



# Standard Test Method for Benzene, Toluene, Xylene (BTX) Concentrates Analysis by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D6563; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the determination of the total nonaromatic hydrocarbons, benzene, toluene, ethylbenzene, xylenes, and total C<sub>9</sub> + aromatic hydrocarbons in BTX concentrates by capillary column gas chromatography. This test method is applicable to materials with a final boiling point below 215°C.

1.2 This test method may also be used to determine the relative distribution of the individual C<sub>8</sub> aromatic hydrocarbon isomers in mixed xylenes.

1.3 Individual components can be determined from 0.01 to 90 %.

1.4 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

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 use.* For a specific precautionary statement, see Section 9.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D3437 Practice for Sampling and Handling Liquid Cyclic Products

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.01 on Benzene, Toluene, Xylenes, Cyclohexane and Their Derivatives.

Current edition approved June 1, 2012. Published July 2012. Originally approved in 2000. Last previous edition approved in 2011 as D6463 – 11a. DOI: 10.1520/D6563-12.

<sup>2</sup> 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.

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E355 Practice for Gas Chromatography Terms and Relationships

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

### 2.2 Other Documents:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200<sup>3</sup>

## 3. Terminology

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

3.1.1 *extracted reformate, n*—an aromatic concentrate obtained by solvent extraction of reformate.

3.1.2 *reformate, n*—the product of a catalytic process that increases the concentration of aromatic hydrocarbons.

3.1.3 *pyrolysis gasoline, n*—depentanized by-product recovered from ethylene manufacture.

3.1.4 *synthetic blend, n*—blend of reagent hydrocarbons that simulate a process product.

3.1.5 *hydrogenated pyrolysis gasoline, n*—pyrolysis gasoline that has been treated with hydrogen to reduce the olefins content.

3.1.6 *crude ethylbenzene, n*—product produced from the reaction of impure fluid cat cracking, (FCC) ethylene and benzene.

3.1.6.1 *Discussion*—It typically contains greater than 40 % of ethylbenzene and benzene.

3.1.7 *light blending aromatics feedstock, n*—light aromatics fraction (with high amounts of benzene and toluene) typically recovered from the isomerization of a *p*-xylene or *m*-xylene depleted C<sub>8</sub> aromatics stream.

<sup>3</sup> Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

\*A Summary of Changes section appears at the end of this standard

3.1.8 *mixed xylenes, n*—a mixture of C<sub>8</sub> aromatic hydrocarbon isomers including ethylbenzene, but excluding styrene.

#### 4. Summary of Test Method

4.1 The specimen to be analyzed is injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column. The peak area of each component is measured and adjusted using effective carbon number (ECN) response factors. The concentration of each component is calculated based on its relative percentages of total adjusted peak area and normalized to 100.00.

4.2 Results can be reported as either volume or weight percent. Volumetric results can be derived by dividing each component's weight percent by its relative density and re-normalizing to 100 %.

#### 5. Significance and Use

5.1 This test method was primarily developed to determine benzene, toluene, and xylenes in chemical intermediate and solvent streams such as reformat, BTX extracts, pyrolysis gasoline, hydrogenated pyrolysis gasoline, crude benzene, crude ethylbenzene, commercial toluene, and light blending aromatic feedstocks. This test method may not detect all components and there may be unknown components that would be assigned inappropriate response factors and thus, the results may not be absolute.

5.2 The relative distribution of C<sub>8</sub> aromatics is useful for determining conformance to *p*-xylene feedstock specifications.

#### 6. Interferences

6.1 Nonaromatic hydrocarbons may interfere with the determination of benzene and toluene when certain columns are used.

6.2 Styrene may be present in some samples. It will elute with C<sub>9</sub>+ aromatics.

#### 7. Apparatus

7.1 *Gas Chromatograph*—Any gas chromatograph having a flame ionization detector and a splitter injector suitable for use with a fused silica capillary column may be used, provided the system has sufficient sensitivity, linearity, and range to obtain a minimum peak height response for a 0.01 % peak of five times the height of the signal background noise, while not exceeding the full scale of either the detector or the electronic integration for the highest peak. The split injection system shall not discriminate over the boiling range of the samples analyzed. The system shall be capable of operating at the conditions given in [Table 1](#).

