



Designation: D3606 – 07

# Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D3606; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the determination of benzene and toluene in finished motor and aviation gasolines by gas chromatography.

1.2 Benzene can be determined between the levels of 0.1 and 5 volume % and toluene can be determined between the levels of 2 and 20 volume %.

1.3 The precision for this test method was determined using conventional gasoline as well as gasolines containing oxygenates (ethers such as methyl *tert*-butyl ether, ethyl *tert*-butyl ether and *tert*-amyl methyl ether).

1.4 Methanol may cause interference. [Appendix X1](#) provides an option for modifying the test method for analyzing samples containing ethanol.

1.5 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.6 *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*:<sup>2</sup>

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[E694 Specification for Laboratory Glass Volumetric Apparatus](#)

[E969 Specification for Glass Volumetric \(Transfer\) Pipets](#)

[E1044 Specification for Glass Serological Pipets \(General Purpose and Kahn\)](#)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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<sup>2</sup> 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.

## E1293 Specification for Glass Measuring Pipets

## 3. Summary of Test Method

3.1 An internal standard, methyl ethyl ketone (MEK), is added to the sample which is then introduced into a gas chromatograph equipped with two columns connected in series. The sample passes first through a column packed with a nonpolar phase such as dimethylpolysiloxane (8.1.1) which separates the components according to boiling point. After octane has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than octane. The octane and lighter components then pass through a column packed with a highly polar phase such as 1,2,3-tris(2-cyanoethoxy) propane (8.1.2) which separates the aromatic and nonaromatic compounds. The eluted components are detected by a thermal conductivity detector. The detector response is recorded, the peak areas are measured, and the concentration of each component is calculated with reference to the internal standard.

## 4. Significance and Use

4.1 Benzene is classed as a toxic material. A knowledge of the concentration of this compound can be an aid in evaluating the possible health hazard to persons handling and using the gasoline. This test method is not intended to evaluate such hazards.

## 5. Apparatus

5.1 *Chromatograph*—Any chromatographic instrument that has a backflush system and thermal conductivity detector, and that can be operated at the conditions given in [Table 1](#), can be employed. Two backflush systems are shown. [Fig. 1](#) is a pressure system and [Fig. 2](#) is a switching valve system. Either one can be used.

### 5.2 Columns:

5.2.1 *Column A*—One 0.8-m (2.5-ft) by 3.2-mm (1/8-in.) outside diameter stainless steel column packed with 10 mass % dimethylpolysiloxane (for example, OV-101) on Chromosorb W, 60 to 80 mesh.

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

**TABLE 1 Instrument Parameters**

Detector	thermal conductivity
Columns:	two, stainless steel
Length, m	(A) 0.8; (B) 4.6
Outside diameter, mm	3.2
Stationary phase	(A) dimethylpolysiloxane, 10 mass % (B) TCEP, 20 mass %
Support	(A) Chromosorb W, 60 to 80-mesh (B) Chromosorb P, 80 to 100-mesh
Reference column	Any column or restriction may be used.
Temperature:	
Sample inlet system, °C	200
Detector, °C	200
Column, °C	145
Carrier Gas:	helium
Linear Gas Rate, cm/s	6
Volume flow rate, cm <sup>3</sup> /min	approximately 30
Column head pressure, kPa (psi)	approximately 200 (30)
Recorder range, mV	0 to 1
Chart speed, cm/min	1
Sample size, µL	2
Total cycle time, min	8
Backflush, min	approximately 0.75 <sup>4</sup>

<sup>4</sup> This back flush time must be determined for each column system.

5.2.2 *Column B*—One 4.6-m (15-ft) by 3.2-mm outside diameter stainless steel column packed with 20 mass % TCEP on Chromosorb P, 80 to 100 mesh.

5.3 *Recorder*, a strip chart recorder. An electronic integrating device or a computer capable of graphical presentation of the chromatogram. The electronic integrating device or computer must be capable of measuring 0.1 volume % MEK with satisfactory signal-to-noise. If a strip chart recorder is to be used, a 0 to 1-mV range recording potentiometer with a response time of 2 s or less and a maximum noise level of  $\pm 0.3$  % of full scale is recommended. The detector strip chart recorder combination must produce a 4-mm deflection for a 2-µL sample containing 0.1 volume % MEK when operated at maximum sensitivity.

5.4 *Microsyringe*, 5-µL capacity.

