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**

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.