



Standard Test Method for Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography¹

This standard is issued under the fixed designation D7576; 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 benzene and total aromatics in finished denatured fuel ethanol by gas chromatography.

1.2 Total aromatics are determined by adding the concentrations of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, and C₉ and heavier aromatics.

1.3 The aromatic hydrocarbons are separated without interferences from other hydrocarbons in denatured fuel ethanol. Nonaromatic hydrocarbons having boiling point greater than that of *n*-dodecane can cause interferences with the determination of the C₉ and heavier aromatics. For the C₈ aromatics, *p*-xylene and *m*-xylene co-elute while ethylbenzene and *o*-xylene are separated. The C₉ and heavier aromatics are determined as a single group.

1.4 This test method covers the following concentration ranges: benzene, 0.01 % to 0.08 % by mass and total aromatics, 0.29 % to 2.67 % by mass.

1.5 Results are reported to the nearest 0.01 % by mass or liquid volume.

1.6 The values stated in SI units are to be regarded as standard.

1.6.1 *Exception*—The values given in parentheses are provided for information only; they may not be exact equivalents.

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.*

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 April 1, 2016. Published April 2016. Originally approved in 2010. Last previous edition approved in 2010 as D7576 – 10. DOI: 10.1520/D7576-16.

2. Referenced Documents

2.1 *ASTM Standards*:²

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C₉ and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions of Terms Specific to This Standard*:

3.1.1 *1,2,3-tris-2-cyanoethoxypropane (TCEP)*—polar gas chromatographic liquid phase.

3.1.2 *aromatic, n*—any organic compound containing a benzene ring.

3.1.3 *low-volume connector, n*—special union for connecting two lengths of narrow bore tubing 1.6 mm (0.06 in.) outside diameter and smaller; sometimes this is referred to as zero dead volume union.

3.1.4 *narrow bore tubing*—tubing used to transfer components prior to or after separation; usually 0.5 mm (0.02 in.) inside diameter and smaller.

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

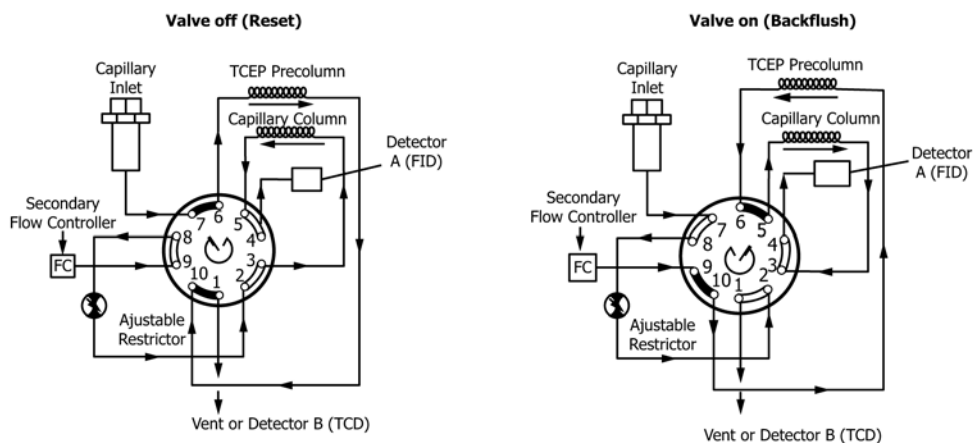


FIG. 1 Valve Diagram, Aromatics in Denatured Fuel Ethanol

3.1.5 *split ratio*—in capillary gas chromatography, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column, expressed by:

$$\text{split ratio} = (S + C)/C \quad (1)$$

where:

S = flow rate at the splitter vent, and

C = flow rate at the column outlet.