7.2 *Columns*—The choice of column is based upon resolution requirements. Any column may be used that is capable of resolving all the components of interest. The column and conditions described in [Table 1](#) have been used successfully and will be the referee in case of dispute.

7.3 *Recorder/Electronic Integration*—Electronic integration with tangent capabilities is recommended.

**TABLE 1 Recommended Operating Conditions**

Column	fused silica capillary
Tubing	50 or 60
Length, m	0.25
Internal diameter, mm	0.25
Stationary phase	bonded polyethylene glycol
Film thickness, μm	0.25
Carrier gas	helium
Flow, linear velocity at 70°C, cm/s	20
Split ratio	200:1
Detector gas	
Hydrogen flow rate, mL/min	30
Air flow rate, mL/min	300
Make-up flow rate, mL/min	30
Sample size, μL	0.5
Temperatures	
Injector, °C	250
Detector, °C	300
Column	
Initial, °C	70
Hold, min	10
Rate, °C/min	5
Final, °C	200
Hold, min	24

#### 8. Reagents

8.1 *Carrier Gas*—Helium with a minimum purity of 99.999 mol %. See [11.1](#) for optional use of hydrogen carrier gas.

8.2 *Detector Gases:*

8.2.1 *Fuel Gas*—Hydrogen with a minimum purity of 99.999 mol %.

8.2.2 *Makeup Gas*—Nitrogen or helium, with a minimum purity of 99.999 mol %.

8.2.3 *Flame Support Gas*—Air, total hydrocarbon less than 0.1 ppm.

8.3 Purify carrier, fuel, and makeup gases by adding traps to reduce the concentration of any remaining oxygen, water, and hydrocarbons. Purify air by adding traps to reduce the concentration of any remaining hydrocarbons and water.

#### 9. Hazards

9.1 Consult current OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all material used in this test method.

#### 10. Sampling

10.1 Sample material in accordance with Practice [D3437](#).

#### 11. Preparation of Apparatus

11.1 *Chromatograph*—Follow manufacturer's instructions for mounting and conditioning the column in the chromatograph. Adjust the instrument to the conditions as described in [Table 1](#) to give the desired separation using the suggested column. Other columns and conditions, including the use of hydrogen carrier gas, may be used to achieve the resolution requirements. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder/electronic baseline. See Practices [E355](#) and [E1510](#) for additional information on gas chromatography practices and terminology.

#### 12. Procedure

12.1 Bring the sample to ambient room temperature.

12.2 Inject an appropriate amount of sample into the chromatograph that meets the criteria outlined in 7.1. See Practices E355 and E1510 for additional information on gas chromatography practices and terminology.

12.3 Sample chromatograms are illustrated in Figs. 1-4.

### 13. Calculation

13.1 Measure the area of all peaks. Total non-aromatics are defined as all components eluting before *o*-xylene, excluding benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, and cumene. Non-aromatics are summed and reported as a group. Total C<sub>9</sub>-plus aromatics are defined as cumene, plus all components eluting after *o*-xylene. C<sub>9</sub>-plus aromatics are summed and reported as a group.

13.2 Calculate the weight percent concentration of each component as follows:

$$C_i = \frac{100 \times A_i \times ECN_i}{\sum_{i=1}^n (A_i \times ECN_i)} \quad (1)$$

where:

- $C_i$  = concentration of component in weight percent,  
 $A_i$  = area of component, *i* peak,  
 $ECN_i$  = effective carbon response factor for component, and  
 $\sum_{i=1}^n (A_i \times ECN_i)$  = the summation of all response corrected areas in the chromatogram.

