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.

Designation: D3606 – 24

Standard Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography[1]

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 quantitation in liquid volume percent 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 column gas chromatography. Procedures A and B have separate precisions.

1.2 The method has been evaluated for benzene using a D6300-compliant Interlaboratory Study (ILS), with the lowest and highest ILS sample concentration means as follows: (*1*) Procedure A between 0.12 % and 5.2 % by volume and (*2*) Procedure B between 0.10 % and 5.0 % by volume.

1.3 The method has been evaluated for toluene using a D6300-compliant Interlaboratory Study (ILS), with the lowest and highest ILS sample concentration means as follows: (*1*) Procedure A between 0.4 % and 19.7 % by volume, and (*2*) Procedure B between 2.0 % and 20.0 % by volume.

1.4 For reporting, the lowest and highest concentration ranges for benzene and toluene for Procedure A of this test method per Practice D6300 see 13.2.

1.5 For reporting, the lowest and highest concentration ranges for benzene and toluene for Procedure B of this test method per Practice D6300 see 25.2.

1.6 For benzene by Procedure A, the following oxygenated fuels are included in the working range: (*1*) ethanol up to 20 % by volume (E20); (*2*) methanol up to 10 % by volume (M10). Fuels M85 and E85 were excluded.

1.7 For benzene by Procedure B the following oxygenated fuels are included in the working range: (*1*) ethanol up to 20 % by volume (E20); (*2*) methanol up to 10 % by volume (M10). Fuels M85 and E85 were excluded.

1.8 For toluene by Procedure A the following oxygenated fuels were included in the working range: (*1*) ethanol up to 20 % by volume (E20); (*2*) M85 and E85.

1.9 For toluene by Procedure B the following oxygenated fuels are included in the working range: (*1*) ethanol up to 20 % by volume (E20); (*2*) M85 and E85.

1.10 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 as *sec*-butanol is an internal standard. For Procedure B, an alternative separation column set described in the annex (A2.3, Annex Approach B) uses MEK as the internal standard when butanols may be blended into gasolines.

1.11 This test method includes a between method bias section for benzene based on Practice D6708 bias assessment between Test Method D3606 Procedure B and Test Method D5769. It is intended to allow Test Method D3606 Procedure B to be used as a possible alternative to Test Method D5769. The Practice D6708 derived benzene correlation equation is applicable for benzene measurements in the reportable range from 0.06 % to 2.76 % by volume as reported by Test Method D3606 Procedure B (see 27.2.1). The correlation complies with EPA's Performance Based Measurement System (PBMS).

1.12 Correlation equations are included in the between test methods bias section 14.2.1 of Procedure A to convert Procedure A to the Procedure B volume percent values for benzene and toluene. The correlations are applicable in the concentration ranges of 0.07 % to 5.96 % by volume for benzene and 0.36 % to 20.64 % by volume for toluene as reported by Procedure A.

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

1.14 *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.*

1.15 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

[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

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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

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

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

E288 Specification for Laboratory Glass Volumetric Flasks

E355 Practice for Gas Chromatography Terms and Relationships

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

3. Terminology

3.1 This test method makes references to terms whose definitions may be found in Practice E355 and Terminology D4175.

PROCEDURE A—CAPILLARY WCOT GAS CHROMATOGRAPHIC SYSTEMS

4. Summary of Test Method

4.1 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 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.

5. Significance and Use

5.1 Knowledge of the concentration of benzene may be required for regulatory use, control of gasoline blending, and/or process optimizations.

6. Apparatus and Chemicals

6.1 *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 8.5 and 12.

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

6.1.2 *Injector*—Capillary split/splitless injector.

6.1.3 *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 8.1.1).

6.2 *Columns:*

6.2.1 *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 µm has been used successfully. Any column with equivalent or better chromatographic efficiency and selectivity may be used.

6.2.2 *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 µm has been used successfully. Any column capable of meeting the resolution requirement in 8.5 may be employed.

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

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

6.4 *Microsyringe*—Capable of making injections from 0.5 µL to 1.0 µL.

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

6.6 *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 9.1).

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 6.5 and 6.6.

6.7 *Flasks*—Volumetric, 25 mL and 100 mL capacity (see Specification E288).

[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.

