Designation: ~~D5580 – 15 (Reapproved 2020)~~ D5580 – 21

Standard 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[1]

This standard is issued under the fixed designation D5580; 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~~ Scope*

1.1 This test method covers the determination of benzene, toluene, ethylbenzene, the xylenes, C_9 and heavier aromatics, and total aromatics in finished motor gasoline by gas chromatography.

1.2 The aromatic hydrocarbons are separated without interferences from other hydrocarbons in finished gasoline. Nonaromatic hydrocarbons having a boiling point greater than *n*-dodecane may 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.

1.3 This test method covers the following concentration ranges, in liquid volume %, for the preceding aromatics: benzene, 0.1 % to 5 %; toluene, 1 % to 15 %; individual C_8 aromatics, 0.5 % to 10 %; total C_9 and heavier aromatics, 5 % to 30 %, and total aromatics, 10 % to 80 %.

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

1.5 This test method includes a relative bias section for U.S. EPA spark-ignition engine fuel regulations reporting for benzene based on Practice D6708 accuracy assessment between Test Method D5580 and Test Method D3606 as a possible Test Method D5580 alternative to Test Method D3606. The Practice D6708 derived correlation equation is only applicable for fuels in the benzene concentration range from 0.0 % to 2.31 % by volume as measured by Test Method D5580. The applicable Test Method D3606 range for benzene is from 0.0 % to 2.38 % by volume as reported by Test Method D3606.

1.6 This test method includes a relative bias section for U.S. EPA spark-ignition engine fuel regulations for total aromatics reporting based on Practice D6708 accuracy assessment between Test Method D5580 and Test Method D5769 as a possible Test Method D5580 alternative to Test Method D5769. The Practice D6708 derived correlation equation(s) is only applicable for fuels in the total aromatic concentration range from 5.4 % to 31.6 % by volume as measured by Test Method D5580 and a distillation temperature T_{95}, at which 95 % of the sample has evaporated, as measured by Test Method D86 is in the range of 149.1 °C to 196.6 °C (300.4 °F to 385.9 °F).

1.6.1 The applicable Test Method D5769 range for total aromatics is from 3.7 % to 29.4 % by volume as reported by Test Method

[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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***A Summary of Changes section appears at the end of this standard**

D5769 and the distillation temperature T_{95}, at which 95 % of the sample has evaporated, when tested according to Test Method D86 ranged from 149.1 °C to 196.6 °C (300.4 °F to 385.9 °F).

1.7 This test method includes a relative bias section for spark-ignition engine fuels (gasolines) for benzene reporting based on Practice D6708 accuracy assessment between Test Method D5580 and Test Method D5769 as a possible Test Method D5580 alternative to Test Method D5769. The Practice D6708 derived correlation equation for benzene is applicable in the test method inclusive valid reporting concentration ranges, as determined from Practice D6708 data set and precision working limits of Test Method D5580, from 0.08 % to 2.34 % by volume as measured by Test Method D5580.

1.8 Many of the common alcohols and ethers that are added to gasoline to reduce carbon monoxide emissions and increase octane, do not interfere with the analysis. Ethers such as methyl *tert*-butylether (MTBE), ethyl *tert*-butylether (ETBE), *tert*-amylmethylether (TAME), and diisopropylether (DIPE) have been found to elute from the precolumn with the nonaromatic hydrocarbons to vent. Other oxygenates, including methanol and ethanol elute before benzene and the aromatic hydrocarbons. 1-Methylcyclopentene has also been found to elute from the precolumn to vent and does not interfere with benzene.

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

1.9.1 *Exception*—The values given in parentheses are for information only.

1.10 *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.*

1.11 *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]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
D3606 Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography
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
D5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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

3.1.2 *low-volume connector, n*—a 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.

3.1.3 *narrow bore tubing, n*—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.

3.1.4 *split ratio, n—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.

3.1.5 *1,2,3-tris-2-cyanoethoxypropane (TCEP),n*—a polar gas chromatographic liquid phase.

3.1.6 *wall-coated open tubular (WCOT), n*—a 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 limiting the concentration of benzene and the total aromatic content of finished gasoline have been established for 1995 and beyond in order to reduce the ozone reactivity and toxicity of automotive evaporative and exhaust emissions. Test methods to determine benzene and the aromatic content of gasoline are necessary to assess product quality and to meet new fuel regulations.

5.2 This test method can be used for gasolines that contain oxygenates (alcohols and ethers) as additives. It has been determined that the common oxygenates found in finished gasoline do not interfere with the analysis of benzene and other aromatics by this test method.

6. Apparatus

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

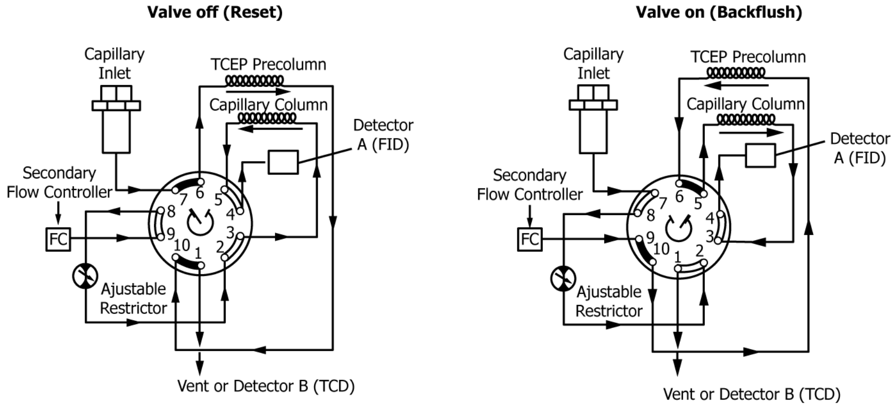

FIG. 1 Valve Diagram, Aromatics in Gasoline

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. Microlitre 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.

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 % by 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 ~~internalvolume~~ 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. Alternatively, 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.

6.1.5.3 An automatic valve switching device is strongly recommended to ensure repeatable switching times.

6.2 *Data Acquisition System:*

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

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

6.2.1.1 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 *Chromatographic Columns (two columns are used):*

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 15.

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.

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.)~~pressure.)

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

7.3 *2,2,4-Trimethylpentane (isooctane)*—Used as a solvent in the preparation of the calibration mixture. Reagent grade. (**Warning—*Iso***octane 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 gasoline 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 Every effort should be made to ensure that the sample is representative of the fuel 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 Appropriate steps should be taken to minimize the loss of light hydrocarbons from the gasoline 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 vaportight container and store at 0 °C to 5 °C (32 °F to 40 °F) until needed for analysis.

10. Preparation of Apparatus and Establishment of Conditions

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 initially to approximately 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 approximately 10 mL ⁄min flow (17 psi to 20 psi). Soap bubble flow meters are suitable. This represents the flow through the polar precolumn.

NOTE 1—The word "approximately" implies to get as close as possible to the stated column flows to initiate the further optimization of the system.

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 approximately 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. (See Note 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 approximately 10 mL ⁄min at the Detector A (FID) exit. (See Note 1.)

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, 10.5.1.2, and 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 5 % each of benzene, ethylbenzene, *o*-xylene, and 2-hexanone in *iso*octane. 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 2—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 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 1.7 % *n*-dodecane in 2,2,4-trimethylpentane ~~(isooctane).~~(*iso*octane). *n*-Dodecane is used to represent the high boiling nonaromatic hydrocarbons in gasoline. Inject 1.0 µL of the mixture under the conditions specified in 10.2 to 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