



# Standard Test Method for Determination of Oxygenates, Benzene, Toluene, C<sub>8</sub>–C<sub>12</sub> Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography/Fourier Transform Infrared Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation D 5986; 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 quantitative determination of oxygenates: methyl-t-butylether (MTBE), di-isopropyl ether (DIPE), ethyl-t-butylether (ETBE), t-amylmethyl ether (TAME), methanol (MeOH), ethanol (EtOH), 2-propanol (2-PrOH), t-butanol (t-BuOH), 1-propanol (1-PrOH), 2-butanol (2-BuOH), i-butanol (i-BuOH), 1-butanol (1-BuOH); benzene, toluene and C<sub>8</sub>–C<sub>12</sub> aromatics, and total aromatics in finished motor gasoline by gas chromatography/Fourier Transform infrared spectroscopy (GC/FTIR).

1.2 This test method covers the following concentration ranges: 0.1–20 volume % per component for ethers and alcohols; 0.1–2 volume% benzene; 1–15 volume % for toluene, 10–40 volume % total (C<sub>6</sub>–C<sub>12</sub>) aromatics.

1.3 The method has not been tested by ASTM for refinery individual hydrocarbon process streams, such as reformates, fluid catalytic cracking naphthas, etc., used in blending of gasolines.

1.4 SI units of measurement are preferred and used throughout this test method.

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 use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method<sup>2</sup>

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter<sup>3</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Product<sup>3</sup>

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards<sup>3</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *aromatics*—refers to any organic compound containing a benzene or naphthalene ring.

3.1.2 *calibrated aromatic component*—in this test method, refers to the individual aromatic components which have a specific calibration.

3.1.3 *cool on-column injector*—in gas chromatography, a direct sample introduction system which 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, or both, on glass liners within injectors. The sample is injected directly into the head of the capillary column tubing or retention gap.

3.1.4 *Gram-Schmidt chromatogram*—a nonselective summation of total intensity from a spectral scan per unit time which resembles in profile a flame ionization detector chromatogram.

3.1.5 *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.

3.1.6 *selective wavelength chromatogram (SWC)*—in this test method, refers to a selective chromatogram obtained by summing the spectral intensity in a narrow spectral wavelength or frequency range as a function of elution time which is unique to the compound being quantitated.

3.1.7 *uncalibrated aromatic component*—in this test method, refers to individual aromatics for which a calibration is not available and whose concentrations are estimated from the response factor of a calibrated aromatic component.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

3.1.8 *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 methylsilicone WCOT column is interfaced to a Fourier transform infrared spectrometer. The sample is injected through a cool on-column injector capable of injecting a small sample size without overloading the column.

4.2 Calibration is performed using mixtures of specified pure oxygenates and aromatic hydrocarbons on a mass basis. Volume % data is calculated from the densities of the individual components and the density of the sample. Multipoint calibrations consisting of at least five levels and bracketing the concentration of the specified individual aromatics is required. Unidentified aromatic hydrocarbons present which have not been specifically calibrated for are quantitated using the response factor of 1,2,3,5-tetramethylbenzene and summed with the other calibrated aromatic components to obtain a total aromatic concentration of the sample.

4.3 Specified quality control mixture(s) are analyzed to monitor the performance of the calibrated GC/FTIR system.

#### 5. Significance and Use

5.1 Test methods to determine oxygenates, benzene, and the aromatic content of gasoline are necessary to assess product quality and to meet new 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 Chromatograph:

6.1.1 System equipped with temperature programmable gas chromatograph suitable for cool-on-column injections. The injector must allow the introduction of small (for example, 0.1  $\mu\text{L}$ ) sample sizes at the head of the WCOT column or a retention gap. An autosampler is mandatory.

6.1.2 WCOT column containing a methylsilicone stationary phase which elutes the aromatic hydrocarbons according to their boiling points. A column containing a relatively thick film of stationary phase, such as 4 to 5  $\mu\text{m}$ , is recommended to prevent column sample overload.

##### 6.2 FTIR Spectrometer:

6.2.1 This test method requires a light-pipe GC/FTIR system (Fig. 1). No data have been acquired with matrix-isolation or other deposition type systems.

6.2.2 The spectrometer must be equipped with a mercury-cadmium-telluride (MCT) detector capable of detecting from at least 4000  $\text{cm}^{-1}$  to 550  $\text{cm}^{-1}$ .

6.2.3 The lower limit of 550  $\text{cm}^{-1}$  is necessary for the accurate determination of benzene. Fig. 2 gives an acceptable infrared spectra of benzene.

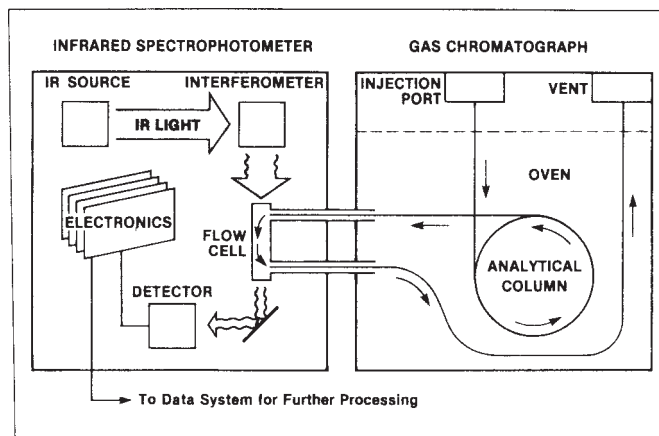


FIG. 1 Light-Pipe GC/FTIR System

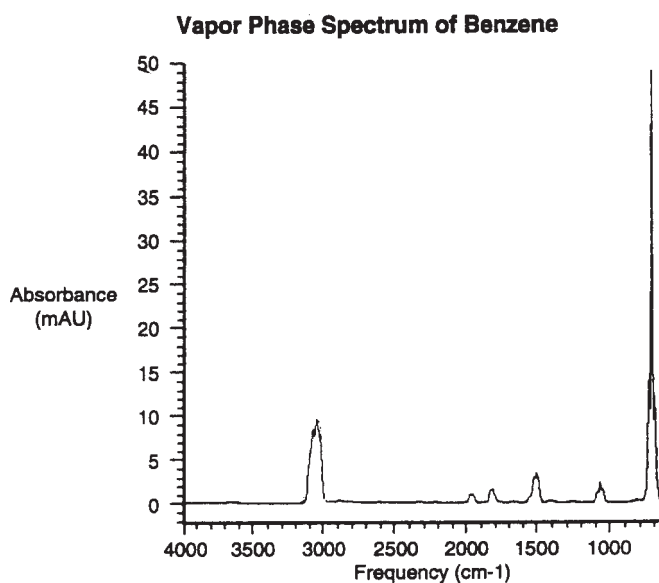


FIG. 2 Vapor Phase Spectrum of Benzene

#### 7. Reagents and Materials

7.1 *Carrier Gas*—Helium and hydrogen have been used successfully. The minimum purity of the carrier gas used must be 99.85 mole %. Additional purification using commercially available scrubbing reagents is recommended to remove trace oxygen which may deteriorate the performance of the GC WCOT column.

7.2 *Dilution Solvents*—*n*-heptane and methylbenzene (toluene) used as a solvent in the preparation of the calibration mixture. Reagent grade. All at 99 % or greater purity. Free from detectable oxygenates and aromatics which may interfere with the analysis.