13.3 Calculate the volume percent concentration of each component as follows; for purposes of the volume percent calculation, the solution is treated as an ideal mixture:

$$V_i = \frac{100 C_i / D_i}{\sum_{i=1}^n (C_i / D_i)} \quad (2)$$

where:

- $V_i$  = calculated vol % concentration of component,  
 $C_i$  = calculated wt % concentration of component from 12.1,  
 $D_i$  = relative density of component, and  
 $\sum_{i=1}^n (C_i \times D_i)$  = sum of the quotients  $C/D$ .

13.4 Use the following effective carbon number (ECN) response factors for the calculations:

Component	ECN Response Factor <sup>A,B</sup>	Relative Density <sup>C</sup> at 20°C
Non Aromatics	1.0000	0.7167 (average)
Benzene	0.9100	0.8789
Toluene	0.9200	0.8670
Ethylbenzene	0.9275	0.8670
<i>p</i> -Xylene	0.9275	0.8610
<i>m</i> -Xylene	0.9275	0.8642
<i>o</i> -Xylene	0.9275	0.8802
C <sub>9</sub> + aromatics	0.9333	0.8712 (average)

<sup>A</sup> Scanlon, J., T., and Willis, D., E., "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept" *Journal of Chromatographic Science*, Vol 23, August, 1985, pp. 333-339.

<sup>B</sup> Response Factors are relative to *n*-heptane.

<sup>C</sup> DS # 4A *Physical Constants of Hydrocarbons C<sub>1</sub> through C<sub>10</sub>*, ASTM, 1971.

### 14. Report

14.1 Report the following information:

14.1.1 All component concentrations to the nearest 0.01 wt (or vol) %.

14.1.2 For concentrations less than 0.01 wt (or vol) %, report as <0.01 wt (or vol) %.

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

15.1 *Precision*—The following criteria should be used to judge the acceptability of results obtained by this test method (95 % confidence level). The precision criteria were derived from an interlaboratory study using data submitted by fourteen laboratories (ten laboratories for mixed xylenes). Each interlaboratory study participant was provided two gravimetrically prepared BTX known samples and three unknown samples of varying concentrations. Each sample was run twice on two days by two different operators. Results of the interlaboratory study were calculated and analyzed using Practice E691.

15.2 *Intermediate Precision, (formerly Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than  $\pm$  the amount shown in Table 2, Table 3, Table 4, Table 5, Table 6, or Table 7. On the basis of test error alone, the difference between two results obtained in the same laboratory on the same material will be expected to exceed this value only 5 % of the time.

15.3 *Reproducibility*—Results submitted by each of two laboratories should not be considered suspect unless they differ by more than  $\pm$  the amount shown in Table 2, Table 3, Table 4, Table 5, or Table 6. On the basis of test error alone, the difference between two results obtained in different laboratories on the same material will be expected to exceed this value only 5 % of the time.

15.4 *Bias*—For mixed xylenes, the interlaboratory test utilized a sample prepared gravimetrically from individual from individual C<sub>8</sub> isomers obtained at the highest purity available. However, this sample has not been approved as an acceptable reference material and consequently bias has not been determined.

15.4.1 As an aid for the users in determining the possibility of bias, calculated C<sub>8</sub> distributed for the round robin sample is listed in Table 7 as the "Expected Concentration." The average value for each C<sub>8</sub> isomer as calculated from the reported concentrations is listed as "Average Concentration Reported."

15.5 The precision using hydrogen carrier gas has not been determined and may not be within the published precision of the method.

### 16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1025. Supporting data for mixed xylenes are available separately: Request Research Report RR:D16-1015. Contact ASTM Customer Service at service@astm.org.

