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.

Designation: D4291 – 21

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 mass ppm 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Section 7.

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

1.3 *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]

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
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
E355 Practice for Gas Chromatography Terms and Relationships
E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355 and E594, and Terminology D4175.

4. Summary of Test Method

4.1 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.

5. Significance and Use

5.1 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.

6. Apparatus

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

6.1.1 *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.

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

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

6.3 *Columns*—1.2 m by 6.4 mm (4 ft by ¼ in.) copper tube packed with 5 % by 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.

6.4 *Integrator*—Manual, mechanical, or electronic integration is required to determine the peak area. However, best

[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.

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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.

***A Summary of Changes section appears at the end of this standard**

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precision and automated operation can be achieved with electronic integration.

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

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

6.7 *Pasteur Pipets.*

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

7. Reagents and Materials

7.1 *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 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.

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

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

7.4 *Calibration Mixtures*—A minimum of three mixtures of water and ethylene glycol are prepared to cover the range from 5 mass ppm 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.

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

7.6 *Ethylene Glycol,* 99 % by mass pure.

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

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

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

7.10 *Water,* deionized or distilled.

8. Preparation of Apparatus

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

TABLE 1 Typical Operating Conditions

Packed Column
Column: 1.2 m (4 ft) by 6.4 mm (¼ in.) OD copper
Packing: 5 % by 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

8.1.1 Prepare the packing, 5 % by 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.

8.1.2 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.

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

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

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

9. Calibration

9.1 Analyze each of the calibration mixtures following the procedure in Section 11, injecting exactly 5 µL and record the area of the ethylene glycol peak.

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

$$F = C/A \quad (1)$$

where:

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

9.3 Calculate an average response factor.

[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.

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