7.2.1 Toluene should be used as a solvent only for the preparation of  $\text{C}_9$  + components and must be free from interfering aromatics. (**Warning**—The gasoline samples and solvents used as reagents such as heptane 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.)

7.3 *Internal Standard*—1,2-dimethoxyethane (DME) or deuterated compounds, or both, have been used successfully. A single internal standard such as DME may be used. If other internal standards are used, a narrow selective wavelength range must be determined to generate a SWC which yields no interference from other components in the sample.

7.4 *Liquid Nitrogen*, supplied from low pressure dewar. Required for cooling of the MCT detector. Dewar may be connected through an electronic solenoid to the MCT cooling reservoir for unattended operation. (**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.)

7.5 *Spectrometer Purge Gas*, N<sub>2</sub> dry air has not been tested, but should be adequate.

NOTE 1—The FTIR spectrometer can be protected by installing appropriate filters to remove volatile oils or contaminants that may be present in commercial low quality nitrogen supplies. A liquid nitrogen dewar may be used as a source for the nitrogen purge.

7.6 *Standards for Calibration and Identification*, all at 99 % or greater purity (Table 1 and Table 2). If reagents of high purity are not available, an accurate assay of the reagent must be performed using a properly calibrated GC or other techniques. The concentration of the impurities which overlap the other calibration components must be known and used to correct the concentration of the calibration components. Because of the error that may be introduced from impurity corrections, the use of only high purity reagents is strongly recommended. Standards are used for calibration as well for establishing the identification by retention time in conjunction with spectral match.

## 8. Sampling

8.1 Make every effort to ensure that the sample is representative of the fuel source from which it is taken. Follow the recommendations of Practice D 4057 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 Take appropriate steps 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 0 to 5°C (32 to 40°F) before and after a sample is obtained for analysis.

**TABLE 1 GC/FTIR Oxygenates Calibration Components**

Compound	CAS
Methyl-t-butyl ether (MTBE)	1634-04-4
Ethyl-t-butyl ether (ETBE)	637-92-3
Methyl-t-amyl ether (TAME)	994-05-8
Di-isopropyl ether (DIPE)	108-20-3
Methanol	67-56-1
Ethanol	64-17-5
2-Propanol	67-63-0
t-Butanol	75-65-0
1-Propanol	71-23-6
2-Butanol	15892-23-6
Isobutanol	78-83-1
1-Butanol	71-36-3
1,2-dimethoxyethane (DME) (Internal Standard)	110-71-4

**TABLE 2 GC/FTIR Aromatic Hydrocarbons Calibration Components (Calibrated Aromatic Components)**

Compound	CAS No.
Benzene	71-43-2
Methylbenzene	108-88-3
Ethylbenzene	100-41-4
1,3-Dimethylbenzene	108-38-3
1,4-Dimethylbenzene	106-42-3
1,2-Dimethylbenzene	95-47-6
(1-Methylethyl)-benzene	98-82-8
Propyl-benzene	103-65-1
1-methyl-3-ethylbenzene	620-14-4
1-methyl-4-ethylbenzene	622-96-8
1,3,5-trimethylbenzene	108-67-8
1-methyl-2-ethylbenzene	611-14-3
1,2,4-trimethylbenzene	95-63-6
1,2,3-trimethylbenzene	526-73-8
Indan	496-11-7
1,4-diethylbenzene	105-05-5
Butylbenzene	104-51-8
1,2-Diethylbenzene	135-01-3
1,2,4,5-Tetramethylbenzene	95-93-2
1,2,3,5-Tetramethylbenzene	527-53-7
Naphthalene	91-20-3
2-methyl-naphthalene	91-57-6
1-methyl-naphthalene	90-12-0

8.3 After the sample is prepared for analysis with internal standard(s), chill the sample and transfer to an appropriate autosampler vial with minimal headspace. Re-chill the remainder of the sample immediately and protect from evaporation for further analyses, if necessary.

## 9. Calibration Procedure

9.1 *Preparation of Calibration Standards*—Prepare multi-component calibration standards using the compounds listed in Table 1 and Table 2 by mass according to Practice D 4307. Prepare calibration solutions as described in 9.1-9.1.4 for each set. 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. The specified volumes of each calibration component are weighed into 100 mL volumetric flasks or 100 mL septum capped vials. Prepare a calibration standard as follows. Cap and record the tare weight of the 100 mL volumetric flask or vial to 0.1 mg. Remove the cap and carefully add components to the flask or vial starting with the least volatile component. Cap the flask and record the net mass (*W<sub>i</sub>*) of the aromatic component added to 0.1 mg. Repeat the addition and weighing procedure for each component. Similarly add the internal standard and record its net mass (*W<sub>s</sub>*) to 0.1 mg. Store the capped calibration standards in a refrigerator at 0 to 5°C (32 to 40°F) when not in use.

NOTE 2—Mix all calibration solutions for at least 30 s on a Vortex mixer after preparation or equivalent. Highly precise sample robotic sample preparation systems are available commercially. These systems may be used provided that the results for the quality control reference material (Section 11) are met when prepared in this manner.

### 9.1.1 Ethers and Alcohols:

9.1.1.1 Three sets of at least six calibration levels each (eighteen total solutions) are prepared bracketing the 0 to 20 volume % range. *Set 1*: for MTBE, DIPE, ETBE, TAME; *Set*

2: MeOH, EtOH, 2-PrOH, t-BuOH; and Set 3: 1-PrOH, 2-BuOH, i-BuOH, 1-BuOH.

9.1.1.2 For each above Set: 1, 3, 5, 10, 15, and 20 mL aliquots of each component are pipetted into respective 100 mL volumetric flasks or vials while accurately recording the masses. For example, for Set 1, into flask one add 1.0 mL MTBE, 1.0 mL DIPE, 1.0 mL ETBE, 1.0 mL TAME; into flask two add 3.0 mL MTBE, 3.0 mL DIPE, 3.0 mL ETBE, 3.0 mL TAME; and so forth. Add the oxygenate in reverse order of their boiling points. The above procedure produces six calibration solutions for each set with the concentrations of each analyte at 1, 3, 5, 10, 15, and 20 volume %. 10.0 mL of DME (internal standard) is then added at constant volumes to each flask or vial while recording its mass. The flasks or vials are then filled to 100 mL total volume with toluene. It is not necessary to weigh the amount of solvent added since the calculations are based on the absolute masses of the calibration components and the internal standard components.

9.1.1.3 For best accuracy at concentrations below 1 %, prepare calibration standard sets to bracket the expected concentration. Some of the alcohols are present at low concentrations in gasoline blends. In this case, for example, if the expected analyte concentration is 0.5 volume %, prepare calibration solutions by mass in the range of 0.1 to 1.0 volume %. Furthermore, if the components in Set 3 are all at these low concentrations then for calibration they can be added to Set 2, thus reducing the calibration solutions to Sets 1 and 2.

9.1.2 *Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)* (Table 3/Set A):

9.1.2.1 To each of six 100 mL volumetric flasks or vials, add 10.0 mL of DME and record the mass.

9.1.2.2 For ethylbenzene, m, p, and o-xylenes (EX): 1, 3, 5, 7, 9 and 10 mL of each analyte is added to the respective flasks above while accurately recording the masses.

9.1.2.3 For toluene (T): 1, 3, 5, 7, 10, 15 mL aliquots are added to respective flasks above (that is, least concentrated toluene is in solution with least concentrated ethylbenzene and xylenes-EX) while accurately recording the masses.