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6.8 *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.

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

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

6.11 *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.

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

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

6.13 *Calibration Standards:*

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

6.13.2 *Toluene*—99.5 % minimum purity.

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

6.14 *Method Chemicals for Resolution Validation:*

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

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

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

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

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

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. Apparatus, Configurations, and Method Setup

8.1 *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 8.5 and Section 12.

8.1.1 *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.

8.1.2 *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.

8.1.3 *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.

8.2 *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.

8.3 *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.

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

8.3.1.1 Establish analytical parameters set forth in Table A1.1 or parameters that have met method separation criteria as outlined in 8.5. Ensure both detector channels are being collected by the CDS.

8.3.1.2 Inject 0.1 µL to 0.5 µL of standard #1 (9.2) or the butanol composite mix (9.5.2) 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 9.5.2 for butanol blend does not need to be prepared. However, if the laboratory wants to prepare this composite mix, the composite mix described in 9.5.2 may be used for establishing backflush time for both blended fuels.

8.3.1.3 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 9.5.2.

8.3.1.4 Next monitor the effluent from the analytical column using the backflush time established in 8.3.1.3. Inject standard #1 (9.2) or composite mix for butanol blend (9.5.2). Record the area for toluene.

8.3.1.5 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.

8.3.1.6 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 9.5.2 is located in Fig. A1.11.

8.3.2 *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—**

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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.

8.3.2.1 Follow procedures from 8.3.1.1 through 8.3.1.3.

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

8.3.2.3 Follow procedures from 8.3.1.4 to 8.3.1.6.

8.3.3 *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.

8.3.3.1 Inject 0.1 µL to 0.5 µL of standard #1 (9.2) or the composite mix (9.5) depending on ethanol or butanol blended gasoline using a backflush time equal to the run-time.

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

8.3.3.3 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.

8.4 *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.

8.5 *Method Criteria:*

8.5.1 *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 9.5.1 or 9.5.2. 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 9.5.2.

8.5.2 *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 9.5.2. 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.

8.5.3 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,
$W_{h1/2}$ = the width of peak 1 at half height, and
$W_{h2/2}$ = the width of peak 2 at half height.

8.5.4 *Determining Method Run Time or Completion of Chromatography for Butanol Blended Gasoline*—Because *n*-butanol may be an isomer in the butanol blend, the runtime and/or temperature needs to be long enough and temperature high enough to ensure *n*-butanol elutes from the analytical column. Use the composite mix in 9.5.2 for this determination. Refer to the chromatogram found in Figs. A1.10 and A1.11.

8.5.5 *Attaining Detection Limit for Benzene*—Using standard mix #7 (9.1), ensure that at least a signal to noise of 50 to 1 is attained for benzene. If this is not achieved, reduce the instrument's split flow or increase the injection volume, not to exceed 0.5 µL until this criteria is attained.

8.5.6 *Calibration Requirements*—A linear regression, or weighted curve, shall meet a criterion correlation coefficient equal to or greater than 0.999.

9. Calibration and Standardization

9.1 *Standards*—Prepare seven standards (Table 1) covering the range 0.06 % to 5 % by volume benzene and 0.5 % to 20 % by volume toluene. For each standard, measure the volume of benzene and of toluene listed below into a 100 mL volumetric flask. Dilute to volume with *iso*octane (*2,2,4-trimethylpentane*), with all components and glassware at ambient temperature.

9.2 *Final Standard Preparation*—Accurately measure 1.0 mL of MIBK into a 25 mL-volumetric flask, and fill to the mark using the first standard (9.1). Continue doing this until all seven (7) blends (concentrations) have been prepared.

NOTE 4—Commercially prepared calibration standards may be used, including those that are pre-mixed with the MIBK internal standard. The purity of target compounds is given in 6.12.

9.3 *Chromatographic Analysis*—Chromatograph each of the calibration blends using the conditions established in Section 8 using the automated sampling system of the gas chromatograph.

9.4 *Calibration*—Using a computer data system (CDS), measure the area of the benzene and toluene aromatic peaks and of the internal standard peak. Calculate the area ratio of the benzene peak area to the MIBK peak area. Plot the concentration of benzene versus the area ratio. Make the same calculation and plot similarly for toluene. Refer to Fig. A1.12 for an example calibration curve. The calibration shall be linear with a correlation coefficient greater than or equal to 0.999. Weighing the calibration curve 1/y is allowed and will provide enhanced accuracy for lower concentration target samples.

