



Designation: D 2360 – 03

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

This standard is issued under the fixed designation D 2360; 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.

*This standard has been approved for use by agencies of the Department of Defense.*

## 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 C<sub>9</sub> aromatics) can be detected by this test method at individual concentrations ranging from 0.001 % to 1.000 weight %.

1.4 The following applies to all specified limits in this test method: for purposes of determining conformance with this standard, 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 E 29.

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.* For specific hazard statement, see Section 9.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 841 Specification for Nitration Grade Toluene<sup>2</sup>

D 2306 Test Method for C<sub>8</sub> Hydrocarbon Analysis by Gas Chromatography<sup>2</sup>

<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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<sup>2</sup> Annual Book of ASTM Standards, Vol 06.04.

D 3437 Practice for Sampling and Handling Liquid Cyclic Products<sup>2</sup>

D 3797 Test Method for Analysis of *o*-Xylene by Gas Chromatography<sup>2</sup>

D 3798 Test Method for Analysis of *p*-Xylene by Gas Chromatography<sup>2</sup>

D 4492 Test Method for Analysis of Benzene by Gas Chromatography<sup>2</sup>

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals<sup>2</sup>

D 5211 Specification for Xylenes for *p*-Xylene Feedstock<sup>2</sup>

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>3</sup>

E 260 Practice for Packed Column Gas Chromatography<sup>4</sup>

E 355 Practice for Gas Chromatography Terms and Relationships<sup>4</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>3</sup>

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs<sup>4</sup>

### 2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200<sup>5</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definition of terms used in this test method see Terminology D 4790.

## 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

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 03.06.

<sup>5</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington DC 20402.

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

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 D 3797, D 3798, and D 4492 for determining the purity of *o*-Xylene, *p*-Xylene, and benzene, respectively.

5.1.2 Refer to Test Method D 2306 for determining the C<sub>8</sub> 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, 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- $\mu$ L capacity.

7.5 *Volumetric Flask*, 50-mL capacity.

**TABLE 1 Instrumental Parameters**

Detector	Flame ionization
Column:	
Tubing	fused silica
Stationary phase	crosslinked polyethylene glycol <sup>A</sup>
Film thickness, $\mu$	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, $\mu$ L	1.0
Analysis time, min	30
Linear velocity @ 145°C, cm/s	20

<sup>A</sup> Polyethylene glycol such as Carbowax 20 M available from most chromatographic suppliers, has been found suitable for this purpose.

## 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.<sup>6</sup>

8.2 *Carrier Gas*—Chromatographic grade helium is recommended.

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

8.3.1 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  $-10 \pm -5^\circ\text{C}$  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.

8.4 *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.

8.4.1 *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.

<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.

## 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 D 3437.

## 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 E 260 and E 355 and E 1510 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  $\mu\text{L}$  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 ( $\text{C}_9$  aromatics).

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:

$$C_i = ((D_i)(V_i))/((V_p)(D_p))(100) \quad (1)$$

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  $\mu\text{L}$  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:

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

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  $\mu\text{L}$  of internal standard into a 50-mL volumetric flask containing 50.00 mLs of sample. Mix well.

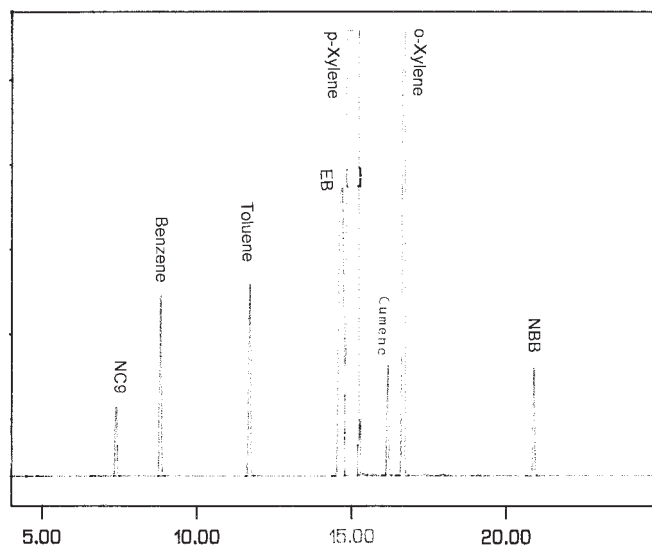
13.2 Depending upon the actual chromatograph's operating conditions, inject an appropriate amount of sample into the instrument. Make sure that the injection amount is consistent with those conditions used to meet the criteria in 7.1.

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. The nonaromatic fraction includes all peaks up to toluene (except for the peak assigned as benzene). Sum together all the nonaromatic peaks and report as a total area. The  $\text{C}_9$  aromatics fraction includes cumene and all peaks emerging after *o*-xylene. Sum together all the  $\text{C}_9$  aromatic peaks and report as a total area.

