Designation: D 5917 – 99

Standard Test Method for
Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and External Calibration[1]

This standard is issued under the fixed designation D 5917; 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 toluene, mixed xylenes, and *p*-xylenes by gas chromatography. The purity of toluene, mixed xylenes, or *p*-xylenes can also be calculated. Calibration of the gas chromatographic system is done by the external standard calibration technique. A similar test method, using the internal standard calibration technique, is Test Method D 2360.

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 0.001 to 2.500 weight %.

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

1.3 Monocyclic aromatic hydrocarbon impurities containing 6 through 9 carbon atoms (benzene through C_9 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 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 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[2]
D 2306 Test Method for C_8 Hydrocarbon Analysis by Gas Chromatography[2]

D 2360 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography[2]
D 3437 Practice for Sampling and Handling Liquid Cyclic Products[2]
D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[3]
D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[3]
D 4534 Test Method for Benzene Content of Cyclic Products by Gas Chromatography[2]
D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals[2]
D 5211 Specification for Xylenes for *p*-Xylene Feedstock[2]
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[4]
E 260 Practice for Packed Column Gas Chromatography[4]
E 355 Practice for Gas Chromatography Terms and Relationships[4]
E 691 Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods[4]
E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[4]

2.2 *Other Document:*
OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200[5]

3. Terminology

3.1 See Terminology D 4790 for definitions of terms used in this test method.

4. Summary of Test Method

4.1 A repeatable volume of the specimen to be analyzed is precisely injected into a gas chromatograph equipped with a flame ionization detector (FID). The peak area of each impurity is measured. Concentration of each impurity is determined from the linear calibration curve of peak area versus concentration. Purity by gas chromatography (GC) is calculated by subtracting the sum of the impurities found from 100.00. Results are reported in weight percent.

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

5. Significance and Use

5.1 Determining the type and amount of hydrocarbon impurities remaining from the manufacture of toluene, mixed xylenes, and *p*-xylenes 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.

5.1.1 Refer to Test Method D 2306 for determining the C_8 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.

5.3 This test method is similar to Test Method D 2360, however, interlaboratory testing has indicated a bias may exist between the two methods. Therefore the user is cautioned that the two methods may not give comparable results.

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 D 4534 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 shall have sufficient sensitivity to obtain a minimum peak height response for 0.001 weight % impurity of twice the height of the background noise.

7.2 *Columns*—A capillary column containing a stationary phase of cross linked polyethylene glycol has been found satisfactory.

TABLE 1 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
Linear velocity, cm/s at 145°C	20
Split ratio	100:1
Sample size, µL	1.0
Detector:	flame ionization
Temperature, °C	300
Analysis time, min	30

7.3 *Recorder*—Electronic integration is recommended.

7.4 *Injector*—The specimen must be precisely and repeatably injected into the gas chromatograph. An automatic sample injection device is highly recommended although manual injection can be employed if the criteria in 12.7 can be satisfied.

7.5 *Volumetric Flask*, 100-mL capacity.

7.6 *Syringe*, 100 µL.

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,[6] where such specifications are available.

8.2 *Carrier Gas*—Chromatographic grade helium or hydrogen 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 a flammable storage freezer at − 10 ± 5°C until approximately ½ to ¾ 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 procedure 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, *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.

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, E 355, and E 1510 for additional information on gas chromatography practices and terminology.

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[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.

12. Calibration

12.1 Prepare a synthetic mixture of high purity *p*-xylene containing impurities at concentrations representative of those expected in the samples to be analyzed. The volume of each hydrocarbon impurity must be measured to the nearest 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. *n*-Nonane will represent the nonaromatic fraction and *o*-xylene the xylene fraction. Cumene will represent the aromatic hydrocarbons containing nine carbon atoms or greater (C_9 aromatics).

12.1.1 Prior to preparing the calibration standard, all reference compounds and any samples to be analyzed must be brought to the same temperature, preferably 25°C.

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

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

where:
D_i = density of impurity *i* from Table 2,
V_i = volume of impurity *i*, mL,
D_p = density of p-xylene from Table 2,
V_t = total volume of standard blend, mL, and
C_i = concentration of impurity *i*, weight %.

12.2.1 Alternatively, calibration standards may be used that have been gravimetrically prepared in accordance with Practice D 4307.

12.3 Inject the resulting solution from 12.1 into the chromatograph, collect and process the data. A typical chromatogram is illustrated in Fig. 1.

12.4 Determine the response factor for each impurity in the calibration mixture as follows:

$$RF_i = C_i / A_i \tag{2}$$

where:
RF_i = response factor for impurity *i*,
A_i = peak area of impurity *i*, and
C_i = concentration of impurity *i*, as calculated in 12.2, weight %.

12.5 Analyze the calibration solution(s) a minimum of three times and calculate an average *RF*.

12.6 Determine the sample standard deviation for *RF* of each impurity using a scientific calculator or spreadsheet program. Determine the coefficient of variation for each *RF* as follows:

$$CV_i = 100 \, SD_i / Avg_i \tag{3}$$

TABLE 2 Preparation of Calibration Blend

Compound	Density[A]	Recommended Vol, µL	Resulting Concentration	
			Volume %	Weight %
p-Xylene (see 8.3.1)	0.857	99.72 (mL)	99.72	99.72
Benzene	0.874	20.0	0.020	0.020
Toluene	0.862	20.0	0.020	0.020
Ethylbenzene	0.863	100.0	0.100	0.101
o-Xylene	0.876	100.0	0.100	0.099
Cumene	0.857	20.0	0.020	0.020
n-Nonane	0.714	20.0	0.020	0.017

[A] Density at 25°C. Values obtained from "Physical Constants of Hydrocarbons C_1 to C_{10}"; ASTM Publication DS 4A, 1971.

where:
CV_i = coefficient of variation for RF_i,
SD_i = standard deviation for RF_i, and
Avg_i = average RF of impurity *i*.

12.7 The coefficient of variation for the response factor of any impurity, as calculated from a minimum of three successive analyses of the standard, shall not exceed 10 %.

13. Procedure

13.1 Bring the sample and calibration mixtures 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.

13.2 Depending upon the actual chromatograph's operating conditions, inject an appropriate amount of sample into the instrument. The injection amount shall be identical to the amount used in 12.3 and must be consistent with those conditions used to meet the criteria in 12.7.

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 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.

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. Use the response factor determined for *n*-nonane for all nonaromatic components, the factor for *o*-xylene for all xylenes, and the factor for cumene for all aromatic hydrocarbons containing nine or more carbon atoms as follows:

$$C_i = A_i RF_i D_c / D_s \tag{4}$$

where:
C_i = concentration of impurity *i*, weight %,
A_i = peak area of impurity *i*,
RF_i = response factor of impurity *i*, from 12.4,
D_c = density of calibration solution (p-xylene), from Table 2, and
D_s = density of sample, from Table 2 or Test Method D 4052.

14.2 Calculate the weight percent purity of the sample as follows:

$$\text{purity, weight \%} = 100.00 - C_t \tag{5}$$

where: C_t = total concentration of all impurities, weight %.

15. Report

15.1 Report individual impurities, total nonaromatics, and total C_9 aromatics, to the nearest 0.001 %.

15.2 For concentrations of impurities less than 0.001 %, report as <0.001 %, and consider as 0.000 in summation of impurities.

15.3 Report the total impurities to the nearest 0.01 %.