NOTE 5—Some CDS systems plot the area ratio versus the concentration ratio of the benzene and toluene to that of the internal standard. Consult the system guidelines.

9.5 *Composite Mix for Ethanol and Butanol Blends*—The composite mix will ensure a necessary separation of ethanol

TABLE 1 Seven Standards

Std #	Benzene		Toluene	
	Volume percent	mL	Volume percent	mL
1	5	5	20	20
2	2.5	2.5	15	15
3	1.25	1.25	10	10
4	0.67	0.67	5	5
5	0.33	0.33	2.5	2.5
6	0.12	0.12	1	1
7	0.06	0.06	0.5	0.5

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from benzene (R > 2), and that possible contaminants in the butanol blend will not co-elute with benzene (R > 2), toluene (R > 0.6) and MIBK (R > 1.5).

9.5.1 *Composite Mix for Ethanol Blend*—Prepare a solution by volume that is 20 % ethanol, 1 % benzene, 4 % MIBK and 20 % toluene in *iso*-octane. This solution may also be used to determine the backflush time.

9.5.2 *Composite Mix for Ethanol and Butanol Blends*—Prepare a solution by volume that is 20 % ethanol, 1 % benzene, 4 % *sec*-butanol, 0.1 % *n*-propanol, 4 % MIBK, 20 % toluene, 20 % *iso*-butanol, 5 % *n*-butanol in *iso*-octane. This solution may also be used to determine the backflush time.

10. Procedure

10.1 *Preparation of Sample*—Accurately measure 1.0 mL of MIBK into a 25 mL volumetric flask. Fill to the mark with the sample to be analyzed and mix well.

10.2 *Chromatographic Analysis*—Chromatograph the sample, using the conditions established in Section 8 and as used for the calibration. The GC column flow must be turned to backflush mode at the time determined in 8.3 so that undesirable components do not enter the analytical column. Fig. A1.13 is an example of a Test Method D3606 proficiency sample analyzed using configuration A.

10.3 *Interpretation of Chromatogram*—Identify the benzene, toluene, and the internal standard MIBK peaks from the retention times of the standards.

NOTE 6—The order of elution will be nonaromatic hydrocarbons, benzene, MIBK and toluene using the dimethyl poly siloxane and polar column combination used in the ILS.

10.4 *Measurement of Area*—Measure the areas under the benzene, toluene aromatic peaks and under the MIBK peak.

11. Calculation

11.1 Calculate the ratios of the peak areas of benzene and toluene to the peak area of MIBK. Determine from the calibration curve the liquid volume percent of benzene and toluene corresponding to the calculated peak ratios. A CDS that has the capability of processing this calibration and quantitating results may be used.

11.2 If the results are desired on a mass basis, convert to mass percent as follows:

$$\text{Benzene, mass percent} = (V_B / D) \times 0.8844 \quad (2)$$

where:

V_B = volume percent benzene, and
D = relative density of sample at 15.6/15.6 °C (60/60 °F).

$$\text{Toluene, mass percent} = (V_T / D) \times 0.8719 \quad (3)$$

where:

V_T = volume percent toluene, and
D = relative density of sample at 15.6/15.6 °C (60/60 °F).

12. Quality Control

12.1 *Test for System Stability and Repeatability*—On setting up the method for the first time and thereafter when major maintenance is performed (change in columns and flows, for example), make six injections of standard #4 (9.2). Calculate the standard deviation from the six results from the six injections. Calculate 2.77 × the standard deviation obtained. This quantity shall meet repeatability as published 14.1.1. Thereafter establish statistical quality control charting (SQC) for each batch of analysis analyzed using a production a sample similar in composition to samples to be analyzed.

12.2 *Reference Material*—Analyze one or more reference material of known accepted reference value (ARV), such as from NIST and/or an independent certified control standard, or meeting the check standard requirement as specified in Practice D6299 upon setting up the test method, post maintenance (calibration, column replacement, cut time adjustments, and so forth) and at least quarterly to confirm proper set-up and calibration of the gas chromatograph. Test results shall agree with within the 95 % confidence level or reproducibility of the benzene or toluene components divided by the square root of 2. In addition follow any other specification requirements per regulatory or commercial application(s). Monitor the performance of the reference material(s) using SQC charting in accordance with Practice D6299.

