



Designation: D3606 – 17

Standard Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography¹

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 (ϵ) 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 spark ignition fuels by gas chromatography. This test method has two procedures: Procedure A uses capillary column gas chromatography and Procedure B uses packed gas chromatography columns. Procedures A and B have separate precisions.

1.2 Benzene can be determined between the levels of: (1) Procedure A 0.1 % and 5.0 % by volume and toluene can be determined between the levels 0.4 % and 20 % by volume, and (2) Procedure B benzene can be determined between the levels of 0.1 % and 5 % by volume and toluene can be determined between the levels of 2 % and 20 % by volume.

1.3 The precision for this test method was determined using conventional spark ignition fuel (motor ‘gasolines’) as well as those containing blended ethanol and such ethers as MTBE, ETBE, TAME, and other alcohols such as methanol and butanols. This method may be used for finished motor and aviation gasolines that contain ethanol blend up to 20 % and butanols blend up to 20 %.

1.4 M85 and E85 fuels were not included in the precision for Procedure A. M85 and E85 fuels cause interference with Procedure B.

1.5 Procedure A uses MIBK as the internal standard. Procedure B uses *sec*-butanol as the internal standard. The use of Procedure B for fuels containing blended butanols requires that *sec*-butanol be below the detection limit in the fuels.

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

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 appro-*

priate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

1.8 *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

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

[D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)

[E288 Specification for Laboratory Glass Volumetric Flasks](#)

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

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

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

[E1293 Specification for Glass Measuring Pipets](#)

PROCEDURE A—CAPILLARY WCOT GAS CHROMATOGRAPHIC SYSTEMS

3. Summary of Test Method

3.1 An internal standard, methyl isobutyl ketone (MIBK) is added to the sample which is then introduced into a heated capillary or programmed temperature vaporization (PTV) injector on a gas chromatograph (GC). The GC is equipped with two columns connected in series. The sample passes first through a column with a nonpolar phase. After toluene has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than toluene. The toluene and lighter components enter a second column which separates

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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

the aromatic and nonaromatic compounds. The eluted components are detected by a flame ionization detector (FID). 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 Knowledge of the concentration of benzene may be required for regulatory use, control of gasoline blending, and/or process optimizations.

5. Apparatus and Chemicals

5.1 *Chromatograph*—Any gas chromatograph that has the capability of performing multidimensional chromatography that can be operated at approximately the conditions described in this method, and meets all the required chromatographic specifications and method criteria specified in 7.5 and 11.

5.1.1 *Sample Introduction System*—Automated sample injection system such as a liquid autosampler.

5.1.2 *Injector*—Capillary split/splitless injector.

5.1.3 *Detector*—At least one flame ionization detector (FID) is required. In a two FID configuration, the optional second detector is used to monitor the effluent from the pre-column (refer to configuration A in 7.1.1).

5.2 Columns:

5.2.1 *Pre-column*—Non-polar, boiling point column, which performs the first separation of the hydrocarbons. A dimethyl polysiloxane phase column with dimensions of 30 m by 0.25 mm by 0.50 μ m has been used successfully. Any column with equivalent or better chromatographic efficiency and selectivity may be used.

5.2.2 *Analytical Column*—This column separates aromatic and non-aromatic compounds. A polyethylene glycol (polar ‘wax’) column with the dimensions 60 m by 0.32 mm by 1.0 μ m has been used successfully. Any column capable of meeting the resolution requirement in 7.5 may be employed.

5.2.3 *Restrictor*—Uncoated deactivated fused silica. A 100 μ m by 42.5 cm restrictor was successfully used when developing this method.

5.3 *Chromatography Data System (CDS)*—An electronic device capable of graphical presentation and integration of the chromatogram peaks.

5.4 *Microsyringe*—Capable of making injections from 0.5 μ L to 1.0 μ L.

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

5.6 *Measuring Pipets*—1 mL 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 Specifications E1044 and E1293) during preparation of standard samples (see 8.1).

NOTE 1—Other manual or automated 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 mL and 100 mL capacity (see Specification E288).

5.8 *GC Carrier Gas*—Helium or hydrogen 99.999 % pure. (**Warning**—Compressed gas under high pressure; hydrogen flammable.) A hydrogen generator may be used.