3.1.6 *wall-coated open tubular (WCOT)*—type of capillary column prepared by coating the inside wall of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 A two-column chromatographic system equipped with a column switching valve and a flame ionization detector is used. A reproducible volume of sample containing an appropriate internal standard, such as 2-hexanone, is injected onto a precolumn containing a polar liquid phase (TCEP). The C_9 and lighter nonaromatics are vented to the atmosphere as they elute from the precolumn. A thermal conductivity detector may be used to monitor this separation. The TCEP precolumn is backflushed immediately before the elution of benzene, and the remaining portion of the sample is directed onto a second column containing a nonpolar liquid phase (WCOT). Benzene, toluene, and the internal standard elute in the order of their boiling points and are detected by a flame ionization detector. Immediately after the elution of the internal standard, the flow through the nonpolar WCOT column is reversed to backflush the remainder of the sample (C_8 and heavier aromatics plus C_{10} and heavier nonaromatics) from the column to the flame ionization detector.

4.2 The analysis is repeated a second time allowing the C_{12} and lighter nonaromatics, benzene and toluene to elute from the polar TCEP precolumn to vent. A thermal conductivity detector may be used to monitor this separation. The TCEP precolumn is backflushed immediately prior to the elution of ethylbenzene and the remaining aromatic portion is directed into the WCOT column. The internal standard and C_8 aromatic components elute in the order of their boiling points and are detected by a flame ionization detector. Immediately after *o*-xylene has eluted, the flow through the nonpolar WCOT

column is reversed to backflush the C_9 and heavier aromatics to the flame ionization detector.

4.3 From the first analysis, the peak areas of benzene, toluene, and the internal standard (2-hexanone) are measured and recorded. Peak areas for ethylbenzene, *p/m*-xylene, *o*-xylene, the C_9 and heavier aromatics, and internal standard are measured and recorded from the second analysis. The backflush peak eluting from the WCOT column in the second analysis contains only C_9 and heavier aromatics.

4.4 The flame ionization detector response, proportional to the concentration of each component, is used to calculate the amount of aromatics that are present with reference to the internal standard.

5. Significance and Use

5.1 Regulations in some jurisdictions, such as California, limit the concentration of benzene and total aromatic content of denatured fuel ethanol in order to reduce the ozone reactivity and toxicity of automotive evaporative and exhaust emissions. Results from this test method may be used to assess product quality and to meet new fuel regulations.

6. Apparatus

6.1 *Chromatographic System*—See Practice E355 for specific designations and definitions. Refer to Fig. 1 for a diagram of the system.

6.1.1 *Gas Chromatograph (GC)*—Capable of operating at the conditions given in Table 1, and having a column switching and backflushing system equivalent to Fig. 1. Carrier gas pressure and flow control devices shall be capable of precise control when column head pressures and flow rates are low.

6.1.2 *Sample Introduction System*—Capable of introducing a representative sample into the gas chromatographic inlet. Microliter syringes and automatic syringe injectors have been used successfully.

6.1.3 *Inlet System (Splitting Type)*—Split injection is necessary to maintain the actual chromatographed sample size within the limits required for optimum column efficiency and detector linearity.

TABLE 1 Typical Chromatographic Operating Parameters 130

Temperatures	
Injection port (split injector)	200 °C
FID (Detector A)	250 °C
TCD (Detector B)	200 °C
Nonpolar WCOT capillary	
Initial	60 °C (6 min)
Program rate	2 °C/min
Final	115 °C (hold until all components elute)
Polar TCEP precolumn (temperature to remain constant before time to BACKFLUSH, T1 or T2. Do not exceed maximum operating temperature.)	60 °C or same as nonpolar WCOT capillary if TCEP/WCOT columns contained in identical heated zone.
Valve	>115 °C or same as nonpolar WCOT capillary if valve and WCOT column contained in identical heated zone.
Flows and Conditions	
Carrier gas	helium
Flow to TCEP precolumn (split injector)	10 mL/min
Flow to WCOT capillary (auxiliary flow)	10 mL/min
Flow from split vent	100 mL/min
Detector gases	as necessary
Split ratio	11:1
Sample size	1 µL

6.1.3.1 Some gas chromatographs are equipped with on-column injectors and autosamplers which can inject submicrolitre sample sizes. Such systems can be used provided that column efficiency and detector linearity are comparable to systems with split injection.

