Designation: D7576 – 16

Standard Test Method for Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography[1]

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 C_9 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 C_9 and heavier aromatics. For the C_8 aromatics, *p*-xylene and *m*-xylene co-elute while ethylbenzene and *o*-xylene are separated. The C_9 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.*

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, C_9 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.

[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**

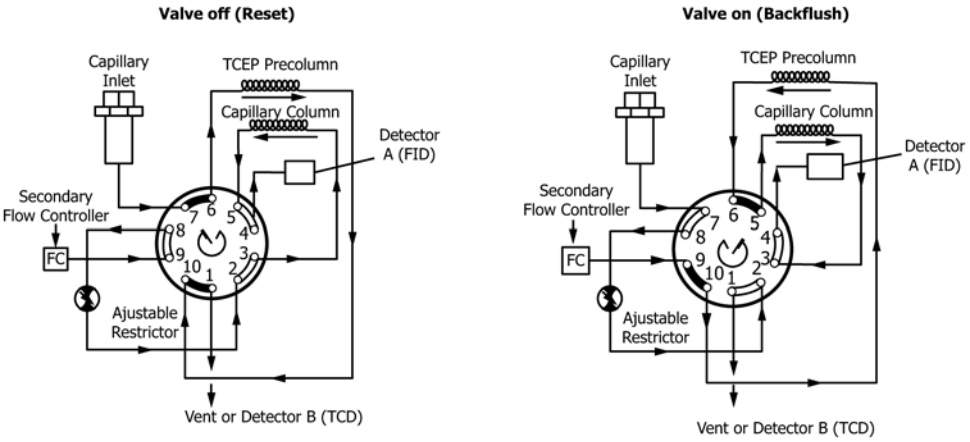

FIG. 1 Valve Diagram, Aromatics in Denatured Fuel Ethanol

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:

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

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.)

7.4 *Standards for Calibration and Identification*—Required for all components to be analyzed and the internal standard. Standards are used for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed. (**Warning—**These materials are flammable and may be harmful or fatal when ingested or inhaled.)

8. Preparation of Columns

8.1 *TCEP Column Packing:*

8.1.1 Use any satisfactory method that will produce a column capable of retaining aromatics from nonaromatic components of the same boiling point range in a denatured fuel ethanol sample. The following procedure has been used successfully.

8.1.2 Completely dissolve 10 g of TCEP in 100 mL of methylene chloride. Next add 40 g of 80/100 mesh Chromosorb P(AW) to the TCEP solution. Quickly transfer this mixture to a drying dish, in a fume hood, without scraping any of the residual packing from the sides of the container. Constantly, but gently, stir the packing until all of the solvent has evaporated. This column packing can be used immediately to prepare the TCEP column.

8.2 *Micro-packed TCEP Column:*

8.2.1 Wash a straight 560 mm (22 in.) length of 1.6 mm (1⁄16 in.) outside diameter, 0.76 mm (0.030 in.) inside diameter stainless steel tubing with methanol and dry with compressed nitrogen.

8.2.2 Insert 6 to 12 strands of silvered wire, a small mesh screen or stainless steel frit inside one end of the tube. Slowly add 0.14 g to 0.15 g of packing material to the column and gently vibrate to settle the packing inside the column. Insert silvered wire, mesh screen, or frit to the other end of the tube to prevent the packing material from falling. When strands of wire are used to retain the packing material inside the column, leave 6.0 mm (0.25 in.) of space at the top of the column.

8.3 *WCOT Methyl Silicone Column*—It is suggested that this column be purchased directly from a suitable capillary column manufacturer (see 6.3.2.1).

9. Sampling

9.1 Ensure that the sample is representative of the source from which it is taken. Follow the recommendations of Practice D4057, or its equivalent, when obtaining samples from bulk storage or pipelines.

9.2 Take appropriate steps to minimize the loss of light hydrocarbons from the denatured fuel ethanol sample to be analyzed. Upon receipt in the laboratory, chill the sample in its original container from 0 °C to 5 °C (32 °F to 40 °F) before and after sub-sampling is performed.

9.3 If necessary, transfer the chilled sample to a vapor tight container and store at 0 °C to 5 °C (32 °F to 40 °F) until needed for analysis.

