Designation: D7716 – 11a

Standard Test Method for Determination of Residual Methanol in Glycerin by Gas Chromatography[1]

This standard is issued under the fixed designation D7716; 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 provides for the quantitative determination of residual methanol in glycerin by gas chromatography. The range of detection for residual methanol is 0.02 to 0.60 mass %.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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]

D1193 Specification for Reagent Water

D7640 Specification for Engine Coolant Grade Glycerin

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E355 Practice for Gas Chromatography Terms and Relationships

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

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions can be found in Practices E355 and E594.

4. Summary of Test Method

4.1 The sample is analyzed by headspace gas chromatography. Calibration is achieved by the use of external standards of methanol in water.

5. Significance and Use

5.1 Methanol content reflects the quality of glycerin for use as an engine coolant. The current specification for the maximum methanol content is 0.1 % weight to weight (w/w).

6. Apparatus

6.1 *Chromatographic System*—See Practice E355 for specific designations and definitions. The gas chromatograph (GC) system shall be capable of operating at the conditions given in Table 1.

6.2 *Autosampler system,* Gerstel multipurpose sampler MPS-2[3] or equivalent. This method can also be run manually.

6.3 *Column,* open tubular column with polyethylene glycol (PEG) bonded and cross-linked phase internal coating. The column should have an upper temperature limit of 260°C. A column 30 m in length, with an internal diameter of 0.32 mm, and a 1.0-µm film thickness has been found satisfactory. Any column with equivalent or better chromatographic efficiency and selectivity can be used.

6.4 *Electronic Data Acquisition System*—A computer capable of providing real-time graphic and digital presentation of the chromatographic data is recommended for use. Peak areas and retention times shall be measured by computer or electronic integration (integrator).

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

[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 D15.93 on Research and Long Range Planning.

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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.

[3] The sole source of supply of the apparatus known to the committee at this time is GERSTEL GmbH & Co.KG, Eberhard- Gerstel-Platz 1, 45473 Mülheim an der Ruhr, Germany. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

TABLE 1 Operating Conditions

Injector: Hot split/splitless, 240°C, 10:1 split ratio
Sample Size: 1.0 mL
Column Temperature Program: Initial temperature: 50°C hold 8 min, ramp at 20°C/min to 200°C, hold for 0 min
Detector: Flame ionization at 250°C
Carrier gas: helium or hydrogen, 1.5 mL/min
Vial incubation time: 20 min
Vial incubation temperature: 80°C
Agitator speed: 600 rpm
Injection speed: 200 µL/s
Pull-up delay: 5 s

such specifications are available.[4] Other grades may be used provided it is first ascertained that the reagent is of sufficient 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 *Methanol,* reagent grade.

7.4 *Glycerin,* meeting Specification D7640.

7.5 *Carrier gas,* hydrogen or helium of high purity. Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure shall be sufficient to ensure a constant carrier gas flow rate.

7.6 *Microlitre syringe on auto sampler,* 2500-µL capacity.

7.7 *Microlitre syringe, gastight,* 1000-µL capacity (needed for manual injections).

7.8 *Screw-cap vials,* with polytetrafluoroethylene (PTFE)-faced septa, 20-mL capacity.

7.9 *Volumetric pipets,* various capacities.

7.10 *Volumetric flasks,* various capacities.

7.11 *Forced-air oven,* 80 ± 1°C (needed for manual injections).

7.12 *Analytical balance,* accurate to 0.1 mg.

8. Preparation of Apparatus

8.1 Install and condition the column in accordance with the manufacturer or supplier's instructions. After conditioning, attach the column outlet to the flame ionization detector inlet and check for leaks throughout the system. If leaks are found, tighten or replace fittings and recheck for leaks before proceeding.

9. Calibration and Standardization

9.1 *Preparation of Calibration Stock Standard*—Prepare a stock methanol standard by weighing approximately 1.5 g of methanol into a clean 100-mL volumetric flask. Record weight to the nearest 0.1 mg. Dilute with Specification D1193 Type II water to the 100-mL mark and mix well. This test method contains approximately 15 000 ppm of methanol.

9.2 *Standard Solutions*—Prepare six calibration standards by first pipeting 2.0 mL of the stock standard into a 100-mL volumetric flask, dilute with Specification D1193 Type II water to the mark and mix well. This standard contains approximately 300 ppm of methanol. Pipette 5 mL of this standard into a 10-mL volumetric flask, dilute with Specification D1193 Type II water to the mark and mix well. This standard contains approximately 150 ppm of methanol. Pipette 5 mL of this standard into a 10-mL volumetric flask, dilute with Specification D1193 Type II water to the mark and mix well. This standard contains approximately 75 ppm of methanol. Make three more dilutions in the same manner to give solutions with methanol concentrations of approximately 37.5, 18.8, and 9.4 ppm. There will be six calibration standards with approximate concentrations of 9.4, 18.8, 37.5, 75, 150, and 300 ppm of methanol.