13. Report

13.1 Report the benzene and toluene contents in liquid volume percent to the nearest 0.01 %, and indicate that the results are from "D3606 Procedure A."

13.2 In accordance with Practice D6300, to accommodate normal random testing variation, the lowest reportable test X result in volume percent is computed as follows:

$$\begin{aligned} X &= \text{lowest reportable test result of this test method} \\ &= [\text{lowest retained ILS sample mean} \\ &\quad - R\ (\text{evaluated at the lowest retained ILS sample mean})] \end{aligned} \quad (4)$$

13.2.1 For benzene: $X_{\text{lowest reportable}} = 0.07$
13.2.2 For toluene: $X_{\text{lowest reportable}} = 0.36$

13.3 In accordance with Practice D6300, to accommodate normal random testing variation, the highest reportable test X result in volume percent is computed as follows:

$$\begin{aligned} X &= \text{highest reportable test result of this test method} \\ &= [\text{highest retained ILS sample mean} \\ &\quad + R\ (\text{evaluated at the highest retained ILS sample mean})] \end{aligned} \quad (5)$$

13.3.1 For benzene: $X_{\text{highest reportable}} = 5.96$
13.3.2 For toluene: $X_{\text{highest reportable}} = 19.7$

14. Precision and Bias[3]

14.1 The following criteria should be used for judging the acceptability of results (95 % confidence). The user should choose the precision statement that reflects the concentration range of each component under study.

14.1.1 *Repeatability*—The difference between two independent results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2004. Contact ASTM Customer Service at service@astm.org.

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constant operating conditions on identical test material within short intervals of time would exceed the values in Table 2 with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would exceed the values in Table 3 with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method.

NOTE 7—The sample compositions and results of the cooperative study are filed at ASTM International.

14.2 *Bias*—Since there is no accepted reference method suitable for measuring bias for this method, no statement of bias can be made.

14.2.1 *Between Method Bias between Procedure A and Procedure B for Benzene:*

14.2.1.1 A between method bias assessment of Test Method D3606 Procedure A versus Procedure B for the determination of benzene in spark-ignition fuel (gasolines) was conducted using data from the ILS of Procedure A which also included a parallel ILS using Procedure B using identical samples. The assessment was performed in accordance with the requirements of Practice D6708 with a successful outcome and is documented in Research Report RR:D02-2004.[3]

NOTE 8—Procedure B is based on the original version of D3606 which uses packed columns and which has been used by regulatory agencies for benzene. Users of this D3606 test method should consult proper regulations on its use as regulations may change.

14.2.1.2 The degree of agreement between results from Test Method D3606 Procedure A versus Procedure B can be further improved by applying a correlation equation (Eq 6) (Research Report RR:D02-2004[3]). There were no discernable sample-specific biases as determined by D6708.

14.2.1.3 *Correlation Equation*:

14.2.1.4

$$\text{Predicted D3606 Procedure B benzene} = \text{bias corrected Procedure A benzene} = C_{procedure\ A} + 0.017 \quad (6)$$

where:

$C_{procedure\ A}$ = volume percent benzene as reported by Test Method D3606 Procedure A.

(1) The correlation equation is applicable to test results in the range of 0.07 % to 5.96 % by volume as determined and reported by Test Method D3606 Procedure A.

14.2.2 *Between Method Bias between Procedures A and B Toluene:*

14.2.2.1 A between method bias assessment of Test Method D3606 Procedure A versus Procedure B for the determination of toluene was conducted using data from the ILS of Procedure A which also included a parallel ILS using Procedure B using identical samples. The assessment was performed in accordance with the requirements of Practice D6708 with a successful outcome and is documented in Research Report RR:D02-2004.[3]

14.2.2.2 The degree of agreement between results from Test Method D3606 Procedure A toluene versus Procedure B toluene can be further improved by applying a correlation equation (Eq 7) (Research Report RR:D02-2004[3]). There were no discernable sample-specific biases as defined in Practice D6708.

