Designation: D5769 – 15

Standard Test Method for
Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry[1]

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 appropriate 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.

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[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:

$$\text{split ratio} = (S+C)/C \tag{1}$$

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	$R = \frac{2(t1 - t2)}{1.699(y2 + y1)}$ $t2$ = retention time of 1,3,5-trimethylbenzene $t1$ = retention time of 1-methyl-2-ethylbenzene $y2$ = peak width at half height of 1,3,5-trimethylbenzene $y1$ = 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 °C, usually 20 °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
n-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

8. Sampling

8.1 Every effort should be made to ensure that the sample is representative of the fuel source from which it is taken. Follow the recommendations of Practice D4057, or its equivalent, when obtaining samples from bulk storage or pipelines. Sampling to meet certain regulatory specifications may require the use of specific sampling procedures. Consult appropriate regulations.

8.2 Appropriate steps should be taken to minimize the loss of light hydrocarbons from the gasoline sample while sampling and during analyses. Upon receipt in the laboratory, chill the sample in its original container to between 0 to 5°C before and after a sample aliquot is removed for analysis.

8.3 After the sample is prepared for analysis with internal standard(s), chill the sample and fill the autosampler vial to approximately 90 % of its volume. The remainder of the sample should be re-chilled immediately and protected from evaporation for further analyses, if necessary. To prevent evaporation of the sample, the autosampler vials should be stored at 0 °C to 5 °C until ready for loading on the autosampler.

9. Calibration

9.1 *Preparation of Calibration Standards*—Multi-component calibration standards using all the compounds listed in Table 1 are prepared by mass according to Practice D4307. The standards may be prepared by combining the specified individual aromatics either into a single mixture or into multiple sets. Multiple sets may be prepared as follows: (*1*) Set I consists of benzene, methylbenzene (toluene), ethylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene, using 2,2,4-trimethylpentane (*iso*octane) as a recommended dilution solvent; (*2*) Set II consists of the remaining C_9+ components using a 50/50 mixture of 2,2,4-trimethylpentane and methylbenzene (toluene) as the recommended dilution solvent. Other solvents, such as *n*-nonane, or co-solvents may be used to improve solubility, chromatographic or mass spectrometric performance, provided these solvents contain no detectable amounts of aromatics which will interfere with the analyses.

NOTE 2—It may be more convenient to prepare gravimetrically pure (solvent free) batches of Set I and Set II components, which then can be weighed into appropriate diluted standards. The internal standards for Set I are benzene-d_6 and ethylbenzene-d_{10}. Toluene-d_8 may be added to the internal standard mixture for the quantitation of toluene. The internal standards for Set II are ethylbenzene-d_{10} and naphthalene-d_8.

NOTE 3—Appropriate internal standards batches may be prepared and then added to calibration standards and samples in a single step.

A *minimum* of five calibration solutions shall be prepared by mass for single mixtures containing all of the specified calibration compounds. For toluene, three of the calibration standards must be above the 50 % point of the calibration range. If nonlinearity is observed, the addition of a sixth calibration standard is recommended to better define its potential nonlinearity at the higher concentration range. If the calibration solutions are prepared in sets, then for each set, five separate solutions must be prepared over the desired concentration range; for example, five calibration solutions for Set I, and five calibration solutions for Set II. Table 2 gives the recommended volumes to be weighed into 100 mL volumetric

TABLE 2 Relative Densities and Calibration Concentrations

Compound	Relative Density 60 °F/60 °F	Target Highest Concentration Calibration Solution (volume % or mL/100 mL)	Calibration Components Prepared into a Single Mixture	Calibration Components Prepared into Two Sets of Mixtures
Benzene	0.8845	5	Set 1	Set 1
Toluene	0.8719	19	Set 1	Set 1
Ethylbenzene	0.8718	5	Set 1	Set 1
1,3-Dimethylbenzene	0.8688	6	Set 1	Set 1
1,4-Dimethylbenzene	0.8657	6	Set 1	Set 1
1,2-Dimethylbenzene	0.8846	6	Set 1	Set 1
(1-Methylethyl)-benzene	0.8664	3	Set 1	Set 2
Propyl-benzene	0.8665	3	Set 1	Set 2
1-Methyl-3-ethylbenzene	0.8691	3	Set 1	Set 2
1-Methyl-4-ethylbenzene	0.8657	3	Set 1	Set 2
1,3,5-Trimethylbenzene	0.8696	3	Set 1	Set 2
1-Methyl-2-ethylbenzene	0.8851	3	Set 1	Set 2
1,2,4-Trimethylbenzene	0.8803	5	Set 1	Set 2
1,2,3-Trimethylbenzene	0.8987	3	Set 1	Set 2
Indan	0.9689	3	Set 1	Set 2
1,4-Diethylbenzene	0.8664	3	Set 1	Set 2
n-Butylbenzene	0.8646	3	Set 1	Set 2
1,2-Diethylbenzene	0.8843	3	Set 1	Set 2
1,2,4,5-Tetramethylbenzene	0.8915	3	Set 1	Set 2
1,2,3,5-Tetramethylbenzene	0.8946	2	Set 1	Set 2
Naphthalene	1.000	2^A	Set 1	Set 2
2-Methyl-naphthalene	1.000	2^A	Set 1	Set 2
1-Methyl-naphthalene	1.0245	2	Set 1	Set 2
Uncalibrated indans	1.000	—		
Uncalibrated C10-benzenes	0.878	—		—
Uncalibrated C11 benzenes	1.000	—		—
Uncalibrated C12-benzenes	1.000	—		—

[A] These components are solids at ambient temperature. The values represent g/100 mL flasks or 100 mL septum capped vials for the most concentrated calibration standard. Adjust these concentrations, as necessary, to ensure that the concentrations of the components in the actual samples are bracketed by the calibration concentrations. Solid components are weighed directly into the flask or vial. Other more dilute standards are prepared separately by weighing appropriate amounts of the pure aromatic components. Prepare a calibration standard according to Practice D4307 as follows:

9.1.1 Cap and record the tare weight of the 100 mL volumetric flask or vial to 0.1 mg.

9.1.2 Remove the cap and carefully add an aromatic component to the flask or vial starting with the least volatile component. Cap the flask and record the net mass (*Wi*) of the aromatic component added to 0.1 mg.