9.1.2.4 For benzene (B): 0.10 mL, 0.30 mL, 0.50 mL, 1 mL, 2 mL, 3 mL of benzene are weighed into respective 100 mL flasks or vials (that is, least concentrated benzene is in solution with least concentrated TEX above).

9.1.2.5 The flasks or vials are then filled to 100 mL with *n*-heptane. This procedure generates calibration solutions containing increasing amounts of benzene from 0.1 to 3 volume %, toluene from 1 to 15 volume %, and ethylbenzene and m, p, and o-xylenes each from 1 to 10 volume % with the internal standard (DME) at a constant 10 volume %.

9.1.3 *C<sub>9</sub>Aromatics (Table 3/Set B):*

9.1.3.1 Add 0.5, 1.0, 2.0, 3.0, 5 mL of each of the C<sub>9</sub>-aromatics in Table 2 to the respective five flasks or vials (that is, add all of the 0.5 mL concentrations together in flask one, all of the 1.0 mL concentrations to flask two, and so forth) while accurately recording the masses.

9.1.3.2 Add 10.0 mL of DME to each of the five flasks or vials and record the mass of DME.

9.1.3.3 The flasks or vials are then filled to 100 mL with *n*-heptane. This procedure generates calibration solutions for the C<sub>9</sub> aromatics in the range of 0.5 to 5 volume %.

9.1.4 *C<sub>10</sub> + Aromatics (Table 3/Set C):*

9.1.4.1 Add 0.5, 1.0, 2.0, 3.0, 4 mL or grams, if solids, of each of the C<sub>10</sub>-aromatics in Table 2 to the respective five flasks or vials (that is, add all of the 0.5 mL concentrations together in flask one, all of the 1.0 mL concentrations to flask two, etc.) while accurately recording the masses.

9.1.4.2 Add 10.0 mL of DME to each of the five flasks or vials and record the mass of DME.

9.1.4.3 The flasks or vials are then filled to 100 mL with toluene. This procedure generates calibration solutions for the C<sub>10</sub> aromatics in the range of 0.5 to 4 volume %.

9.1.4.4 Ensure that all of the prepared standards are thoroughly mixed and transfer approximately 2 mL of the solution to a vial compatible with the autosampler. Chill the vials until ready for loading on the autosampler.

9.2 *GC/FTIR Procedure:*

9.2.1 Before initiating the calibration procedure ensure that the GC/FTIR system has been set up according to the manufacturer's instructions.

9.2.2 The WCOT must meet the resolution requirements described in Table 4 when installed in the GC/FTIR system.

**TABLE 3 Relative Densities and Calibration Procedure for Aromatic Hydrocarbons**

Compound	Relative Densities 60°F/60°F	Calibration Set
Benzene	0.8845	Set A
Methylbenzene	0.8719	Set A
Ethylbenzene	0.8717	Set A
1,3-Dimethylbenzene	0.8687	Set A
1,4-Dimethylbenzene	0.8657	Set A
1,2-Dimethylbenzene	0.8848	Set A
(1-Methylethyl)-benzene	0.8663	Set B
Propyl-benzene	0.8666	Set B
1-Methyl-3-ethylbenzene	0.8690	Set B
1-Methyl-4-ethylbenzene	0.8657	Set B
1,3,5-Trimethylbenzene	0.8696	Set B
1-Methyl-2-ethylbenzene	0.8852	Set B
1,2,4-Trimethylbenzene	0.8802	Set B
1,2,3-Trimethylbenzene	0.8987	Set B
Indan	0.9685	Set B
1,4-Diethylbenzene	0.8663	Set C
Butylbenzene	0.8646	Set C
1,2-Diethylbenzene	0.8843	Set C
1,2,4,5-Tetramethylbenzene	0.8918	Set C
1,2,3,5-Tetramethylbenzene	0.8946	Set C
Naphthalene	1.000	Set C
2-Methyl-Naphthalene	1.000	Set C
1-Methyl-Naphthalene	1.000	Set C
Uncalibrated aromatics	1.000	...

**TABLE 4 Gas Chromatographic WCOT Resolution Requirement**

Resolution "R" between ethylbenzene and p + m xylene at the 3 mass % level each must be equal to or greater than 1
$R = \frac{2(t_2 - t_1)}{1.699(y_2 + y_1)}$
t <sub>2</sub> = retention time of p + m xylenes
t <sub>1</sub> = retention time of ethylbenzene
y <sub>2</sub> = peak width at half height of p + m xylenes
y <sub>1</sub> = peak width at half height ethylbenzene



9.2.3 Prepare a solution of 0.01 mass % of naphthalene and ensure that it is detected with at least a signal/noise ratio of five.

9.2.4 Sequentially analyze all of the calibration standards.

9.2.5 Table 5 gives suggested operating conditions.

9.3 Calibration Calculations:

9.3.1 After the analyses of the calibration standards is complete, the GC/FTIR is calibrated by generating the selective reconstruction chromatograms for each analyte and the internal standard from the frequency ranges in Table 6. These GC peaks are integrated and calibration curves for each analyte are obtained.

9.3.2 Plot the response ratio  $rsp_i$ :

$$rsp_i = (Ai/As) \tag{1}$$

where:

$Ai$  = area of aromatic compound “i”, and

$As$  = area of internal standard.

as the y-axis versus the amount ratio  $amt_i$ :

$$amt_i = W_i / W_s \tag{2}$$

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 oxygenate and aromatic component in Table 1 and Table 2.

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:

TABLE 5 GC/FTIR Conditions

Recommended Conditions	
Gas Chromatography (GC)	
Column	60 m × 0.53 mm ID, df = 5.0 μm polymethylsiloxane
Injector type	cool on-column. A section of deactivated or polymethylsiloxane coated 0.53 mm ID fused silica tubing can be connected between the injector and the column with a low dead volume union to allow use of an on-column autosampler
Injection size (μl)	0.5
Injector temperature (°C)	track oven temperature
Oven temperature	50°C (0 min), 2°C/min to 190°C (0 min); 30°C/min to 300°C (1 min)
Carrier gas	hydrogen or helium
Carrier gas linear velocity (cm/s)	hydrogen: 42 cm/s at 300°C
GC/FTIR Interface	
Interface temperature (°C)	approximately 300°C
FTIR Spectrometer	
Cell	light pipe at 300°C
Detector	mercury-cadmium-telluride (MCT)
MCT range	at least 4000 cm <sup>-1</sup> to 550 cm <sup>-1</sup>
Resolution	8 cm <sup>-1</sup>
Scan rate	1 spectrum/s, all data points stored
Selective absorbance reconstructions	Second difference with function width = 75. A different reconstruction frequency range is used for each analyte (Table). Reference spectra are taken by averaging the first 0.5 min of the chromatogram at which time no compounds elute

