



Designation: D7504 – 15

## 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 A small amount of benzene in toluene, ethylbenzene, *p*-xylene, *o*-xylene, styrene and mixed xylenes may not be distinguished from the non-aromatics and the concentrations are determined as a composite (see 6.1).

1.3 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.

1.4 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.*

<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.

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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
- 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 ASTM Test Methods

<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

- 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> response 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 response factors and thus, the results may not be absolute.

### 6. Interferences

6.1 In some cases for toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene and styrene, it may be difficult to resolve benzene from the nonaromatic hydrocarbons. Therefore the concentrations are determined as a composite. In the event that the benzene concentration must be determined, an

alternate method such as Test Method D6229 must be selected to ensure an accurate assessment of the benzene concentration.

6.2 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.

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 repeatably injected into the gas chromatograph. An automatic sample injection device is highly recommended.

7.5 Syringe—chromatographic, capable of delivering appropriate  $\mu\text{L}$  volumes.

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, $\mu\text{m}$  | 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, $\mu\text{L}$     | 0.6                             |
| Detector:                      | flame ionization                |
| Temperature, °C                | 300                             |
| Analysis time, min             | 38                              |

<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.

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

| Component                       | ECN Response Factor <sup>A</sup> | Density at 20°C               |
|---------------------------------|----------------------------------|-------------------------------|
| Non Aromatics                   | 1.0000                           | 0.7255 (average) <sup>B</sup> |
| Benzene                         | 0.9100                           | 0.8780 <sup>C</sup>           |
| Toluene                         | 0.9200                           | 0.8658 <sup>C</sup>           |
| Ethylbenzene                    | 0.9275                           | 0.8658 <sup>C</sup>           |
| <i>p</i> -Xylene                | 0.9275                           | 0.8597 <sup>C</sup>           |
| <i>m</i> -Xylene                | 0.9275                           | 0.8630 <sup>C</sup>           |
| <i>o</i> -Xylene                | 0.9275                           | 0.8786 <sup>C</sup>           |
| Cumene                          | 0.9333                           | 0.8605 <sup>C</sup>           |
| 1,4-Dioxane                     | 3.0800                           | 1.0329 <sup>D</sup>           |
| C <sub>9</sub> + Aromatics      | 0.9333                           | 0.8715 <sup>E</sup> average   |
| Styrene                         | 0.91                             | 0.9048 <sup>C</sup>           |
| C <sub>10</sub> Aromatics       | 0.938                            | 0.8694 <sup>E</sup> average   |
| <i>p</i> -diethylbenzene (PDEB) | 0.938                            | 0.8620 <sup>E</sup>           |

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

<sup>B</sup> DS # 4A *Physical Constants of Hydrocarbons C<sub>7</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.

## 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.

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.

<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.

8.4 *Calibration Check Standard*. This standard may be purchased if desired.

## 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 acceptable precision and bias can be obtained using a synthetic mixture of known composition (Calibration check sample).

