



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 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).

1.2 This test method has been tested for the following concentration ranges, in liquid volume percent, for the following aromatics: benzene, 0.1 % to 4 %; toluene, 1 % to 13 %; and total (C6 to C12) aromatics, 10 % to 42 %. The round-robin study did not test the method for *individual* hydrocarbon process streams 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.

1.4 This test method includes a relative bias section for EPA spark-ignition engine fuel benzene regulations reporting based on Practice [D6708](#) accuracy 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 in the benzene concentration range from 0.0 % to 2.50 % by volume as measured by Test Method D5769. The applicable Test Method [D3606](#) range for benzene is from 0.0 % to 2.47 % by volume as reported by Test Method [D3606](#).

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 appro-*

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

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 Finished Motor and Aviation Gasoline 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

[D4307](#) Practice for Preparation of Liquid Blends for Use as Analytical Standards

[D6708](#) Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *aromatic*—any hydrocarbon compound containing a benzene or naphthalene ring.

3.1.2 *calibrated aromatic component*—the individual aromatic components that have a specific calibration.

3.1.3 *cool on-column injector*—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.

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 Spectroscopy.

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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

3.1.4 *open split interface*—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.

3.1.5 *reconstructed ion chromatogram (RIC)*—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.

3.1.6 *retention gap—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.

3.1.7 *split ratio—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.

3.1.8 *total ion chromatogram (TIC)*—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.

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

3.1.10 *wall coated open tubular (WCOT)*—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 a thicker film of stationary phase, such as 4–5 μm , is recommended to prevent column sample overload.

Resolution R between 1,3,5-trimethylbenzene and 1-methyl-2-ethylbenzene at the 3 mass % level each must be equal to or greater than 2.0

$$R = \frac{2(t_1 - t_2)}{1.699(y_2 + y_1)}$$

t_2 = retention time of 1,3,5-trimethylbenzene

t_1 = retention time of

1-methyl-2-ethylbenzene

y_2 = peak width at half height of 1,3,5-trimethylbenzene

y_1 = peak width at half height 1-methyl-2-ethyl benzene

6.2 Mass Spectrometry:

6.2.1 Mass spectrometer capable of producing electron impact spectra at 70, or higher, electron volts or equivalent, and capable of scanning the range of the specified quantitation masses or m/e . The mass scan range shall cover the masses of interest for quantitation and should yield at least 5 scans across the peak width at half peak width for a 1 to 3 mass percent toluene and cover the masses of interest for quantitation. A scan range of 41 to 200 daltons is adequate.

6.2.2 The mass spectrometer must be capable of being interfaced to a gas chromatograph and WCOT columns. The interface must be at a high enough temperature to prevent condensation of components boiling up to 220 $^{\circ}\text{C}$, usually 20 $^{\circ}\text{C}$ above the final column temperature is adequate. Direct column interface to the mass spectrometer can be used. An open split interface with computer controlled programmable flow controller(s) can also be used, particularly with cool

on-column injections, to maintain all aromatic components within the linearity of the mass spectrometer and at the same time maintain detectability of lower concentration aromatic components. For example, a higher open-split-interface make-up gas flow can be used for the high concentration components, such as toluene and xylenes, and a lower make-up gas flow rate may be used during the elution of the lower concentration benzene and C9+ components. Other interfaces may be used provided the criteria specified in Sections 9 and 10 are met.

6.2.3 A computer system shall be interfaced to the mass spectrometer to allow acquisition of continuous mass scans or total ion chromatogram (TIC) for the duration of the chromatographic program and be able to analyze repeatedly 0.01 mass percent 1,4-diethylbenzene with the specified signal/noise ratio of 5. Software must be available to allow searching any GC/MS run for specific ions or reconstructed ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantitation. The quantitation software must allow linear least squares or quadratic nonlinear regression and quantitation with multiple internal standards. It is also recommended that software be available to automatically perform the identification of aromatic components as specified in 13.1.1.

7. Reagents and Materials

7.1 *Carrier Gas*—Helium and hydrogen have been used successfully. The recommended minimum purity of the carrier gas used is 99.999 mol percent. Additional purification using commercially available scrubbing reagents may be necessary to remove trace oxygen, which may deteriorate the performance of the GC WCOT. (**Warning**—Helium and hydrogen are supplied under high pressure. Hydrogen can be explosive and requires special handling. Hydrogen monitors that automatically shut off supply to the GC in case of serious leaks are available from GC supply manufacturers.)