9.1.3 Repeat the addition and weighing procedure for each aromatic component.

9.1.4 If Sets I and II components were *pre-mixed* gravimetrically, then to each calibration solution, volumetric flask, or vial, weigh appropriate volumes to yield the ten calibration solutions. Calculate the actual mass of each component by multiplying the total mass of the combined mixture by the mass fraction of the individual components in the pre-mixed undiluted mixture.

9.1.5 Similarly add each internal standard and record its net mass (*Ws*) to 0.1 mg. If standards are prepared in multiple sets; for Set I weigh 2 mL each of benzene-d6 and ethylbenzene-d10, and for Set II weigh 2 mL of ethylbenzene-d10 and 1 g naphthalene-d8.

9.1.6 Dilute to 100 mL total volume the standard with the recommended solvents above or equivalent. It is not necessary to weigh the amount of solvent added since the calculations are based on the absolute masses of the aromatic and internal standard components.

9.1.7 Similarly prepare four additional standards to cover the concentration range of interest. For example, for benzene, prepare 0.1, 0.5, 1.0, 3.0, and 5.0 targeted volume percent standards; for toluene, prepare 2.0, 5.0, 10.0, 15.0, and 19.0 targeted volume percent equivalent standards. If the calibration response for toluene is nonlinear, then add a sixth calibration standard, such as 2.0, 5.0, 10.0, 15.0, 17.0, and 19.0 targeted volume percent.

9.1.8 Store the capped calibration standards in a refrigerator at 0 °C to 5 °C when not in use.

9.1.9 Thoroughly mix the prepared standards using a vortex mixer, or equivalent, and transfer approximately 2 mL of the solution to a vial compatible with the autosampler if such equipment is used. Chill the vials until ready for loading on the autosampler.

NOTE 4—Highly precise robotic or semi-automated sample preparation systems are available commercially. These systems may be used to prepare mass percent calibration standards and samples for analyses provided that the results for the quality control reference material (Section 10) are met when prepared with the automated systems.

9.2 *GC/MS Calibration Procedure :*

9.2.1 Prepare the GC/MS system according to manufacturer's instructions and set analysis operating conditions. Table 3 gives suggested operating conditions for split and on-column injection modes.

TABLE 3 Examples of GC/MS Conditions[A]

	Condition 1	Condition 2	Condition 3
Gas Chromatography (GC):			
Column	60 m × 0.25 mm df=1.0 um dimethyl polysiloxane	60 m × 0.32 mm i.d., df=5.0 um dimethyl polysiloxane	20 m × 0.18 mm i.d., df=0.4 um dimethyl polysiloxane
Injector type	splitter	cool on-column	splitter
Injector split ratio	250:1	—	approximately 700:1
Injection size (ul)	0.1–0.5	0.1	0.1 ul
Injector temperature (C)	250 °C	track oven temperature	250 °C
Oven temperature	60 °C (0 min), 3 °C ⁄min to 120 (0 min) 10 °C ⁄min to 250 °C.	50 °C (0 min), 2 °C ⁄min to 190 °C (0 min); 30 °C ⁄min to 300 °C (1 min).	35 °C (1 min), 25 °C ⁄min to 210 °C (1 min)
Carrier gas	helium	hydrogen	helium
Carrier gas linear velocity (cm/s)	35 at 50 °C	42 at 300 °C	30 cm/s at 50 °C
GC/MS Interface:			
GC/MS interface type	direct	open-split with variable flow	direct
Interface temperature (C)	280	280	250
Mass Spectrometry (MS):			
MS Type	quadrupole	quadrupole	quadrupole
MS data acquisition mode	full scan[B]	full scan[B]	full scan[B]
Scan Rate (scan/s)	>1	>1	10
Source temperature (C)	approximately 250	approximately 250	approximately 250
Ionization voltage (eV)	70[B]	70[B]	70[B]
Mass scan range	45–300	45–200	70–170

[A] The above are approximate conditions reported by several laboratories. Other conditions that meet the specifications in the method may be used also.
[B] Fixed operating conditions; must be used as indicated.

9.2.2 Before initiating the calibration procedure, tune the mass spectrometer according to manufacturer's instructions. Set the mass spectrometer data system to acquire data in the full scan (TIC-RIC) mode.

9.2.3 The WCOT shall meet the resolution requirements described in 6.1.2 when installed in the GC/MS system.

9.2.4 Prepare a solution of 0.01 mass % of 1,4-diethylbenzene and verify that it is detected with a signal/noise ratio of at least 5 at mass 134.

9.2.5 Inject a solution of 3 mass % of 1,2,3-trimethylbenzene and confirm that the mass spectrometer provides a fragmentation pattern as specified in Table 4.

9.2.6 Sequentially analyze the calibration standards.

9.3 *Calibration Calculations:*

TABLE 4 Mass Spectrometer Spectral Requirement for 3 Mass % 1,2,3–Trimethylbenzene

Ion (m/e)	Relative Intensity
120	30–60
105	100
91	7–15

9.3.1 After the analyses of the calibration standards are complete, integrate the peak area of each calibration component and internal standards using the reconstructed ion chromatogram (RIC) of the characteristic calibration ion listed in Table 1. Obtain the area under the extracted ion at the retention time of the expected aromatic component (or internal standard).

