



Standard Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography¹

This standard is issued under the fixed designation D2360; 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 determination of the total nonaromatic hydrocarbons, and trace monocyclic aromatic hydrocarbons in the purity of toluene and mixed xylenes by gas chromatography.

1.2 Nonaromatic aliphatic hydrocarbons containing 1 through 10 carbon atoms (methane through decanes) can be detected by this test method at concentrations ranging from 0.001 % to 2.500 weight %.

1.2.1 A small amount of benzene in mixed xylenes may not be distinguished from the nonaromatics and the concentrations are determined as a composite.

1.3 Monocyclic aromatic hydrocarbon impurities containing 6 through 9 carbon atoms (benzene through C₉ aromatics) can be detected by this test method at individual concentrations ranging from 0.001 % to 1.000 weight %.

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 applica-*

bility of regulatory limitations prior to use. For specific hazard statement, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

D841 Specification for Nitration Grade Toluene

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D3797 Test Method for Analysis of *o*-Xylene by Gas Chromatography

D4492 Test Method for Analysis of Benzene by Gas Chromatography

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D5211 Specification for Xylenes for *p*-Xylene Feedstock

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

D7504 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number

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

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

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.

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

2.2 Other Document:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200³

3. Terminology

3.1 Definitions:

3.1.1 For definition of terms used in this test method see Terminology D4790.

4. Summary of Test Method

4.1 A known amount of an internal standard is added to the specimen that is then introduced into a gas chromatograph (GC) equipped with a flame ionization detector (FID). The peak area of each impurity and the internal standard is measured and the amount of each impurity is calculated from the ratio of the peak area of the internal standard versus the peak area of the impurity. Purity by GC is calculated by subtracting the sum of the impurities found from 100.00. Results are reported either in weight percent or volume percent.

5. Significance and Use

5.1 The determination of hydrocarbon impurities contained in toluene and mixed xylenes used as chemical intermediates and solvents is typically required. This test is suitable for setting specifications and for use as an internal quality control tool where aromatic monocyclic hydrocarbons are produced or are used. This test method is applicable for determining the impurities from the aromatic hydrocarbon production process. Typical impurities are alkanes containing 1 to 10 carbon atoms, benzene, toluene, ethylbenzene (EB), xylenes, and aromatic hydrocarbons containing nine carbon atoms.

5.1.1 Refer to Test Methods D3797, D4492, and D7504 for determining the purity of *o*-Xylene, *p*-Xylene, and benzene.

5.1.2 Refer to Test Method D6563 or D7504 for determining the C₈ aromatic hydrocarbon distribution in mixed xylenes.

5.2 Purity is commonly reported by subtracting the determined expected impurities from 100.00. However, a gas chromatographic analysis cannot determine absolute purity if unknown or undetected components are contained within the material being examined.

6. Interferences

6.1 The internal standard chosen must be satisfactorily resolved from any impurity and the product peak. A peak will be satisfactorily resolved from a neighboring peak if the distance from the valley to the baseline between the two peaks is not greater than 50 % of the peak height of the smaller of the two peaks.

6.2 In some cases for mixed xylenes, it may be difficult to resolve benzene from the nonaromatic hydrocarbons and therefore the concentrations are determined as a composite. In the event that the benzene concentration must be determined,

TABLE 1 Instrumental Parameters

Detector	Flame ionization
Column:	
Tubing	fused silica
Stationary phase	crosslinked polyethylene glycol ⁴
Film thickness, μ	0.25
Length, m	60
Diameter, mm	0.32 ID
Temperatures:	
Injector, °C	270
Detector, °C	300
Oven:	
Initial, °C	60
Time 1, min	10
Final, °C	150
Rate, °C/min	5
Time 2, min	10
Carrier gas	helium
Flow rate, mL/min	1.0
Split ratio	100:1
Sample size, μL	1.0
Analysis time, min	38
Linear velocity at 145°C, cm/s	20

⁴ Polyethylene glycol such as Carbowax 20 M available from most chromatographic suppliers, has been found suitable for this purpose.

an alternate method must be selected to ensure an accurate assessment of the benzene concentration.