TABLE 6 GC/FTIR Selective Reconstruction Frequencies

Compound	Frequencies cm <sup>-1</sup>
Benzene	670–678
Methylbenzene	724–732
Ethylbenzene	694–702
1,3-Dimethylbenzene	687–695
1,4-Dimethylbenzene	790–798
1,2-Dimethylbenzene	736–744
(1-Methylethyl)-benzene	695–703
Propyl-benzene	695–703
1-Methyl-3-ethylbenzene	775–783
1-Methyl-4-ethylbenzene	807–815
1,3,5-Trimethylbenzene	831–839
1-Methyl-2-ethylbenzene	741–749
1,2,4-Trimethylbenzene	801–809
1,2,3-Trimethylbenzene	762–770
Indan	739–747
1,4-Diethylbenzene	826–834
n-Butylbenzene	694–702
1,2-Diethylbenzene	748–756
1,2,4,5-Tetramethylbenzene	863–871
1,2,3,5-Tetramethylbenzene	844–852
Naphthalene	777–785
2-Methyl-Naphthalene	803–811
1-Methyl-Naphthalene	782–790
Uncalibrated Aromatics	600–900 <sup>A</sup>
Methyl-t-butyl ether (MTBE)	1205–1213
Ethyl-t-butyl ether (ETBE)	1199–1207
Methyl-t-amyl ether (TAME)	1185–1193
Di-isopropyl ether (DIPE)	1122–1130
Methanol	1055–1063
Ethanol	1052–1060
2-Propanol	1141–1149
t-Butanol	1207–1215
1-Propanol	1056–1064
2-Butanol	1128–1136
Isobutanol	1037–1045
1-Butanol	3665–3673
1,3-Dimethoxyethane (DME) (Internal Standard)	1123–1131

<sup>A</sup>Use the calibration curve of 1,2,3,5-tetramethylbenzene at the SWC of 600–900 cm<sup>-1</sup> for quantitation of uncalibrated aromatics. See 12.2.2 and Fig. 4 and Fig. 5 for the location and SWCs for each of the uncalibrated compounds.

$$r^2 = \frac{(\sum xy)^2}{(\sum x^2)(\sum y^2)} \tag{3}$$

where:

$$x = X_i - \bar{x} \tag{4}$$

$$y = Y_i - \bar{y} \tag{5}$$

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.

Table 7 gives an example of the calculation for an ideal data set  $X_i$  and  $Y_i$ .

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

$$(rsp_i) = (m_i)(amt_i) + b_i \tag{6}$$

where:

$rsp_i$  = response ratio for aromatic “P” (y-axis),

$m_i$  = slope of linear equation for aromatic “P”,

$amt_i$  = amount ratio for aromatic “P” (x-axis), and

$b_i$  = y-axis intercept.

The values  $m_i$  and  $b_i$  are calculated as follows:

**TABLE 7 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

$$\begin{aligned} \bar{x} &= 3 \\ \bar{y} &= 1.5 \\ (\sum xy)^2 &= 25.0 \\ \sum x^2 &= 10.0 \\ \sum y^2 &= 2.5 \\ r^2 &= \frac{(\sum xy)^2}{(\sum x^2)(\sum y^2)} \\ r^2 &= \frac{25.0}{(10.0)(2.5)} = 1.0 \end{aligned}$$

$$m_i = \frac{\sum xy}{\sum x^2} \quad (7)$$

and

$$b_i = \bar{y} - m_i \bar{x} \quad (8)$$

For the example in Table 7:

$$m_i = 5/10 = 0.5 \quad (9)$$

and

$$b_i = 1.5 - (0.5)(3) = 0 \quad (10)$$

Therefore, the least square equation for the above example in Table 7 is:

$$(rsp_i) = 0.5(amt_i) + 0 \quad (11)$$

NOTE 3—Normally the  $b_i$  term is not zero and may be positive or negative.

9.3.4.1 The calibration response for benzene with a MCT detector may be nonlinear. In the round robin of this test method a linear fit was used for concentrations up to approximately one mass % benzene and a point to point or quadratic fit used for higher concentrations. The region of linearity may vary among instrument types and needs to be determined during calibration.

9.3.5 *Y-intercept Criteria*—For an optimum calibration, the absolute of the  $y$ -intercept  $b_i$  must be at a minimum, that is, the calibration curves must not deviate significantly from a  $y$ -intercept equal to zero value.  $A_i$  approaches zero when  $w_i$  is less than 0.1 mass %. As  $A_i$  approaches zero, the equation to determine the mass % aromatics reduces to Eq 12. Therefore, the  $y$ -intercept can be tested using Eq 12:

$$w_i = (b_i / m_i)(W_s / W_g)100 \% \quad (12)$$

where:

$w_i$  = mass % aromatic “ $T$ ”, where  $w_i$  is <0.1 mass %,  
 $W_s$  = mass of internal standard added to the gasoline samples for the quantitation of the aromatic component “ $T$ ”, g, and  
 $W_g$  = mass of gasoline samples, g.

NOTE 4—Since in practice  $W_s$  and  $W_g$  vary slightly from sample to sample, typical values for these parameters are used to test the  $y$ -intercept.

9.3.6 The GC/FTIR system must be recalibrated whenever results of the quality control reference material do not agree within the tolerance levels specified in 11.1.

## 10. Sample Analysis Procedure

10.1 Add 1.0 mL of internal standard into a 10.0 mL volumetric flask or vial and record the mass ( $W_s$ ). Add 9.0 mL of gasoline sample to the flask or vial, and record the mass ( $W_g$ ). The sample/internal standard solution is then mixed 30 s on a vortex mixer and analyzed by GC/FTIR according to the instrument manufacturer’s directions using the same conditions as for calibrations.

## 11. Quality Control Reference Material

11.1 After the calibration has been completed, prepare the quality control reference material outlined in Table 8. Analyze the reference material as described in the sample preparation procedure below. The individual aromatic and total aromatics values obtained must agree within  $\pm 5$  % relative of the values in the prepared reference material (for example, benzene  $1.0 \pm 0.05$ ). If the individual values are outside the specified range verify calibration and instrument parameters, accuracy of the preparation of quality control reference material, and so forth. Do NOT analyze samples without meeting the quality control specifications.

11.1.1 If samples containing oxygenated fuel additives such as ethanol, methyl-t-butylether (MTBE) are also analyzed in addition to conventional oxygenates free gasolines, then several quality control reference materials must be prepared containing the major oxygenated additives at levels found in gasoline samples.

11.2 Analyze the quality control reference materials before every batch of samples. Bracket the samples with the reference material. If the reference material does not meet the specifications in 11.1, the samples analyzed immediately preceding the reference material are considered suspect and should be rerun.

## 12. Calculations

### 12.1 Oxygenates:

12.1.1 After identifying the various oxygenates, measure the areas of each oxygenate peak and that of the internal standard. Fig. 3 gives the elution order of the various oxygenates. From the least squares fit calibrations, Eq 13, calculate the *absolute* mass of each oxygenate components ( $W_i$ ) in grams in

**TABLE 8 Composition of Quality Control Reference Material for Aromatic Hydrocarbon Analysis<sup>A</sup>**

Compound	Concentration (mass %)
n-Hexane	12
n-Heptane	17
n-Octane	17
n-Decane	12
n-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	3
Total aromatics	25

<sup>A</sup>If sample contains oxygenates, then include the major oxygenate(s) in the QC sample.

