



Designation: ~~D2360-07~~ Designation: D 2360 – 08

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

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 (ϵ) 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 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 E 29.

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.* For specific hazard statement, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

D 841 Specification for Nitration Grade Toluene

~~D2360 Test Method for C₈ Aromatic Hydrocarbon Analysis by Gas Chromatography~~

Ð 3437 Practice for Sampling and Handling Liquid Cyclic Products

D 3797 Test Method for Analysis of *o*-Xylene by Gas Chromatography

D 3798 Test Method for Analysis of *p*-Xylene by Gas Chromatography

D 4492 Test Method for Analysis of Benzene by Gas Chromatography

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D 5211 Specification for Xylenes for *p*-Xylene Feedstock

D 6563 Test Method for Benzene, Toluene, Xylene (BTX) Concentrates Analysis by Gas Chromatography

D 6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E 260 Practice for Packed Column Gas Chromatography

E 355 Practice for Gas Chromatography Terms and Relationships

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E 1510 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 1910.1200 ³

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 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

5.1.2 Refer to Test Method D 6563 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, an alternate method must be selected to ensure an accurate assessment of the benzene concentration.

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>.

TABLE 1 Instrumental Parameters

| | |
|-------------------------------|--|
| Detector | Flame ionization |
| Column: | |
| Tubing | fused silica |
| Stationary phase | crosslinked polyethylene glycol ^A |
| 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 | 30 |
| Analysis time, min | 38 |
| Linear velocity @ 145°C, cm/s | 20 |

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

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- μ L 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

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*—zero grade or better. Purify air to remove hydrocarbons and water.

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 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 μ 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 (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:

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

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.