7. Apparatus

7.1 *Gas Chromatograph*—Any instrument having a flame ionization detector that can be operated at the conditions given in Table 1. The system should have sufficient sensitivity to obtain a minimum peak height response for 10 mg/kg *n*-butylbenzene of twice the height of the signal to background noise.

7.2 *Columns*—Both capillary and packed columns containing a stationary phase of cross-linked polyethylene glycol have been found satisfactory. The column must give satisfactory resolution of the internal standard from the solvent and the impurity peaks, and should be such that benzene is eluted between *n*-nonane and *n*-decane. Table 1 contains a description of a column that has been found satisfactory.

7.3 *Recorder*—Electronic integration is recommended.

7.4 *Microsyringe*, 10 and 50, and 500-μL capacity.

7.5 *Volumetric Flask*, 50-mL capacity.

8. Reagents

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, where such specifications are available.⁴

⁴ *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.

³ 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>.

8.2 *Carrier Gas*—Helium is recommended. However, hydrogen may be used. Carrier, makeup and detector gases should have 99.999 % minimum purity. Oxygen in carrier gas should be 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*—Purify air to remove hydrocarbons and water. Air for a FID should contain less than 0.1 ppm THC.

8.4 *High Purity p-Xylene*, 99.999 weight % or greater purity.

8.4.1 Most *p*-xylene is available commercially at a purity less than 99.9 % and can be purified by recrystallization. To prepare 1.9 L of high purity *p*-xylene, begin with approximately 3.8 L of material and cool in an explosion-proof freezer at $-0 \pm -5^{\circ}\text{C}$ until approximately $\frac{1}{2}$ to $\frac{3}{4}$ of the *p*-xylene has frozen. This should require about 5 h. Remove the sample and decant the liquid portion. The solid portion is the purified *p*-xylene. Allow the *p*-xylene to thaw and repeat the crystallization step on the remaining sample until the *p*-xylene is free of contamination as indicated by gas chromatography.

8.5 *Pure Compounds*, for calibration, shall include *n*-nonane, benzene, toluene, ethylbenzene (EB), *o*-xylene and cumene. The purity of all reagents should be >99 weight %. If the purity is less than 99 %, the concentration and identification of impurities must be known so that the composition of the standard can be adjusted for the presence of the impurities.

8.5.1 *Internal Standard*—*n*-butylbenzene (NBB) is the recommended internal standard of choice, however, other compounds may be found acceptable provided they meet the criteria as defined in Section 6.

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 and E355 and E1510 for additional information on gas chromatography practices and terminology.

12. Calibration

12.1 Prepare a synthetic mixture of high purity *p*-xylene with representative impurities. The volume of each hydrocarbon impurity must be measured to the nearest 0.1 μL and all liquid reference compounds must be brought to the same temperature before mixing. Refer to Table 2 for an example of a calibration blend. The nonaromatic fraction is represented by *n*-nonane, while *o*-xylene represents the xylene fraction. Cumene will represent the aromatic hydrocarbons containing nine carbon atoms or greater (C_9 aromatics).

TABLE 2 Preparation of Calibration Blend

Compound	Density ^A g/cc	Recommended Volume (μL)	Resulting Concentration	
			Volume Percent	Weight Percent
<i>p</i> -Xylene (see 8.4.1)	0.857	50.00 mL	99.72	99.72
Benzene	0.874	10.0	0.020	0.020
Toluene	0.862	10.0	0.020	0.020
Ethylbenzene	0.863	50.0	0.100	0.101
<i>o</i> -Xylene	0.876	50.0	0.100	0.102
Cumene	0.857	10.0	0.020	0.020
<i>n</i> -Nonane	0.714	10.0	0.020	0.017

^A Density at 25°C. Values obtained from *Physical Constants of Hydrocarbons C₁ to C₁₀*, ASTM Publication Data Series 4A, 1971.