9.3.1.1 Erroneous aromatic concentrations may result when the deuterated internal standards used for calibrations are from a different batch or lot used for the samples. The most accurate results are obtained when using the same batch of internal standards for the calibration and the sample. However, if the ratio of the intensities of (M-1)/M for the internal standards in the calibration standards divided by the ratio of the intensities of (M-1)/M of the corresponding internal standards in the sample being analyzed is less than 0.97 or greater than 1.03 (±3 % relative difference), then use the SUM of M and (M-1) for the total intensities of the deuterated internal standards for quantitation. If the result is within 0.97 to 1.03 or if the same batch of internal standards is used for the calibration standards and the samples, then the molecular ion M of the internal standards may be used for quantitation. Table 1 lists the M and M-1 ions for the specified deuterated internal standards.

9.3.1.2 The deuterated internal standards may show multiple peaks or shoulders due to the resolution of their various deuterated homologues. If this occurs, sum all of the peaks or shoulders, or both.

9.3.2 Plot the response ratio rsp_i:

$$rsp_i = (A_i/A_s) \tag{2}$$

where:

A_i = area of aromatic compound i, and
A_s = area of internal standard.

as the y-axis versus the amount ratio amt_i:

$$amt_t = W_i/W_s \tag{3}$$

where:

W_i = mass of aromatic compound i in the calibration standard, and
W_s = mass of internal standard in the calibration standard.

as the x-axis to generate calibration curves for each aromatic component specified in Table 2. See Fig. 1 for an example plot.

9.3.3 Check the correlation r^2 value for each aromatic calibration. The value r^2 should be at least 0.99 or better and is calculated as follows:

$$r^2 = \frac{\left(\sum xy\right)^2}{\left(\sum x^2\right)\left(\sum y^2\right)} \tag{4}$$

where:

$$x = X_i - \bar{x} \tag{5}$$

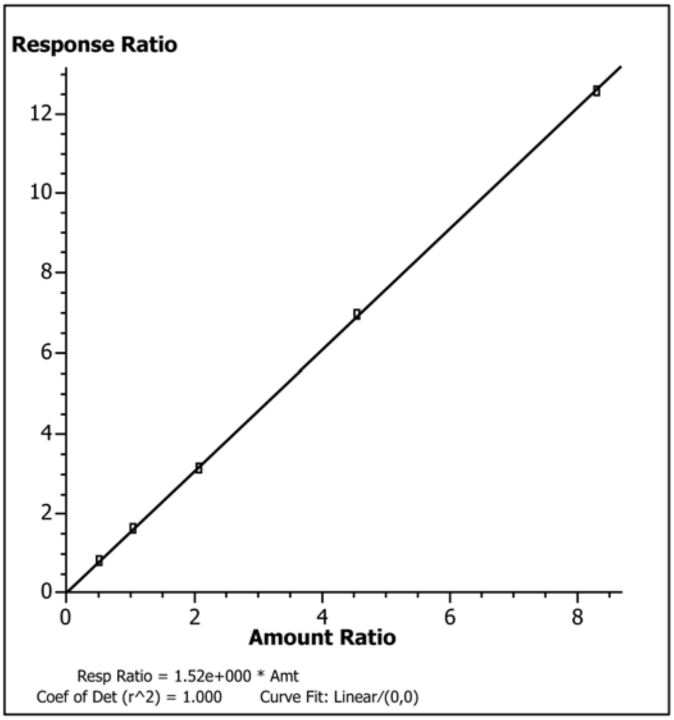

FIG. 1 Example Plot

$$y = Y_i - \bar{y} \tag{6}$$

and:

X_i = amt_t ratio data point,
$\bar{x}$ = average values for all (amt_t) data points,
Y_i = corresponding rsp_i ratio data point, and
$\bar{y}$ = average values for all amt_i data points.

Using the example ideal data set shown in Table 5, r^2 would be calculated as follows:

$$r^2 = \frac{\left(\sum xy\right)^2}{\left(\sum x^2\right)\left(\sum y^2\right)} = \frac{(5)(5)}{(10.0)(2.5)} = 1.0 \tag{7}$$

9.3.4 *Linear Least Squares Fit*—For each aromatic i calibration data set, obtain the linear least squares in the form:

$$(rsp_i) = (m_i)(amt_i) + b_i \tag{8}$$

rsp_i = response ratio for aromatic I (y − axis),

m_i = slope of linear equation for aromatic I, and

amt_i = amount ratio for aromatic I (x − axis).

b_i = y − axis intercept

TABLE 5 Example of Data Set For r^2 Calculation

	Xi	Yi	$x = Xi - \bar{x}$	$y = Yi - \bar{y}$	xy	x^2	y^2
	1.0	0.5	–2.0	–1.0	2.0	4.0	1.0
	2.0	1.0	–1.0	–0.5	0.5	1.0	0.25
	3.0	1.5	0.0	0.0	0.0	0.0	0.0
	4.0	2.0	1.0	0.5	0.5	1.0	0.25
	5.0	2.5	2.0	1.0	2.0	4.0	1.0
Sum	15.0	7.5	0.0	0.0	5.0	10.0	2.5
Average	3.0 ($\bar{x}$)	1.5 ($\bar{y}$)					

The values m_i and b_i are calculated as follows:

$$m_i = \sum xy / \sum x^2 \tag{9}$$

and

$$b_i = \bar{y} - mi\bar{x} \tag{10}$$

For the example in Table 5:

$$m_i = 5/10 = 0.5 \tag{11}$$

and

$$b_i = 0 \tag{12}$$

Therefore, the least square equation for the above example in Table 5 is:

$$(rsp_i) = 0.5(amti) + 0 \tag{13}$$

NOTE 5—Normally the b_i term is not zero and may be positive or negative. It may be more appropriate to force the calibration through the zero intercept, that is, $b_i = 0$, to prevent calculating negative results for components present in the samples at very low concentrations, such as the uncalibrated components. Software is available on commercial GC/MS systems for performing this. Fig. 1 is an example of a calibration curve forced through the origin with a resulting zero intercept value.

