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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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.

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.

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

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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.

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 Glycols tend to be sticky molecules that can lead to small carryover into blank injections.

6.2 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.

6.3 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.

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

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

6.6 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.

6.7 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.

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

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

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

6.11 Split injection has been shown to cause ethylene glycol carryover in the injector. Therefore, direct column connection between the headspace sampler and the analytical column is used.

6.12 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, with a direct connection of the headspace device to the analytical column without exposing the sample to a GC injector.

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.

7.5.1 Open tubular column with a cross bond 5 % diphenyl 95 % dimethyl polysiloxane phase internal coating, 15 m by 0.32 mm I.D. with a 0.25 µm film thickness. Never use a polar column.

7.6 *Sample Introduction Devices:*

7.6.1 *Headspace Automatic Sampler*—An automatic sampling device for heating samples to transfer volatile components into the vapor phase and injecting a reproducible and representative aliquot of the vapor phase into the gas chromatograph.

7.7 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantification of these analyses must meet or exceed these minimum requirements:

7.7.1 Normalized percent calculations based on peak area or peak height.

7.7.2 Ability to construct a first order linear regression calibration curve up to five levels of calibration.

7.7.3 Identification of individual components based on retention time.

7.7.4 Baseline corrections for positive or negative sloping baseline.

7.7.5 Ability to turn on and off integration.

7.7.6 Ability to adjust integration stop and start of each component.

8. Reagents and Materials

8.1 *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.

8.1.1 *Phenylboronic acid CAS# 98-80-6,* 99+ percent pure. Used as a derivatizing reagent to convert ethylene glycol and other low molecular weight glycols to the phenylboronic derivative of the glycol.

8.1.2 *Ethylene glycol CAS# 107-21-1,* 99+ percent pure. Used as a calibration standard for retention time and quantitative response by concentration.

8.1.3 *Propylene glycol CAS# 57-55-6,* 99+ percent pure. Also known as 1,2-propanediol. Used as a calibration standard for retention time and quantitative response by concentration.

8.1.4 *1,3-propanediol CAS# 504-63-2,* 99+ percent pure. Used as a calibration standard for retention time and quantitative response by concentration. Not essential in most antifreeze formulations. Used primarily to insure resolution of 1,2-propanediol from 1,3-propanediol.

8.1.5 *Acetone, CAS# 67-64-1,* 99+ percent pure. (**Warning—**Extremely flammable and toxic liquid.) One of the solvents that can be used to dissolve the phenylboronic acid.

8.1.6 *2,2-dimethoxypropane CAS# 77-76-9,* 99+ percent pure. (**Warning—**Extremely flammable and toxic liquid.) One of the solvents that can be used to dissolve the phenylboronic acid.

8.1.7 *Derivitization Reagent Solution*—Prepared by dissolving dry phenylboronic acid into solvent such as acetone or 2,2-dimethoxypropane. A high concentration or saturated solution is preferred. 0.5 g/mL phenylboronic acid in acetone will dissolve very slowly to overnight with agitation. A gentle heating to 50 °C for 5 min will facilitate PBA into solution. Make enough volume for weekly use. Do not make large volumes that will be deactivated by humidity.

8.2 *Gas*—The following compressed gases are utilized for the operation of the gas chromatograph.

8.2.1 *Helium,* 99.999 %. (**Warning—**Compressed gas under high pressure.) This gas can be used as carrier gas. Ensure sufficient pressure for a constant carrier gas flow rate. Precision is based on helium as the carrier gas; however, hydrogen and nitrogen have been successfully used as carrier gas.

8.2.2 *Hydrogen,* 99.999 %. (**Warning—**Extremely flammable compressed gas under high pressure.) This gas is used to supply fuel to the flame ionization detector (FID) detector. Hydrogen is the preferred carrier. A hydrogen generator is preferred to cylinders.

8.2.3 *Nitrogen,* 99.999 %. (**Warning—**Compressed gas under high pressure.) Used as an alternative carrier gas.

8.2.4 *Air*—(**Warning—**Compressed gas under high pressure.) The gas is used to supply oxidant to the flame ionization detector (FID). A zero air generator is preferred.