5.5 *Volumetric Pipets, Class A*, 0.5, 1, 5, 10, 15, and 20-mL capacities (see Specification E694 and E969).

5.6 *Measuring Pipets*, 1 and 2-mL capacities calibrated in 0.01 mL; 5-mL calibrated in 0.1-mL, for use in dispensing volumes of benzene and toluene not covered by the volumetric pipets (see Specification E1044 and E1293) during preparation of standard samples (see 11.1).

NOTE 1—Other volume dispensing equipment capable of delivering the specified volumes within the stated tolerance limits may be used as an alternative to the requirements stated in 5.5 and 5.6.

5.7 *Flasks*, volumetric, 25 and 100-mL capacity.

5.8 *Vibrator*, electric.

5.9 *Vacuum Source*.

5.10 *Evaporator*, vacuum, rotary.

5.11 *Flask*, boiling, round-bottom, short-neck, with <sup>24</sup>/<sub>40</sub> standard taper joint, 500-mL capacity. Suitable for use with evaporator (5.10).

5.12 *Lamp*, infrared.

5.13 *Burets*, automatic, with integral reservoir, 25-mL capacity.

## 6. Materials

6.1 *Carrier Gas*—Helium, 99.99 % pure. (**Warning**—Compressed gas under high pressure.)

6.2 *Support*—Crushed firebrick, acid-washed, 60 to 80-mesh and 80 to 100-mesh.

6.3 *Liquid Phases*—1,2,3-Tris(2-cyanoethoxy) propane (TCEP) and methyl silicone.<sup>3</sup>

6.4 *Solvents*:

6.4.1 *Methanol*, reagent grade. (**Warning**—Flammable. Vapor harmful. Can be fatal or cause blindness if swallowed or inhaled.)

6.4.2 *Chloroform*, reagent grade. (**Warning**—Can be fatal if swallowed. Harmful if inhaled.)

6.4.3 *Methylene Chloride*, for cleaning columns. (**Warning**—Harmful if inhaled. High concentrations can cause unconsciousness or death.)

6.4.4 *Acetone*, for cleaning columns. (**Warning**—Extremely flammable. Vapors can cause flash fires.)

6.5 *Internal Standard*:

6.5.1 *Methyl Ethyl Ketone (MEK)*, 99.5% minimum purity. (**Warning**—Flammable. Vapor can be harmful.)

6.6 *Calibration Standards*:

6.6.1 *Benzene*, 99<sup>+</sup> mol %. (**Warning**—Poison. Carcinogen. Harmful or fatal if swallowed. Extremely flammable. Vapors can cause flash fires.)

6.6.2 *Isooctane (2,2,4-trimethyl pentane)*, 99<sup>+</sup> mol %. (**Warning**—Extremely flammable. Harmful if inhaled.)

6.6.3 *Toluene*, (**Warning**—Flammable. Vapor harmful.)

6.6.4 *n-Nonane*, 99<sup>+</sup> mol %. (**Warning**—Flammable. Vapor harmful.)

## 7. Sampling

7.1 *Gasoline*—(**Warning**—Extremely flammable. Vapors harmful if inhaled.) Samples to be analyzed by this test method shall be obtained using the procedures outlined in Practice D4057.

## 8. Preparation of Column Packings

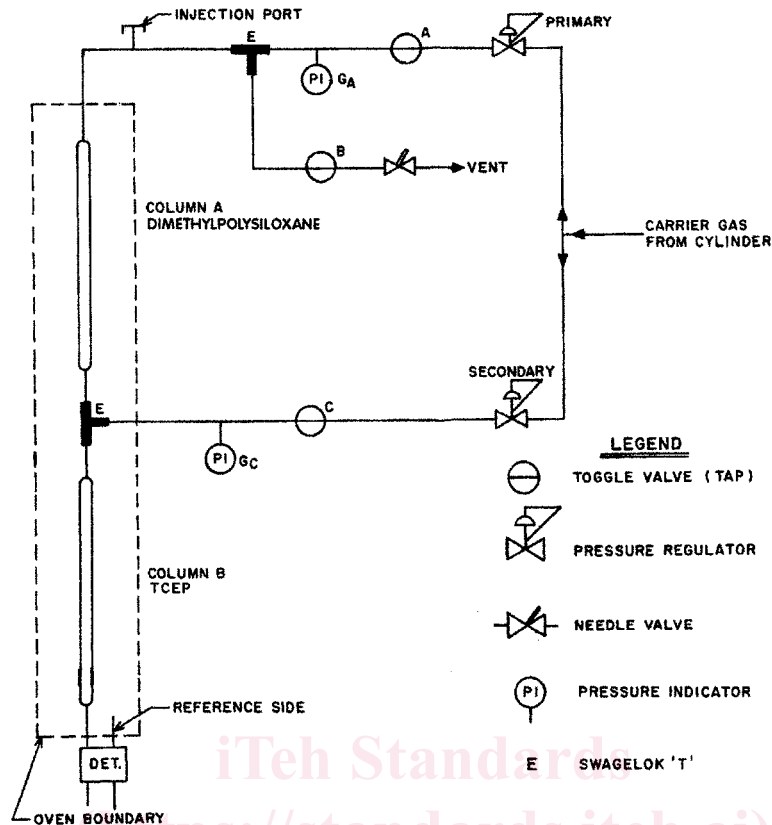
8.1 Prepare two packing materials (one packing material consists of 10 mass % dimethylpolysiloxane on Chromosorb W; the other, 20 mass % TCEP on Chromosorb P) in accordance with the following procedures:

