



Designation: D7504 – 17a

## Standard Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number<sup>1</sup>

This standard is issued under the fixed designation D7504; 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 total nonaromatic hydrocarbons and monocyclic aromatic hydrocarbons in benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, styrene and mixed xylenes by gas chromatography. The purity of benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, styrene and mixed xylenes is also calculated. Similar test methods, using the internal standard calibration technique and the external standard calibration technique, are Test Methods D2360, D3797, D4492, D5060, D5135, D5917, and D6563 respectively.

1.2 The limit of detection (LOD) is 0.0002 wt % and limit of quantitation (LOQ) is 0.0006 wt % for impurities in toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene, benzene, and styrene.

1.3 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.

1.4 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 use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

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### 2. Referenced Documents

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

- D841 Specification for Nitration Grade Toluene
- D1555M Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons and Cyclohexane [Metric]
- D2360 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography (Withdrawn 2016)<sup>3</sup>
- D3437 Practice for Sampling and Handling Liquid Cyclic Products
- D3797 Test Method for Analysis of *o*-Xylene by Gas Chromatography (Withdrawn 2014)<sup>3</sup>
- D4492 Test Method for Analysis of Benzene by Gas Chromatography
- D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
- D5060 Test Method for Determining Impurities in High-Purity Ethylbenzene by Gas Chromatography
- D5135 Test Method for Analysis of Styrene by Capillary Gas Chromatography
- D5136 Specification for High Purity *p*-Xylene
- D5211 Specification for Xylenes for *p*-Xylene Feedstock
- D5917 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and External Calibration
- D6229 Test Method for Trace Benzene in Hydrocarbon Solvents by Capillary Gas Chromatography
- D6563 Test Method for Benzene, Toluene, Xylene (BTX) Concentrates Analysis by Gas Chromatography
- 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
- E177 Practice for Use of the Terms Precision and Bias in

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

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

## ASTM Test Methods

**E260** Practice for Packed Column Gas Chromatography

**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 Document:

**OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200**<sup>4</sup>

## 3. Terminology

3.1 See Terminology **D4790** for definitions of terms used in this test method.

## 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)<sup>5</sup> correction factors. The concentration of each component is calculated based on its relative percentages of total adjusted peak area and normalized to 100.0000 %.

## 5. Significance and Use

5.1 Determining the type and amount of hydrocarbon impurities remaining from the manufacture of toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene, benzene, and styrene used as chemical intermediates and solvents is often required. This test method is suitable for setting specifications and for use as an internal quality control tool where these products are produced or are used. Typical impurities are: alkanes containing 1 to 10 carbons atoms, benzene, toluene, ethylbenzene (EB), xylenes, and aromatic hydrocarbons containing nine carbon atoms or more.

5.2 This method may not detect all components and there may be unknown components that would be assigned inappropriate correction factors and thus, the results may not be absolute.

## 6. Interferences

6.1 The complete separation of *p*-xylene from ethylbenzene, or ethylbenzene and *m*-xylene from *p*-xylene can be difficult when either ethylbenzene or *p*-xylene is analyzed, respectively. The separation can be considered adequate if the distance from the baseline to the valley between the two peaks is not greater than 50 % of the peak height of lower of the two peaks.

## 7. Apparatus

7.1 Chromatographic data system is required.

**TABLE 1 Recommended Method Parameters**

Inlet	Split
Temperature, °C	270
Column:	
Tubing	fused silica
Length, m	60
Internal diameter, mm	0.32
Stationary phase	crosslinked polyethylene glycol
Film thickness, µm	0.25
Column temperature program	
Initial temperature, °C	60
Initial time, min	10
Programming rate, °C/min	5
Final, °C	150
Time 2, min	10
Carrier gas	helium or hydrogen
Linear velocity, cm/s at 145°C	20 helium or 45 hydrogen
Split ratio	100:1
Sample size, µL	0.6
Detector:	flame ionization
Temperature, °C	300
Analysis time, min	38

7.2 *Columns*—The choice of column is based on resolution requirements. Any column may be used that is capable of resolving all significant impurities from the major component. The column and conditions described in **Table 1** have been used successfully and shall be used as a referee in cases of dispute.

