



Designation: D5769 – 10

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

1.5 *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](#)

[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](#)

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.

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:

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

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.

Current edition approved May 1, 2010. Published August 2010. Originally approved in 1995. Last previous edition approved in 2004 as D5769-04. DOI: 10.1520/D5769-10.

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.

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°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.

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 to 5°C until ready for loading on the autosampler.

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 |

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 (*isooctane*) as a recommended dilution solvent; (2) Set II consists of the remaining C₉+ 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-d₆ and ethylbenzene-d₁₀. Toluene-d₈ may be added to the internal standard mixture for the quantitation of toluene. The internal standards for Set II are ethylbenzene-d₁₀ and naphthalene-d₈.

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 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 (*W_i*) 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

TABLE 2 Relative Densities and Calibration Concentrations

| Compound | Relative Density 60°F/60°F | Target Highest Concentration Calibration Solution (volume % or mL/100mL) | 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 |
| <i>n</i> -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 | — | — | — |

^AThese components are solids at ambient temperature. The values represent g/100 mL

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 (*W_s*) 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 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.

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:

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).

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.

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 |

9.3.1.1 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 ($\pm 3\%$ 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 :

$$rsp_i = (A_i/A_s) \quad (2)$$

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 :

$$amt_i = W_i/W_s \quad (3)$$

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:

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

where:

$$x = X_i - \bar{x} \quad (5)$$

$$y = Y_i - \bar{y} \quad (6)$$

and:

X_i = amt_i ratio data point,

\bar{x} = average values for all (amt_i) 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:

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

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

$$(rsp_i) = (m_i)(amt_i) + b_i \quad (8)$$

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

The values m_i and b_i are calculated as follows:

$$m_i = \sum xy / \sum x^2 \quad (9)$$

and

$$b_i = \bar{y} - m_i\bar{x} \quad (10)$$

For the example in Table 5:

$$m_i = 5/10 = 0.5 \quad (11)$$

and

$$b_i = 0 \quad (12)$$

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

$$(rsp_i) = 0.5(amt_i) + 0 \quad (13)$$

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.

TABLE 5 Example of Data Set For r^2 Calculation

| | X_i | Y_i | $x = X_i - \bar{x}$ | $y = Y_i - \bar{y}$ | 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 | 1.5 | | | | | |
| | (\bar{x}) | (\bar{y}) | | | | | |

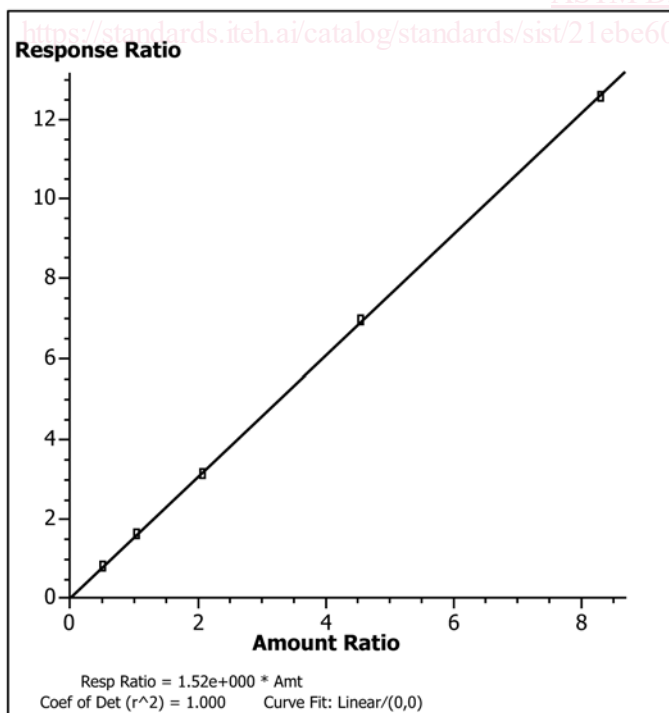


FIG. 1 Example Plot