NOTE 2—When using hydrogen carrier gas, use precautions such as installation of hydrogen sensors in the gas chromatograph oven. It is recommended that the hydrogen excess flow, such as from the splitter inlet, should be vented to a safe area such as a ventilated hood or appropriate exhaust approved for such use. Use caution when performing maintenance by isolating the hydrogen source.

5.9 *FID Gas*—Air chromatographic grade, dry (**Warning**—Compressed gas under high pressure.) An air generator may be used with purifier.

5.10 *FID Gas*—Hydrogen, 99.999 % pure (**Warning**—Compressed gas under high pressure; hydrogen flammable.) A hydrogen generator may be used.

5.11 *FID Make-up Gas, if Required (Refer to Manufacturer’s Requirements)*—Nitrogen, 99.999 % pure. (**Warning**—Compressed gas under high pressure.)

NOTE 3—Reference the instrument manual for specifics on how to establish required flow rates for a particular vendor’s instrument.

5.12 *Chemicals*—(**Warning**—These chemicals are dangerous, harmful, or fatal if swallowed or inhaled. They are flammable to extremely flammable. Vapors can cause flash fires.)

5.12.1 *Internal Standard*—Methyl Isobutyl Ketone (MIBK) 99.5 % pure.

5.13 Calibration Standards:

5.13.1 *Benzene*—99.5 % minimum purity. (**Warning**—Carcinogen.)

5.13.2 *Toluene*—99.5 % minimum purity.

5.13.3 *Isooctane (2,2,4-trimethyl pentane)*—99.5 % minimum purity. This is the solvent used for dilution.

5.14 Method Chemicals for Resolution Validation:

5.14.1 *Sec-butanol*—99.5 % minimum purity.

5.14.2 *Iso-butanol*—99.5 % minimum purity.

5.14.3 *n-butanol*—99.5 % minimum purity.

5.14.4 *n-propanol*—99.5 % minimum purity.

5.14.5 *Ethanol*—99.5 % minimum purity (200 proof).

6. Sampling

6.1 *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.

7. Apparatus, Configurations, and Method Setup

7.1 *Configuration*—Illustrated and discussed in this test method are three configurations used by the laboratories that have participated in the interlaboratory study (ILS). Figs. A1.5 and A1.6 contain graphical representations of these configurations and Table A1.1 provides the method parameters. Valve-based systems for backflushing may be used and such a configuration is displayed in Fig. A1.7 and was also used in the ILS. Other configurations may be used provided all of the requirements and criteria in this test method are met, such as

signal to noise (S/N), resolution, calibration, quality control requirements, and so forth, which are discussed in 7.5 and Section 11.

7.1.1 *Configuration A*—Has the capability of monitoring the effluent from the pre-column via a restrictor. This is a dual detector system. One FID is used to monitor the analytical column's effluent, and the other to monitor the effluent from the pre-column. The second FID provides a quicker approach in determining backflush time. Figs. A1.1 and A1.2 represent examples of this configuration.

7.1.2 *Configuration B*—Has the capability of monitoring the effluent from the pre-column via a restrictor; however, only one FID is installed. Figs. A1.3 and A1.4 represent examples of this configuration.

7.1.3 *Configuration C*—Does not have the capability to monitor the effluent from the pre-column. Figs. A1.5 and A1.6 represent an example of this configuration.

7.2 *Conditioning Column*—Install the pre-column, analytical column, and the restrictor, if the restrictor is being used as in configurations A and B. Condition the columns per manufacturer's instructions.

7.3 *Determine Time to Backflush (BF)*—Or backflush time, must be empirically determined for each system and column set used by the laboratory. Optimization of backflush time is dependent upon the configuration used.

7.3.1 *Configuration A, Dual Detector Configuration*—Follow the instrument setup as shown in Figs. A1.1 and A1.2.

7.3.1.1 Establish analytical parameters set forth in Table A1.1 or parameters that have met method separation criteria as outlined in 7.5. Ensure both detector channels are being collected by the CDS.