7.3 *Gas Chromatograph*—Any instrument 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 determine 0.0001 wt %, while not exceeding the full scale of either the detector or the electronic integration for the major component. It shall have a split injection system that will not discriminate over the boiling range of the samples analyzed. The system should be capable of operating at conditions given in **Table 1**.

7.4 *Injector*—The specimen must be precisely and repeatedly injected into the gas chromatograph. An automatic sample injection device is highly recommended.

7.5 *Syringe*—chromatographic, capable of delivering appropriate µL volumes.

## 8. Reagents and Materials

8.1 *Purity of Reagent*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,<sup>6</sup> where such specifications are available. Reagents with an establish purity greater than ACS reagent grade may be used.

<sup>4</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>.

<sup>5</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>6</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2 *Carrier Gas, Makeup Gas and Detector Gases 99.999 % Pure.* Oxygen in carrier gas less than 1 ppm, less than 0.5 ppm is preferred. Purify carrier, makeup and detector gases to remove oxygen, water, and hydrocarbons.

8.3 Air for the FID should contain less than 0.1 ppm total hydrocarbon.

#### 8.4 *Equipment Set-up Check Sample*

8.4.1 *High Purity p-Xylene (99.99 wt.% or greater purity)*—Most *p*-xylene is available commercially at a purity less than 99.9 wt. %, but can be purified by recrystallization. To prepare 2 qt. of high-purity *p*-xylene, begin with approximately 1 gal of reagent-grade *p*-xylene and cool in an explosion-proof freezer at between  $-10\text{ }^{\circ}\text{C}$  to  $+10\text{ }^{\circ}\text{C}$  until approximately  $\frac{1}{2}$  to  $\frac{3}{4}$  of the *p*-xylene has frozen. Remove the sample and decant the liquid portion. Allow the *p*-xylene to thaw and repeat the crystallization step on the remaining sample until the *p*-xylene is free of contamination (no peaks detected other than *p*-xylene) as indicated by gas chromatography.

8.4.2 Fill a 100 mL volumetric flask approximately  $\frac{3}{4}$  full of the high purity *p*-xylene.

8.4.3 Add 0.1 mL *m*-xylene.

8.4.4 Add 0.01 mL of toluene, ethylbenzene, cumene, *o*-xylene, styrene, alpha methylstyrene, and phenylacetylene.

8.4.5 Add 0.001 mL benzene and 1, 4-dioxane.

8.4.6 Dilute to volume with high purity *para*-xylene.

8.4.7 Impurities that are not present in the samples being analyzed may be omitted from the check sample.

8.4.8 The purpose of the set-up check sample is to help determine the retention time of the various components and that the *para*-xylene and *meta*-xylene are adequately separated. This sample should not be used for calibration.

## 9. Hazards

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

## 10. Sampling

10.1 Sample the material in accordance with Practice D3437.

## 11. Preparation of Apparatus

11.1 Follow manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the conditions described in Table 1, allowing sufficient time for the equipment to reach equilibrium. See Practices E260, E355, and E1510 for additional information on gas chromatography practices and terminology.

## 12. Calibration

12.1 Prior to implementation of the ECN method, a laboratory should demonstrate that the equipment is set up properly using an equipment set-up check sample. This sample should be used to: determine retention times of each component, and that the separation of *meta*-xylene from *para*-xylene is satisfactory. See 6.1 for the definition of an adequate separation.

## 13. Procedure

13.1 Bring the sample to room temperature.

13.2 Check the chromatography performance to make sure that the column is properly resolving peaks.

13.3 Inject an appropriate amount of sample into the instrument.

13.4 Review the chromatographic data system result. Measure the area of all peaks. The non-aromatics fraction includes all peaks up to ethylbenzene except for the peaks assigned to benzene and toluene. Sum together all the non-aromatic peaks as a total area. When either benzene or toluene is analyzed and 1,4-dioxane is required to be reported, the non-aromatic fraction does not include the peak assigned to 1,4-dioxane.