9.3.5 *Y-intercept Criteria for Calibrations Curves Not Forced Through Zero*—For an optimum calibration, the absolute value of the *y*-intercept (b_i) must be at a minimum, that is, A_i approaches zero when w_i is less than 0.1 mass %. As A_i approaches zero, the equation to determine the mass % aromatics *i* or w_i reduces to Eq 14.

$$w_i = (b_i/m_i)(W_s/W_g)100\ \% \tag{14}$$

where:

w_i = mass % aromatic *i*,
W_s = mass of internal standard added to the gasoline samples for the quantitation of the aromatic component *i*, g, and
W_g = mass of gasoline samples, g.

Determine the acceptability of the *y*-intercept of the calibration curve of each aromatic component by substituting in Eq 14 the corresponding slope (m_i) and intercept (b_i) along with typical (or average) values for sample mass (W_i). If the calculated mass % aromatic *i* (W_i) is not less than 0.1 mass %, verify the integrity of the GC/MS system and all calibration standards and recalibrate.

9.3.6 Every effort shall be made to obtain linear calibration curves to ensure optimum chromatographic performance and to ensure that the MS signal is not saturated. However, for certain components present in large concentrations in the samples, such as toluene, some nonlinearity may exist. For such compounds the following quantitation procedure must be used:

9.3.6.1 Plot component concentration versus compound response factor of each calibration standard.

9.3.6.2 If the deviation of the response factors for the higher concentration standards is less than 5 % relative than the response factors of the lower concentration standards that are in the linear range, then use a linear fit for all calibration points.

9.3.6.3 If the deviation in 9.3.6.2 is in the range of 5 % to 10 % relative, then use a quadratic fit.

9.3.6.4 If the deviation in 9.3.6.2 is greater than 10 % relative, then no samples can be analyzed until the deviation is corrected.

9.3.7 The GC/MS system shall be recalibrated whenever results of the quality control reference material do not agree within the tolerance levels specified in 10.1.

10. Quality Control Reference Material

10.1 After the calibration has been completed, prepare the quality control reference material outlined in Table 6. Analyze the reference material as described in Sections 11 – 13. The individual aromatic and total aromatics values obtained shall agree within ±5 % relative of the values in the prepared reference material (for example, benzene 1.0 ± 0.05) except for 1,2,4,5-tetramethylbenzene and naphthalene, which must be within ±10 % relative of the values specified. If the individual values are outside the specified range, verify calibration and instrumental parameters, including linearity of injection port splitter (both in concentration and boiling point) for calibration solutions, linearity of mass spectrometer response, purity of reagents, stability or repeatability of GC/MS system, accuracy of the preparation of quality control reference material, and so forth. DO NOT analyze samples without meeting the quality control specifications.

10.2 If samples containing oxygenated fuel additives, such as ethanol or methyl-t-butyl ether (MTBE), are to be analyzed in addition to conventional oxygenates-free gasolines, then it is recommended that several quality control reference materials be prepared containing the major oxygenated additives at levels found in gasolines to demonstrate that the injection/chromatographic performance is independent of sample types.

10.3 If the linear least squares calibration does not yield results that meet the ±5 % specification for the reference material above, then try forcing the calibration through the origin, that is, $b_i = 0$, using the GC/MS quantitation software and recalculate the results for the reference material. For components present in high concentrations, such as toluene, try using a quadratic fit as described in 9.3.6. If the results for the reference material are still in error, verify the calibration and instrument set-up.

10.4 Analyze the quality control reference materials before every batch of samples. It is recommended that the samples are bracketed by the reference materials specified in 10.1. If the reference material does not meet the specifications in 10.1, the

TABLE 6 Composition of Quality Control Reference Material

Compound	Concentration (mass %)
Hexane	12
Heptane	17
Octane	17
Decane	12
Dodecane	5
2,2,4-Trimethylpentane	12
Benzene	1
Toluene	9
1,3-Dimethylbenzene	3
1,2-Dimethylbenzene	3
Ethylbenzene	3
1,2,4-Trimethylbenzene	3
1,2,4,5-Tetramethylbenzene	2
Naphthalene	1
Total Aromatics	25

samples analyzed immediately preceding the reference material are considered suspect and should be rerun. *Returning of the mass spectrometer and drift with time may require recalibration of the GC/MS system.* See Section 9.

10.5 In addition to the analysis of the QC sample in Table 6, it is strongly recommended that a gasoline reference material be analyzed routinely as part of the QC program. Such gasoline reference materials are available from commercial vendors.

11. Sample Preparation Procedure

11.1 Tare a leak proof sample container (volumetric flask or septum sealed vial). Transfer approximately 10 g of chilled sample and record its mass (Wg) to nearest 0.1 mg. Tare the container and add gravimetrically each of the internal standards as follows. For the three internal standard version, add a quantity (Ws) of benzene-d6, ethylbenzene-d10, and naphthalene-d8 internal standards at the following approximate mix ratio: 2 mL, 2 mL, and 1 g, respectively. For the four internal standard version, add a quantity of benzene-d6, ethylbenzene-d10, napththalene-d8 and toluene-d8 internal standards at the following approximate mix ratio 2 mL, 2 mL, 1 g, and 7 mL, respectively. Tare the container for each addition, starting with the least volatile internal standard. Record the mass of each internal standard to nearest 0.1 mg.

NOTE 6—For convenience, the individual internal standards may be gravimetrically pre-mixed into a single larger stock solution and then added as a single addition and weighing into the samples. The amount of internal standards added should be approximately in the same proportion as that added to the calibration solutions. For example, if 2 g of benzene-d6 was added per 100 mL solutions for calibrations, then add 0.2 g for 10 mL of sample or 0.1 g for 5 mL of sample equivalent for each internal standard. The sample solution is then mixed 30 s on a vortex mixer and analyzed by GC/MS, as described previously.

12. Sample Analyses Procedure

12.1 Ensure that the GC/MS operating conditions are identical to those used for calibration, that the system is properly calibrated, and that all of the criteria in Sections 9 and 10 are met.

12.2 Transfer a sufficient quantity of the chilled sample containing the appropriate internal standards from Section 11 to fill a GC autosampler vial and seal with a leak free septum cap.