14.2.2.3 *Correlation Equation*:

TABLE 2 Repeatability–Procedure A (WCOT Column)

NOTE 1—X = the average of two results in volume percent of the component; each result is to be within the ranges below.

Component	Volume percent	Repeatability
Benzene	0.12 to 5.2	0.03202 (X + 0.2)
Toluene	0.4 to 19.7	0.01767 (X + 0.5)

TABLE 3 Reproducibility–Procedure A (WCOT Column)

NOTE 1—X = the average of two results in volume percent of the component; each result is to be within the ranges given below.

Component	Volume percent	Reproducibility
Benzene	0.12 to 5.2	0.1462 (X + 0.2)
Toluene	0.4 to 19.7	0.04659 (X + 0.5)

TABLE 4 Repeatability/Reproducibility Example (Benzene)–Procedure A (WCOT Column)

Benzene Volume percent	Repeatability	Reproducibility
0.10	0.010	0.044
0.20	0.013	0.058
0.30	0.016	0.073
0.40	0.019	0.088
0.50	0.022	0.102
0.60	0.026	0.117
0.70	0.029	0.132
0.80	0.032	0.146
0.90	0.035	0.161
1.00	0.038	0.175
2.00	0.070	0.322
3.00	0.102	0.468
4.00	0.134	0.614
5.00	0.167	0.760

TABLE 5 Repeatability/Reproducibility Example (Toluene)–Procedure A (WCOT Column)

Toluene Volume percent	Repeatability	Reproducibility
0.4	0.016	0.042
1.0	0.027	0.070
2.0	0.044	0.116
3.0	0.062	0.163
4.0	0.080	0.210
5.0	0.097	0.256
6.0	0.115	0.303
7.0	0.133	0.349
8.0	0.150	0.396
9.0	0.168	0.443
10.0	0.186	0.489
11.0	0.203	0.536
12.0	0.221	0.582
13.0	0.239	0.629
14.0	0.256	0.676
15.0	0.274	0.722
16.0	0.292	0.769
17.0	0.309	0.815
18.0	0.327	0.862
19.0	0.345	0.909
20.0	0.362	0.955

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TABLE 6 Comparison of Precision between Procedure A and Procedure B in the Range of 0.10 % to 1.50 % Volume for Benzene

Benzene percent volume	Procedure A		Procedure B	
	Repeatability	Reproducibility	Repeatability	Reproducibility
0.10	0.010	0.044	0.013	0.063
0.30	0.016	0.073	0.019	0.089
0.50	0.022	0.102	0.025	0.115
0.70	0.029	0.132	0.031	0.141
0.90	0.035	0.161	0.037	0.167
1.10	0.042	0.190	0.043	0.193
1.30	0.048	0.219	0.049	0.219
1.50	0.054	0.249	0.055	0.245

14.2.2.4

$$\text{Predicted D3606 Procedure B toluene} = \text{bias corrected Procedure A toluene} = 1.01 * C_{Procedure\ A} - 0.025 \quad (7)$$

where:

$C_{Procedure\ A}$ = volume percent toluene as reported by Test Method D3606 Procedure A.

(1) The correlation equation is applicable to test results as determined and reported by Test Method D3606 Procedure A in the range of 0.36 % to 20.64 % by volume toluene.

15. Keywords

15.1 aviation gasoline; benzene; gas chromatography; gasoline; multidimensional gas chromatography; spark ignition fuels; toluene

PROCEDURE B—PACKED GAS CHROMATOGRAPHIC COLUMNS

16. Summary of Test Method

16.1 An internal standard, *sec*-butanol, is added to the sample. The sample is then introduced into a gas chromatograph (GC) equipped with two packed GC columns connected in series. The sample passes first through a pre-column packed with a nonpolar or equivalent phase, which separates the lighter components according to boiling point. After toluene has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than toluene. The lighter components then pass through an analytical column packed with a stationary phase capable of separating benzene and toluene from ethanol and other hydrocarbons and oxygenates such as methanol, MTBE, TAME, ETBE, and butanols. The eluted components are detected by a thermal conductivity detector (TCD). The detector response is recorded, the peak areas are measured and the concentration of each component is calculated with reference to the internal standard.