NOTE 1—A poorly resolved peak, such as *p*-xylene from high purity ethylbenzene or *m*-xylene from high purity *p*-xylene, will often require a tangent skim from the neighboring peak.

13.5 See Figs. 1-8 for representative chromatograms.

## 14. Calculation or Interpretation of Results

14.1 Using the ECN weight correction factors listed in Table 2, calculate the concentration of each component as follows:

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

where:

$C_i$  = concentration for component *i*, weight %,

$A_i$  = peak area of component *i*, and

$R_i$  = ECN correction factor for component *i*.

14.2 Calculate the volume percent concentration of each component using the density in Table 2 as follows:

**TABLE 2 Effective Carbon Number Correction Factors and Density**

Component	ECN Correction Factor <sup>A</sup>	Density at 20°C
Non Aromatics	1.0000	0.7255 (average) <sup>B</sup>
Benzene	0.9095	0.8780 <sup>C</sup>
Toluene	0.9195	0.8658 <sup>C</sup>
Ethylbenzene	0.9271	0.8658 <sup>C</sup>
<i>p</i> -Xylene	0.9271	0.8597 <sup>C</sup>
<i>m</i> -Xylene	0.9271	0.8630 <sup>C</sup>
<i>o</i> -Xylene	0.9271	0.8786 <sup>C</sup>
Cumene	0.9329	0.8605 <sup>C</sup>
1,4-Dioxane	3.0774	1.0329 <sup>D</sup>
C <sub>9</sub> + Aromatics	0.9329	0.8715 <sup>E</sup> average
Styrene	0.9210	0.9048 <sup>C</sup>
C <sub>10</sub> Aromatics	0.9376	0.8694 <sup>E</sup> average
<i>p</i> -diethylbenzene (PDEB)	0.9376	0.8620 <sup>E</sup>
Phenylacetylene	0.8296	0.9300 <sup>F</sup>
Alpha-methylstyrene	0.9276	0.9077 <sup>F</sup>
AMS		

<sup>A</sup> Correction factors are relative to *n*-heptane.

<sup>B</sup> DS # 4A *Physical Constants of Hydrocarbons C<sub>1</sub> through C<sub>10</sub>*, ASTM, 1971. Average of hexane, methylcyclopentane, methylcyclohexane, heptane, and ethylcyclopentane.

<sup>C</sup> Test Method D1555M.

<sup>D</sup> Keith, L. H., Walters, D B., Compendium of Safety Data Sheets for Research and Industrial Chemicals, Part II, VCH Publishers, Deerfield Beach, p. 726, 1985.

<sup>E</sup> CRC Handbook of Chemistry and Physics, David R. Lide, 88th Ed., 2007–2008.

<sup>F</sup> CRC Handbook of Chemistry and Physics, David R. Lide, 84th Ed., 2003–2004.