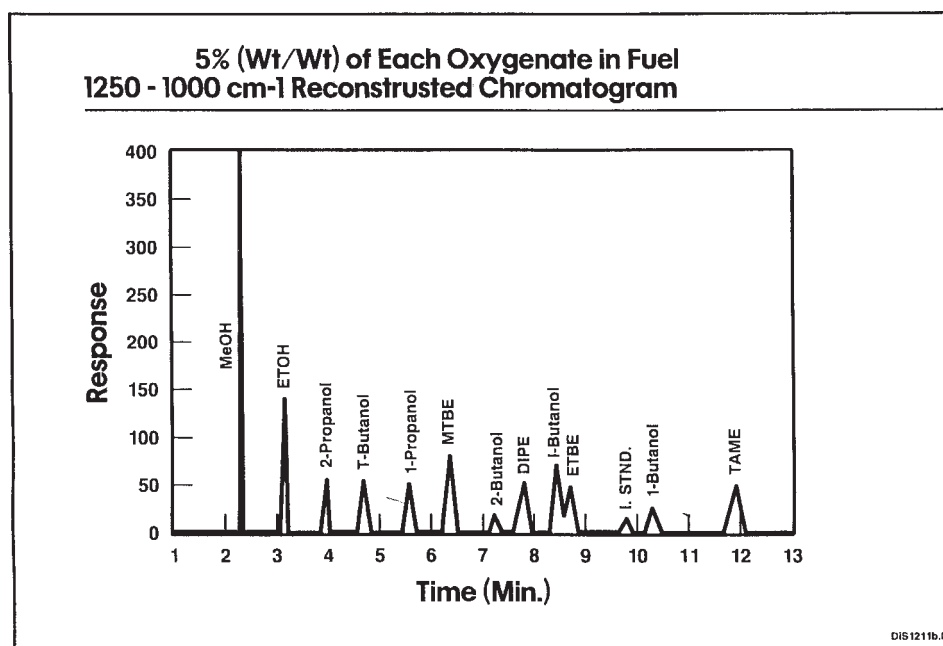


FIG. 3 5% (wt/wt) of Each Oxygenated In Fuel 1250-1000 cm-1 Reconstructed Chromatogram

the gasoline samples using the response ratio ( $rsp_i$ ) of the areas for the oxygenates components to that of the internal standard as follows:

$$W_i = \left[ \left( \frac{A_i}{A_s} - b_i \right) / m_i \right] W_s \quad (13)$$

12.1.2 To obtain mass % ( $w_o$ ) results for each oxygenate Tables 9-11:

$$w_o = (W_i / W_g)(100 \%) \quad (14)$$

where:

$W_g$  = mass of gasoline sample.

12.1.3 *Mass % Oxygen*—To determine the oxygen content of the fuel, sum the mass of oxygen contents of all oxygenated components determined above according to the following equation:

TABLE 9 Relative Densities and Molecular Masses of Oxygenates

Compound	Relative Densities 60°F/60°F	Relative Molecular Mass
Methyl-t-butyl ether (MTBE)	0.7460	88.2
Ethyl-t-butyl ether (ETBE)	0.7452	102.18
Methyl-t-amyl ether (TAME)	0.7758	102.18
Di-isopropyl ether (DIPE)	0.7300	102.18
Methanol	0.7963	32.04
Ethanol	0.7939	46.07
2-Propanol	0.7899	60.09
t-Butanol	0.7922	74.12
1-Propanol	0.8080	60.09
2-Butanol	0.8114	74.12
Isobutanol	0.8058	74.12
1-Butanol	0.8137	74.12
1,3-dimethoxyethane (DME)	0.8720	...

TABLE 10 Range and Repeatability

Component	Range (Mass/Volume %)	Repeatability
Aromatics, volume %	13-41	0.55
Aromatics, mass %	16-49	$0.23X^{0.3333}$
Benzene, volume %	0.1-2	$0.0099(X + 0.6824)$
Benzene, mass %	0.1-2	$0.012(X + 0.48)$
Toluene, volume %	2-9	0.10
Toluene, mass %	2-10	0.057
1-Butanol, mass %	0.5-1	0.082
1-Propanol, mass %	0.2-1	0.050
2-Butanol, mass %	0.6-3	0.081
2-Propanol, mass %	1-2	0.073
DIPE, mass %	0.3-2	$0.026X^{0.4}$
ETBE, mass %	1-18	$0.066X^{0.5}$
Ethanol, mass %	1-12	$0.052X^{0.5}$
Isobutanol, mass %	0.1-2.0	0.057
Methanol, mass %	1-5	0.035
MTBE, mass %	1-15	$0.032X^{0.5}$
TAME, mass %	1-18	$0.068X^{0.6}$
tert-Butanol, mass %	1-2	0.051

$$w_{ot} = \sum \frac{(w_o)(16)(N_i)}{M_i} \quad (15)$$

where:

- $w_o$  = mass % of each oxygenates,
- $w_{ot}$  = total mass % oxygen in the fuel,
- $M_i$  = relative molecular mass of the oxygenate as given in, Table 9,
- 16.0 = atomic mass of oxygen, and
- $N_i$  = number of oxygen atoms in the oxygenate molecule.

12.1.4 If the volumetric concentration of each oxygenate component is desired, calculate the volumetric concentration according to Eq 16:

**TABLE 11 Range and Reproducibility**

Component	Range (Mass/ Volume% )	Reproducibility
Aromatics, volume %	13–41	1.65
Aromatics, mass %	16–49	0.69X <sup>0.3333</sup>
Benzene, volume %	0.1–2	0.054 (X + 0.68)
Benzene, mass %	0.1–2	0.063 (X + 0.48)
Toluene, volume %	2–9	0.23
Toluene, mass %	2–10	0.20
1-Butanol, mass %	0.5–1	0.12
1-Propanol, mass %	0.2–1	0.078
2-Butanol, mass %	0.6–3	0.45
2-Propanol, mass %	1–2	0.10
DIPE, mass %	0.3–2	0.066X <sup>0.4</sup>
ETBE, mass %	1–18	0.19X <sup>0.5</sup>
Ethanol, mass %	1–12	0.11X <sup>0.5</sup>
Isobutanol, mass %	0.1–2.0	0.12
Methanol, mass %	1–5	0.45
MTBE, mass %	1–15	0.17X <sup>0.5</sup>
TAME, mass %	1–18	0.15X <sup>0.6</sup>
tert-Butanol, mass %	1–2	0.18

$$v_i = w_i(D_f/D_i) \quad (16)$$

where:

$v_i$  = volume % of each oxygenate to be determined,

$D_i$  = relative density at 15.56°C (60°F) of the individual oxygenates as found in Table 9, and

$D_f$  = relative density of the fuel under study as determined by Practice D 1298 or Test Method D 4052.

### 12.2 Aromatic Hydrocarbons:

12.2.1 After identifying the various calibrated aromatic hydrocarbons in Table 2, including benzene, (Fig. 4) measure the areas of each aromatic peak at the selective reconstruction frequency in Table 6 and that of the DME internal standard. From the least squares fit calibrations, Eq 13, calculate the *absolute* mass of each aromatic components ( $W_i$ ) in grams in the gasoline samples using the response ratio ( $rsp_i$ ) of the areas for the aromatic components to that of the internal standard.

12.2.2 *Uncalibrated Aromatic Components (3.1.5)*—The calibration components in Table 2 may not account for all of the aromatic hydrocarbons present in the gasoline sample. For the uncalibrated components (Fig. 4 and Fig. 5) follow the chromatographic fingerprint in Fig. 5 to selectively quantitate each uncalibrated compound using the specified SWC in Fig. 4. Use a SWC of 600 to 900 cm<sup>-1</sup> as a guide in detecting the uncalibrated aromatics (Fig. 4 was obtained with a SWC of 600 to 900 cm<sup>-1</sup>). Use the least square linear fit of 1,2,3,5-tetramethylbenzene obtained using the SWC of 600 to 900 cm<sup>-1</sup> for the quantitation of the uncalibrated aromatic components.

