatograms Using Option B*:

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

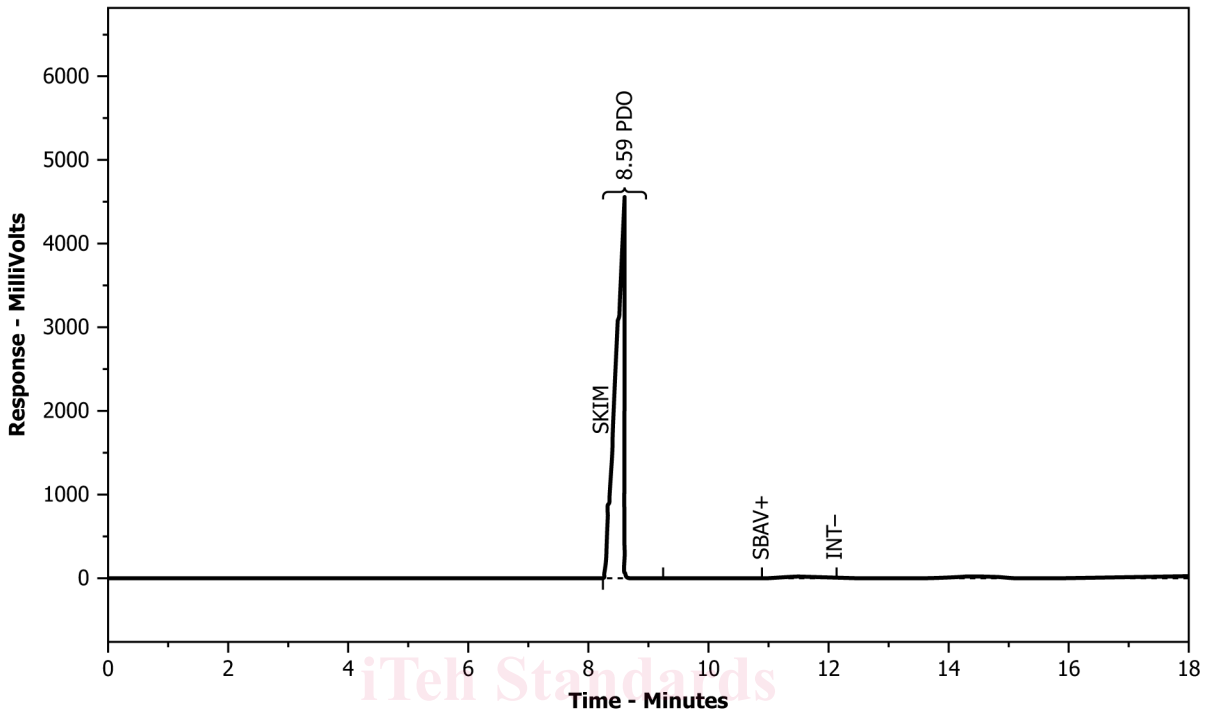

FIG. A1.3 Chromatogram of PDO