12.2 Using the exact volumes and densities in Table 2, calculate the weight percent concentration for each impurity in the calibration blend as follows:

$$C_i = ((D_i)(V_i))/((V_p)(D_p))(100) \tag{1}$$

where:

- D_i = density of impurity *i* from Table 2,
- V_i = volume of impurity *i*, mLs,
- D_p = density of *p*-xylene from Table 2,
- V_p = volume of *p*-xylene, mLs, and
- C_i = concentration of impurity *i*, weight percent.

12.3 Into a 50-mL volumetric flask, add 50.0 μL of *n*-butylbenzene (NBB) to 50.00 mLs of the calibration blend and mix well. Assuming a density of 0.857 for the calibration blend and 0.856 for NBB, the resulting NBB concentration will be 0.100 weight %, as determined from the equation in 12.2.

12.3.1 All solutions and reference compounds must be brought to the same temperature, preferably 25°C, prior to adding the internal standard.

12.4 Inject the resulting solution from 12.3 into the chromatograph. A typical chromatogram is illustrated in Fig. 1.

12.5 Determine the response factor for each impurity relative to NBB by measuring the area under each peak and calculate the relative response factor as follows:

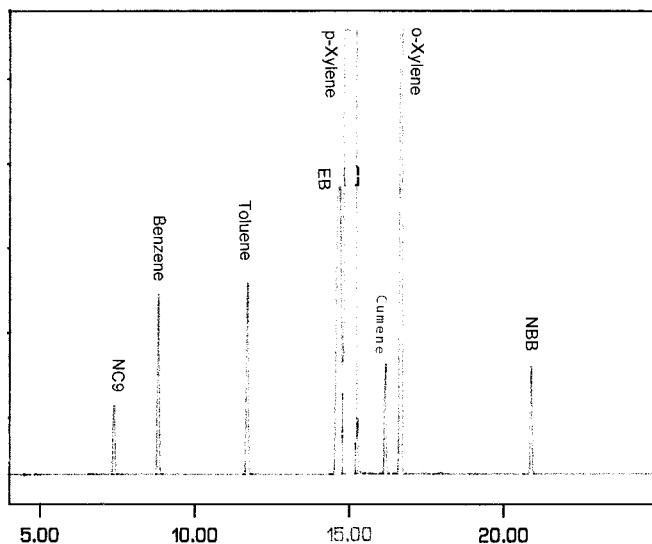


FIG. 1 Typical Analysis of Calibration Standard

$$RRF_i = \frac{(A_s)(C_i)}{(C_s)(A_i)} \quad (2)$$

where:

RRF_i = response factor for impurity i relative to the internal standard,

A_i = peak area of impurity, i ,

A_s = peak area of the internal standard, NBB,

C_s = concentration of the internal standard, NBB, weight percent, and

C_i = concentration of impurity i , as calculated in 12.2, weight percent.

12.6 Calculate the response factors to the nearest 0.001.

13. Procedure

13.1 Bring the internal standard and the sample to be analyzed to identical temperatures, preferably 25°C. Make sure that the temperature of the sample is consistent with that of the calibration standard prepared in Section 12. Pipet 50.0 μ L of internal standard into a 50-mL volumetric flask containing 50.00 mLs of sample. Mix well.

13.2 Depending upon the actual chromatograph's operating conditions, inject an appropriate amount of sample into the instrument. Make sure that the injection amount is consistent with those conditions used to meet the criteria in 7.1.

13.3 Measure the area of all peaks except the major component(s). Measurements on the sample must be consistent with those made on the calibration blend.

13.4 Fig. 2 illustrates the analysis of Specification D841 toluene. Fig. 3 illustrates the analysis of Specification D5211 mixed xylenes.