NOTE 5—Consider all peaks between the retention time of indan and the end of the 600 to 900 cm<sup>-1</sup> chromatogram (end of GC analysis time) as uncalibrated aromatic components *except* for the calibrated components in Table 2.

12.2.3 To obtain mass percent ( $W_a$ ) results for each aromatic hydrocarbon, including uncalibrated aromatics:

$$w_a = (W_f/W_g)(100\%) \quad (17)$$

where:

$W_g$  = mass of gasoline sample.

12.2.4 To obtain the mass % of the total aromatic concentration  $W_r$ , sum the mass % of each aromatic component, including the mass percent of the uncalibrated components:

$$w_r = \sum w_a \quad (18)$$

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

12.2.6 If the volumetric concentration of each aromatic component is desired, calculate the volumetric concentration according to Eq 19:

$$v_i = w_a(D_f/D_i) \quad (19)$$

where:

$v_i$  = volume % of each aromatic to be determined,

$D_i$  = relative density at 15.56°C (60°F) of the individual aromatics as found in Table 3, and

$D_f$  = relative density of the fuel under study as determined by Practice D 1298 or Test Method D 4052.

12.2.7 To obtain the volume % of the total aromatic concentration  $V_r$ , sum the volume % of each aromatic component, including the volume percent of the uncalibrated components:

$$V_r = \sum V_i \quad (20)$$

12.2.8 Report results to nearest 0.1 volume % for total aromatics and to nearest 0.01 volume % for benzene.

## 13. Precision and Bias <sup>4</sup>

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

13.1.1 *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:

where:

$X$  = the mean mass or volume % of the component.

13.1.2 *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:

where:

$X$  = the mean mass or volume % of the component.

13.2 *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. Keywords

14.1 aromatics; benzene; gas chromatography; GC/IR; gasolines; oxygenates; toluene

<sup>4</sup> Supporting data is available from ASTM Headquarters in the form of a research report. Request RR:D02-1399. The volume % repeatability and reproducibility were determined for constant fuel densities given to round robin participants.