9. Preparation of Apparatus

9.1 *Gas Chromatograph Setup:*

9.1.1 Install the gas chromatograph and place into operation in accordance with the manufacturer's instructions. Recommended operating conditions are listed in Section 7. Example conditions are listed in Appendix X1.

9.1.2 Any injector may be used on the gas chromatograph as a firm mounting point for the automated headspace sampling device.

9.2 *Column Conditioning*—Open tubular columns with cross-linked and bonded stationary phases containing 5 % diphenyl 95 % dimethyl polysiloxane are available from many manufacturers and are usually pre-conditioned. Column conditioning is still recommended. The column can be conditioned very rapidly and effectively using the following guidelines outlined in Practice E1510.

9.3 *System Performance Specification:*

9.3.1 *Column Resolution*—Resolution between ethylene glycol phenyl boronate and 1,2-propylene glycol phenyl boronate is required to differentiate glycols found in common antifreeze formulations. A resolution of at least 2.0 is required where resolution is calculated by:

$$R = 2\cdot(t_{r2} - t_{r1})/(w_1 + w_2) \tag{1}$$

where:

R = resolution,

t_{r2} = retention time of 1,2-Propylene Glycol phenyl boronate (seconds),

t_{r1} = retention time of Ethylene Glycol phenyl boronate (seconds),

w_1 = width of peak Ethylene Glycol phenyl boronate (seconds), and

w_2 = width of peak 1,2-Propylene Glycol phenyl boronate (seconds).

10. Calibration

10.1 *Calibration Mixtures*—A minimum of three mixtures of glycols covering the range of up to 50 µg/g to 1000 µg/g.

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[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

This test method has been shown to be linear from 50 µg/g to 1000 µg/g for ethylene glycol and propylene glycol. See Fig. 1. If a sample result is above the calibration range, it is recommended to dilute the sample to bring the concentration into the calibration dynamic range. Commercially available calibration mixtures are available at concentrations of 100 µg/g, 500 µg/g and 1000 µg/g each of ethylene glycol and 1,2-propylene glycol in 7.5 × 10^{-5} m^2/s (75 cSt) base oil.

10.2 *Preparing Your Own Calibration Mixtures*—The following procedure has been used successfully to create calibration standards. Prepare a stock solution or 1 % m/m glycols for use in dilution to working calibration standards. Mass to mass dilutions are performed due to the high viscosity of engine oils and base oil. Stock Solution: In a 250 mL polyethylene screw cap bottle, accurately weigh 2 g (±0.002 g) each of ethylene glycol and 1,2-propylene glycol. Add 7.5 × 10^{-5} m^2/s (75 cSt) base oil to bring mass of solution to a total of 200 g. This represents a 1 % (10,000 µg/g) mixture of each glycol. Shake briskly for 20 s. Let mixture stand 1 h, shake again briskly for 20 s. Repeat stand and shake routine for at least five times to ensure adequate mixing.

10.3 *Working Standards*—Dilute 1 % glycol stock to make working standards. Do not use less than 50 mL volume for mixing. Mixing is poor for low volumes. Use large enough container to allow adequate mixing.

10.3.1 *1000 µg/g working standard*—In a 125 mL polyethylene screw cap bottle, weigh out 90 g of 7.5 × 10^{-5} m^2/s (75 cSt) base oil and 10 g glycol stock solution. Briskly mix five times by stand/shake.

10.3.2 *500 µg/g working standard*—In a 125 mL polyethylene screw cap bottle, weigh out 95 g of 7.5 × 10^{-5} m^2/s (75 cSt) base oil and 5 g of glycol stock solution. Briskly mix five times by stand/shake.

10.3.3 *100 µg/g working standard*—In a 125 mL polyethylene screw cap bottle, weigh out 99 g of 7.5 × 10^{-5} m^2/s (75 cSt) base oil and 1 g of glycol stock solution. Briskly mix five times by stand/shake.

10.4 Brisk shaking is absolutely essential to the complete mixing of polar glycols into the non-polar base oil. The mixture is to be considered a suspension as opposed to a solution. The most common failure for this glycol method is the improperly agitated standards which allow settling of glycols out of the base oil. Every time the standards are used, the bottle must be briskly shaken again to ensure mixing and a uniform suspension.