## 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.

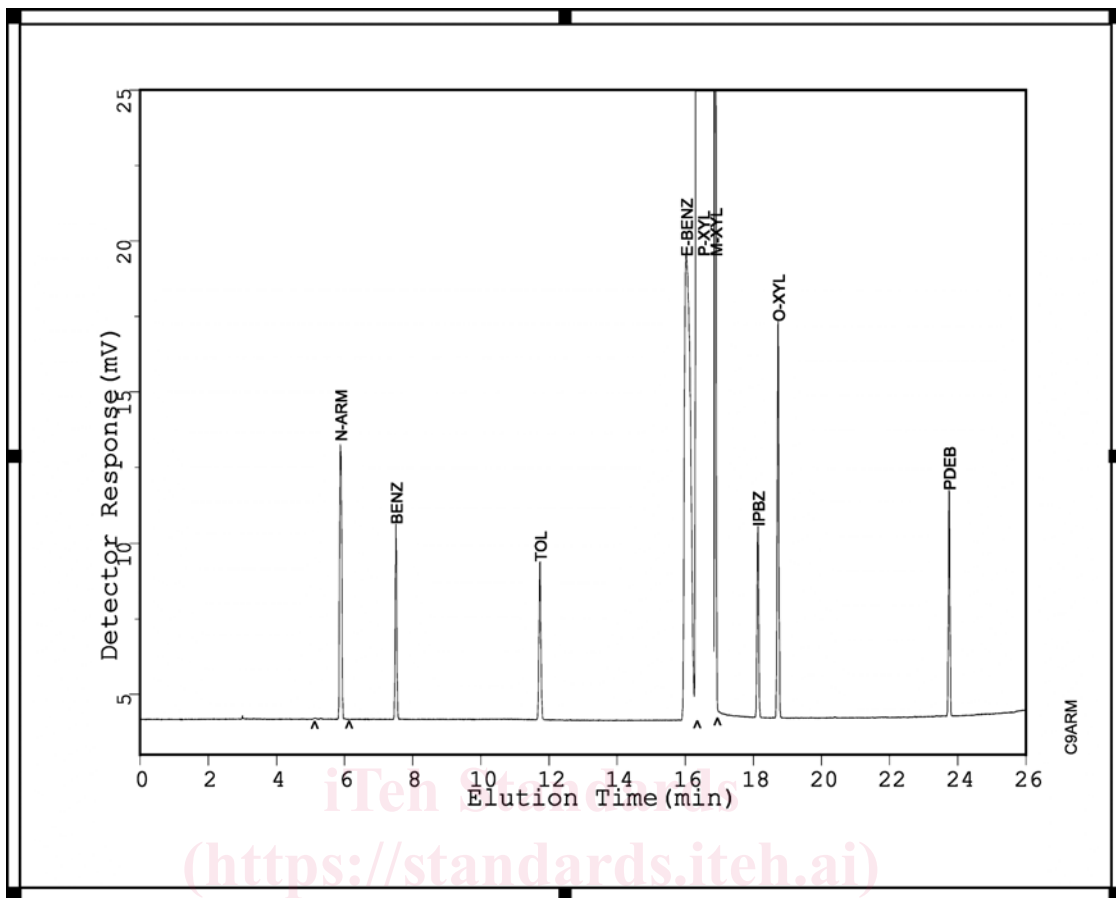


FIG. 1 Typical Chromatogram of Synthetic Blend

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[ASTM D7504-15](https://standards.iteh.ai/catalog/standards/sist/35916706-f6ca-4be4-8419-31ee0bfbd529/astm-d7504-15)

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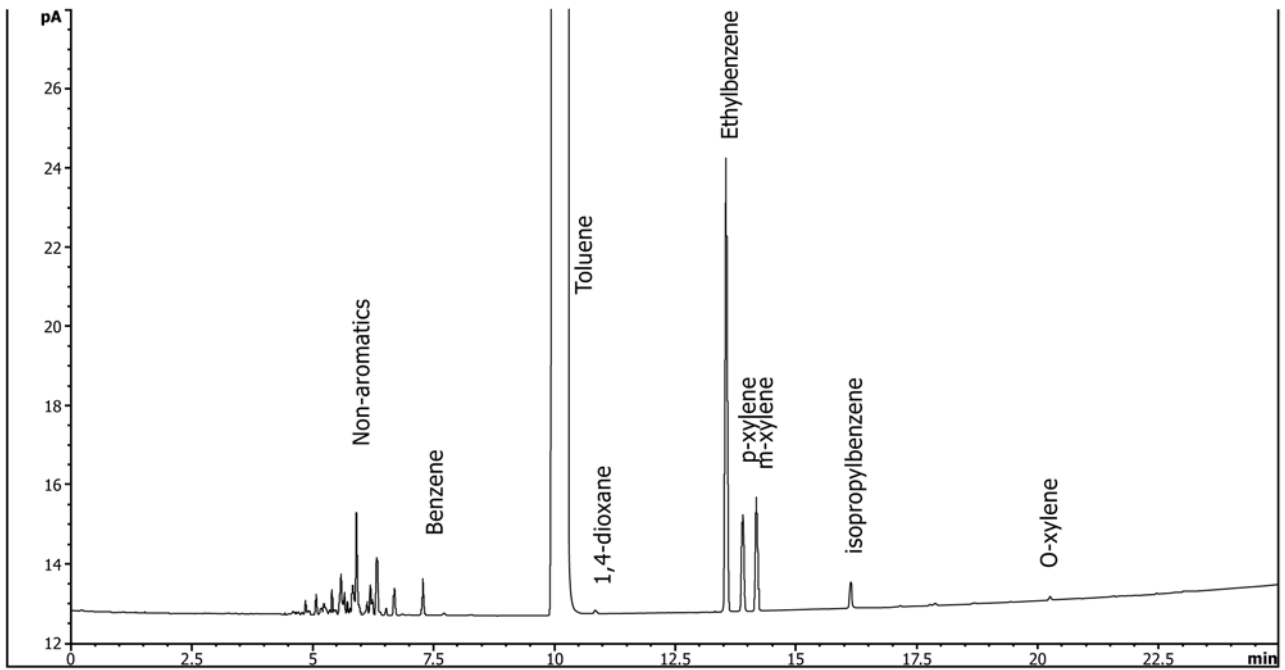