12.3 Place the sample vial on the autosampler and start the analysis.

13. Calculation

13.1 *Mass Concentration of Aromatic Hydrocarbon:*

13.1.1 *Calibrated Aromatic Components (3.1.5)*—Identify the various aromatic components in Table 2 from their retention times and mass spectrum. To identify a compound, obtain a RIC for the primary ion (molecular ion used for quantitation) and the two other major secondary ions listed in Table 7. The criteria below must be met for a *qualitative* identification:

13.1.1.1 The three characteristic ions for the compound shall be found to maximize in the same or within one spectrum or scan of each other.

13.1.1.2 The ratio of the intensities of the three characteristic ions for the compound must agree within ±30 %, ±50 %, and ±100 % relative for ions with a relative intensities of >50 %, 20 % to 50 %, and <20 %, respectively, when compared to the relative ion intensity ratios obtained for a calibration standard containing the compound at approximately the same concentration.

TABLE 7 Mass Spectrometer Qualitative Ions for Calibrated Sample Components

Compound	Primary Ion	Secondary Ion 2	Secondary Ion 3
Benzene	78	77	79
Toluene	92	91	89
Ethylbenzene	106	91	77
1,3-Dimethylbenzene	106	91	105
1,4-Dimethylbenzene	106	91	105
1,2-Dimethylbenzene	106	91	105
(1-Methylethyl)-benzene	120	105	77
Propyl-benzene	120	91	92
1-Methyl-3-ethylbenzene	120	105	91
1-Methyl-4-ethylbenzene	120	105	91
1,3,5-Trimethylbenzene	120	105	119
1-Methyl-2-ethylbenzene	120	105	91
1,2,4-Trimethylbenzene	120	105	119
1,2,3-Trimethylbenzene	120	105	119
Indan	117	118	115
1,4-Diethylbenzene	134	105	91
n-Butylbenzene	134	120	91
1,2-Diethylbenzene	134	105	91
1,2,4,5-Tetramethylbenzene	134	120	91
1,2,3,5-Tetramethylbenzene	134	120	91
Naphthalene	128	127	102
2-Methyl-naphthalene	142	141	115
1-Methyl-naphthalene	142	141	115

13.1.1.3 The retention time at the maximum intensity scan in 13.1.1.1 must be within ±15 s of the retention time of the authentic compound from the calibration analyses.

13.1.2 *Uncalibrated Aromatic Components (3.1.2)*—The calibration components in 6.1.2 may not account for all of the aromatic hydrocarbons present in the gasoline sample. Uncalibrated aromatics are identified by the existence of peaks with characteristic ions in specified retention time ranges (see Figs. 2-4). The concentration of the uncalibrated components is estimated using the calibration curves of several of the calibrated components (see 13.1.3).

13.1.3 After the compounds in Table 2 have been properly identified, measure the areas of each peak at the specified primary quantitation mass and that of the internal standards using the same procedure used for the calibration solutions. Using the sample RIC plots in Figs. 2-5, follow the steps below for quantitation.

13.1.3.1 *Mass 78*—Use to quantitate benzene from its calibration curve. Ignore any other mass 78 peaks.

13.1.3.2 *Mass 92*—Use to quantitate toluene from its calibration curve. Ignore any other mass 92 peaks.

13.1.3.3 *Mass 106*—Use to quantitate ethylbenzene and the three xylene isomers from their respective calibrations. 1,3-dimethylbenzene and 1,4-dimethylbenzene may be unresolved or poorly resolved and may be combined for quantitation. Ignore any other mass 106 peaks.

13.1.3.4 *Mass 120*—Use to quantitate C9-benzenes using their respective calibration curves. Ignore any other mass 120 peaks.

13.1.3.5 *Mass 134*—Use to quantitate C10-benzenes. Assume all mass 134 response up to the retention time of