9.3 *Chromatographic Analysis*—Pipette 1.0 mL of each of the prepared standards into each of six 20-mL headspace vials. Pipette 5.0 mL of Specification D1193 Type II water into each of the vials and cap tightly with a PTFE-lined septa.[5] Also prepare two air blank vials that should be run for the first vial to check the system background and also after the highest calibration standard to check for carryover.

9.4 Analyze the calibration standards under the same operating conditions as the sample solutions. If using a manual injection technique, place the first calibration standard vial into an 80°C forced-air oven and allow to incubate for 20 min. Also place the 1-mL syringe into the oven to become equilibrated with the standard vial. When the time has elapsed, remove the syringe using heat-resistant gloves. Remove the calibration standard vial and insert the syringe needle into the vial through the septa. Withdraw the headspace gas up past the 1-mL mark and inject back into the vial. Repeat this two more times. Withdraw headspace gas again up past the 1-mL mark and allow the pressure in the syringe to equilibrate for 5 s before bringing the plunger down to the 1.0-mL mark. Withdraw the syringe from the vial and immediately inject the headspace sample into the GC and press the Start button on the GC front panel. Repeat this process with the remaining standards and samples. If using an automated headspace sampling system, inject 1.0 mL of each of the calibration standards (after the 20-min incubation time at 80°C) to obtain a chromatogram and peak integration report. Identify the methanol peak by comparison of retention time to the retention time shown in Fig. 1. Review the integration of the methanol peak ensure it was integrated properly. If not, reintegrate the peak manually to obtain the peak area.

9.5 Input the integrated peak areas and corresponding concentrations into an Excel spreadsheet to generate a linear calibration curve. The curve should have a correlation coefficient r^2 of 0.99 or greater. If this criterion is not met, rerun the calibration or check the instrument parameters and hardware. If

[4] *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.

[5] Over tightening could cause the vial to crack. Use caution.

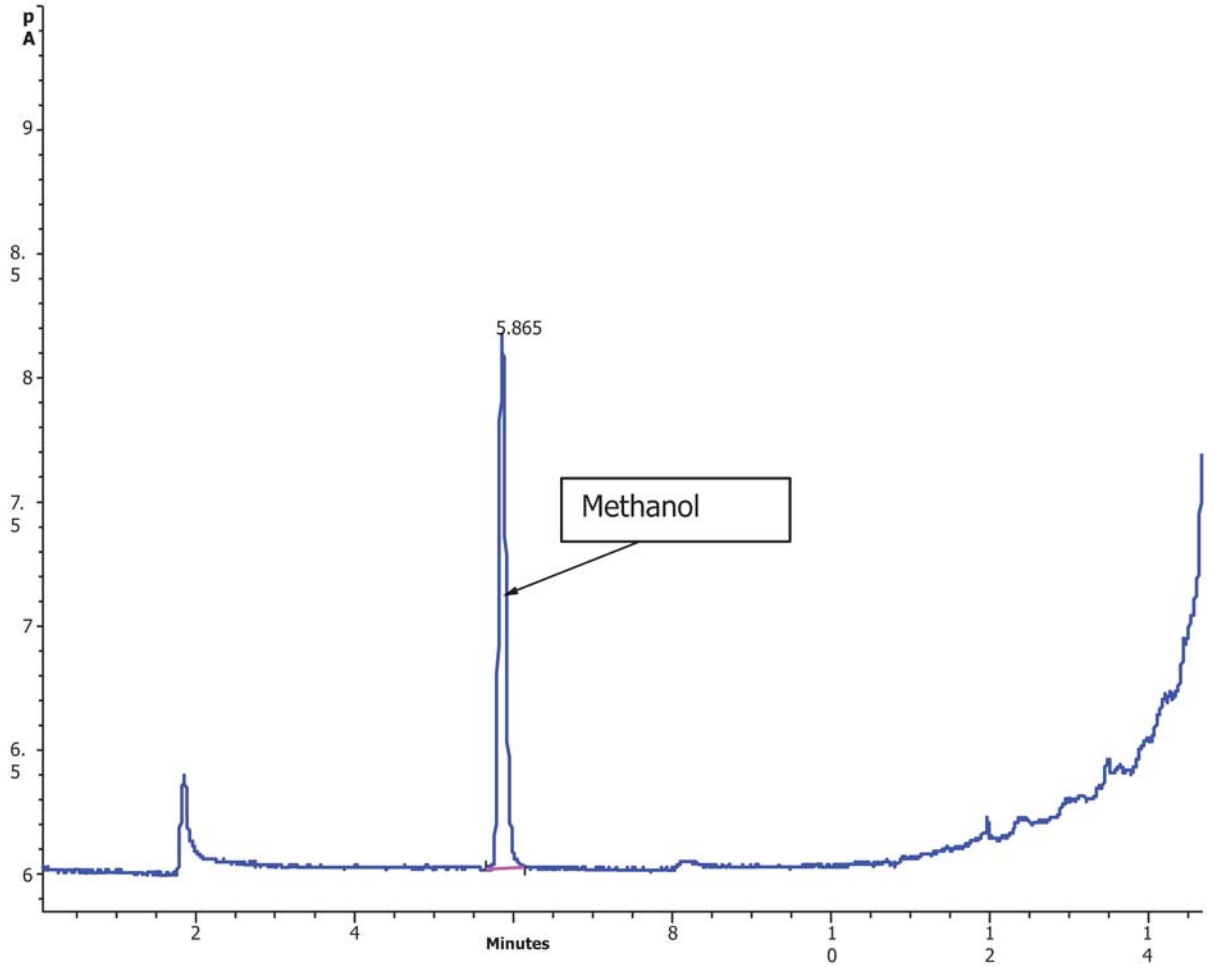

FIG. 1 Reference Chromatogram

some chromatographic processing software is available, this step can be automated to produce the calibration curve.