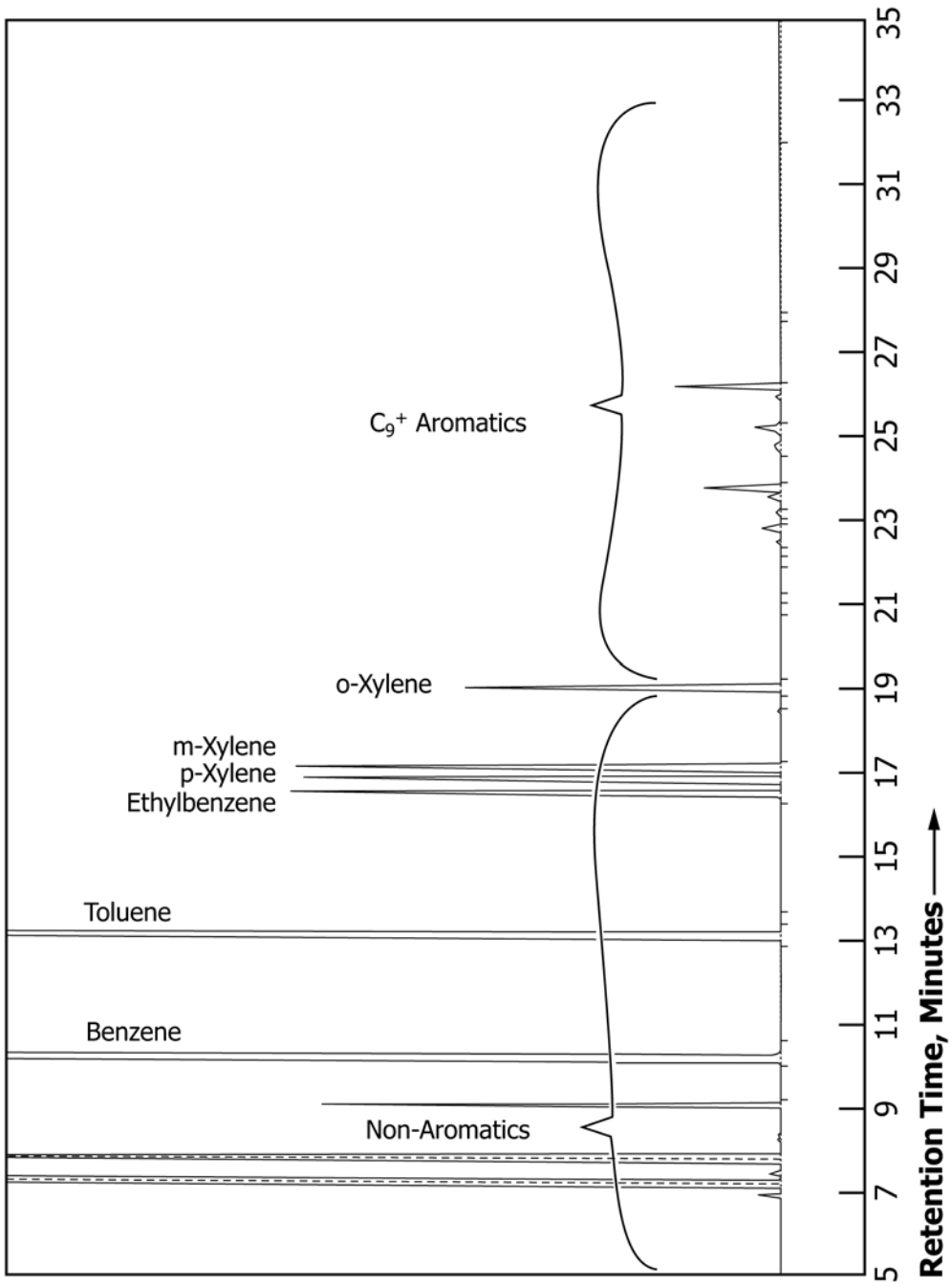


FIG. 1 Synthetic Blend

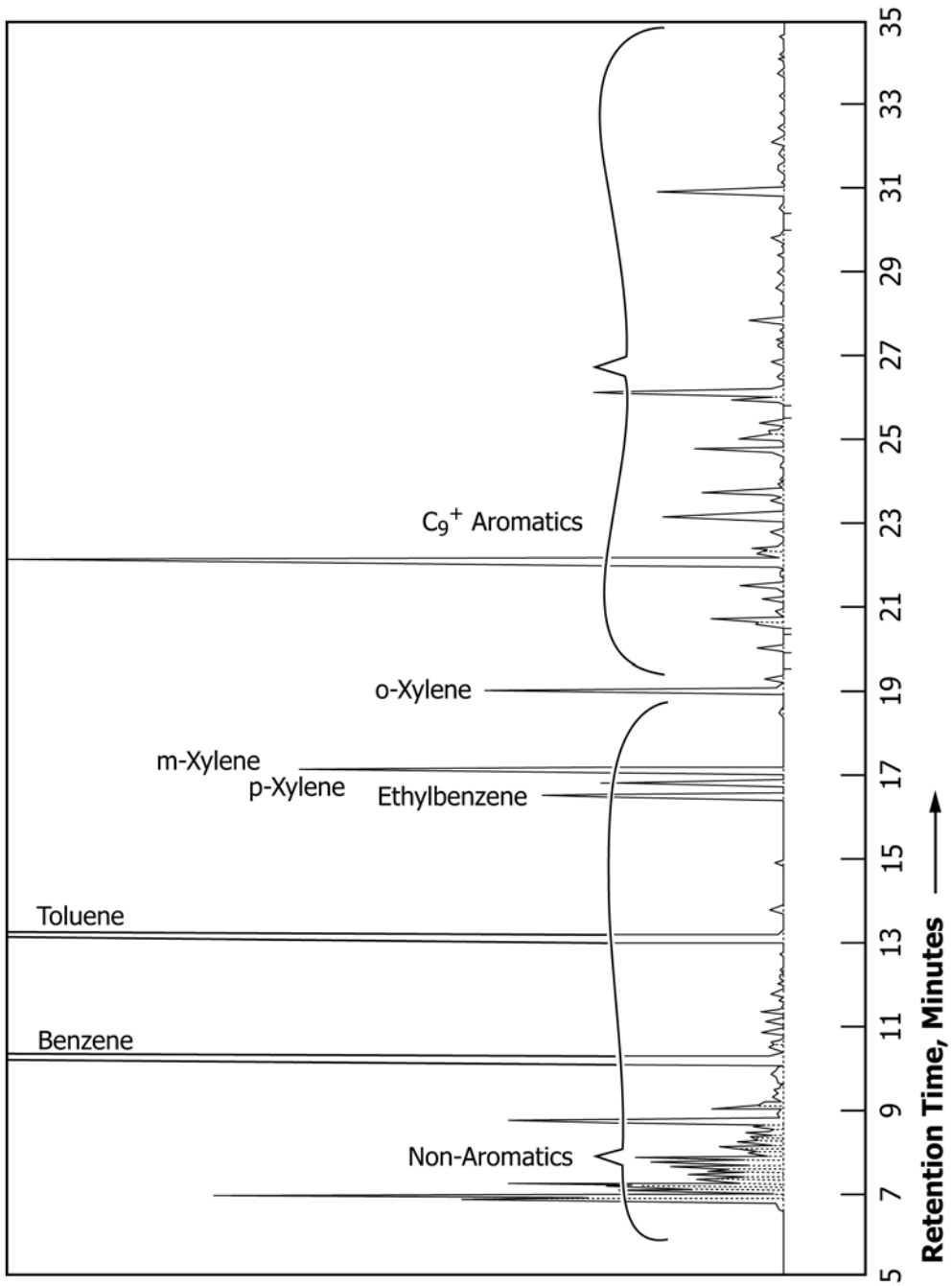


FIG. 2 Pyrolysis Gasoline

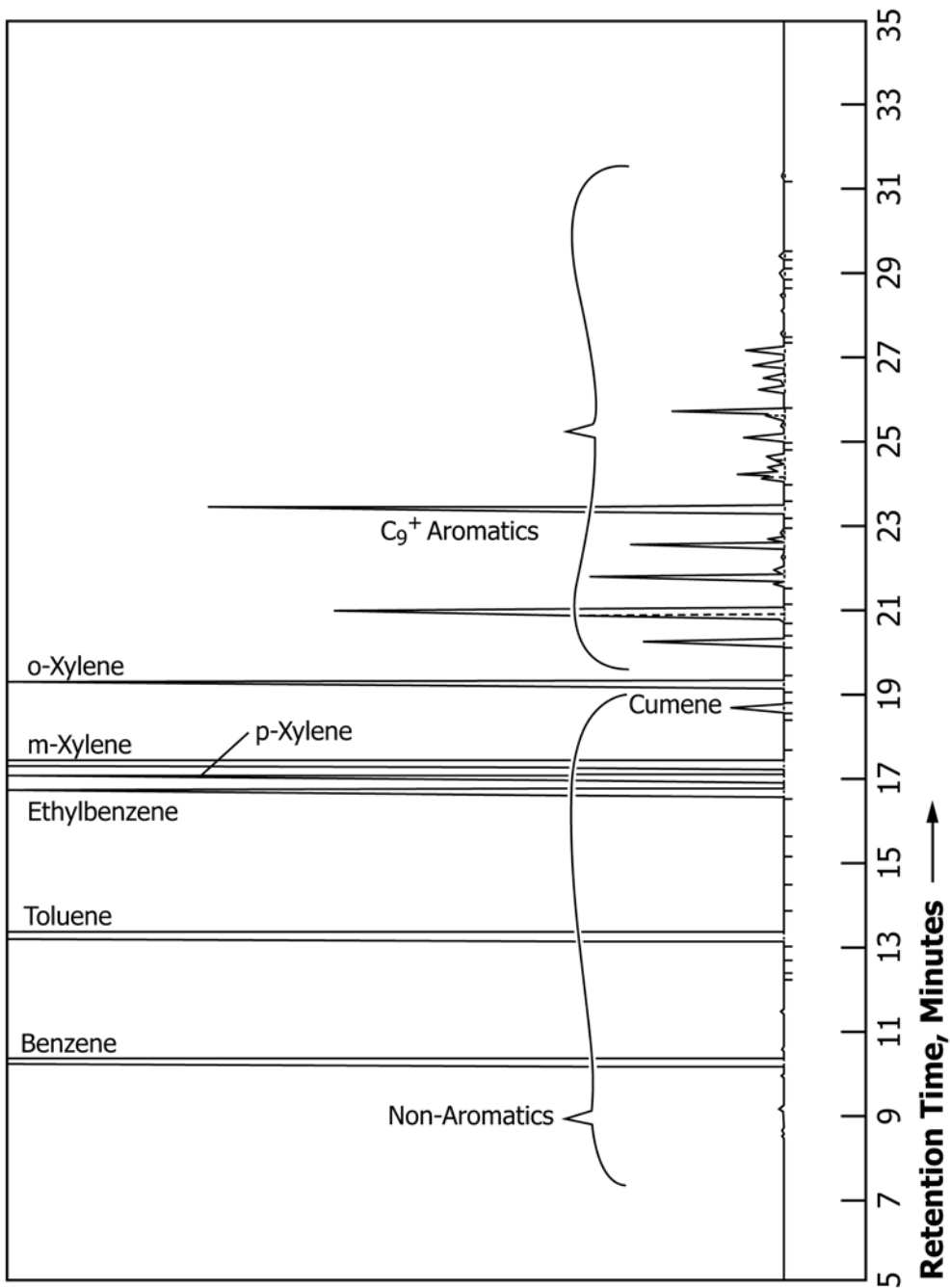