8.1.1 *Dimethylpolysiloxane Packing*—Weigh 45 g of the Chromosorb W, 60 to 80 mesh and pour into the 500-mL flask (5.11). Dissolve 5 g of the dimethylpolysiloxane in approximately 50 mL of chloroform. (**Warning**—Can be fatal if swallowed. Harmful if inhaled.) Pour the methyl silicone-chloroform solution into the flask containing the Chromosorb W. Attach the flask to the evaporator (5.10), connect the vacuum, and start the motor. Turn on the infrared lamp and allow the packing to mix thoroughly until dry.

8.1.2 *1,2,3-Tris(2-cyanoethoxy) Propane (TCEP) Packing*—Weigh 80 g of Chromosorb P, 80 to 100 mesh and pour into the 500-mL flask (5.11). Dissolve 20 g of TCEP in

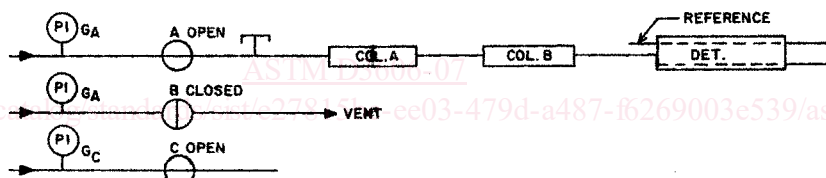
<sup>3</sup> Packed column liquid phases such as OV 101 are considered to be of the dimethylpolysiloxane type. Other equivalent phases can also be used. Consult with the column manufacturer or phase supplier for information.