7.2 *Dilution Solvents*—Reagent grade 2,2,4-trimethylpentane (*iso*-octane), *n*-heptane, *n*-nonane, cyclohexane, or toluene, or a combination thereof, used as a solvent in the preparation of the calibration mixtures. (**Warning**—The gasoline samples and solvents used as reagents such as *iso*-octane, cyclohexane, *n*-heptane, *n*-octane, and toluene, are flammable and may be harmful or fatal if ingested or inhaled. Benzene is a known carcinogen. Use with proper ventilation. Safety glasses and gloves are required while preparing samples and standards. Samples should be kept in well ventilated laboratory areas.)

NOTE 1—Toluene should be used as a solvent only for the preparation of C9+ components and shall be free from interfering aromatics.

7.3 *Internal Standards*—Deuterated analogs of benzene, ethylbenzene, and naphthalene, as specified in Table 1, shall be used as internal standards because of their similar chromatographic characteristics as the components analyzed. The use of a fourth internal standard toluene-d8 is recommended. Deuterated naphthalene is hygroscopic and should be stored away from high humidity.

7.4 *Standards for Calibration and Identification*—Aromatic hydrocarbons used to prepare standards should be 99 % or greater purity (see Table 1). If reagents of high purity are not available, an accurate assay of the reagent shall be performed using a properly calibrated GC or other techniques. The concentration of the impurities that overlap the other calibration components shall be known and used to correct the concentration of the calibration components. The use of only high purity reagents is strongly recommended because of the error that may be introduced from impurity corrections. Standards are used for calibration as well as for establishing the identification by retention time in conjunction with mass spectral match (see 13.1.1). Naphthalene is hygroscopic and should be stored away from high humidity.

TABLE 1 Mass Spectrometer Quantitation Ions for Sample Components and Internal Standards

Compound	CAS No.	Primary Ion (Dalton)	Internal Standard (ISTD)	ISTD ION (Dalton)
Benzene	71-43-2	78	Benzene-d6	84 + 83
Toluene	108-88-3	92	Ethylbenzene-d10 or toluene-d8	116 + 115 or 100 + 99
Ethylbenzene	100-41-4	106	Ethylbenzene-d10	116 + 115
1,3-Dimethylbenzene	108-38-3	106	Ethylbenzene-d10	116 + 115
1,4-Dimethylbenzene	106-42-3	106	Ethylbenzene-d10	116 + 115
1,2-Dimethylbenzene	95-47-6	106	Ethylbenzene-d10	116 + 115
(1-Methylethyl)-benzene	98-82-8	120	Ethylbenzene-d10	116 + 115
Propyl-benzene	103-65-1	120	Ethylbenzene-d10	116 + 115
1-Methyl-3-ethylbenzene	620-14-4	120	Ethylbenzene-d10	116 + 115
1-Methyl-4-ethylbenzene	622-96-8	120	Ethylbenzene-d10	116 + 115
1,3,5-Trimethylbenzene	108-67-8	120	Ethylbenzene-d10	116 + 115
1-Methyl-2-ethylbenzene	611-14-3	120	Ethylbenzene-d10	116 + 115
1,2,4-Trimethylbenzene	95-63-6	120	Ethylbenzene-d10	116 + 115
1,2,3-Trimethylbenzene	526-73-8	120	Ethylbenzene-d10	116 + 115
Indan	496-11-7	117	Ethylbenzene-d10	116 + 115
1,4-Diethylbenzene	105-05-5	134	Naphthalene-d8	136 + 135
<i>n</i> -Butylbenzene	104-51-8	134	Naphthalene-d8	136 + 135
1,2-Diethylbenzene	135-01-3	134	Naphthalene-d8	136 + 135
1,2,4,5-Tetramethylbenzene	95-93-2	134	Naphthalene-d8	136 + 135
1,2,3,5-Tetramethylbenzene	527-53-7	134	Naphthalene-d8	136 + 135
Naphthalene	91-20-3	128	Naphthalene-d8	136 + 135
2-Methyl-naphthalene	91-57-6	142	Naphthalene-d8	136 + 135
1-Methyl-naphthalene	90-12-0	142	Naphthalene-d8	136 + 135