10. Preparation of Apparatus

10.1 *Assembly*—Connect the TCEP and WCOT column to the valve system (Fig. 1) using low-volume connectors and narrow bore tubing. It is important to minimize the volume of the chromatographic system that comes in contact with the sample, otherwise peak broadening will occur.

10.2 *Initial Operating Conditions*—Adjust the operating conditions to those listed in Table 1, but do not turn on the detector circuits. Check the system for leaks before proceeding further.

10.2.1 If different polar and nonpolar columns are used, or WCOT capillary columns of smaller inner diameter or different film thickness, or both, are used, it may be necessary to use different optimum flows and temperatures.

10.2.2 Conditions listed in Table 1 are applicable to the columns described in 6.3. If a WCOT column of a different film thickness is used, the conditions chosen for the analysis must sufficiently separate toluene from the internal standard (first analysis) and ethylbenzene from the xylenes (second analysis).

10.3 *Flow Rate (Carrier Gas) Adjustments:*

10.3.1 Attach a flow measuring device to the precolumn vent (or Detector B) with the valve in the RESET or forward flow position and adjust the pressure of the capillary injection port (Fig. 1) to give 10.0 mL/min flow (17 psi to 20 psi). Soap bubble flow meters are suitable. This represents the flow through the polar precolumn.

10.3.2 Attach a flow measuring device to the split injector vent and adjust the flow from the split vent using the flow controller to provide a flow of 100 mL/min. Recheck the column vent flow set in 10.3.1 and adjust, if necessary. The split ratio should be approximately 11:1.

10.3.3 Switch the valve to BACKFLUSH position and adjust the variable restrictor to give the same precolumn vent flow set in 10.3.1. This is necessary to minimize flow changes when the valve is switched.

10.3.4 Switch the valve to the RESET position and adjust the auxiliary flow controller to give a flow of 10 mL/min at the Detector A (FID) exit.

10.4 *Detector Setup*—Depending on the particular type of instrumentation used, adjust the hydrogen, air, and makeup flows to the flame ionization detector and ignite the flame. If a thermal conductivity detector (Detector B) is being used to monitor the vent effluent in the valve RESET position, set the reference flow and turn on the detector circuit.

10.5 *Valve Backflush and Reset Times:*

10.5.1 The time to BACKFLUSH and RESET the valve will vary slightly for each column system and must be determined as described in 10.5.1.1 – 10.5.1.3. The start time of the integrator or computer system and valve timer must be synchronized with the injection to accurately reproduce the backflush time. This procedure assumes that a thermal conductivity detector is installed on the precolumn vent line as Detector B (see 6.1.4.1). If a detector is not available, the appropriate valve BACKFLUSH times, T1 and T2, must be determined experimentally. If the BACKFLUSH times, T1 and T2, are not set correctly (switched too late), it is possible that part of the benzene and ethylbenzene peaks will be vented.