10.5 Analyze each of the calibration mixtures prepared in 10.3. Inject the same volume as chosen for the sample. Record the area due to the glycol portion in each mixture.

10.6 Prepare a linear regression calibration curve by plotting the area of each specific glycol versus the concentration of glycol in micrograms per gram. The correlation coefficient for each component should meet or exceed $r^2 = 0.998$. See Fig. 1. Volatiles in the oil matrix will also enter the headspace vapor and contribute a slight amount to the total peak area. This matrix contribution is small and consistent from run to run so calibration will negate the effects of the matrix, but can result in a small negative intercept on the calibration curve causing increased error at very low concentrations below the lowest calibration level.

$$(rsp_i) = (m_i)(amt_i)+b_i \tag{2}$$

where:

(rsp_i) = response for glycol (y-axis),
m_i = slope of linear equation,
amt_i = amount for glycol (x-axis), and
b_i = y-axis intercept.

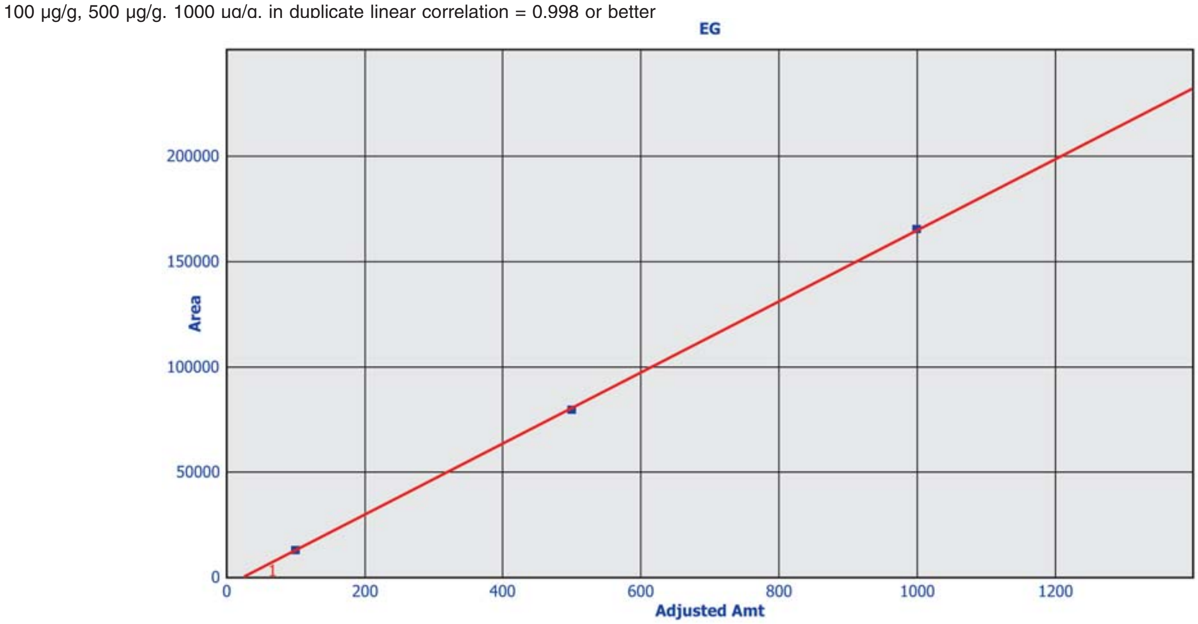

FIG. 1 Ethylene Glycol Calibration Curve

11. Procedure

11.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule will include setting the heated zones to the analysis temperature, establishing set carrier pressure/flow, injecting sample into the gas chromatograph, chromatography software collecting and processing data.

11.2 *Baseline Blank*—Perform a baseline blank base oil free of glycols.

11.3 *Sample Preparation*—Briskly shake sample. A 100 µL representative aliquot of in-service engine oil is transferred into the appropriate headspace sampler vial using a positive displacement syringe. 50 µL derivatization reagent is added to the headspace vial using a micropipette. The vial should be sealed with the appropriate vial cap specified by the vendor of the instrumentation.