ESTIMATED AROMATICS' RECONSTRUCTION FREQUENCIES

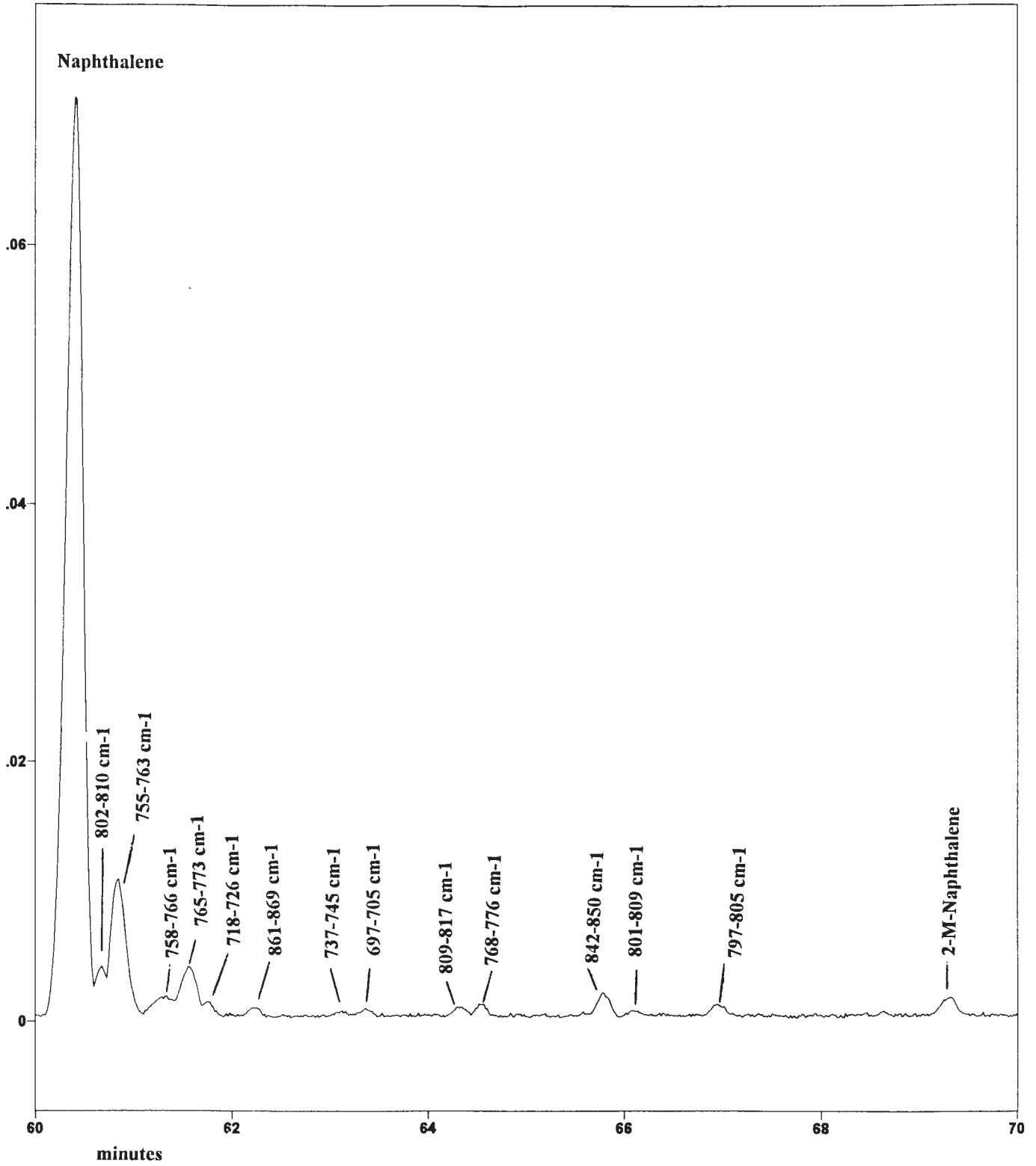
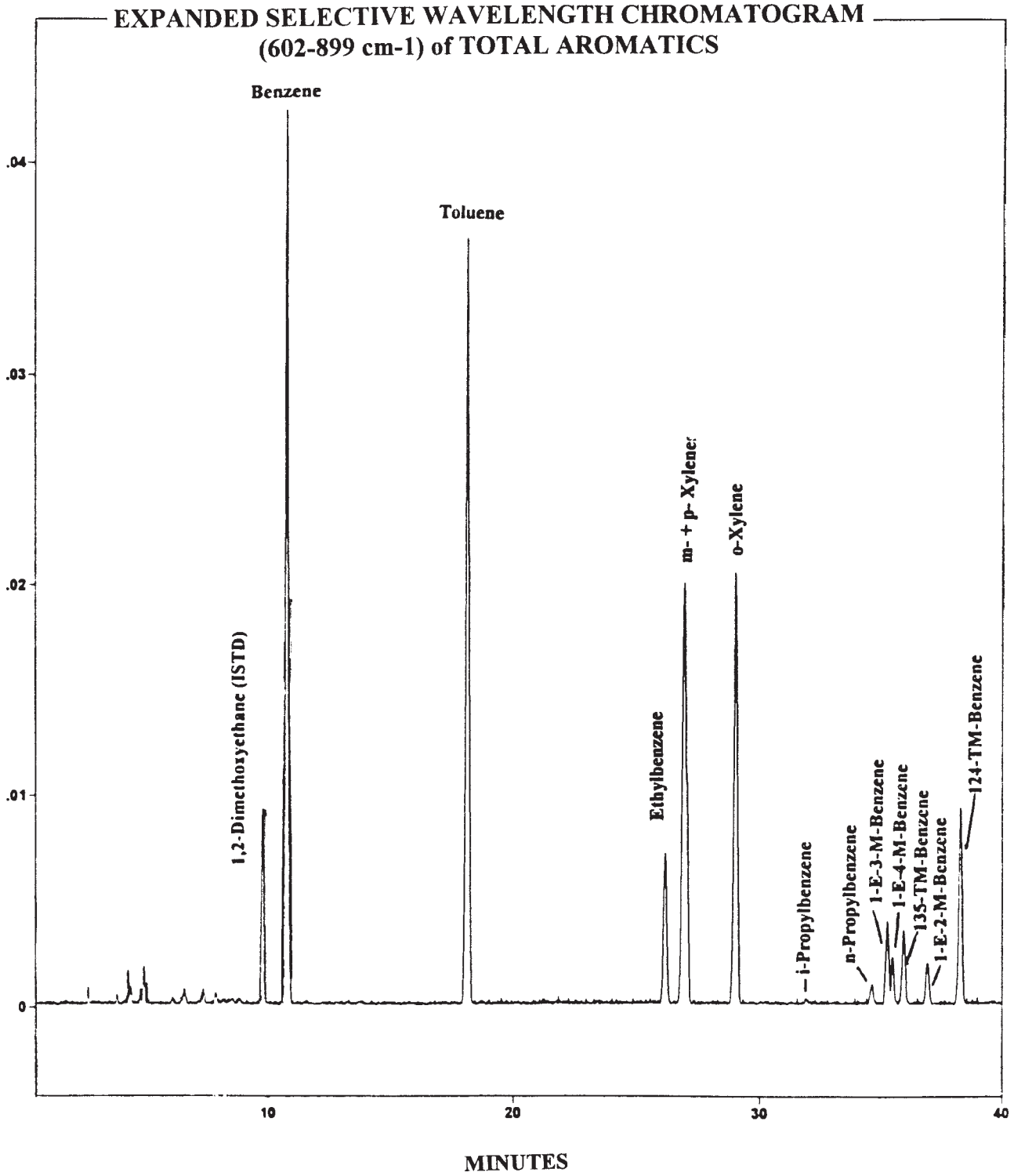
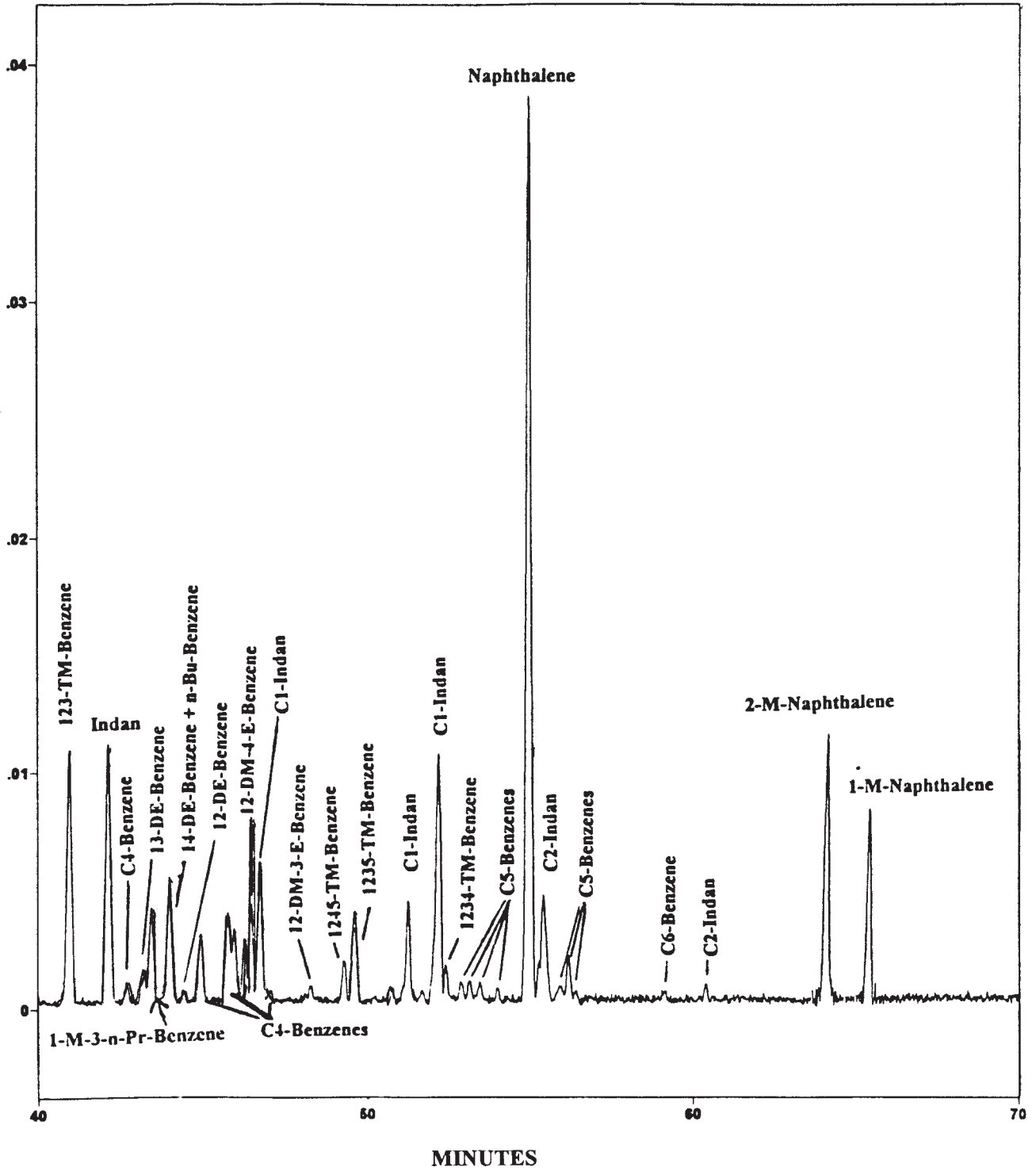


FIG. 4 Expanded Selective Wavelength Chromatogram (602-899 cm-1) of Total Aromatics



SWC of 602-899 cm<sup>-1</sup>

FIG. 4 (continued)