10.5.1.1 Adjust the valve to RESET (forward flow) and inject 1.0 µL of a blend containing approximately 0.5 % each

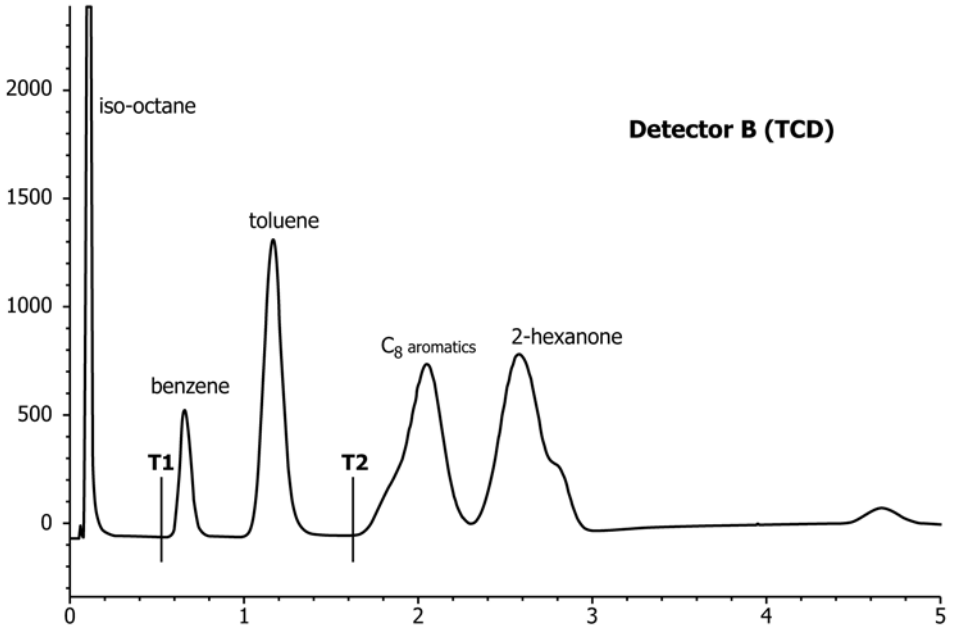

FIG. 2 Determination of Precolumn Backflush Times, T1 and T2

of benzene, ethylbenzene, *o*-xylene, and 2-hexanone in ethanol. This mixture is used to set the valve timing, therefore, the exact concentration need not be known. Alternatively, the calibration mixture can be used for this test. Determine retention time in seconds at which benzene and ethylbenzene start to elute as measured by Detector B. Subtract 6 s from each of these and call these times to BACKFLUSH, T1 and T2, respectively. The correct time for T1 and T2 is just prior to the elution of benzene and ethylbenzene from the TCEP precolumn.

NOTE 1—Fig. 2 is an example chromatogram illustrating the elution of a calibration mixture from the polar precolumn using the procedure described in 10.5.1.1. Times to BACKFLUSH, T1 and T2, are indicated on the chromatogram. The times to BACKFLUSH, T1 and T2, should be optimized for each chromatographic system.

10.5.1.2 Reinject the calibration blend and turn the valve to BACKFLUSH at time T1. When the internal standard peak (2-hexanone) returns to baseline, switch the valve back to RESET (forward flow) position. Call this time T3.

10.5.1.3 Reinject the calibration blend and BACKFLUSH at time T2. When the *o*-xylene peak returns to baseline, switch the valve back to RESET (forward flow). Call this time T4.

10.6 *Polar Precolumn Selectivity Check:*

10.6.1 The selectivity of the polar precolumn is critical to allow for accurate determination of the C_9 and heavier aromatics without non-aromatic interferences. The selectivity must be verified so that for the second analysis, when the time to BACKFLUSH T2 is properly adjusted, all of the C_{12} and lighter nonaromatic hydrocarbons are vented from the polar precolumn while the heavier aromatics are retained. The following test can be used to verify the precolumn performance.

10.6.1.1 Prepare a blend containing approximately 1.5 % *n*-dodecane in 2,2,4-trimethylpentane (isooctane). *n*-Dodecane is used to represent the high boiling nonaromatic hydrocarbons in denatured fuel ethanol. Inject 1.0 µL of the mixture under the conditions specified in 10.2 – 10.5 and actuate the valve at time T2 (BACKFLUSH) and time T4 (RESET). Record the signals from both the flame ionization (Detector A) and thermal conductivity (Detector B) detectors. Verify that *n*-dodecane fully elutes from the polar precolumn before BACKFLUSH time T2. When monitoring the thermal conductivity detector (Detector B), the *n*-dodecane peak should return to baseline before BACKFLUSH time T2. If not, part of the *n*-dodecane peak will be backflushed to the non-polar WCOT column and be detected by the flame ionization detector after the valve RESET time T4. If a thermal conductivity detector is not available on the precolumn vent line, the chromatogram obtained by the flame ionization detector can be used to verify that all the *n*-dodecane is being vented. This chromatogram should not show any significant response from *n*-dodecane after the RESET time T4.

10.6.1.2 If all of the *n*-dodecane peak is not completely vented from the polar precolumn, as measured by the thermal conductivity or flame ionization detector, recheck instrument parameters and valve backflush times (10.5) or replace the polar precolumn. If the valve is contained in a separate isothermal heated zone, it may be necessary to use a higher temperature to prevent absorption of small amounts of *n*-dodecane on the rotor or transfer tubing surfaces.