17. Significance and Use

17.1 Knowledge of the concentration of benzene may be required for regulatory use, control of gasoline blending, and/or process optimizations.

18. Apparatus

18.1 *Chromatograph*—Any multidimensional packed column gas chromatographic instrument configuration that has a backflush system and thermal conductivity detector, and that can meet the specification of this test method, such as column resolution, can be used.

18.1.1 Two backflush systems are shown. Fig. A2.1 is a switching valve system and Fig. A2.2 is a pressure system. Either one can be used.

18.2 *Columns:*

18.2.1 *Columns A (Precolumn) and B (Analytical Column)*—Annex A2.2 gives an example of a commercial column set that has been used successfully for samples containing ethanol. In addition, Annex A2.4 gives an additional column set originally proposed by the U.S. Environmental Protection Agency (EPA) that may be adequate for this analyses. Other packed column sets that give a resolution from ethanol as specified in 21.3 may be used.

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

18.4 *Microsyringe*—5 µL capacity.

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

18.6 *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.

NOTE 9—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 18.5 and 18.6.

18.7 *Flasks*—Class A volumetric (see Specification E288), 25 mL and 100 mL capacity.

19. Materials

19.1 *Carrier Gas*—Helium, 99.99 % mol pure or better. (**Warning—**Compressed gas under high pressure.)

19.2 *Solvents:*

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

19.3 *Internal Standard:*

19.3.1 sec-*butanol*—99.5 % mol minimum purity. Free of benzene and toluene. (**Warning—**Flammable. Vapor can be harmful.)

19.4 *Calibration Standards:*

19.4.1 *Benzene*—99^+ % mol. (**Warning—**Poison. Carcinogen. Harmful or fatal if swallowed. Extremely flammable. Vapors can cause flash fires.)

19.4.2 *Isooctane (2,2,4–trimethyl pentane)*—99^+ % mol. (**Warning—**Extremely flammable. Harmful if inhaled.)

19.4.3 *Toluene*—(**Warning—**Flammable. Vapor harmful.)

19.4.4 *n-nonane*—99^+ % mol. (**Warning—**Flammable. Vapor harmful.)

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20. Sampling

20.1 *Spark Ignition Fuel (for example, "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.

21. Configuration of Apparatus and Establishment of Conditions

21.1 Following manufacturer's guidelines and/or suggested details in A2.2, A2.3, and A2.4 optimize the chromatographic system.

21.1.1 *Column System Setup for Valve Backflushing*—The following procedure provides a general guideline for optimizing a system using valve switching as shown in Fig. A2.1. Several operational conditions are given in Table A2.1.

21.1.1.1 Set the valve in the *forward flow* mode with columns A and B in series (Fig. A2.2), and adjust the primary flow control to give the desired flow. Measure the flow rate at the detector vent, sample side.

21.1.1.2 Set the valve in the *backflush* position, measure the flow rate at the detector vent, sample side. If the flow has changed, adjust the secondary or auxiliary flow control to obtain the correct flow. Flows should match to within ±1 cm^3/min.

21.1.1.3 Change the valve from *forward flow* to the *backflush* position several times and observe the baseline. There should be no baseline shift or drift after the initial valve kick that results from the pressure surge. If there is a baseline shift, increase or decrease the secondary flow control slightly to balance the baseline. A persistent drift could indicate leaks somewhere in the system.

21.2 *Determine Time to Backflush*—The time to backflush will vary for each column system and must be determined experimentally as follows. Table A2.1 gives examples of backflush times. Prepare a mixture of 5 % by volume *iso*octane in *n*-nonane. With the valve configuration in the *forward flow* mode, inject 1 µL of the *iso*octane-*n*-nonane mixture. Allow the chromatogram to run until the *n*-nonane has eluted and the detector signal has returned to baseline. Measure the time in seconds, from the injection until the detector signal returns to baseline between the *iso*octane and *n*-nonane peaks. At this point all of the *iso*octane, but essentially none of the *n*-nonane, should have eluted. Repeat the run, including the injection, but switching the system to the *backflush* mode at the predetermined "time to backflush." This should result in a chromatogram of *iso*octane with little or no *n*-nonane visible. If necessary, make additional runs, adjusting the "time to backflush" until this condition of all the *iso*octane and little or no *n*-nonane is attained. The "time to backflush" so established, including the *actual valve operations, must be used* in all subsequent calibrations and analyses. It is also valid to set backflush time after toluene elutes.