7.3.1.2 Inject 0.1 μL to 0.5 μL of standard #1 (8.2) or the butanol composite mix (8.5.2) depending on ethanol or butanol blended gasoline, respectively. If the gasoline being tested is blended with ethanol and not butanol, the composite mix described in 8.5.2 for butanol blend does not need to be prepared. However, if the laboratory wants to prepare this composite mix, the composite mix described in 8.5.2 may be used for establishing backflush time for both blended fuels.

7.3.1.3 Record the time when toluene returns to baseline from the pre-column via the restrictor. A chromatogram from the pre-column through the restrictor demonstrating this is shown in Fig. A1.8 for standard #1, and in Fig. A1.9 for the composite mix in 8.5.2.

7.3.1.4 Next monitor the effluent from the analytical column using the backflush time established in 7.3.1.3. Inject standard #1 (8.2) or composite mix for butanol blend (8.5.2). Record the area for toluene.

7.3.1.5 Reduce the backflush time by 0.02 min. Inject standard #1 or composite mix. Record the area for toluene. Repeat this step until the response for toluene begins to decrease.

7.3.1.6 The backflush time for the method will be the time recorded before the time when toluene decreased. An example chromatogram from the analytical column of standard #1 is in Fig. A1.10 and an example chromatogram of composite mix described in 8.5.2 is located in Fig. A1.11.

7.3.2 *Configuration B, Single Detector Configuration*—To monitor the flow from the pre-column to establish the backflush time, the analytical column is removed from the FID and left in the GC oven as displayed in Fig. A1.3. (**Warning**—Use caution if using hydrogen as carrier gas; if possible, vent externally of the gas chromatograph's oven.) The restrictor is installed into the FID.

7.3.2.1 Follow procedures from 7.3.1.1 through 7.3.1.3.

7.3.2.2 Remove restrictor from the detector and install the analytical column in the detector for analysis as shown in Fig. A1.4.

7.3.2.3 Follow procedures from 7.3.1.4 to 7.3.1.6.

7.3.3 *Configuration C, No Pre-column Configuration*—This configuration is not capable of monitoring the chromatography from the pre-column. An example of this configuration is shown in Figs. A1.5 and A1.6 configuration C.

7.3.3.1 Inject 0.1 μL to 0.5 μL of standard #1 (8.2) or the composite mix (8.5) depending on ethanol or butanol blended gasoline using a backflush time equal to the run-time.

7.3.3.2 Decrease the backflush time by 1 min intervals until toluene is no longer present in the chromatogram.

7.3.3.3 Increase the backflush time by 0.02 min until toluene provides a stable area count. The shortest time when the toluene has a stable response is the backflush time.

7.4 *Re-establishing Backflush Time*—As the column ages with use, retention times will become shorter. If the quality control samples fail, backflush time may need to be re-established on the same column, set especially if a retention time shift is when a new pre-column, analytical column, and/or restrictor are employed, the backflush time will need to be re-established.

7.5 *Method Criteria:*

7.5.1 *Verify Resolution for Gasoline Blended With Ethanol*—Using the injection volume and other parameters that will be used for sample analysis, inject either composite mix described in 8.5.1 or 8.5.2. Benzene shall be sufficiently resolved from ethanol and having a resolution (R) value >2 . The internal standard (MIBK) shall have an R value >1.5 . Refer to Fig. A1.10 for standard #1 or Fig. A1.11 for an example chromatogram displaying resolution for composite mix from 8.5.2.

7.5.2 *Verify Resolution for Gasoline Blended With Butanol*—Using the injection volume and parameters established above and that will be used for sample analysis, inject composite mix described in 8.5.2. The resolution requirements are as follows: benzene $R > 2$; MIBK $R > 1.5$; toluene $R > 0.6$. Refer to an example chromatogram found in Fig. A1.11.

7.5.3 Resolution calculation may be performed by the CDS or manually. If using a CDS, ensure the CDS is using the proper resolution calculation, as follows:

$$R_{p2} = \frac{1.18(T_{p2} - T_{p1})}{W_{h1/2} + W_{h2/2}} \quad (1)$$

where:

R_{p2} = the resolution of peak 2,
 T_{p1} = the retention time of peak 1,
 T_{p2} = the retention time of peak 2,