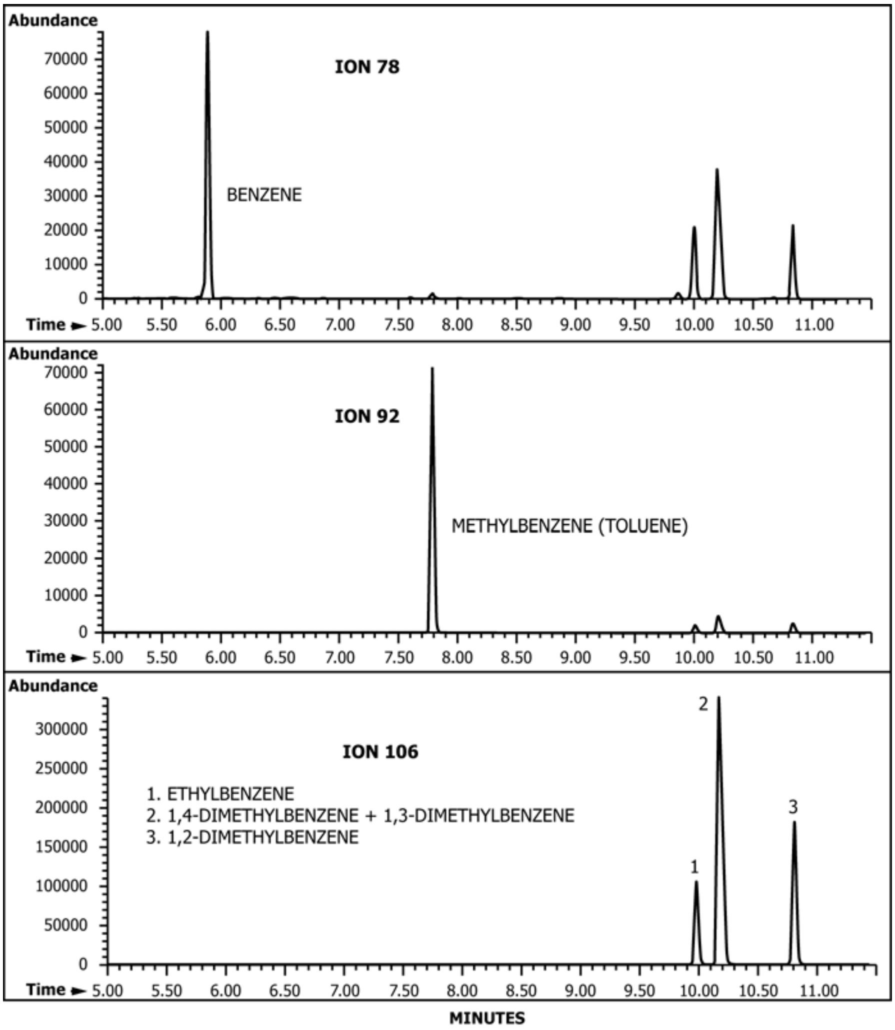

FIG. 2 Reconstructed Ion Chromatograms (RIC) for Quantitated Hydrocarbons

1,2,3,4-tetramethyl benzene are C10-benzenes. For calibrated components use their corresponding calibration curves. For *n*-butylbenzene and 1,4-diethylbenzene, which may coelute, use the combined calibration curve of *n*-butylbenzene and 1,4-diethylbenzene. For the uncalibrated C10-benzenes, sum all of the areas and use the calibration curve of 1,2-diethylbenzene.

13.1.3.6 *Mass 117*—Use to quantitate indan and substituted alkylindans. Assume all mass 117 peak eluting after indan are substituted alkyl indans. Use the calibration curve for indan to quantitate all mass 117 peaks.

13.1.3.7 *Mass 148*—Use to quantitate C11 benzenes. Use the calibration curve of 1,2-diethylbenzene for quantitation of all detected uncalibrated components with mass 148.

13.1.3.8 *Mass 162*—Use to quantitate C12 benzenes. The concentrations of these components may be at or below detection limits. If detected, use the calibration curve of 1,2-diethylbenzene for quantitation of all detected uncalibrated components with mass 162.

13.1.3.9 *Mass 128*—Use to quantitate naphthalene from its calibration curve. Ignore all other mass 128 peaks.

13.1.3.10 *Mass 142*—Use to quantitate the two methylnaphthalene isomers from their corresponding calibration curves. Ignore all other mass 142 peaks.

13.1.3.11 For the quantitation of the *uncalibrated* components, DO NOT include the peak areas of any resolved *calibrated* components having a similar reconstructed (RIC) ion response with the summed areas of the uncalibrated components. The calibrated components are quantitated separately using their respective calibrations.

13.1.4 From the linear least squares fit calibrations, Eq 15, calculate the *absolute* mass of each aromatic (W_i) in grams in the gasoline samples using the response ratio ($\mathrm{rsp_i}$) of the areas for the sample of the aromatic component to that of the internal standard as follows:

$$W_i = \left[\left(\frac{A_i}{A_s} - b_i\right)/m_i\right]W_s \qquad (15)$$

13.1.4.1 If the calibration curves were obtained by forcing the intercept to be zero, then $b_i = 0$.

13.1.4.2 For components that yielded nonlinear calibrations as specified in 9.3.6, calculate W_i using appropriate software.

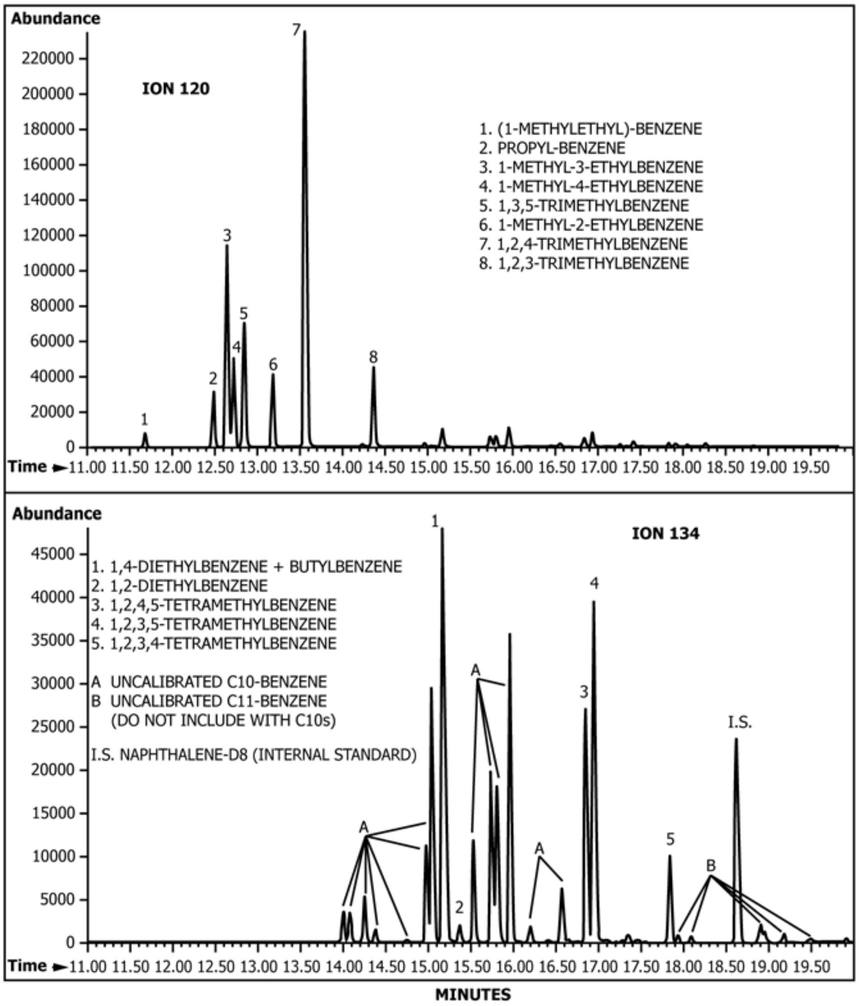

FIG. 3 Reconstructed Ion Chromatograms (RIC) for Quantitated Hydrocarbons

13.1.5 For the uncalibrated components, either sum all of their peak areas and treat the total area as a single component for quantitation or treat each uncalibrated component as a single component for quantitation and then sum their total concentrations.