21.3 *Resolution of Ethanol/Benzene and Sec-butanol Benzene Pairs*—Resolution calculation may be performed by the CDS or manually. The resolution shall be greater than 1.5 using calibration standard 4 (Table 7) for benzene. If using a CDS, ensure the CDS is using the proper resolution calculation, as follows:

TABLE 7 Seven Standard Samples

Std #	Benzene		Toluene	
	Volume %	mL	Volume %	mL
1	5	5	20	20
2	2.5	2.5	15	15
3	1.25	1.25	10	10
4	0.67	0.67	5	5
5	0.33	0.33	2.5	2.5
6	0.12	0.12	1	1
7	0.06	0.06	0.5	0.5

$$R_{p2} = \frac{1.18(T_{p2} - T_{p1})}{W_{h1/2} + W_{h2/2}} \quad (8)$$

where:

R_{p2} = the resolution of peak 2,
T_{p1} = the retention time of peak 1,
T_{p2} = the retention time of peak 2,
$W_{h1/2}$ = the width of peak 1 at half height, and
$W_{h2/2}$ = the width of peak 2 at half height.

21.4 To ensure proper resolution at low concentration ranges, the ethanol needs to have minimal peak tailing. A2.2 and A2.4 describe the recommended peak symmetry for ethanol and the ethanol/benzene resolution required. It is recommended that final system optimization be verified against certified reference materials containing benzene at several concentration levels of interest and ethanol present at a level in the expected samples to confirm the accuracy of the analyses.

22. Calibration and Standardization

22.1 *Standard Samples*—Prepare seven standard samples (Table 7) covering the range 0.06 % to 5 % by volume benzene and 0.5 % to 20 % by volume toluene as follows: For each standard, measure the volume of benzene and of toluene listed below into a 100 mL volumetric flask. Dilute to volume with *iso*octane (*2,2,4–trimethyl pentane*), with all components and glassware at ambient temperature.

22.2 *Calibration Blends*—Accurately measure 1.0 mL of *sec*-butanol into a 25 mL volumetric flask, and fill to the mark with the first standard sample (22.1). Continue doing this until all blends have been prepared.

NOTE 10—Commercially prepared calibration standards may be used, including those that are pre-mixed with the *sec*-butanol internal standard.

22.3 *Chromatographic Analysis*—Chromatograph each of the calibration blends using the conditions established in 21.4 using the following injection technique:

22.4 *Injection of Sample:*

22.4.1 Use an automatic liquid sample injection system. If manual injections are to be made, the injection technique in 22.4.2 is necessary so that sharp symmetrical peaks will be obtained.

NOTE 11—ILS precision was based using automated injection systems.

22.4.2 Flush the 5 µL microsyringe at least three times with the sample mixture and then fill with about 3 µL of the sample. (Avoid including any air bubbles in the syringe). Slowly eject the sample until 2.0 µL remains in the syringe; wipe the needle with tissue and draw back the plunger to admit 1 µL to 2 µL of air into the syringe. Insert the needle of the syringe through the

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septum cap of the chromatograph and push until the barrel of the syringe is resting against the septum cap; then push the plunger to the hilt and remove the syringe immediately from the chromatograph.

22.5 *Calibration*—Measure the area of both aromatic peaks and of the internal standard peak. Calculate the ratio of the benzene peak area to the *sec*-butanol and the ratio of concentrations of benzene to that of the *sec*-butanol. Plot the area ratios versus and concentration ratios. Make the same calculation and plot for toluene. The calibrations shall be linear (Fig. A2.6).

NOTE 12—Some CDS systems plot the area ratio versus the concentration ratio of the benzene and toluene to that of the internal standard. Consult the system guidelines.

23. Procedure

23.1 *Preparation of Sample*—Accurately measure 1.0 mL of *sec*-butanol into a 25 mL volumetric flask. Fill to the mark with the sample to be tested and mix well.