11.4 *Quality Control Check*—A quality control sample representative of the type and range of glycols expected should be run on a daily basis to check instrument conditions.

11.5 *Sample Analysis*—Using the analysis sequence protocol, sample is heated for sufficient time to reach headspace equilibrium with the vapor phase. Derivitization of glycols takes place in-situ in the headspace vial during vial thermostat period. Inject headspace aliquot of in-service oil into the gas chromatograph. Collect the entire analysis and let the chromatographic software process the data with the calibrated analytical method. Typical in-service oil chromatograms are presented in Fig. 2 and Fig. 3.

12. Interpretation of Results

12.1 Determine the concentration of glycols in the samples by relating the area from the glycol components obtained to the previously determined calibration curve.

13. Report

13.1 Using the chromatography software report the results of glycols in the sample in micrograms per gram or other dimensions such as milligrams per kilogram mass or percent mass may be used.

14. Precision and Bias

14.1 *Precision*—See Note 1. The repeatability for glycol dilution of in-service oils was determined by one laboratory analyzing three different levels of in-service oil samples from 100 µg/g to 1000 µg/g 30 times.

NOTE 1—The precision statement of this test method was established using helium as the carrier gas. Other carrier gases such as hydrogen and nitrogen have demonstrated equivalent results but the precision statement of this test method only applies when using helium as the carrier gas.

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials is calculated by the formula:

$$Repeatability = (STDEV \cdot 2.8) \qquad (3)$$

14.1.1.1 30 replicates of a 500 µg/g standard showed a standard deviation of 12.

14.1.1.2 Repeatability is calculated as 500 µg/g ethylene glycol ±33.6 µg/g.

14.1.2 *Reproducibility*—The reproducibility of this test method is being determined and will be available on or before December 2018.

15. Keywords

15.1 antifreeze; ethylene glycol; gas chromatography; glycol; headspace; in-service oil; lubricating oil