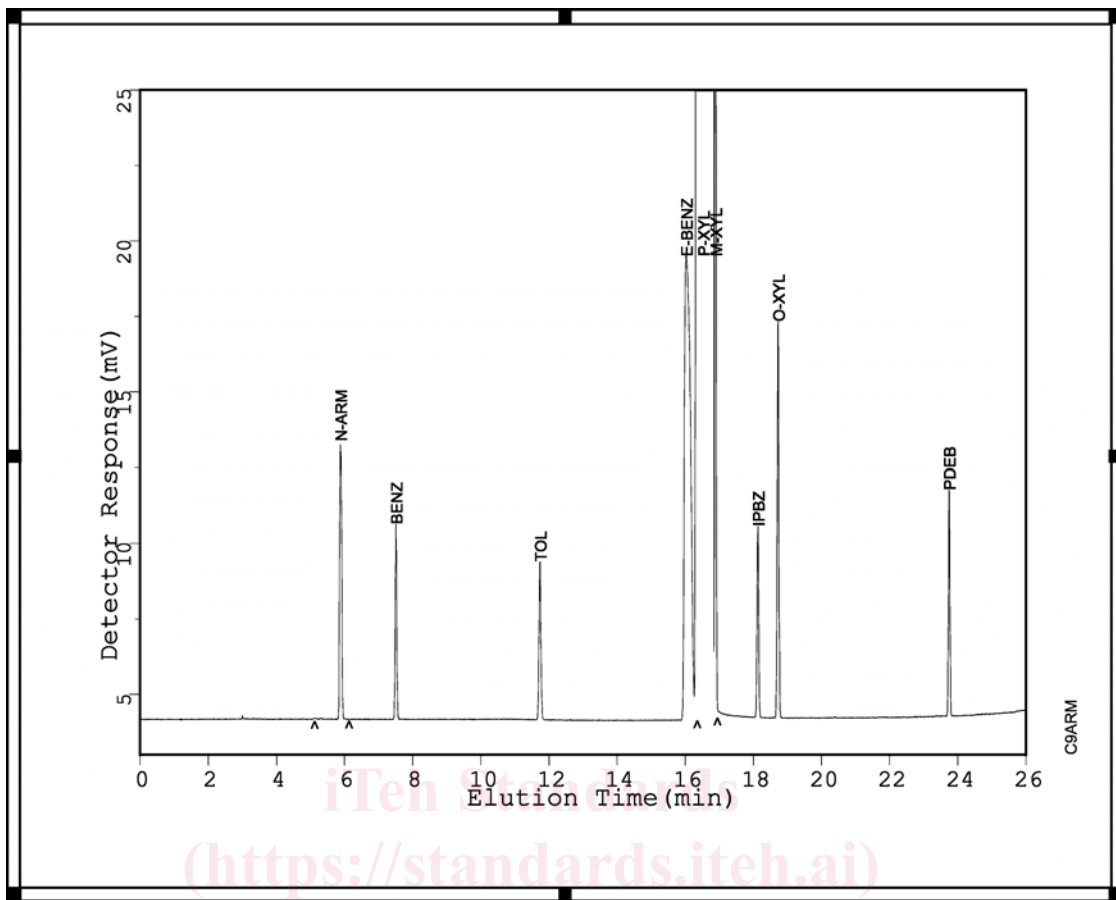


FIG. 1 Typical Chromatogram of Synthetic Blend

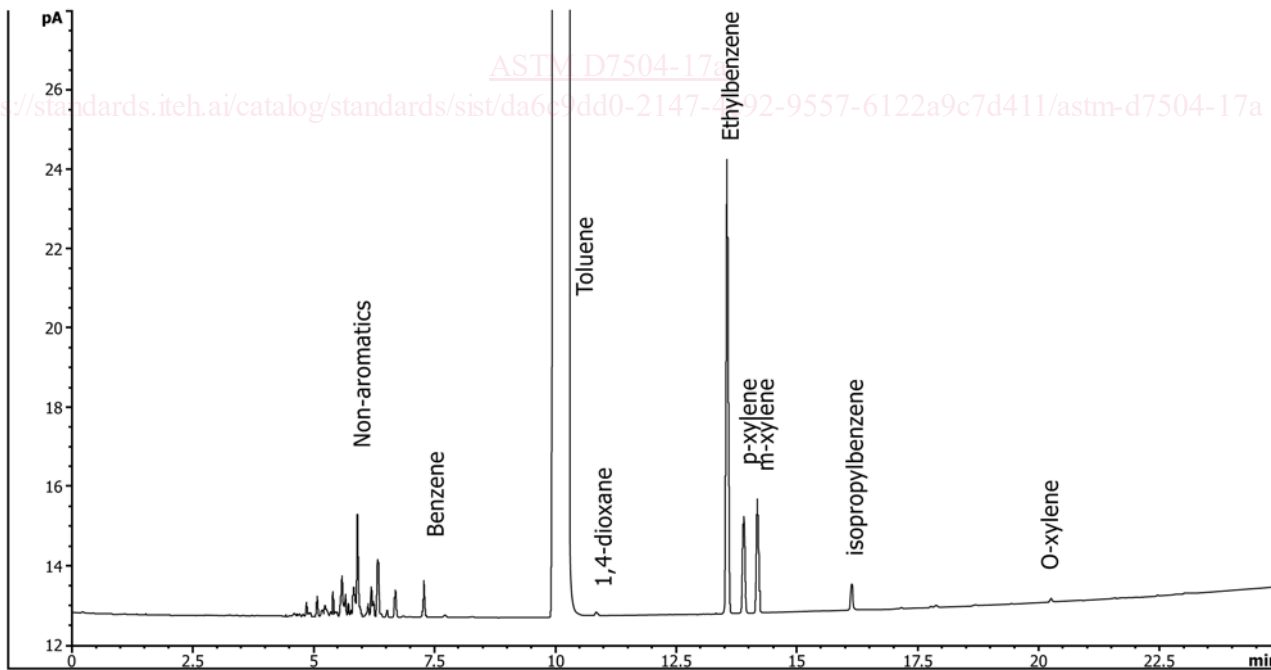


FIG. 2 Typical Chromatogram of Toluene

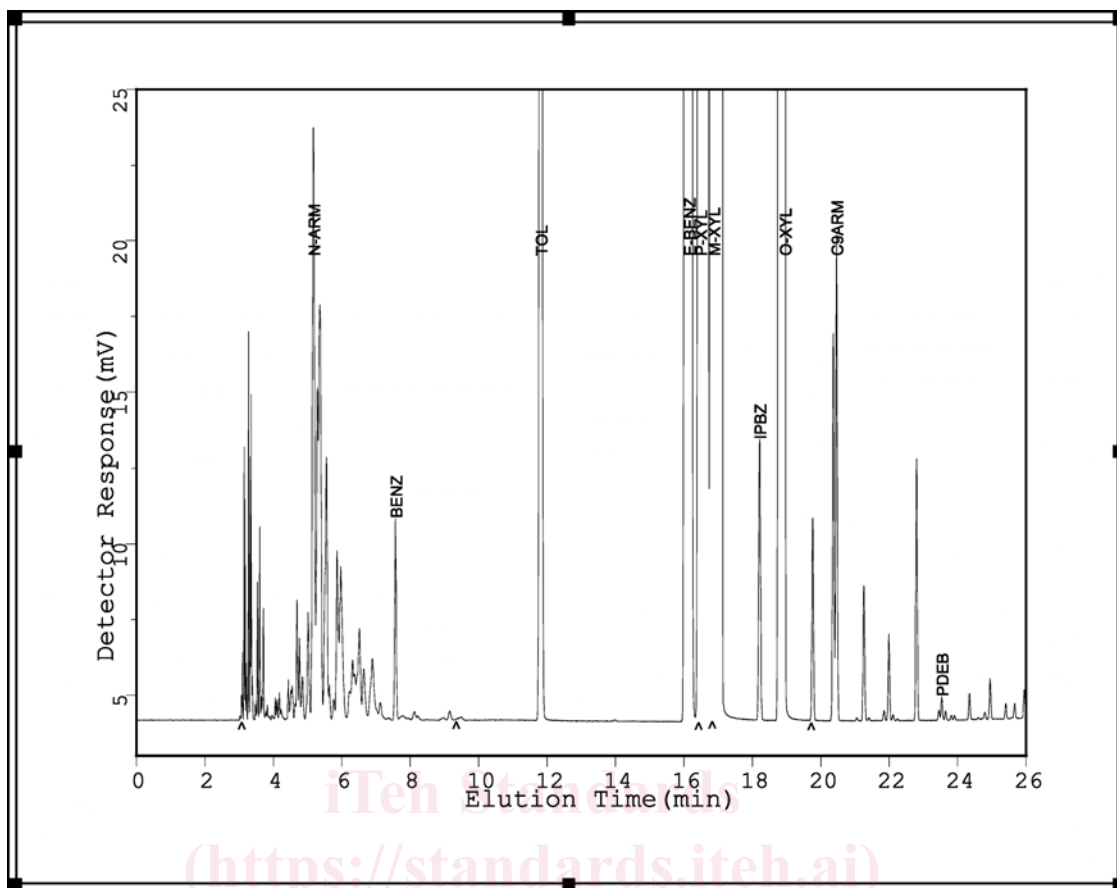


FIG. 3 Typical Chromatogram of Specification D5211, Xylenes

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

where:

- $V_i$  = calculated vol % concentration of component  $i$ ,
- $C_i$  = calculated wt % concentration of component  $i$  from 14.1, and
- $D_i$  = density of component  $i$ .