**TABLE 2 Preparation of Calibration Blend**

Compound	Density <sup>A</sup>	Recommended Volume ( $\mu\text{L}$ )	Resulting Concentration	
			Volume Percent	Weight Percent
<i>p</i> -Xylene (see 8.3.1)	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	0.099
Cumene	0.857	10.0	0.020	0.020
<i>n</i> -Nonane	0.714	10.0	0.020	0.017

<sup>A</sup>Density at 25°C. Values obtained from *Physical Constants of Hydrocarbons C<sub>1</sub> to C<sub>10</sub>*, ASTM Publication Data Series 4A, 1971.



**FIG. 1 Typical Analysis of Calibration Standard**

13.4 Fig. 2 illustrates the analysis of Specification D 841 toluene. Fig. 3 illustrates the analysis of Specification D 5211 mixed xylenes.

**14. Calculations**

14.1 Calculate the weight percent concentration of the total nonaromatics and each impurity as follows:

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

14.2 Calculate the volume concentration of the total nonaromatics, total C<sub>9</sub> aromatics and each trace aromatic as follows:

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

where:

V<sub>i</sub> = concentration of impurity i, volume percent, and

D<sub>i</sub> = density of impurity i from Table 2.

D<sub>s</sub> = density of sample

14.3 Calculate the purity of the sample as follows:

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

where:

C<sub>t</sub> = total concentration of all impurities, weight percent.

**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 %.

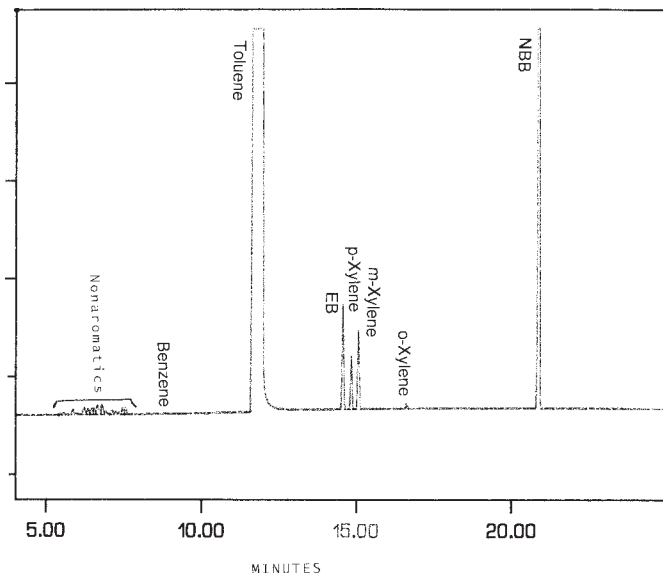


FIG. 2 Typical Analysis of Specification D 841 on Toluene

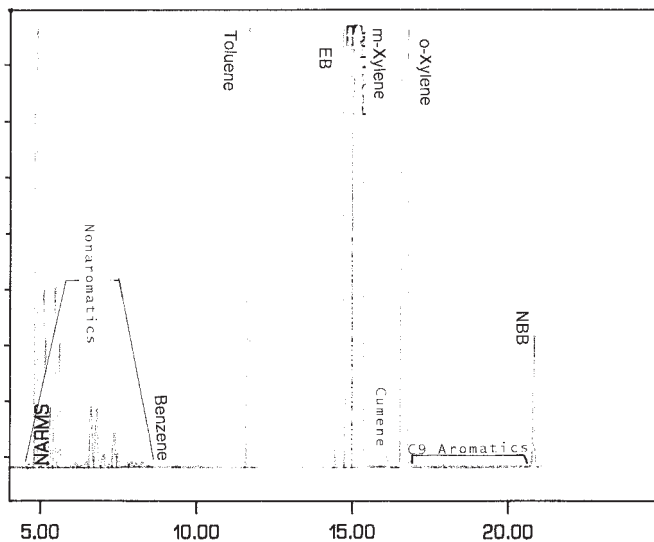


FIG. 3 Typical Analysis of Specification D 5211 for Xylenes

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

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 E 691.

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

TABLE 3 Repeatability and Reproducibility

Toluene	Intermediate Precision	Reproducibility
Nonaromatics (0.023)	0.0067	0.0110
Ethylbenzene (0.017)	0.0041	0.0063
p-Xylene (0.010)	0.0038	0.0038
m-Xylene (0.012)	0.0031	0.0040
o-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

impurities.

<sup>7</sup> Supporting data are available from ASTM International Headquarters. Request RR: D16-1020.

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. Keywords

17.1 impurities; purity; toluene; xylenes

## SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last date of issue (D 2360 - 00) that may impact the use of this standard.

- (1) Corrected Equation 4.
- (2) Added definition of  $D_s$  after Equation 4.
- (3) Corrected Table 2 reference to *p*-Xylene from 7.3.1 to 8.3.1.

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