NOTE 7—It may be more appropriate to force the calibration curves used to quantitate the uncalibrated components through the zero intercept, that is, $b_i = 0$, to prevent calculating negative results for the uncalibrated components that are present in the samples at very low concentrations.

13.1.6 To obtain mass % (w_i) results for each aromatic hydrocarbon, including uncalibrated aromatics:

$$w_i = (W_i/W_g)(100\,\%) \tag{16}$$

where:

W_g = mass of gasoline sample

13.1.7 To obtain the mass % of the total aromatic concentration W_t, sum the mass % of each aromatic component, including the mass percent of the uncalibrated components:

$$W_t = \sum W_i \tag{17}$$

13.1.8 Report results for total aromatics to nearest 0.1 mass % and for benzene to 0.01 mass %.

13.2 *Volumetric Concentration of Aromatics:*

13.2.1 Calculate the volumetric concentration according to Eq 18:

$$v_i = w_i\,(D_f/D_i) \tag{18}$$

where:

v_i = volume % of each aromatic to be determined,
D_i = relative density at 60 °F (15.56 °C) of the individual aromatics as found in Table 2, and
D_f = relative density of the fuel under study as determined by Practice D1298 or Test Method D4052.

13.2.2 To obtain the volume percent of the total aromatic concentration V_t, sum the volume percent of each aromatic component, including the volume percent of the uncalibrated components:

$$v_t = \sum v_i \tag{19}$$

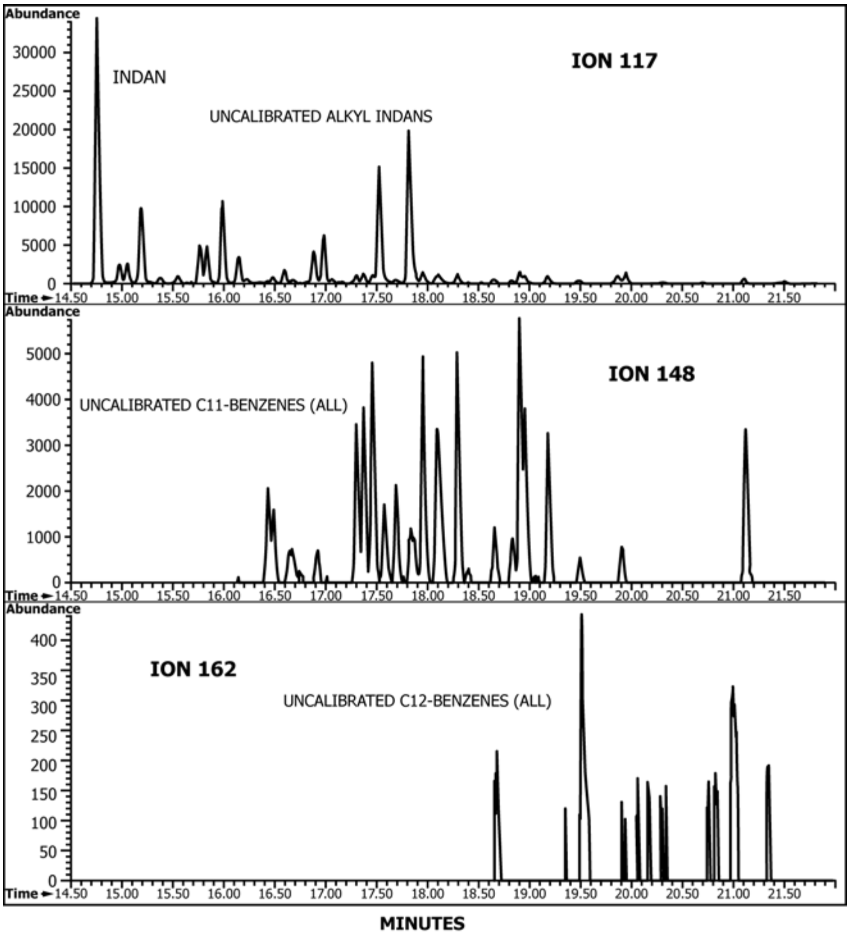

FIG. 4 Reconstructed Ion Chromatograms (RIC) for Quantitated Hydrocarbons

13.2.3 Report results for total aromatics to nearest 0.1 volume percent and for benzene to 0.01 volume percent.

14. Precision and Bias[3]

14.1 *Precision*—The precision of this test method as determined by a statistical examination of interlaboratory results is as follows:

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Component	Range (volume %)	Repeatability
Benzene	0.09–4.0	$0.046(X^{0.67})$
Toluene	1.0–13	$0.117(X^{0.40})$
Total aromatics	9–42	$0.0761(X^{0.75})$

where X is the volume percent of the component.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Component	Range (volume %)	Reproducibility
Benzene	0.09–4.0	$0.221(X^{0.67})$
Toluene	1.0–13	$0.695(X^{0.40})$
Total aromatics	9–42	$0.244(X^{0.75})$

where X is the volume percent of the component.

Table 8 summarizes the repeatability and reproducibility as a function of concentration volume %.

14.2 *Bias*—Since there is no certified reference material suitable for determining the bias for the procedures in this test method, bias cannot be determined.

14.3 *Relative Bias*—A relative bias assessment of Test Method D5769 versus Test Method D3606 for the determination of benzene in spark-ignition fuel was conducted using data from the ASTM D02 Interlaboratory Crosscheck Program. The assessment was performed in accordance with the requirements of Practice D6708 with a successful outcome. It was based on

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1382. Contact ASTM Customer Service at service@astm.org.