FIG. 3 Extracted Reformat

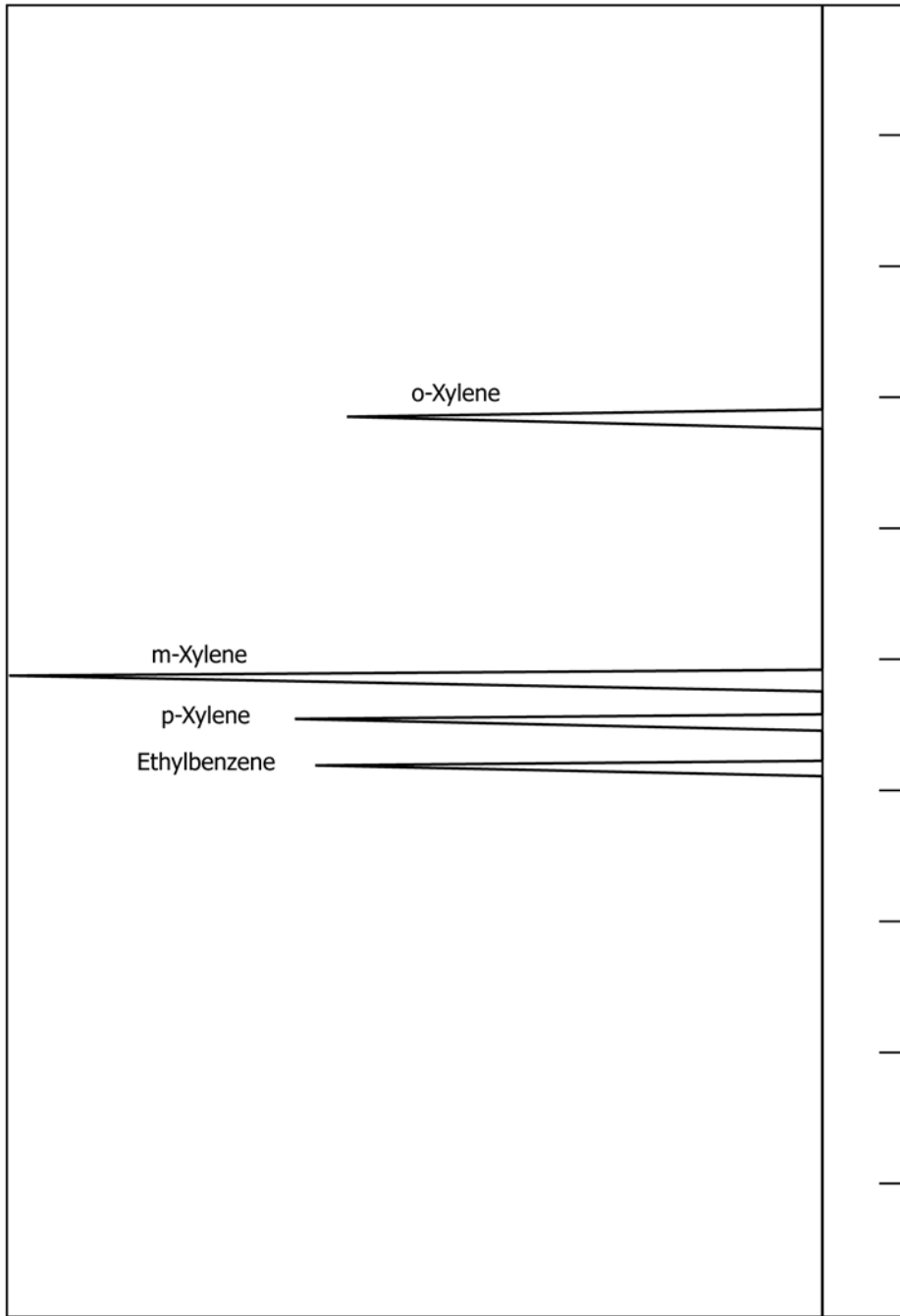


FIG. 4 Mixed Xylenes

**TABLE 2 Interlaboratory Precision and Reproducibility for Synthetic Blend Sample**

NOTE 1—This data was calculated after removal of outliers using Practice E691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	22.447	0.296	1.746
Benzene	42.891	0.781	1.887
Toluene	19.961	0.212	0.715
Ethylbenzene	3.061	0.055	0.191
Total xylenes	7.921	0.195	0.512
C <sub>9</sub> + aromatics	4.192	0.169	1.009