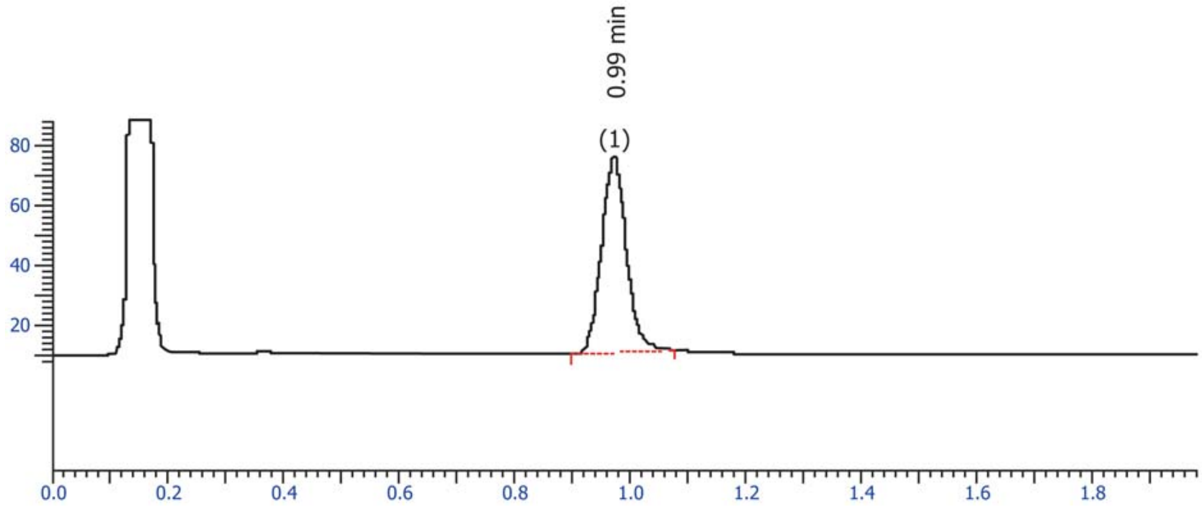

FIG. 2 Chromatogram—Ethylene Glycol Phenyl Boronate, Helium Carrier

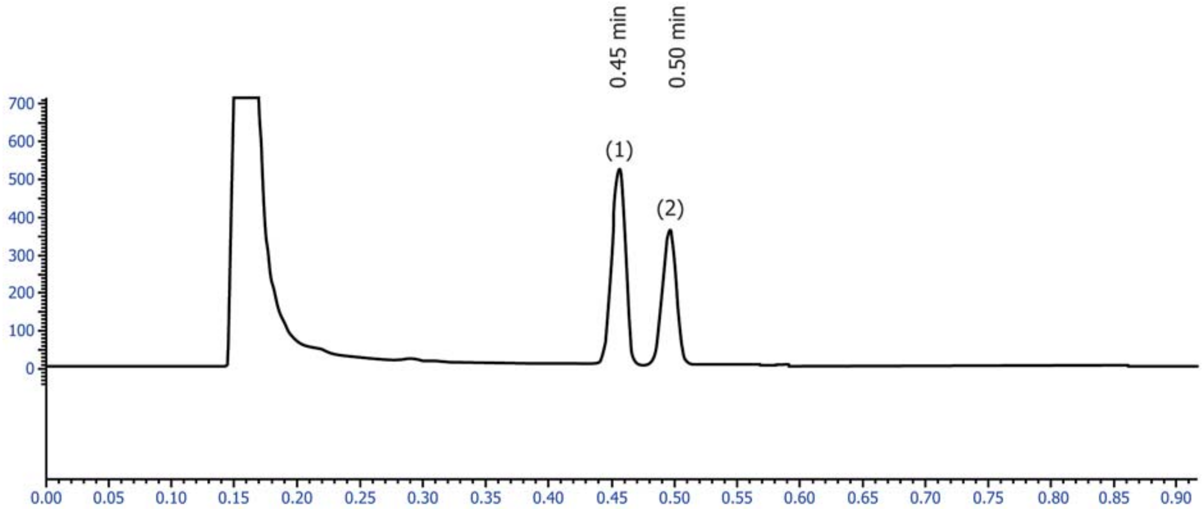

FIG. 3 Chromatogram—Ethylene Glycol Phenyl Boronate (1) and 1,2-Propylene Glycol Phenyl Boronate (2) with Hydrogen Carrier

APPENDIX

(Nonmandatory Information)

X1. TYPICAL OPERATING CONDITIONS

TABLE X1.1 Typical Operating Conditions

Gas Chromatograph	Any gas chromatograph meeting the following criteria
Injector	Any injector, used only to mount autosampler, 180 °C
Detector	FID Temp: 250 °C Air and Hydrogen per manufacturers recommendation Adjust total FID hydrogen to factor in hydrogen carrier[A]
Column	15 m × 0.32 mm I.D. × 0.25 µm 5 % diphenyl 95 % dimethyl polysiloxane capillary column
GC Oven	120 °C to 130 °C isothermal for 2.0 min for helium carrier EG: ~0.9 min to 1.2 min 90 °C to 100 °C isothermal for 1.0 min for hydrogen carrier EG: ~0.45 min to 80 min Adjust GC oven temperature to achieve resolution of at least R = 2.0 between ethylene glycol and 1,2-propylene glycol
Autosampler	Automated Headspace sampler
Headspace Temperature	Vial Oven: 140 °C to 150 °C for 18 min Needle: 160 °C , Transfer line: 200 °C
Pneumatics	276 kPa (40 psig) helium carrier ~ 10 mL/min 276 kPa (40 psig) hydrogen carrier ~ 17 mL/min
Column Connection	1 m to 2 m × 320 µm fused silica transfer line Direct connect transfer line from HS to analytical column inside GC oven with glass press-tight union Do not use split injection inside capillary injector
Injection volume	About 300 µL ~ 0.02 min inject time
Remaining parameters	According to HS manufacturer recommendation

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[A] If hydrogen is used as carrier gas, reduce FID hydrogen by the measured flow of hydrogen carrier to result in a desired total flow of hydrogen delivered to the detector. H2 carrier + H2 flame gas = manufacturer's recommended flow.