11. Calibration and Standardization

11.1 *Preparation of Calibration Samples*—Prepare multicomponent calibration standards of benzene, toluene, ethylbenzene, *o*-xylene, and 1,2,4-trimethylbenzene at concentrations of interest by mass in accordance with Practice D4307. *o*-Xylene is used to represent the xylenes while 1,2,4-trimethylbenzene is used for the C_9 and heavier aromatics. For each aromatic component, use at least five calibration points and ensure that the concentration of each aromatic component

TABLE 2 Physical Constants

Component	Relative Density (15.56/15.56 °C)[A]
Benzene	0.8845
Toluene	0.8719
Ethylbenzene	0.8717
p/m-Xylene	0.8679
o-Xylene	0.8848
1,2,4-Trimethylbenzene	0.8806
C_9 plus aromatics	0.8764
2-hexanone	0.8162

[A] STP 109A, *Physical Constants of Hydrocarbons C 1–C10*, ASTM International, West Conshohocken, PA. The mixed xylene (*p/m*-xylene) density based upon a 1:3 ratio of *p*-xylene to *m*-xylene. C_9 plus aromatics based upon the average relative density values of the 30 C_9-C_{10} aromatics.

is within its calibration range. For benzene, calibration concentrations of 0.02, 0.04, 0.06, 0.08, and 0.10 volume percent can be used. For toluene and 1,2,4-trimethylbenzene: 0.05, 0.10, 0.20, 0.40, and 0.60 volume percent. For ethylbenzene and *o*-xylene: 0.02, 0.05, 0.10, 0.15, and 0.20 volume percent can be used. The relative densities listed in Table 2 shall be used as a guide in determining the proper mass of aromatic components that need to be added in order to arrive at a target volume percent concentration.

11.2 Before preparing the standards, determine the purity of the aromatics by capillary GC and make corrections for the impurities found. Whenever possible, use stocks of at least 99.9 % purity.

11.3 Prepare standards by transferring a fixed volume of aromatic component using pipettes, eye droppers, or syringes to 100 mL volumetric flasks or 100 mL septum-capped vials as follows. Cap and record the tare weight of the volumetric flask or vial to 0.1 mg. Remove the cap and carefully add the aromatic components to the flask or vial starting with the least volatile (1,2,4-trimethylbenzene). Cap the flask and record the net mass (*Wi*) of the aromatic component added to 0.1 mg. Repeat the addition and weighing procedure for each aromatic component. Do not exceed 5 volume % for all aromatics added. Similarly, add 1 mL of the internal standard, 2-hexanone, and record its net mass (*Ws*) to 0.1 mg. Dilute each standard to the mark with aromatics free ethanol. Store the capped calibration standards in a refrigerator at 0 °C to 5 °C (32 °F to 40 °F) when not in use.

11.4 *Calibration Procedure*—With the valve initially in the RESET mode, chromatograph each of the calibration mixtures (11.1) twice using valve timing procedures in accordance with 10.5. For the first analysis, use times T1 (BACKFLUSH) and T3 (RESET) to actuate the valve. For the second analysis, use times T2 (BACKFLUSH) and T4 (RESET) to actuate the valve.

NOTE 2—The first analysis is used to calibrate the gas chromatograph for benzene and toluene. The second analysis is used to calibrate for ethylbenzene, the xylenes (*o*-xylene), and the C_9 and heavier aromatics (1,2,4-trimethylbenzene).

11.4.1 *Linearity Test*—Analyze the calibration standards in accordance with the procedure in 11.4. Measure the peak areas of benzene, toluene, and internal standard peaks from the first analysis. From the second analysis measure the peak areas of internal standard, ethylbenzene, *o*-xylene, and 1,2,4-trimethylbenzene. Determine the response ratio (rsp_i) and amount ratio (amt_i) for each component in each standard using Eq 2 and Eq 3.

$$rsp_i = (Ai/As) \tag{2}$$

where:

Ai = area of aromatic component, and
As = area of internal standard.

$$amt_i = (Wi/Ws) \tag{3}$$

where:

Wi = mass of aromatic component, and
Ws = mass of internal standard.