**TABLE 3 Interlaboratory Precision and Reproducibility for Pyrolysis Gasoline Sample**

NOTE 1—This data was calculated after removal of outliers using Practice E691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	17.918	0.237	1.394
Benzene	36.580	0.666	1.610
Toluene	17.117	0.181	0.613
Ethylbenzene	1.519	0.027	0.095
Total xylenes	6.271	0.154	0.406
C <sub>9</sub> + aromatics	20.419	0.823	4.917

**TABLE 4 Interlaboratory Precision and Reproducibility for Extracted Reformate Sample**

NOTE 1—This data was calculated after removal of outliers using Practice E691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	0.264	0.003	0.021
Benzene	21.015	0.382	0.925
Toluene	34.516	0.366	1.236
Ethylbenzene	5.473	0.098	0.342
Total xylenes	24.173	0.595	1.564
C <sub>9</sub> + aromatics	14.744	0.594	3.550

16.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

16.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

16.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

**TABLE 5 Interlaboratory Precision and Reproducibility for Hydrogenated Pyrolysis Gasoline**

NOTE 1—This data was calculated after removal of outliers using Practice E691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	27.871	0.368	2.168
Benzene	61.111	1.112	2.689
Toluene	10.966	0.116	0.391
Ethylbenzene	trace	...	...
Total xylenes	trace	...	...
C <sub>9</sub> + aromatics	trace	...	...

**TABLE 6 Interlaboratory Precision and Reproducibility for Standard Sample**

NOTE 1—This data was calculated after removal of outliers using Practice E691.

Component	Concentration Weight %	Intermediate Precision	Reproducibility
Nonaromatics	4.538	0.060	0.353
Benzene	50.0655	0.911	2.203
Toluene	30.039	0.318	1.075
Ethylbenzene	5.067	0.091	0.316
Total xylenes	5.069	0.125	0.328
C <sub>9</sub> + aromatics	5.308	0.214	1.278

**TABLE 7 Intermediate Precision and Reproducibility for Mixed Xylenes**

Component	Expected Concentration Weight %	Average Concentration Reported Weight %	Intermediate Precision (formerly called Repeatability)	Reproducibility
Ethylbenzene	17.93	17.92	0.077	0.153
<i>p</i> -xylene	20.16	20.07	0.073	0.193
<i>m</i> -xylene	44.09	43.96	0.101	0.369
<i>o</i> -xylene	17.83	17.98	0.116	0.193

16.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

## 17. Keywords

17.1 BTX concentrates; BTX extracts; capillary gas chromatography; commercial toluene; crude benzene; crude ethylbenzene; hydrogenated pyrolysis gas; light blending aromatic feedstock; mixed xylenes; pyrolysis gas



**SUMMARY OF CHANGES**

Committee D16 has identified the location of selected changes to this standard since the last issue (D6563 - 11a) that may impact the use of this standard. (Approved June 1, 2012.)

- |   |   |
|---|---|
| (1) Paragraphs 8.2 and 8.3 were revised to current guidelines.                          | (5) The densities listed in paragraph 13.4 were changed to 20°C; the values were taken from ASTM Publication DS 4A. |
| (2) A sentence was added to paragraph 11.1 to clarify the used of hydrogen carrier gas. | (6) The title of Table 1 was changed.   |
| (3) Paragraph 12.4 was moved from Procedure to Calculation.                             | (7) Figures 1–3 were revised to fit the new definitions for non-aromatics and C <sub>9</sub> -plus aromatics.       |
| (4) An “ideal mixture” phrase was added to paragraph 13.3.                              |   |

Committee D16 has identified the location of selected changes to this standard since the last issue (D6563 – 11a) that may impact the use of this standard. (Approved June 1, 2011.)

- (1) Paragraphs 8.1 and 11.1 were revised to permit the use of hydrogen carrier gas.

Committee D16 has identified the location of selected changes to this standard since the last issue (D6563 - 05 (2010) <sup>e1</sup>) that may impact the use of this standard. (Approved February 1, 2011.)

- (1) Deleted paragraph 13.4.

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; <http://www.copyright.com/>*