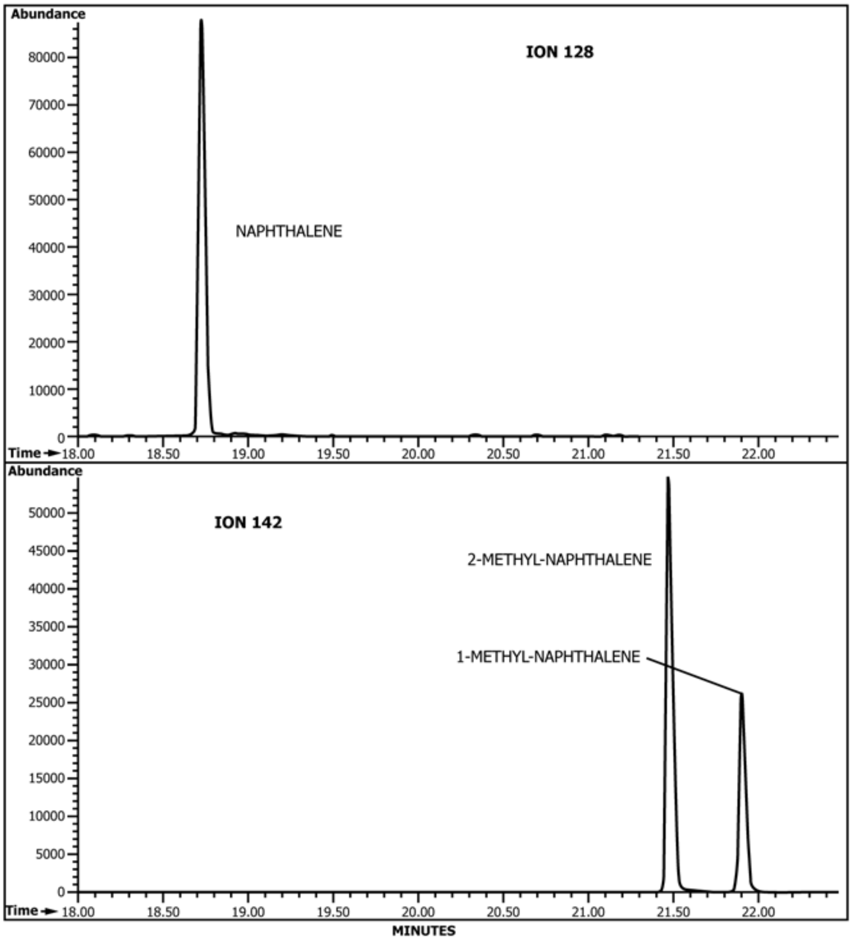

FIG. 5 Reconstructed Ion Chromatogram (RIC) for Quantitated Hydrocarbons

TABLE 8 Repeatability and Reproducibility

Components	Concentration Volume %	Repeatability	Reproducibility
Benzene	0.10	0.01	0.05
	0.20	0.02	0.08
	0.30	0.02	0.10
	0.40	0.02	0.12
	0.50	0.03	0.14
	0.60	0.03	0.16
	0.70	0.04	0.17
	0.80	0.04	0.19
	0.90	0.04	0.21
	1.00	0.05	0.22
	1.50	0.06	0.29
	2.00	0.07	0.35
	3.00	0.10	0.46
	4.00	0.12	0.56
Toluene	1.0	0.1	0.7
	3.0	0.2	1.1
	5.0	0.2	1.3
	7.0	0.3	1.5
	9.0	0.3	1.7
	10.0	0.3	1.7
	13.0	0.3	1.9
Total aromatics	10.0	0.4	1.4
	15.0	0.6	1.9
	20.0	0.7	2.3
	25.0	0.9	2.7
	30.0	1.0	3.1
	35.0	1.1	3.5
	40.0	1.2	3.9
	42.0	1.3	4.0

measurements of benzene in spark-ignition engine fuels supplied between January 2006 and October 2014 by the Reformulated Gasoline program of the ASTM Proficiency Testing Program (Interlaboratory Crosscheck Program) and is documented in Research Report RR:D02-1816.[4]

NOTE 8—In the United States, the U.S. EPA requires the measurement of benzene in spark-ignition engine fuels by Test Method D3606. Effective Jan. 1, 2016, there is an allowance in the regulation to use other test methods if they are formally correlated with the specified test method by a consensus organization, for example, ASTM. This relative bias statement is intended to satisfy the requirement and allow use of Test Method D5769 bias-corrected results in the stated concentration ranges in place of Test Method D3606 for benzene.

14.3.1 The degree of agreement between results from Test Method D5769 and Test Method D3606 can be further improved by applying a correlation equation (Eq 20) (Research Report RR:D02-1816),[4] and this correlation equation shall be utilized when reporting compliance with EPA fuels program. There were no discernable sample-specific biases as defined in Practice D6708.

14.3.2 *Correlation Equation:*

$$\text{Predicted D3606} = \text{bias corrected D5769} = C_{D5769} + 0.01 \quad (20)$$

where:

C_{D5769} = volume percent benzene as reported by Test Method D5769.

14.3.2.1 The correlation equation is only applicable for fuels in the concentration range from 0.0 % to 2.50 % by volume as reported by Test Method D5769.

14.3.2.2 The correlation equation is applicable for fuels that when determined by Test Method D3606 are in the concentration range of 0.0 % to 2.47 % by volume.

NOTE 9—The Test Method D3606 concentration range used to develop the Practice D6708 assessment may not cover the entire scope indicated in the scope of Test Method D3606 for benzene.

NOTE 10—The correlation equation was developed from a variety of fuel samples from the ASTM Interlaboratory Crosscheck programs; however, it is recommended that the correlation equation be verified for samples of interest to ensure applicability.

15. Keywords

15.1 aromatics; benzene; gas chromatography; gasolines; GC/MS; mass spectrometry; toluene

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1816. Contact ASTM Customer Service at service@astm.org.

SUMMARY OF CHANGES

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D5769 – 10 (2015)) that may impact the use of this standard. (Approved Dec. 1, 2015.)

(1) Added new subsections 1.4 and 14.3.