## 15. Report

15.1 Report individual impurities and total non-aromatics, to the nearest 0.0001 %.

15.1.1 If required, report total  $C_9^+$  aromatics to the nearest 0.0001 %. It is the sum of cumene and all peaks emerging after *o*-xylene.

15.1.2 If required, report total xylenes to the nearest 0.0001 %. It is the sum of *m*-xylene, *o*-xylene, *p*-xylene, and ethylbenzene by industry convention.

15.2 For concentrations of impurities less than 0.0002 %, report as <0.0002 %, and consider as 0.0000 in summation of impurities.

15.3 Report the total impurities to the nearest 0.01 %.

15.4 Report purity as “purity (by GC)” to the nearest 0.01 %.

## 16. Precision and Bias<sup>7</sup>

16.1 An ILS was conducted which included 14 laboratories analyzing 7 different materials. Each material was at 4 different levels and each level was analyzed 3 times. Practice E691 was followed for the design and analysis of the data; the details are given in Research Report RR:D16-1056.<sup>7</sup> The outliers for para-xylene were identified and removed using the t test.

16.1.1 The para-xylene samples were prepared by purifying para-xylene. Level 1 was the purified material. Levels 2, 3, and 4 had increasing amounts of the concentrated impurities from the purification process added.

16.1.2 The benzene, ethylbenzene, mixed xylenes, *ortho*-xylene, styrene, and toluene had known amounts added to levels 2, 3, and 4. See 16.4 for levels and recovery.

16.2 *Repeatability (r)*—Results should not be suspect unless they differ by more than shown in Tables 3-9. Results differing by less than  $r$  have a 95 % probability of being correct.

16.3 *Reproducibility (R)*—Results submitted by two labs should not be considered suspect unless they differ by more

<sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1056. Contact ASTM Customer Service at service@astm.org.