11.4.1.1 Prepare a calibration curve for each aromatic component by plotting the response ratios (rsp_i), as the *y*-axis, versus the amount ratios (amt_i), as the *x*-axis. Fig. 3 is an example of such a plot.

11.4.1.2 Calculate the correlation coefficient r^2 value for each aromatic component in the calibration using Eq 4. The r^2 value should be at least 0.980 or greater. If the above criteria for r^2 is not met, rerun the calibration or check instrument parameters and hardware.

$$r^2 = \frac{(\sum xy)^2}{(\sum x^2)(\sum y^2)} \tag{4}$$

where:

$$x = X_i - \bar{x} \tag{5}$$

$$y = Y_i - \bar{y} \tag{6}$$

and:

X_i = amt_i ratio data point,
$\bar{x}$ = average values for all amt_i data points,
Y_i = corresponding rsp_i ratio data point, and
$\bar{y}$ = average values for all rsp_i data points,

11.4.1.3 Table 3 gives an example on the calculation of r^2 for an ideal data set.

11.4.2 *Linear Least Square Fit*—For each aromatic *i* calibration data set, obtain the linear least square fit equation in the form:

$$(rsp_i) = (m_i)(amt_i) + b_i \tag{7}$$

where:

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

11.4.2.1 The values m_i and b_i are calculated as follows:

$$m_i = \sum xy / \sum x^2 \tag{8}$$

and

$$b_i = \bar{y} - m_i \bar{x} \tag{9}$$

11.4.2.2 For the example in Table 3:

$$m_i = 5/10 = 0.5 \tag{10}$$

and

$$b_i = 1.5 - (0.5)(3) = 0 \tag{11}$$

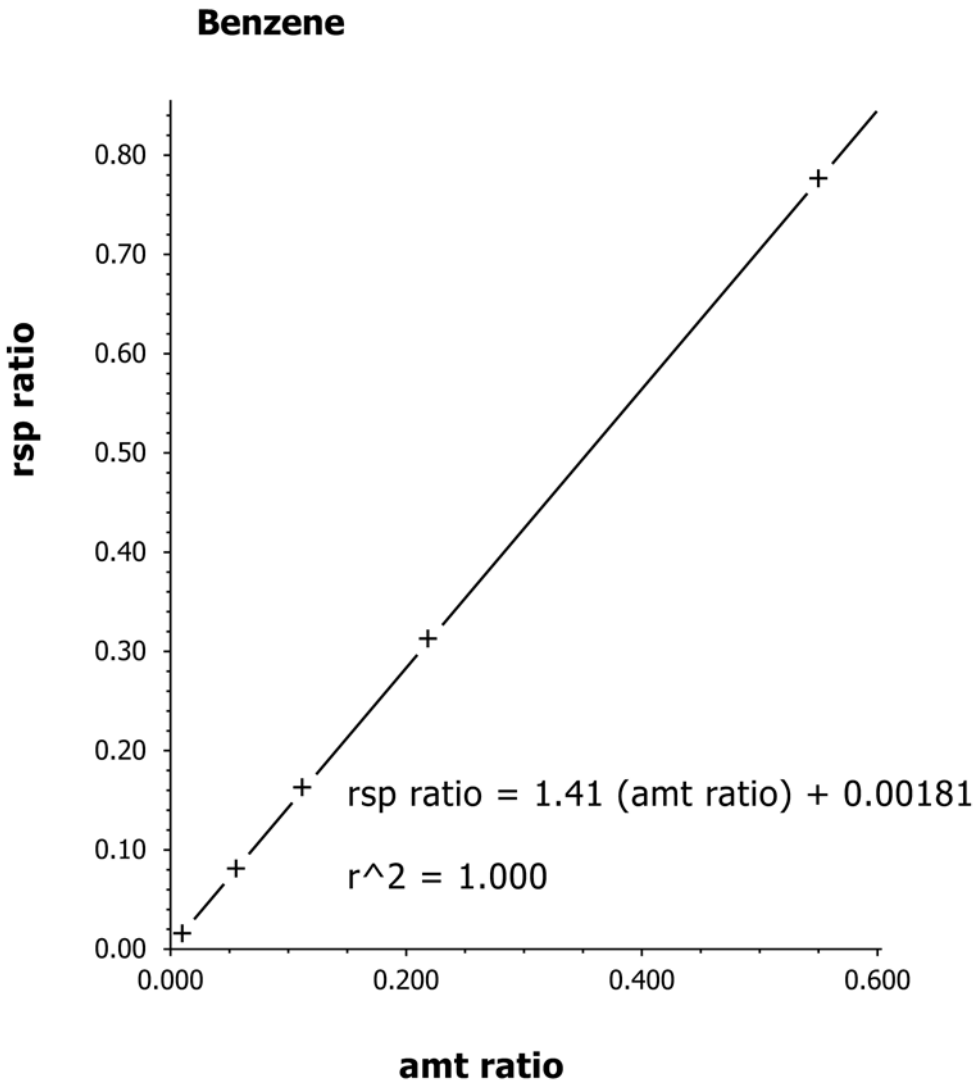

FIG. 3 Typical Benzene Calibration Curve

TABLE 3 Example of Data Set for r^2 Calculation[A]

X_i	Y_i	$x = Xi - \bar{x}$	$y = Yi - \bar{y}$	xy	x^2	y^2
1.0	0.5	–2.0	1.0	2.0	4.0	1.0