14. Calculations

14.1 The nonaromatic fraction includes all peaks up to toluene (except for the benzene peak). Sum together all the nonaromatic peaks and report as a total area.

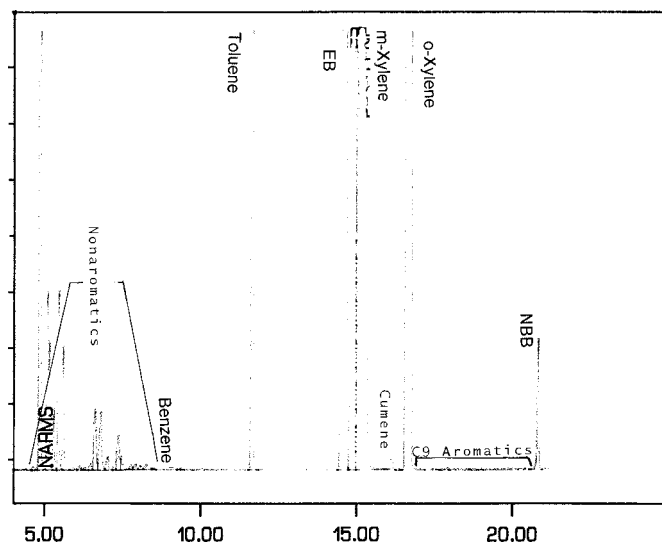


FIG. 3 Typical Analysis of Specification D5211 for Xylenes

14.2 The C_9 aromatics fraction includes cumene and all peaks emerging after o -xylene. Sum together all the C_9 aromatic peaks and report as a total area.

14.3 Calculate the weight percent concentration of the total nonaromatics, C_9 aromatics and each trace aromatic (<1 %) as follows:

$$C_i = \frac{(A_i)(RRF_i)(C_s)}{(A_s)} \quad (3)$$

14.4 Calculate the volume concentration of the total nonaromatics, total C_9 aromatics and each trace aromatic (<1 %) as follows:

$$V_i = (C_i)(D_s)/(D_i) \quad (4)$$

where:

V_i = concentration of impurity i , volume percent,

D_i = density of impurity i from Table 2, and

D_s = density of sample.

14.5 Calculate the purity of the sample as follows:

$$\text{purity, weight percent} = 100.00 - C_t \quad (5)$$

where:

C_t = total concentration of all impurities, weight percent.

