Designation: D4291 – 04 (Reapproved 2013)

Standard Test Method for
Trace Ethylene Glycol in Used Engine Oil[1]

This standard is issued under the fixed designation D4291; 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 covers the determination of ethylene glycol as a contaminant in used engine oil. This test method is designed to quantitate ethylene glycol in the range from 5 to 200 mass ppm.

1.2 *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 warning statements, see Section 6.

NOTE 1—A qualitative determination of glycol-base antifreeze is provided in Test Methods D2982. Procedure A is sensitive to about 100 ppm.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D2982 Test Methods for Detecting Glycol-Base Antifreeze in Used Lubricating Oils

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 The sample of oil is extracted with water and the analysis is performed on the water extract. A reproducible volume of the extract is injected into a gas chromatograph using on-column injection and the eluting compounds are detected by a flame ionization detector. The ethylene glycol peak area is determined and compared with areas obtained from the injection of freshly prepared known standards.

4. Significance and Use

4.1 Leakage of aqueous engine coolant into the crank case weakens the ability of the oil to lubricate. If ethylene glycol is present, it promotes varnish and deposit formation. This test method is designed for early detection to prevent coolant from accumulating and seriously damaging the engine.

5. Apparatus

5.1 *Gas Chromatograph*—Any gas chromatograph equipped with the following:

5.1.1 *Flame Ionization Detector,* capable of operating continuously at a temperature equivalent to the maximum column temperature employed, and connected to the column so as to avoid any cold spots.

5.1.2 *Sample Inlet System,* providing for on-column injection and capable of operating continuously at a temperature equivalent to the maximum column temperature employed.

5.2 *Recorder*—Recording potentiometer with a full-scale response time of 2 s or less may be used.

5.3 *Columns*—1.2-m (4-ft) by 6.4-mm (¼-in.) copper tube packed with 5 mass % Carbowax 20-M liquid phase on 30/60 mesh Chromosorb T solid support. As an alternative, a fused silica capillary column, 15 m long with a 0.53–mm ID and 2.0–micron film thickness of a bonded polyethylene glycol can be used.

5.4 *Integrator*—Manual, mechanical, or electronic integration is required to determine the peak area. However, best precision and automated operation can be achieved with electronic integration.

5.5 *Centrifuge*—RCF 600 minimum and centrifuge tubes with stoppers.

5.6 *Syringe*—A microsyringe, 10 µL is needed for sample introduction.

5.7 *Pasteur Pipets.*

5.8 *Vials,* 2 mL, with crimped septum caps.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

---

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

Current edition approved Oct. 1, 2013. Published October 2013. Originally approved in 1983. Last previous edition approved in 2009 as D4291 – 04 (2009). DOI: 10.1520/D4291-04R13.

[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.

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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

6.3 *Air and Hydrogen*—(**Warning—**The air supply may be from a cylinder under high pressure. Hydrogen is an extremely flammable gas under pressure.)

6.4 *Calibration Mixtures*—A minimum of three mixtures of water and ethylene glycol are prepared to cover the range from 5 to 200 mass ppm. Prepare one blend of approximately 2000 mass ppm ethylene glycol in water to provide for accurate weighing; then, prepare dilutions of that solution.

6.5 *Carrier Gas,* helium or nitrogen may be used with the flame ionization detector. (**Warning—**Helium and nitrogen are compressed gases under high pressure.)

6.6 *Ethylene Glycol,* 99 mass % pure.

6.7 *n-Hexane,* 99 mol % pure. (**Warning—***n*-Hexane is extremely flammable, harmful if inhaled, may produce nerve cell damage.)

6.8 *Liquid Phase and Solid Support,* 5 mass % Carbowax 20-M liquid phase on 30/60 mesh Chromosorb T solid support.

6.9 *Tubing,* 6.4 mm (¼ in.) in outside diameter, 1.2 m (4 ft) long of copper.

6.10 *Water,* deionized or distilled.

7. Preparation of Apparatus

7.1 *Packed Column Preparation*—If a packed column is used, prepare it using the following steps:

7.1.1 Prepare the packing, 5 mass % Carbowax 20-M liquid phase on 30/60 mesh Chromosorb T solid support, by any satisfactory method used in the practice of gas chromatography.

NOTE 2—Care should be taken in handling Chromosorb T solid support because of its static charge and softness. Chilling may be helpful in improving its handling properties.

7.1.2 Add the prepared packing to the copper tubing using only gentle tapping. Do not use vacuum or mechanical vibration to pack the column. Chromosorb T solid support is a resin which will deform under pressure or severe vibration.

7.2 *Column Installation*—The column must be attached to the injection port in such a way as to allow on-column injection.

7.3 *Column Conditioning*—The column must be conditioned at the operating temperature to reduce baseline shift due to bleeding of column substrate.

TABLE 1 Typical Operating Conditions

Packed Column

Column: 1.2 m (4 ft) by 6.4 mm (¼ in.) OD copper
Packing: 5 mass % Carbowax 20-M liquid phase on 30/60 mesh Chromosorb T solid support
Detector: FID
Detector Temperature: 200°C
Injection Port Temperature: 150°C
Column Oven Temperature: 130°C
Carrier Gas Flow: 60 mL/min
Sample Size: 5 µL

Capillary Column

Column: 15 m by 0.53–mm fused silica capillary with 2 µm of bonded polyethylene glycol stationary phase
Detector: FID
Detector Temperature: 300°C
Injection Port Temperature: 250°C
Column Oven Initial Temperature: 150°C
Column Oven Initial Hold Time: 0 min
Column Oven Temperature Program Rate: 10°C/min
Column Oven Program Final Temperature: 200°C
Column Oven Program Final Hold Time: 5 min
Carrier Gas Flow: 22 mL/min
Sample Size: 1 µL

7.4 *Chromatograph*—Place in service in accordance with manufacturer's instructions. Typical operating conditions are shown in Table 1.