2.0	1.0	–1.0	–0.5	0.5	1.0	0.25
3.0	1.5	0.0	0.0	0.0	0.0	0.0
4.0	2.0	1.0	0.5	0.5	1.0	0.25
5.0	2.5	2.0	0.0	2.0	4.0	1.0

[A] $\bar{x} = 3$

$\bar{y} = 1.5$

$(\sum xy)^2 = 25.0$

$\sum x^2 = 10.0$

$\sum y^2 = 2.5$

$$r^2 = \frac{(\sum x \cdot y)^2}{(\sum x^2) \cdot (\sum y^2)}$$

$$r^2 = \frac{25.0}{(10.0)(2.5)} = 1.0$$

11.4.2.3 Therefore, the least square equation (Eq 7) for the example in Table 3 is:

$$(rsp_i) = 0.5(amt_i) + 0 \quad (12)$$

NOTE 3—Normally the b_i value is not zero and can be positive or negative. Fig. 3 gives an example of linear least square fit for benzene and the resulting equation in the form of Eq 7.

12. Column Conditioning

12.1 Both the TCEP and WCOT columns are to be briefly conditioned before use. Connect the columns to the valve (see Fig. 1 and 10.1) in the chromatographic oven. Adjust the carrier gas flows in accordance with 10.3 and place the valve in the RESET position. After several minutes, increase the column oven temperature to 120 °C and maintain these conditions for 20 min. Cool the columns below 60 °C before shutting off the carrier gas.

13. Procedure

13.1 *Preparation of Sample*—Transfer 0.1 mL of internal standard (*Ws*) by way of a volumetric pipette into a tared and capped 10 mL volumetric flask or capped vial. Record the net mass of the internal standard added to the nearest 0.1 mg. Retare the capped flask or vial. Fill the volumetric flask or vial with 9.9 mL of chilled sample, cap, and record the net mass (*Wg*) of the sample added. Mix thoroughly. If using an automatic sampler then transfer an aliquot of the solution into