6.1.4 *Detector*—A flame ionization detector (Detector A) is employed for quantitation of components eluting from the WCOT column. The flame ionization detector used for Detector A shall have sufficient sensitivity and stability to detect 0.01 volume % of an aromatic compound.

6.1.4.1 It is strongly recommended that a thermal conductivity detector be placed on the vent of the TCEP precolumn (Detector B). This facilitates the determination of valve BACKFLUSH and RESET times (10.5) and is useful for monitoring the separation of the polar TCEP precolumn.

6.1.5 *Switching and Backflushing Valve*—To be located within a temperature-controlled heated zone and capable of performing the functions in accordance with Section 10, and illustrated in Fig. 1. The valve shall be of low internal volume design and not contribute significantly to deterioration of chromatographic resolution.

6.1.5.1 A 10-port valve with 1.6 mm (0.06 in.) outside diameter fittings is recommended for this test method. Alternately, and if using columns of 0.32 mm inside diameter or smaller, a valve with 0.8 mm (0.03 in.) outside diameter fittings should be used.

6.1.5.2 Some gas chromatographs are equipped with an auxiliary oven which can be used to contain the valve. In such a configuration, the valve can be kept at a higher temperature than the polar and nonpolar columns to prevent sample condensation and peak broadening. The columns are then located in the main oven and the temperature can be adjusted for optimum aromatic resolution.

6.2 Data Acquisition System:

6.2.1 *Integrator or Computer*—Capable of providing real-time graphic and digital presentation of the chromatographic data is recommended for use. Peak areas and retention times can be measured by computer or electronic integration.

6.2.1.1 It is recommended that this device be capable of performing multilevel internal-standard-type calibrations and

be able to calculate the correlation coefficient (r^2) and linear least square fit equation for each calibration data set in accordance with 11.4.

6.3 Two Chromatographic Columns:

6.3.1 *Polar Precolumn*—To perform a pre-separation of the aromatics from nonaromatic hydrocarbons in the same boiling point range. Any column with equivalent or better chromatographic efficiency and selectivity in accordance with 6.3.1.1 can be used.

6.3.1.1 *TCEP Micro-Packed Column*—560 mm (22 in.) by 1.6 mm ($1/16$ in.) outside diameter by 0.76 mm (0.030 in.) inside diameter stainless steel tube packed with 0.14 g to 0.15 g of 20 % (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW). This column was used in the cooperative study to provide the precision and bias data referred to in Section 16.

6.3.2 *Nonpolar (Analytical) Column*—Any column with equivalent or better chromatographic efficiency and selectivity in accordance with 6.3.2.1 can be used.

6.3.2.1 *WCOT Methyl Silicone Column*—30 m long by 0.53 mm inside diameter fused silica WCOT column with a 5.0 µm film thickness of cross-linked methyl siloxane.

6.4 *Compatibility with D5580*—An instrument configured to run Test Method D5580 can be used for this test method with no modification of hardware or columns.

7. Reagents and Materials

7.1 *Carrier Gas*—Appropriate to the type of detector used. Helium has been used successfully. The minimum purity of the carrier gas used must be 99.95 mol %. Additional purification may be necessary to remove trace amounts of oxygen. (**Warning**—Helium is usually supplied as a compressed gas under high pressure.)

7.2 *Methylene Chloride*—Used for column preparation. Reagent grade, free of nonvolatile residue. (**Warning**—Harmful when ingested or inhaled at high concentrations.)

7.3 *2,2,4-Trimethylpentane (Isooctane)*—Used as a solvent in the preparation of the calibration mixture. Reagent grade. (**Warning**—Isooctane is flammable and can be harmful or fatal when ingested or inhaled.)