SWC of 602-899 cm-1

FIG. 5 Estimated Aromatics' Reconstruction Frequencies

ESTIMATED AROMATICS' RECONSTRUCTION FREQUENCIES

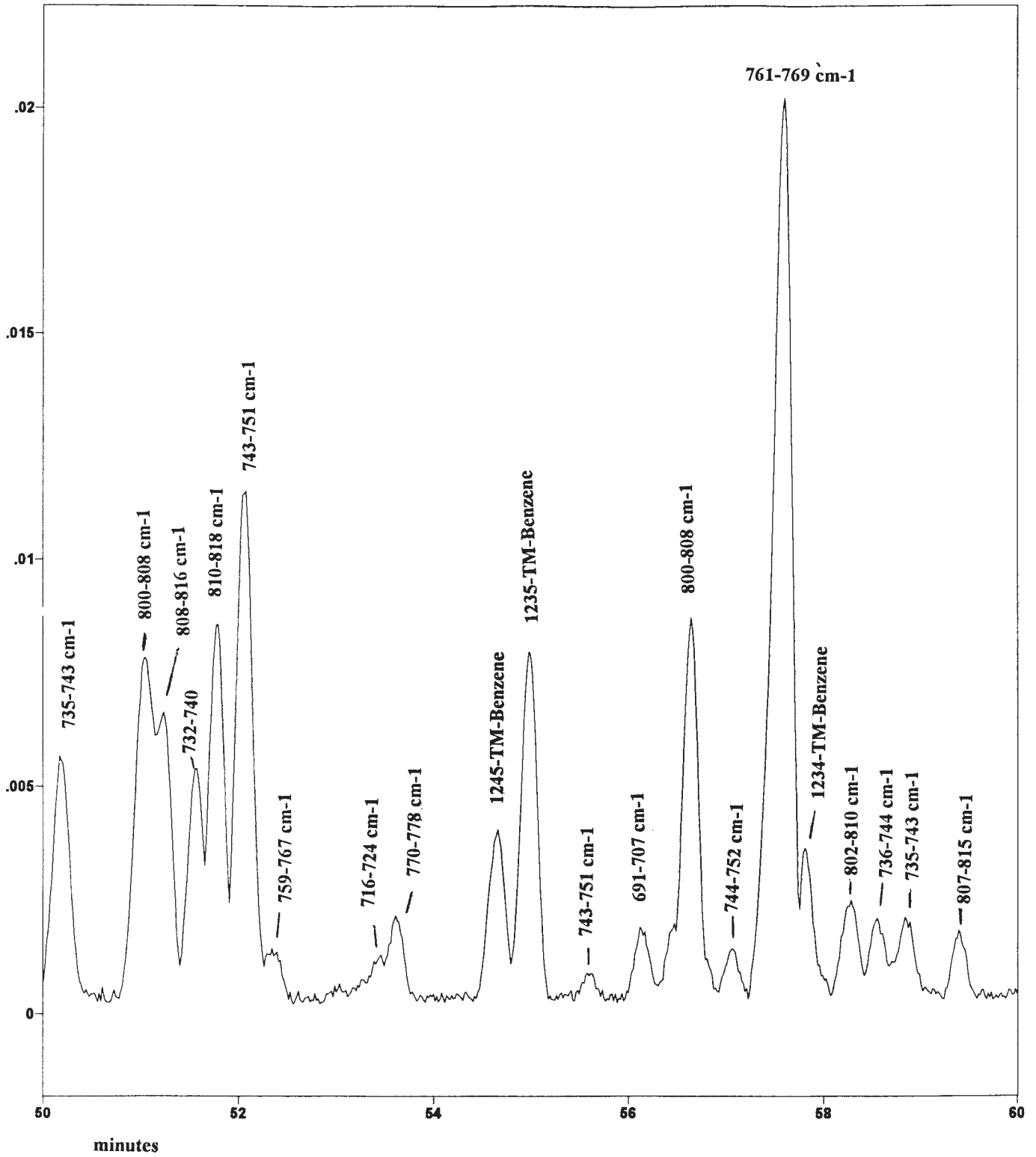


FIG. 5 (continued)



ESTIMATED AROMATICS' RECONSTRUCTION FREQUENCIES

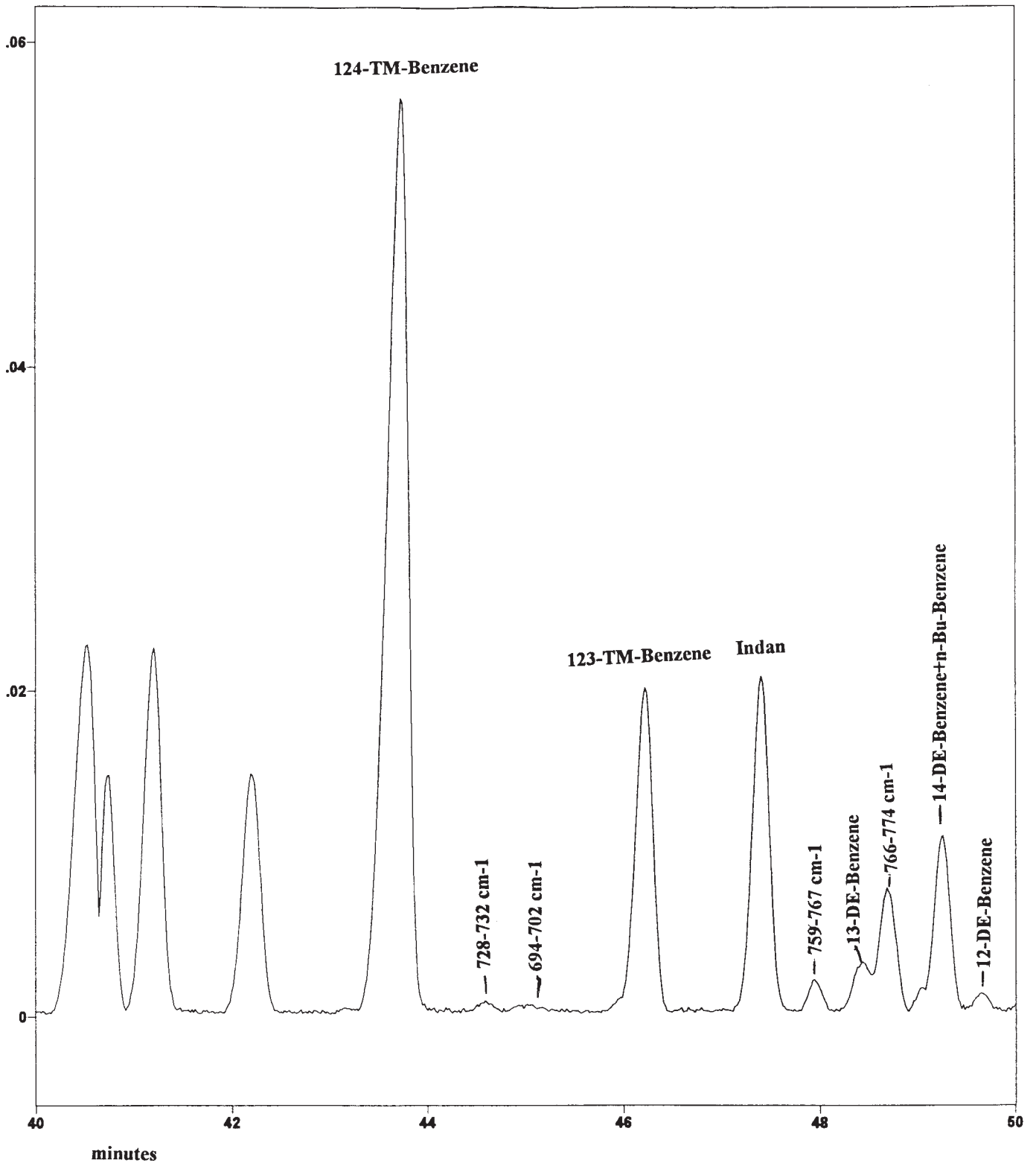


FIG. 5 (continued)

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