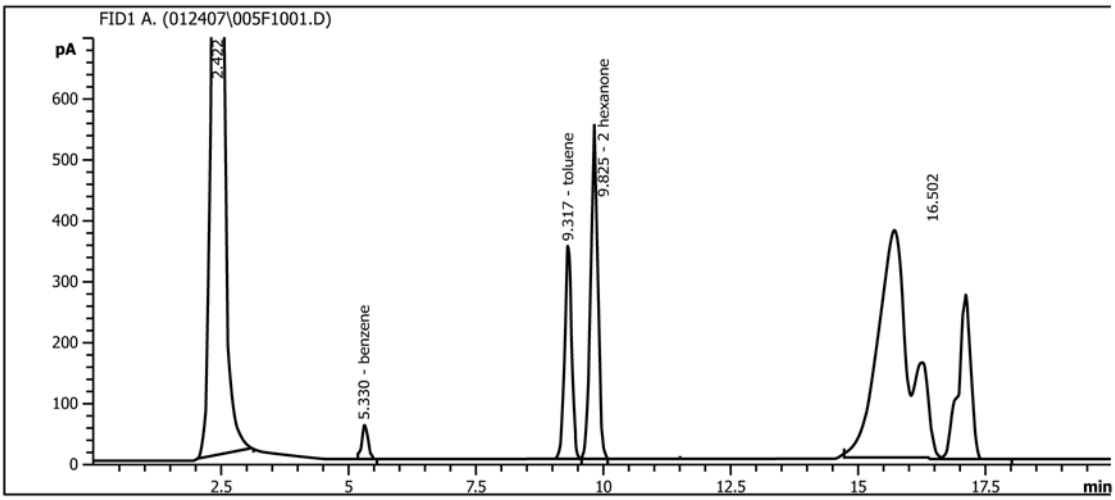

FIG. 4 Aromatics in Denatured Fuel Ethanol, Analysis No. 1

a glass GC vial. Seal the GC vial with a TFE-fluorocarbon-lined cap. If the sample is not immediately analyzed, store at 0 °C to 5 °C (32 °F to 40 °F).

13.2 *Chromatographic Analysis*—Introduce an aliquot of the sample, containing internal standard, into the gas chromatograph using the same technique and sample size as used for the calibration analysis. An injection volume of 1 µL with an 11:1 split ratio has been used successfully. Chromatograph the sample twice using valve timing procedures in accordance with 10.5. Use times T1 and T3 for the first analysis to BACK-FLUSH and RESET the valve. Use times T2 and T4 for the second analysis.

13.3 *Interpretation of Chromatogram*—Compare the retention times of sample components to those of the calibration analysis to determine the identities of the aromatics. Identify benzene, toluene, and the internal standard from the first analysis. Identify the internal standard, ethylbenzene, *p/m*-xylene, *o*-xylene, C_9 and heavier aromatic composite from the second analysis. Refer to Fig. 4 and Fig. 5 for sample chromatograms.

NOTE 4—Denatured fuel ethanols containing styrene will have an additional peak in the chromatogram. Styrene elutes just before *o*-xylene; the two peaks are partially, but not baseline, resolved. If quantitation of styrene is desired, use the *o*-xylene calibration.

14. Calculation

14.1 *Mass Concentration of Aromatics*—After identifying the peaks, measure the areas of benzene, toluene, and the internal standard from the first analysis and the internal standard, ethylbenzene, *p/m*-xylene, *o*-xylene, C_9 and heavier aromatics from the second analysis. Using the slope and *y*-intercept of the least square fit calibrations in 11.4.2, calculate the mass of each aromatic component (*Wi*) in the denatured fuel ethanol samples using the response ratio (rsp_i) of the areas of the aromatic component to the internal standard as follows:

$$Wi = \left[\left(\frac{Ai}{As} - b_i \right) / m_i \right] Ws \quad (13)$$

where:

Wi = mass of aromatic component *i*,
Ai = area of aromatic component *i*,
As = area of internal standard, and
Ws = mass of internal standard added.

14.1.1 To obtain mass percent (w_i) results for each component:

$$w_i = \frac{Wi(100)}{Wg} \quad (14)$$

where:

Wg = mass of denatured fuel ethanol sample.

14.1.2 To obtain the total mass percent aromatics, sum the mass percent (w_i) results of all the individual aromatic components *i*.

14.2 *Volumetric Concentration of Aromatic Components*—If the volumetric concentration of each aromatic component *i* is desired, calculate the volumetric concentration in accordance with Eq 15:

$$v_i = w_i \left(\frac{D_f}{D_i} \right) \quad (15)$$

where:

v_i = volume percent of each aromatic component to be determined,
D_f = relative density of the denatured fuel ethanol under study as determined in accordance with Test Method D1298 or Test Method D4052, and
D_i = relative density at 15.56°C (60°F) of the individual aromatics (Table 2).