A. PIPING AND INSTRUMENTATION



B. FLOW SWITCHING SYSTEM

1. FORWARD FLOW



2. BACKFLUSH

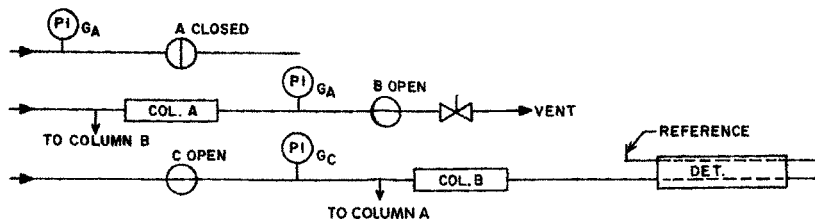


FIG. 1 Pressure Backflush

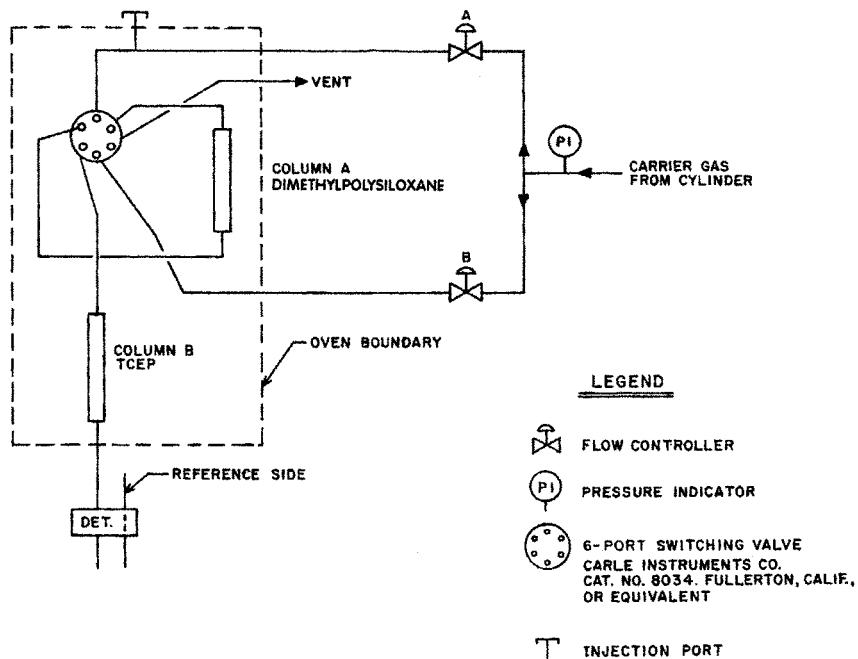
200 mL of methanol and pour into the flask containing the Chromosorb P. Attach the flask to the evaporator (5.10), connect the vacuum, and start the motor. Turn on the infrared lamp and allow the packing to mix thoroughly until dry. (Do not heat the packing over 180°C.)

9. Preparation of Column

9.1 *Cleaning Column*—Clean the stainless steel tubing as follows. Attach a metal funnel to one end of the steel tubing.

Hold or mount the stainless steel tubing in an upright position and place a drain beaker under the outlet end of the tubing. Pour about 50 mL of methylene chloride (**Warning**—Harmful if inhaled. High concentrations can cause unconsciousness or death) into the funnel and allow it to drain through the steel tubing and into the drain beaker. Repeat the washing procedure with 50 mL of acetone. (**Warning**—Harmful if inhaled. High concentrations can cause unconsciousness or death.) Remove

A. PIPING AND INSTRUMENTATION



B. FLOW SWITCHING SYSTEM

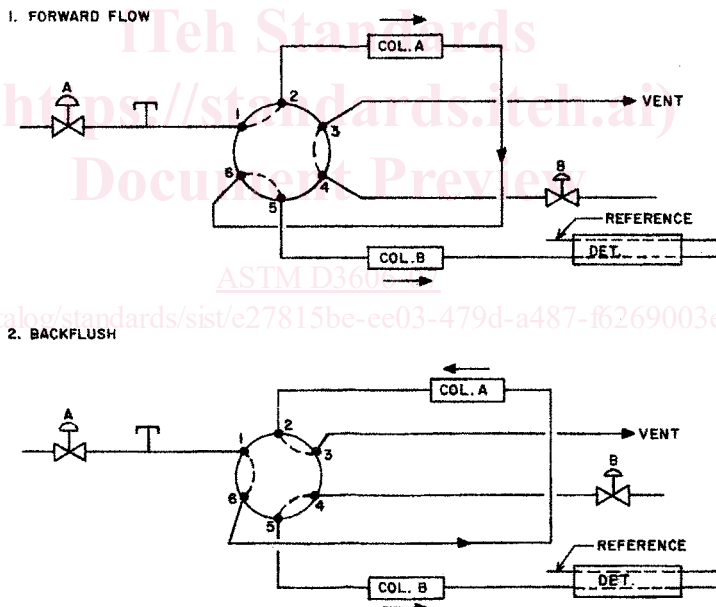


FIG. 2 Valve Backflush

the funnel and attach the steel tubing to an air line, using vinyl tubing to make the connection. Remove all solvent from the steel tubing by blowing filtered, oil-free air through or pulling a vacuum.

9.2 *Packing Columns*—Preform Columns A and B separately to fit the chromatograph. Pack the 0.8-m tubing (Column A) with the dimethylpolysiloxane packing (8.1.1) and the 4.6-m tubing (Column B) with the TCEP packing (8.1.2) using the following procedure. Close one end of each tubing with a

small, glass wool plug, and connect this end to a vacuum source by means of a glass wool-packed tube. To the other end connect a small polyethylene funnel by means of a short length of vinyl tubing. Start the vacuum and pour the appropriate packing into the funnel until the column is full. While filling each column, vibrate the column with the electric vibrator to settle the packing. Remove the funnel and shut off the vacuum source. Remove the top 6 mm (1/4-in.) of packing and insert a glass wool plug in this end of the column.