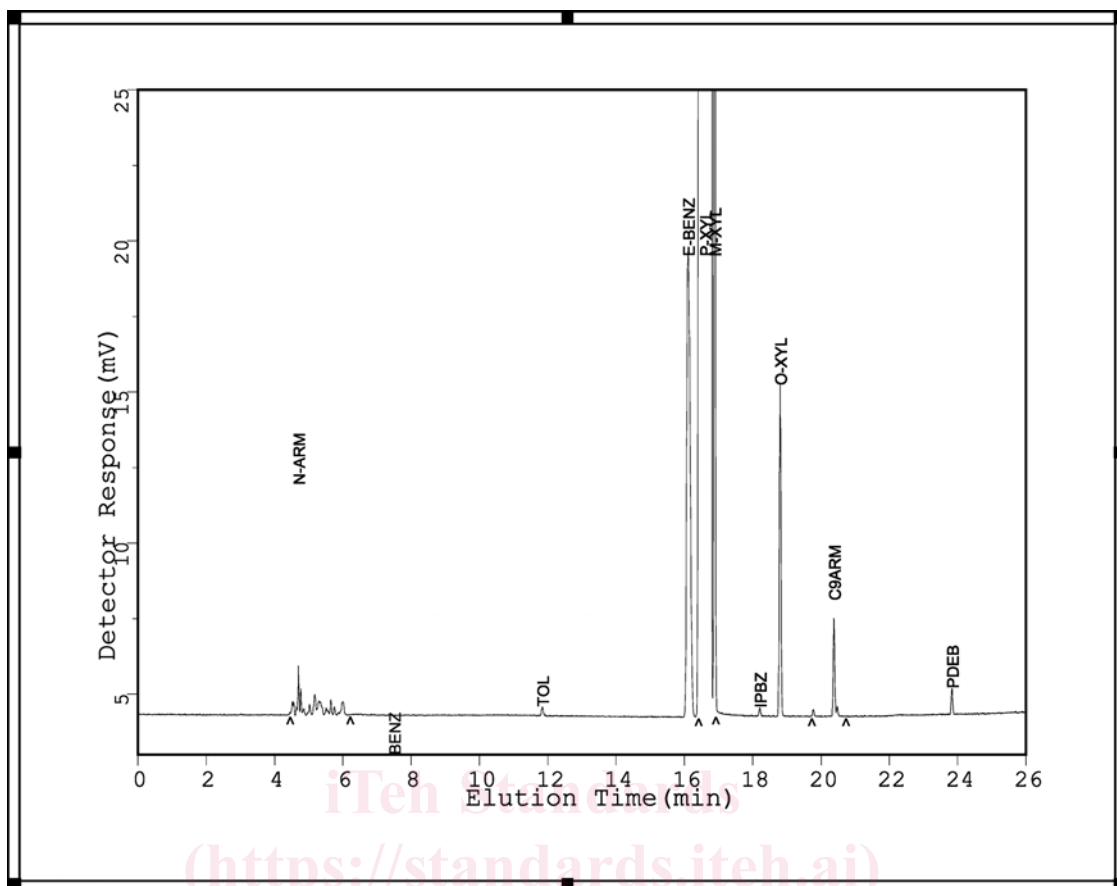


FIG. 4 Typical Chromatogram of Specification D5136, *p*-Xylene

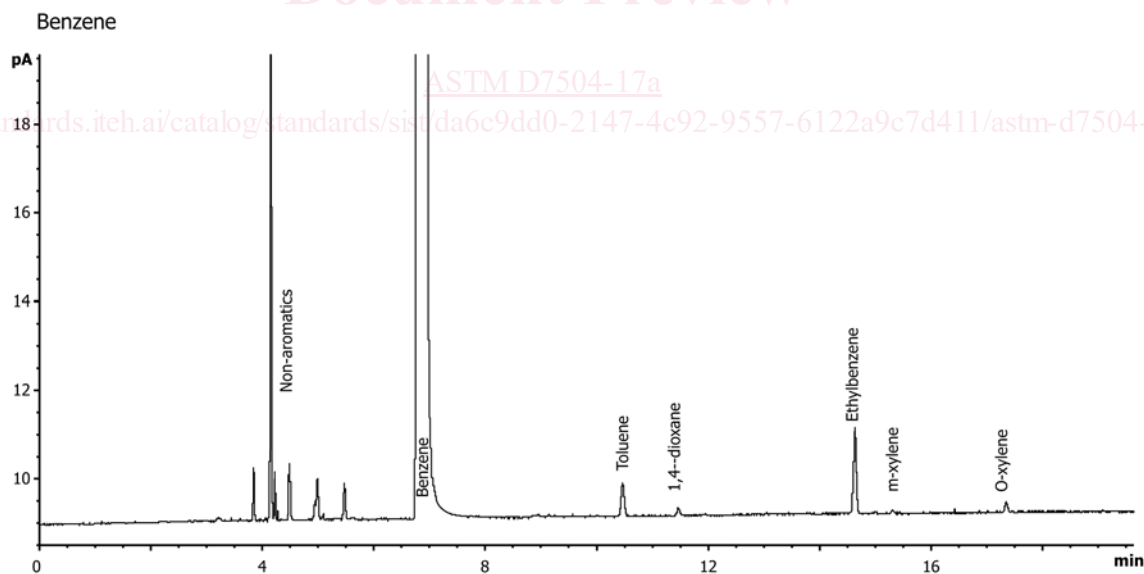


FIG. 5 Typical Chromatogram of Benzene

than shown in Tables 3-9. Results differing by less than *R* have a 95 % probability of being correct.

16.4 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method, bias has

not been determined. Recovery of added impurities is reported in Tables 10-15. These values are based on impurities that were added to the sample versus the result reported.