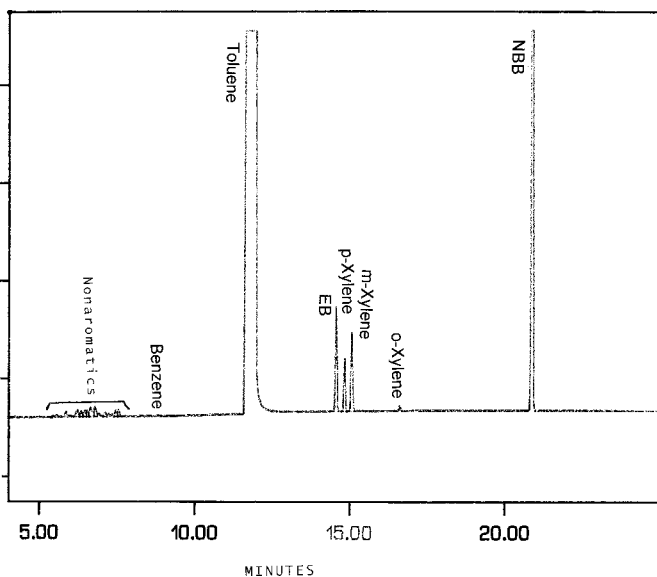


FIG. 2 Typical Analysis of Specification D841 on Toluene

TABLE 3 Repeatability and Reproducibility

Toluene	Intermediate Precision	Reproducibility
Nonaromatics (0.023)	0.0067	0.0110
Ethylbenzene (0.017)	0.0041	0.0063
<i>p</i> -Xylene (0.010)	0.0038	0.0038
<i>m</i> -Xylene (0.012)	0.0031	0.0040
<i>o</i> -Xylene (0.001)	0.0003	0.0003
Toluene (99.94)	0.0160	0.0210
Mixed Xylenes	Intermediate Precision	Reproducibility
Nonaromatics (2.526)	0.150	0.816
Toluene (0.649)	0.052	0.153
Cumene (0.010)	0.0007	0.0013
Xylenes (96.82)	0.180	0.819

14.5.1 Mixed xylenes is the sum of *m*-xylene, *o*-xylene, *p*-xylene, and ethylbenzene by industry convention. The above calculations may be used to determine total mixed xylenes but should not be used for determining individual C₈ components in a mixed xylene sample. Test Methods **D6563** or **D7504** should be used for the individual C₈ components in mixed xylenes.

15. Report

15.1 Report the following information:

15.1.1 Individual impurities to the nearest 0.001 %.

15.1.2 Concentrations of impurities less than 0.001 %, report as <0.001 %, and consider as 0.000 in summation of impurities,

15.1.3 Total impurities to the nearest 0.01 %, and

15.1.4 Purity as “purity (by GC)” to the nearest 0.01 %.

16. Precision and Bias⁵

16.1 *Precision*—The following criteria should be used to judge the acceptability of the 95 % probability level of the results obtained by this test method. The criteria was derived from the round-robin between seven different laboratories. The data from five laboratories was used in calculating the precision data for toluene. Two samples were analyzed. Each sample was run twice in two days by two different operators. Results of the interlaboratory study were calculated and analyzed using Practice **E691**.

16.1.1 The numbers in parentheses shown in the left hand column of **Table 3** are reported average concentrations of the impurities.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1020. Contact ASTM Customer Service at service@astm.org.

16.2 *Intermediate Precision*, (formerly called Repeatability)—Duplicate results by the same operator should not be considered suspect unless they differ by more than \pm the amount shown in **Table 3**. All values are in weight percent.

16.3 *Reproducibility*—The results between two laboratories should not be considered suspect unless they differ by more than \pm the amount shown in **Table 3**. All values are in weight percent.

16.4 *Bias*—Since there was no accepted reference material available at the time of interlaboratory testing, no statement on bias can be made at this time. All values are in weight percent.

17. Quality Guidelines

17.1 Laboratories shall have a quality control system in place.

17.1.1 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.

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

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

17.1.4 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.

18. Keywords

18.1 impurities; purity; toluene; xylenes

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D2360 - 08) that may impact the use of this standard. (Approved June 1, 2011.)

(1) 2.1 — Added Test Method **D7504**.

(2) 5.1.1 — Added Test Method **D7504**.

(3) 5.1.2 — Refer to Test Method **D6563** or **D7504** for determining the C₈ aromatic hydrocarbon distribution in mixed xylenes.

(4) Modified 8.3 to specify that air should contain less than 0.1 THC.

(5) Moved what nonaromatics and C₉ consist of and to sum peaks from 13.3 to 14.1 and 14.2.

(6) Modified Section 17, Quality Control Guidelines, to latest D16 Editorial Guidelines.

(7) 14.3 — Calculate the weight percent concentration of the total nonaromatics, C₉ aromatics and each trace aromatic (<1 %) as follows:

(8) 14.4 — Calculate the volume concentration of the total nonaromatics, total C₉ aromatics and each trace aromatic (<1 %) as follows:

(9) Modified 14.5.1 which defined mixed xylenes to include “The above calculations may be used to determine total mixed xylenes but should not be used for determining individual C₈ components in a mixed xylene sample. Test Methods **D6563** or **D7504** should be used for the individual C₈ components in mixed xylenes.”

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