



Standard Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number¹

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 (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Table 1 was corrected editorially in March 2010.

1. Scope

1.1 This test method covers the determination of the total nonaromatic hydrocarbons and trace monocyclic aromatic hydrocarbons in toluene, mixed xylenes, and *p*-xylene by gas chromatography. The purity of toluene, mixed xylenes, or *p*-xylene can also be calculated. Similar test methods, using the internal standard calibration technique and the external standard calibration technique, are Test Method [D2360](#) and [D5917](#) respectively.

1.2 Total aliphatic hydrocarbons containing 1 through 10 carbon atoms (methane through decanes) can be detected by this test method at concentrations ranging from 0.0001 to 2.5000 weight %. The limit of detection is 0.00003 weight % and the limit of quantitation is 0.0001 weight %.

1.2.1 A small amount of benzene in mixed xylenes or *p*-xylene may not be distinguished from the non-aromatics and the concentrations are determined as a composite (see [6.1](#)).

1.3 Monocyclic aromatic hydrocarbon impurities containing 6 through 10 carbon atoms (benzene through C₁₀ aromatics) can be detected by this test method at individual concentrations ranging from 0.0001 to 1.0000 weight %.

1.4 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, an observed value or a calculated value shall be rounded off “to the nearest unit” in the last right-hand digit used in expressing the specification limit, 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 appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:²

- [D841](#) Specification for Nitration Grade Toluene
- [D2360](#) Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography
- [D3437](#) Practice for Sampling and Handling Liquid Cyclic Products
- [D4534](#) Test Method for Benzene Content of Cyclic Products by Gas Chromatography³
- [D4790](#) Terminology of Aromatic Hydrocarbons and Related Chemicals
- [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
- [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
- [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:

¹ 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 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.

³ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200⁴

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)⁵ 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, and *p*-xylene 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.

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 mixed xylenes and *p*-xylene, 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 **D4534** must be selected to ensure an accurate assessment of the benzene concentration.

6.2 Complete separation of ethylbenzene and *m*-xylene for *p*-xylene is difficult and can be considered adequate if the distance from baseline to valley between peaks is not greater than 50 % of the peak height of the impurity.

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.

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

7.3 **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 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,⁶ 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.

8.4 **Calibration check standard**. This standard may be purchased if desired.

⁴ 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>.

⁵ 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. 35, August 1985, pp. 333–339.

⁶ *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.

9. Hazards

9.1 Consult current OSHA regulations, supplier's Material 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. 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. The C₉ aromatics fraction includes cumene and all peaks emerging after *o*-xylene, with exception of para-diethylbenzene (PDEB). Sum together all the C₉ aromatic peaks and report as a total area. If PDEB is included in the calibration, report PDEB.

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

13.5 See [Figs. 1-4](#) for representative chromatograms.

14. Calculation or Interpretation of Results

14.1 Using the ECN weight response factors listed in [Table 2](#), calculate the concentration of each component as follows:

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

TABLE 2 Effective Carbon Number Response Factors

Component	Response Factor (Weight) ^A
Non-aromatics	1.0000
Benzene	0.9100
Toluene	0.9200
Ethylbenzene	0.9275
<i>p</i> -Xylene	0.9275
<i>m</i> -Xylene	0.9275
<i>o</i> -Xylene	0.9275
Cumene	0.9333
<i>p</i> -diethylbenzene (PDEB)	0.9380

^A Response factors are relative to *n*-heptane.

TABLE 3 *p*-Xylene Sample 1

Analyte	Average (wt %) \bar{x}	Repeatability Standard Deviation S_r	Repeatability Limit r
Non-aromatics	0.0272	0.0003	0.0008
Benzene	0.0003	0.00001	0.00004
Toluene	0.0044	0.00002	0.00006
Ethylbenzene	0.0231	0.0001	0.0002
<i>m</i> -Xylene	0.0420	0.0001	0.0004
<i>o</i> -Xylene	0.0150	0.00002	0.00004
C ₉ aromatics	0.0079	0.0001	0.0003
PDEB	0.0040	0.00003	0.00008
<i>p</i> -Xylene	99.8761	0.0003	0.0009

where:

C_i = concentration for component i , weight %,

A_i = peak area of component i , and

R_i = ECN response factor for component i .

15. Report

15.1 Report individual impurities, total non-aromatics, and total C₉ aromatics, to the nearest 0.0001 %.

15.2 For concentrations of impurities less than 0.0001 %, report as <0.0001 %, and consider as 0.0000 in summation of impurities.

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

15.4 Report the total impurities to the nearest 0.01 %.

15.5 Report purity as "purity (by GC)" to the nearest 0.01 %.

16. Precision and Bias⁷

16.1 The precision of this test method is based on an intralaboratory study of Test Method D7504 conducted in 2008. One laboratory tested five different materials (two samples of *p*-xylene, two samples of mixed xylene, and a single toluene) for a number of impurities. Every test result represents an individual determination. The laboratory reported 20 replicate results for each analysis/material combination in order to estimate the repeatability limits of the standard. Practice [E691](#) was followed for the design and analysis of the repeatability data; the details are given in Research Report No. D16-1036.

16.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the " r " value for that material; " r " is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

16.1.1.1 Repeatability limits are listed in [Tables 3-7](#).

16.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the " R " value for that material; " R " is the interval representing the critical

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1036.