Designation: D7922 – 23

Standard Test Method for Determination of Glycol for In-Service Engine Oils by Gas Chromatography[1]

This standard is issued under the fixed designation D7922; 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 glycol based antifreeze for in-service engine oil by derivative headspace/gas chromatography.

1.2 Sample is derivatized in-situ directly in a headspace sampling vial prior to vapor phase extraction and injection into a gas chromatograph.

1.3 The chemistry of the derivatization is unique to the detection of the molecules of ethylene glycol and 1,2-propylene glycol. 1,3-propylene glycol could also be detected but is not used in any known anti-freeze at this time. Other coolant analyses are beyond the scope of this test method.

1.4 The derivatization process does not affect glycol breakdown products such as glycolate and formate and hence the presence of these compounds in the oil will not be quantified.

1.5 The test method concentration range is from 50 µg/g to 1000 µg/g. Lower levels are possible by method modifications. Higher levels are possible through sample dilution.

1.6 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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.*

1.8 *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]

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4291 Test Method for Trace Ethylene Glycol in Used Engine Oil

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

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.

3.1.2 *antifreeze, n*—antifreeze is typically a dilution of ethylene glycol and possibly other glycols, and additives, in water to act as a machine coolant. 1,2-propanediol is found in some antifreeze formulations.

3.1.3 *derivitization reagent, n*—a saturated solution of phenylboronic acid (PBA) in solvent. Acetone and 2,2-dimethoxypropane have been used successfully. Gentle warming at 50 °C will hasten dissolution. Solution is stable for three months at room temperature if kept away from moisture.

3.1.4 *glycol, n*—the amount, expressed as a percentage, of glycol found in the in-service lubricating oil. The most common glycol formulated into antifreeze is ethylene glycol (CAS# 107-21-1) with some antifreeze also containing 1,2-propanediol also known as propylene glycol (CAS# 57-55-6). Another glycol such as 1,3-propanediol (CAS# 504-63-2) is detected by this test method but is not commonly used in antifreeze formulations.

[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, 2023. Published October 2023. Originally approved in 2014. Last previous edition approved in 2021 as D7922 – 21. DOI: 10.1520/D7922-23.

[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**

3.1.5 *glycols, n*—the summed amount of individual glycols found in the in-service lubricating oil.

3.1.6 *in-service oil, n*—lubricating oil that is present in a machine that has been at operating temperature for at least 1 h.

4. Summary of Test Method

4.1 A representative aliquot of in-service engine oil is introduced into a headspace sampling vial along with a derivatizing agent. The headspace vial is heated to volatilize the derivatized glycol into the vapor phase. Using a small aliquot of sample and derivatization reagent approaches a total vaporization technique to minimize partition coefficient differences in in-service oil samples. A representative aliquot of the vapor sample is introduced to the gas chromatograph. Carrier gas transports the vaporized aliquot through the dimethyl polysiloxane bonded phase capillary column where the glycols are separated by the chromatographic process. The detector signal is processed by an electronic data acquisition system. The components are identified by comparing their retention times to ones identified by analyzing standards under identical conditions. The concentrations of all components are determined by percent area by normalization of the peak areas.

5. Significance and Use

5.1 Some glycol/antifreeze dilution of in-service engine oil is normal under typical operating conditions. However, excessive glycol dilution can lead to decreased performance, premature wear, or sudden engine failure. This test method provides a means of quantifying the level of glycol based antifreeze dilution, allowing the user to take necessary action.

6. Interferences

6.1 PBA is slightly volatile and can reach the headspace (HS) injector head and the transfer line. It is recommended to periodically inspect a blank injection chromatogram for carry over caused by condensation of PBA in the headspace sampling head and/or transfer line. Several 10 µL injections of water:methanol (50:50) through the headspace will consume any residual derivatizing reagent.

6.2 The most common failure for this glycol method is improperly agitated standards which allow settling of glycols out of the oil base. Polar glycols do not stay in the non-polar oil. It is more correctly considered a suspension rather than a solution. Every oil, sample or standard, must be shaken briskly for 15 s to 20 s before sampling.

6.3 Water/humidity reaching PBA will deactivate the PBA and inhibit derivatization of glycols. PBA will derivatize any hydroxyl functional group. Store PBA in a desiccator, never in a refrigerator.

6.4 Buy PBA in small quantities to be replaced at six month intervals rather than larger, more cost effective quantities.

6.5 Headspace carrier pressure must be higher than pressure in the heated vial to allow pressurization of the vial to a constant pressure. This vial pressure is a function of which solvent is used and the thermostatting temperature of the vial. A pressure of 276 kPa (40 psi) has been shown to be successful.

6.6 Diesel fuel in the oil along with the glycols will be seen in the chromatogram. Oven conditions are chosen to minimize co-elution of diesel peaks with the ethylene glycol. Other medium petroleum distillates in the oil could interfere with the ethylene glycol peak but will be noticeable on the chromatogram.

6.7 Headspace vial crimp is extremely critical to completely seal the vial.

6.8 As an external standard method, measurement of oil volume is critical and should be performed with a positive displacement pipette.

6.9 Daily column bake-out is recommended to get rid of fuel and high molecular weight artifacts.

6.10 Some higher quality oils may have a small quantity of ethylene glycol in the new, unused motor oil as part of the oil formulation. This concentration has been observed at about 30 µg/g to 75 µg/g which is well under the level of interest of 100 µg/g to 1000 µg/g. This ethylene glycol will typically boil off in the heat of the engine. But a small level of ethylene glycol should not be considered as a definite coolant leak without considering the possibility of ethylene glycol in new or recently topped off engine oil.

7. Apparatus

7.1 *Gas Chromatograph (GC)*—The following gas chromatographic system performance characteristics are required:

7.2 *Detector*—This test method requires a flame ionization detector (FID). The detector must have sufficient sensitivity to detect 50 µg/g ethylene glycol by area on the data acquisition device under the conditions prescribed in this test method. The detector must meet or exceed the specifications as detailed in Practice E594. The detector must be capable of operating continuously at 250 °C and connected to the column such that no temperature zones below the column temperature (cold spots) exist.

7.3 *Injector*—The preferred injector is an automated headspace sampling device. Connection of the headspace device to the GC column can be direct or interfaced using a split/spitless GC inlet.

7.4 *Pneumatic Controllers*—The headspace sampler and gas chromatograph must be capable of maintaining carrier gas pressure constant to ±1 % for both the injector and the detector. Most modern gas chromatographs can control carrier gas in either pressure control mode or flow control mode. This analysis uses isothermal oven temperature therefore constant flow control will not improve chromatographic throughput or efficiency. At isothermal oven temperatures, both pressure and flow will remain constant.

7.5 *Column Conditions*—This test method utilizes a fused silica open tubular column with 5 % diphenyl and 95 % dimethyl polysiloxane crossbonded phase internal coating operating isothermally at 90 °C to 140 °C, depending on the carrier gas used.