



Designation: D5769 – 22

Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry¹

This standard is issued under the fixed designation D5769; 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 in volume percent of benzene, toluene, other specified individual aromatic compounds, and total aromatics in finished motor gasoline, including gasolines containing oxygenated blending components, by gas chromatography/mass spectrometry (GC/MS). Precision is calculated for benzene, toluene and total aromatics.

1.2 This test method has been evaluated using a **D6300**-compliant Interlaboratory Study (ILS), with the lowest and highest ILS sample averages listed as follows: benzene, 0.09 % to 4.00 %; toluene, 1.0 % to 13.0 %; and total (C6 to C12) aromatics, 10.0 % to 42.0 %. The ILS study did not test the method for *individual* hydrocarbon process streams produced in a refinery, such as reformates, fluid catalytic cracked naphthas, and so forth, used in the blending of gasolines.

1.3 Results are reported to the nearest 0.01 % for benzene and 0.1 % for the other aromatics by liquid volume. The Report Section (14) describes the applicable reporting ranges of this test method.

1.4 This test method includes a between test method bias section for spark-ignition engine fuel benzene reporting based on Practice **D6708** assessment between Test Method D5769 and Test Method **D3606** as a possible Test Method D5769 alternative to Test Method **D3606**. The Practice **D6708** derived correlation equation is only applicable for blended fuels with benzene results concentration range from 0.05 % to 2.50 % by volume as measured and reported by Test Method D5769.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to its use.*

1.7 *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

- 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
- D4175** Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4307** Practice for Preparation of Liquid Blends for Use as Analytical Standards
- 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

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 **D02.04.0M** on Mass Spectrometry.

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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

3. Terminology

3.1 This test method makes reference to common terms, procedures, and relationships. Detailed definitions of these may be found in Practice E355 and Terminology D4175.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *aromatic, n*—any hydrocarbon compound containing a benzene or naphthalene ring.

3.2.2 *calibrated aromatic component, n*—the individual aromatic components that have a specific calibration.

3.2.3 *cool on-column injector, n*—in gas chromatography, a direct sample introduction system that is set at a temperature at or below the boiling point of solutes or solvent on injection and then heated at a rate equal to or greater than the column. Normally used to eliminate boiling point discrimination on injection or to reduce adsorption on glass liners within injectors, or both. The sample is injected directly into the head of the capillary column tubing.

3.2.4 *open split interface, n*—GC/MS interface used to maintain atmospheric pressure at capillary column outlet and to eliminate mass spectrometer vacuum effects on the capillary column. Can be used to dilute the sample entering the mass spectrometer to maintain response linearity.

3.2.5 *reconstructed ion chromatogram (RIC), n*—a limited mass chromatogram representing the intensities of ion mass spectrometric currents for only those ions having particular mass to charge ratios. Used in this test method to selectively extract or identify aromatic components in the presence of a complex hydrocarbon matrix, such as gasoline.

3.2.6 *retention gap, n*—in gas chromatography, refers to a deactivated precolumn which acts as a zone of low retention power for reconcentrating bands in space. The polarity of the precolumn must be similar to that of the analytical column.

3.2.7 *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.

3.2.8 *total ion chromatogram (TIC), n*—mass spectrometer computer output representing either the summed intensities of all scanned ion currents or a sample of the current in the ion beam for each spectrum scan plotted against the corresponding spectrum number. Generally, it can be correlated with a flame ionization detector chromatogram.

3.2.9 *uncalibrated aromatic component, n*—individual aromatics for which a calibration is not available. These components are estimated from the calibration of several calibrated aromatic components.

3.2.10 *wall coated open tubular (WCOT), n*—a type of capillary column prepared by coating or bonding the inside wall of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 A gas chromatograph equipped with a dimethylpolysiloxane WCOT column is interfaced to a fast scanning mass spectrometer that is suitable for capillary column GC/MS analyses. The sample is injected either through a capillary splitter port or a cool-on-column injector capable of introducing a small sample size without overloading the column. The capillary column is interfaced directly to the mass spectrometer or by way of an open split interface or other appropriate device.

4.2 Calibration is performed on a mass basis, using mixtures of specified pure aromatic hydrocarbons. Volume percent data is calculated from the densities of the individual components and the density of the sample. A multipoint calibration consisting of at least five levels and bracketing the expected concentrations of the specified individual aromatics is required. Specified deuterated hydrocarbons are used as the internal standards, for example, d6-benzene for quantitating benzene. Unidentified aromatic hydrocarbons present that have not been specifically calibrated for are quantitated using the calibration of an adjacent calibrated compound and summed with the other aromatic components to obtain a total aromatic concentration of the sample.

4.3 Specified quality control mixture(s), such as synthetic quality control mixtures must be analyzed to monitor the performance of the calibrated GC/MS system. Analysis of a gasoline as a reference material is strongly recommended.

5. Significance and Use

5.1 Test methods to determine benzene and the aromatic content of gasoline are necessary to assess product quality and to meet 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 Gas Chromatography:

6.1.1 System equipped with temperature-programmable gas chromatograph suitable for split injections with WCOT column or cool-on-column injector that allows the injection of small (for example, 0.1 µL) samples at the head of the WCOT column or a retention gap. An autosampler is mandatory for the on-column injections.

6.1.2 WCOT column containing dimethylpolysiloxane bonded stationary phase, meeting the specification in the following table. For on-column injections, a column containing