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 D5917; 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—Research Report information was added editorially in September 2015.

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. 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 D2360.

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 10 carbon atoms (benzene through C_{10} 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 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 applicability 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
D2360 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography
D3437 Practice for Sampling and Handling Liquid Cyclic Products
D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
D5136 Specification for High Purity *p*-Xylene
D5211 Specification for Xylenes for *p*-Xylene Feedstock
D6526 Test Method for Analysis of Toluene by Capillary Column Gas Chromatography
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
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**

TABLE 1 Recommended Operating Conditions

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	1.0
Detector:	flame ionization
Temperature, °C	300
Analysis time, min	30

2.2 *Other Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200[3]

3. Terminology

3.1 See Terminology D4790 for definitions of terms used in this test method.

3.2 Mixed xylenes are a mixture of C_8 aromatics including *m*-xylene, *o*-xylene, and *p*-xylene. Industry convention includes ethylbenzene as a 'mixed xylene' though ethylbenzene is not technically a xylene. Styrene is excluded.

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.

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.

5.2 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 D2360, 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 D6526 must be selected to ensure an accurate assessment of the benzene concentration.

6.2 Complete separation of ethylbenzene and *m*-xylene from *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 *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*—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.

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,[4] where such specifications are available.

8.2 *Carrier Gas*—Chromatographic grade helium or hydrogen, 99.999 % is recommended. Purify carrier, fuel and

[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.

[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.

makeup gases by adding traps to reduce the concentration of any remaining oxygen, water, and hydrocarbons. Purify air by adding traps to reduce the concentration of any remaining hydrocarbons and water.

8.3 *Air,* Chromatographic grade, containing 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 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.

8.5 Pure compounds for calibration, shall include *n*-nonane, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and cumene. If applicable, the calibration may include paradiethylbenzene (PDEB). 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 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 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, *o*-xylene the *o*-xylene fraction, *m*-xylene the *m*-xylene fraction. Cumene will represent the aromatic hydrocarbons containing nine carbon atoms or greater, with exception of PDEB. If PDEB is included in the calibration, PDEB will represent PDEB.

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 ambient or 20°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:

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

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 D4307.

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:

TABLE 2 Preparation of Calibration Blend

Compound	Density[A]	Recommended Vol, µL	Resulting Concentration (including PDEB)		Resulting Concentration (excluding PDEB)	
			Volume %	Weight %	Volume %	Weight %
p-Xylene	0.861	99.60-99.62 ml	99.60	99.60	99.62	99.62
Benzene	0.879	20	0.020	0.020	0.020	0.020
Toluene	0.867	20	0.020	0.020	0.020	0.020
Ethylbenzene	0.867	100	0.100	0.100	0.100	0.100
o-Xylene	0.880	100	0.100	0.102	0.100	0.102
Cumene	0.862	20	0.020	0.020	0.020	0.020
n-Nonane	0.718	20	0.020	0.017	0.020	0.017
m-Xylene	0.864	100	0.100	0.101	0.100	0.101
PDEB	0.866	20	0.020	0.020	n/a	n/a

[A] Density at 20°C. Values obtained from "Physical Constants of Hydrocarbons C_1 to C_{10};" ASTM Publication DS 4A, 1971.