23.2 *Chromatographic Analysis*—Chromatograph the sample, using the conditions established in Section 21 "time to backflush" and the injection technique described in 22.4. The valves must be turned to backflush mode at the time determined in 21.2 so that undesirable components do not enter Column B.

23.3 *Interpretation of Chromatogram*—Identify on the chromatogram the benzene, toluene, and the internal standard *sec*-butanol peaks from the retention times of the standards.

NOTE 13—The order of elution will be nonaromatic hydrocarbons, ethanol, benzene, *sec*-butanol, and toluene using the prescribed column system in A2.2. Figs. A2.5 and A2.6 are examples of typical chromatograms.

23.4 *Measurement of Area*—Measure the areas under the aromatic peaks and under the internal standard peak by CDS.

NOTE 14—The precision statement in Section 26 was developed from data obtained using electronic integrators or on-line computers. The precision statement may not apply if other methods of integration or peak area measurement are used.

24. Calculation

24.1 Calculate the ratios of the peak areas of benzene and toluene to the peak area of the internal standard or if using concentration ratios also ratio of benzene and aromatics to that of the internal standard. Determine from the appropriate calibration curve the liquid volume percent of benzene and toluene corresponding to the calculated peak ratios.

24.2 If the results are desired on a mass basis, convert to mass percent as follows:

$$\text{Benzene, mass percent} = (V_B / D) \times 0.8844 \quad (9)$$

where:

V_B = volume percent benzene, and
D = relative density of sample at 15.6/15.6 °C (60/60 °F).

$$\text{Toluene, mass percent} = (V_T / D) \times 0.8719 \quad (10)$$

where:

V_T = volume percent toluene, and
D = relative density of sample at 15.6/15.6 °C (60/60 °F).

25. Report

25.1 Report the benzene and toluene contents in liquid volume percent to the nearest 0.01 %. Indicate that result is from "D3606 Procedure B."

25.2 In accordance with Practice D6300, to accommodate normal random testing variation, the lowest reportable test X result in volume percent is computed as follows:

$$\begin{aligned} X &= \text{lowest reportable test result of this test method} \\ &= [\text{lowest retained ILS sample mean} \\ &\quad - R\ (\text{evaluated at the lowest retained ILS sample mean})] \end{aligned} \quad (11)$$

25.2.1 For benzene: $X_{\text{lowest reportable}} = 0.04$
25.2.2 For toluene: $X_{\text{lowest reportable}} = 1.7$

25.3 In accordance with Practice D6300, to accommodate normal random testing variation, the highest reportable test X result in volume percent is computed as follows:

$$\begin{aligned} X &= \text{highest reportable test result of this test method} \\ &= [\text{highest retained ILS sample mean} \\ &\quad + R\ (\text{evaluated at the highest retained ILS sample mean})] \end{aligned} \quad (12)$$

25.3.1 For benzene: $X_{\text{highest reportable}} = 5.25$
25.3.2 For toluene: $X_{\text{highest reportable}} = 21.2$

26. Quality Control

26.1 *Test for System Stability and Repeatability*—On setting up the method for the first time and thereafter when major maintenance (change in columns and flows, for example) is performed, make six injections of standard #4 (Table 7). Calculate the standard deviation from the six results from the six injections. Calculate 2.77 × the standard deviation obtained. This quantity shall meet repeatability as published in 27.1.1. Thereafter, establish statistical quality control charting (SQC) for each batch of analysis analyzed using a production sample similar in composition to samples to be analyzed.

26.2 *Reference Material*—Analyze one or more reference material of known accepted reference value (ARV), such as from NIST and/or an independent certified control standard, or meeting the check standard requirement as specified in Practice D6299 upon setting up the test method, post maintenance (calibration, column replacement, cut time adjustments, and so forth) and at least quarterly to confirm proper set-up and calibration of the gas chromatograph. Test results shall agree with within the 95 % confidence level or reproducibility of the benzene or toluene components divided by the square root of 2. In addition follow any other specification requirements per regulatory or commercial application(s). Monitor the performance of the reference material(s) using SQC charting in accordance with Practice D6299.

27. Precision and Bias

27.1 The following criteria should be used for judging the acceptability of results (95 % confidence). The user should choose the precision statement that reflects the concentration range of each component under study.

27.1.1 *Repeatability*—The difference between two independent results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under

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