8. Calibration

8.1 Analyze each of the calibration mixtures following the procedure in Section 10, injecting exactly 5 µL and record the area of the ethylene glycol peak.

8.2 Calculate a response factor for each calibration mixture as follows:

$$F = C/A \tag{1}$$

where:

F = response factor for ethylene glycol,
C = concentration in mass ppm of ethylene glycol in water, and
A = peak area for ethylene glycol.

8.3 Calculate an average response factor.

NOTE 3—A calibration curve may be employed to obtain the response factor.

9. Preparation of Sample

9.1 Weigh approximately 3 g of sample, obtained as recommended in Practice D4057, to the nearest 0.1 mg into the stoppered centrifuge tube. Add approximately 3 g of water, weighed to the nearest 0.1 mg, to the centrifuge tube. Add 5 mL of *n*-hexane.

9.2 Stopper and vigorously agitate the centrifuge tube for approximately 5 min.

9.3 Centrifuge the tube for 30 min.

9.4 If there is no clear water layer, remove and discard the upper oil layer, taking care not to remove any of the water emulsion. Add another 5 mL of *n*-hexane and centrifuge for 30 min.

---

[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 *Annual 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.

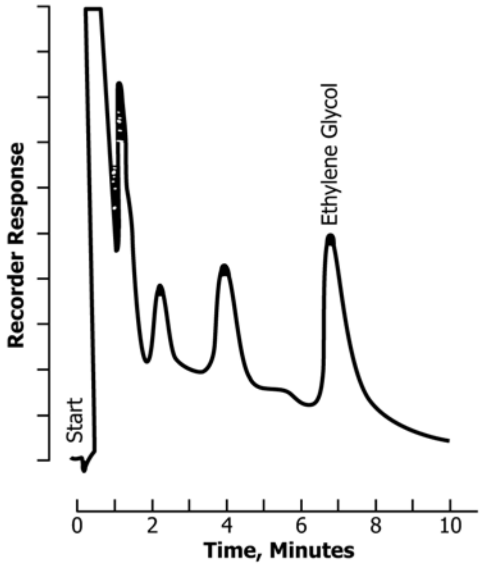

FIG. 1 Typical Packed Column Chromatogram

9.5 Remove an aliquot of the clear water layer from the centrifuge tube with a Pasteur pipet and place in a 2-mL vial. Crimp a cap on the vial.

10. Procedure

10.1 Set the operating conditions of the chromatograph as described in 7.4. Inject exactly 5 µL of water extract directly on the column. Record the peaks at a sensitivity that allows the maximum peak size compatible with the method of measurement.

NOTE 4—A typical chromatogram obtained with packed columns is shown in Fig. 1. A typical chromatogram obtained with capillary columns is shown in Fig. 2.

10.2 After each sample analysis is completed, inject 5 µL of water and allow to elute.

NOTE 5—Small amounts of ethylene glycol are retained by the chromatographic column when higher concentrations of the glycol are injected. Therefore, when analyzing for very low concentrations of ethylene glycol, make repeated injections of water until no peak is found at the ethylene glycol retention time.

11. Calculations

11.1 The concentration of ethylene glycol in the original oil sample is calculated as follows:

$$\text{Ethylene glycol, mass ppm} = F \times A \times W_W / W_S \qquad (2)$$

where:

F = response factor for ethylene glycol as calculated in 8.3,
A = peak area for ethylene glycol,
W_W = weight of the water as determined in 9.1, and
W_S = weight of the oil sample as determined in 9.1.

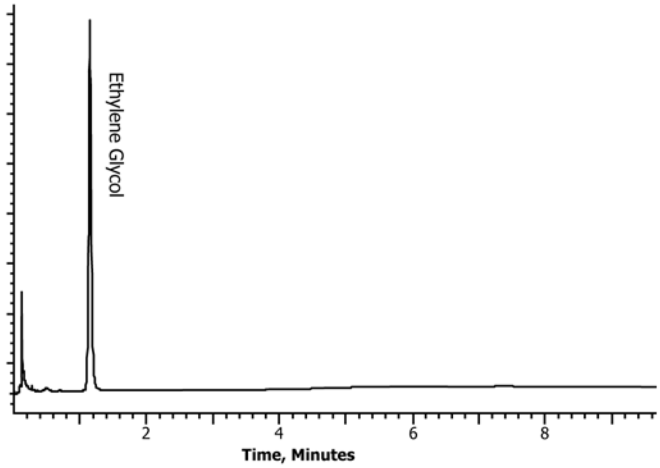

FIG. 2 Typical Capillary Column Chromatogram

12. Precision and Bias[4]

12.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of test method, exceed the following values only in one case in twenty.

$$\text{Repeatability, } n = 0.212X \qquad (3)$$

where:

X = ethylene glycol content, mass ppm.

12.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators, working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$\text{Reproducibility, R} = 0.528X \qquad (4)$$

where:

X = ethylene glycol content, mass ppm.

NOTE 6—The precision stated in this test method was determined using packed columns.

12.2 *Bias*—Bias cannot be determined because there is no acceptable reference material suitable for determining the bias for the procedure in this test method.

13. Keywords

13.1 antifreeze; ethylene glycol; gas chromatography; used engine oil

---

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1167.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/