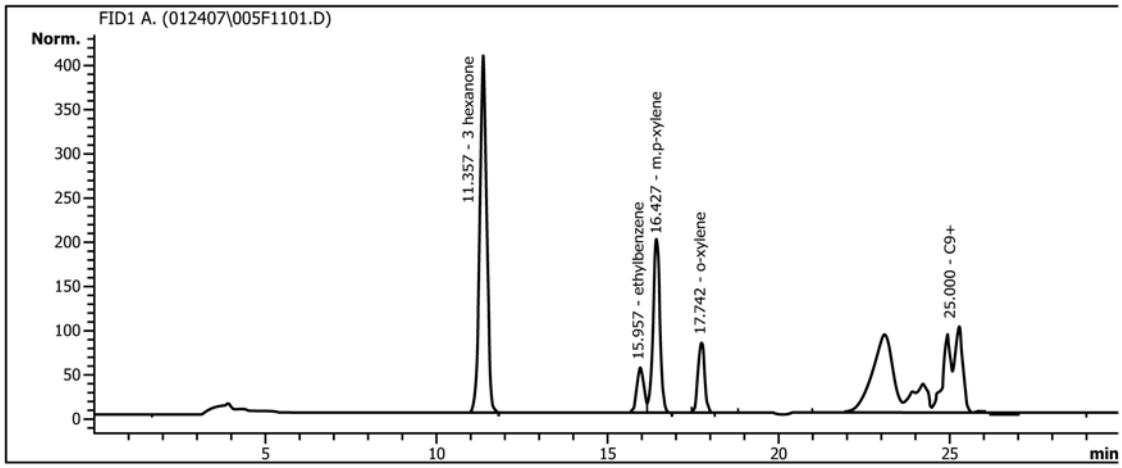

FIG. 5 Aromatics in Denatured Fuel Ethanol, Analysis No. 2

14.2.1 To obtain total volume percent aromatics, sum the volume percent (v_i) results of all the individual aromatic components *i*.

15. Report

15.1 Report the mass percent results of benzene and total aromatics to the nearest 0.01 and reference this test method. See 14.1.

15.2 Report the volume percent results of benzene and total aromatic components to the nearest 0.01 and reference this test method. See 14.2.

16. Precision and Bias[3]

16.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory test reports is as follows:

NOTE 5—The following precision data were developed in a 2015 interlaboratory cooperative test program. Participants analyzed sample sets comprised of ten types of denatured fuel ethanol with blinded replicates. The benzene content ranged from 0.00 to 0.08 % by mass nominal and the total aromatic content ranged from 0.29 to 2.67 % by mass nominal. A total of seven laboratories participated. The degrees of freedom associated with the reproducibility estimate from this round robin study are 5 for benzene and 9 for total aromatics. Since the minimum requirement of 30 (in accordance with Practice D6300) is not met, users are cautioned that the actual repeatability/reproducibility may be significantly different than these estimates. Practice D6300 does not recommend publishing precision estimates with degrees of freedom less than 15 as the reliability of such estimates is highly questionable. However, this test method is a regulatory requirement in California. A new interlaboratory study will be performed in the future in order to generate an improved precision statement.

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1829. Contact ASTM Customer Service at service@astm.org.

TABLE 4 Repeatability Estimates for Aromatics in Denatured Fuel Ethanol

Component	Range, (mass %)	Repeatability (X = mass %)
Benzene	0.01–0.08	0.0014
Total aromatics	0.29–2.67	$0.0308(X^{1.185})$

TABLE 5 Reproducibility Estimates for Aromatics in Denatured Fuel Ethanol

Component	Range, (mass %)	Reproducibility (X = mass %)
Benzene	0.01–0.08	0.142(X + 0.03)
Total aromatics	0.29–2.67	$0.444(X^{1.185})$

16.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method exceed the following values in only one case in twenty. See Table 4.

16.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material, would in the long run, exceed the following values in one case in twenty. See Table 5.

16.1.3 *Bias*—Since there is no accepted reference material suitable for determining bias for the procedure in this test method, no statement of bias is being made.

17. Keywords

17.1 aromatics; benzene; denatured fuel ethanol; ethylbenzene; gas chromatography; toluene; xylenes

SUMMARY OF CHANGES

Subcommittee D02.40 has identified the location of selected changes to this standard since the last issue (D7576 – 10) that may impact the use of this standard. (Approved April 1, 2016.)

(1) Revised Section 16.