10. Procedure

10.1 Set the instrument to the operating conditions specified in Table 1. Weigh to the nearest 0.1 mg approximately 1.0 g of the glycerin sample directly into a clean 100-mL volumetric flask and record the weight. Dilute to the mark with Specification D1193 Type II water, cap, and mix well. Prepare another glycerin sample in the same manner so that the sample is analyzed in duplicate. Pipette 1.0 mL of Specification D1193 Type II water and 5.0 mL of the sample solution into a 20-mL headspace vial and cap tightly.[5]

10.2 If using a manual injection technique, place the first sample vial into an 80°C forced-air oven and allow to incubate for 20 min. Also place the 1-mL syringe into the oven to become equilibrated with the sample vial. When the time has elapsed, remove the syringe using heat-resistant gloves. Remove the sample vial and insert the syringe needle into the vial through the septa. Withdraw the headspace gas up past the 1-mL mark and inject back into the vial. Repeat this two more times. Withdraw the headspace gas again up past the 1-mL mark and allow the pressure in the syringe to equilibrate for 5 s before bringing the plunger down to the 1.0-mL mark. Withdraw the syringe from the vial and immediately inject the headspace sample into the GC and press the start button on the GC front panel. If using an automated headspace sampling system, inject 1.0 mL of each of the samples (after the 20-min incubation time at 80°C) to obtain a chromatogram (see Fig. 1) and peak integration report. Review the integration of the methanol peak to make sure it was integrated properly. If not, reintegrate the peak manually to obtain the peak area.

11. Calculation or Interpretation of Results

11.1 After identifying the methanol peak in the chromatograms (by retention time) and obtaining the properly integrated peaks, use the slope and *b*-intercept of the calibration curve to calculate the mass of methanol in the unknowns. Divide the mass of methanol by the mass of sample in grams (approximately 0.05 g) to obtain the final result in parts per million (ppm). Report the average from the duplicate samples. If some chromatographic processing software is available, this step can be automated to calculate the final results.

11.2 *Example:*

$$\textit{Weight of sample}: 1.0511\ g/100\ mL = 0.010\ 511\ g/mL$$
$$\textit{Calibration formula}: y = 0.0892x + 0.1128\ (y = mx + b)$$
$$\textit{Area of methanol peak} = 13.0$$
$$x = [(13.0 - 0.1128)/0.0892)/(0.010\quad 511 \cdot 5\quad mL$$

TABLE 2 Residual Methanol (ppm)

Material	Number of Data Sets Contributing to Precision Calculations	Average, $\bar{\chi}$	Repeatability Standard Deviation, s_r	Reproducibility Standard Deviation, s_R	Repeatability Limit, r	Reproducibility Limit, R
5441.72-A	7	0.0	0.0	0.0	0.0	0.0
5441.72-B	7	734.7	20.6	99.0	57.6	277.1
5441.72-C	6	1146.3	64.8	145.2	181.5	406.7

$$x = 2749 - ppm\ methanol\ (0.27\ \%\ methanol)$$

12. Precision and Bias

12.1 *Precision*—The precision of this test method is based on an interlaboratory study conducted in 2010. A total of seven laboratories participated in this study, testing samples of three different glycerin samples for residual methanol content. Each test result reported represents an individual determination, and all participants were asked to report duplicate test results for material. Practice E691 was followed for the design and analysis of the data; the details are given in RR:D15-1029.[6]

12.1.1 *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.

12.1.1.1 Repeatability limits are listed in Table 2.

12.1.2 *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.

12.1.2.1 Reproducibility limits are listed in Table 2.

12.1.3 The above terms (*repeatability limit* and *reproducibility limit*) are used as specified in Practice E177.

12.1.4 Any judgment made in accordance with statements 12.1.1 and 12.1.2 would have an approximate 95 % probability of being correct.

12.2 *Bias*—As there were no certified reference materials tested as part of this study, no statement on bias is being made.

12.3 The precision statement was determined through statistical examination of 40 test results, submitted by seven laboratories, measuring residual methanol in three glycerin samples.

12.3.1 The three materials were described as follows:

Material 1	99.5% glycerin, no spike
Material 2	99.5% glycerin, spiked with 805 ppm methanol
Material 3	99.5% glycerin, spiked with 1097 ppm methanol

12.4 To judge the equivalency of two test results, it is recommended to choose the material that is closest in characteristics to the test material.

13. Keywords

13.1 gas chromatography; glycerin; headspace; methanol

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D15-1029.