FIG. 2 Typical Chromatogram of Toluene

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<https://standards.itih.ai/catalog/standards/sist/35916706-ffca-4be4-8419-31ee0bfb529/astm-d7504-15>

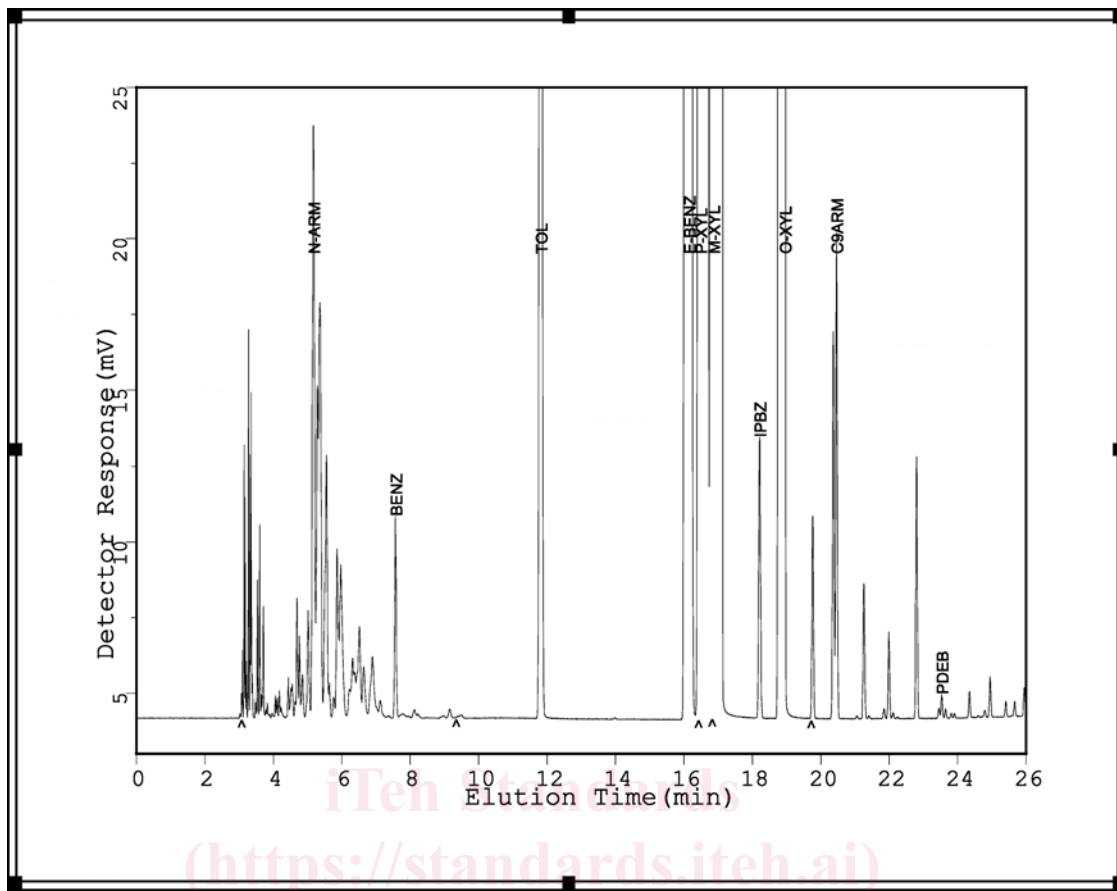


FIG. 3 Typical Chromatogram of Specification D5211, Xylenes

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