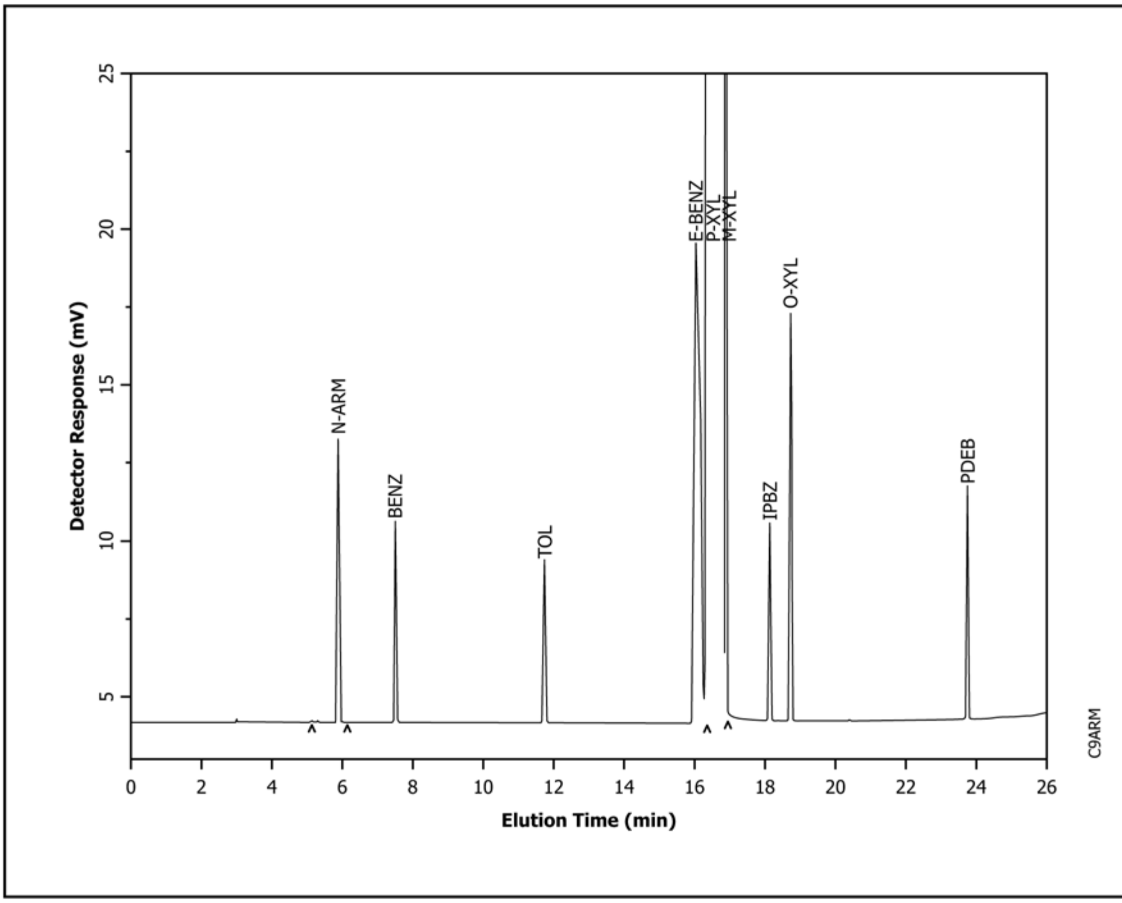

FIG. 1 Typical Chromatogram of Calibration Standard

$$RF_i = C_i/A_i \quad (2)$$

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:

$$CV_i = 100\ SD_i/Avg_i \quad (3)$$

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 ambient or 20°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.

14. Calculations

14.1 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. Total non-aromatics are defined as all components eluting before *o*-xylene, excluding benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, and cumene (IPBZ in Fig. 1). Total C_9-plus aromatics are defined as cumene, plus all components eluting after *o*-xylene. Generally, C_9-plus aromatics are summed and reported as a group. In certain cases, one or more individual C_9-plus aromatic components, such as cumene or *p*-diethylbenzene (PDEB in Fig. 1), may be reported separately. In those cases, the grouping would not include the separately reported component(s) and the remaining C_9-plus aromatics would be reported as C_9-plus aromatics other than component(s).

14.2 A poorly resolved peak, such as *m*-xylene, will often require a tangent skim from the neighboring peak. Make consistent measurements on the specimen and calibration chromatograms for tangents or poorly resolved peaks.

14.3 Fig. 2 illustrates the analysis of Specification D841, Toluene. Fig. 3 illustrates the analysis of Specification D5211, Mixed Xylene. Fig. 4 illustrates the analysis of Specification D5136, *p*-xylene.

14.4 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 *o*-xylene, the factor for *m*-xylene for *m*-xylene, the factor for cumene for all aromatic hydrocarbons containing nine or more carbon atoms with exception of PDEB, and if PDEB is included in the calibration, the PDEB factor for PDEB 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 D4052.

14.5 Calculate the weight percent purity of the major component or components of the sample as follows:

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

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

14.5.1 If the major component of the sample is a mixture, for example, mixed xylenes, and not a single aromatic, report the major components as a total. Subtract the total minor impurities from 100 for the total mixed xylenes. This method is not to be used for the distribution of major components. Test Method D6563 may be used for the distribution of mixed xylenes.

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 %.

15.4 Report purity of the major component or components as "purity (by *GC*)" to the nearest 0.01 %.

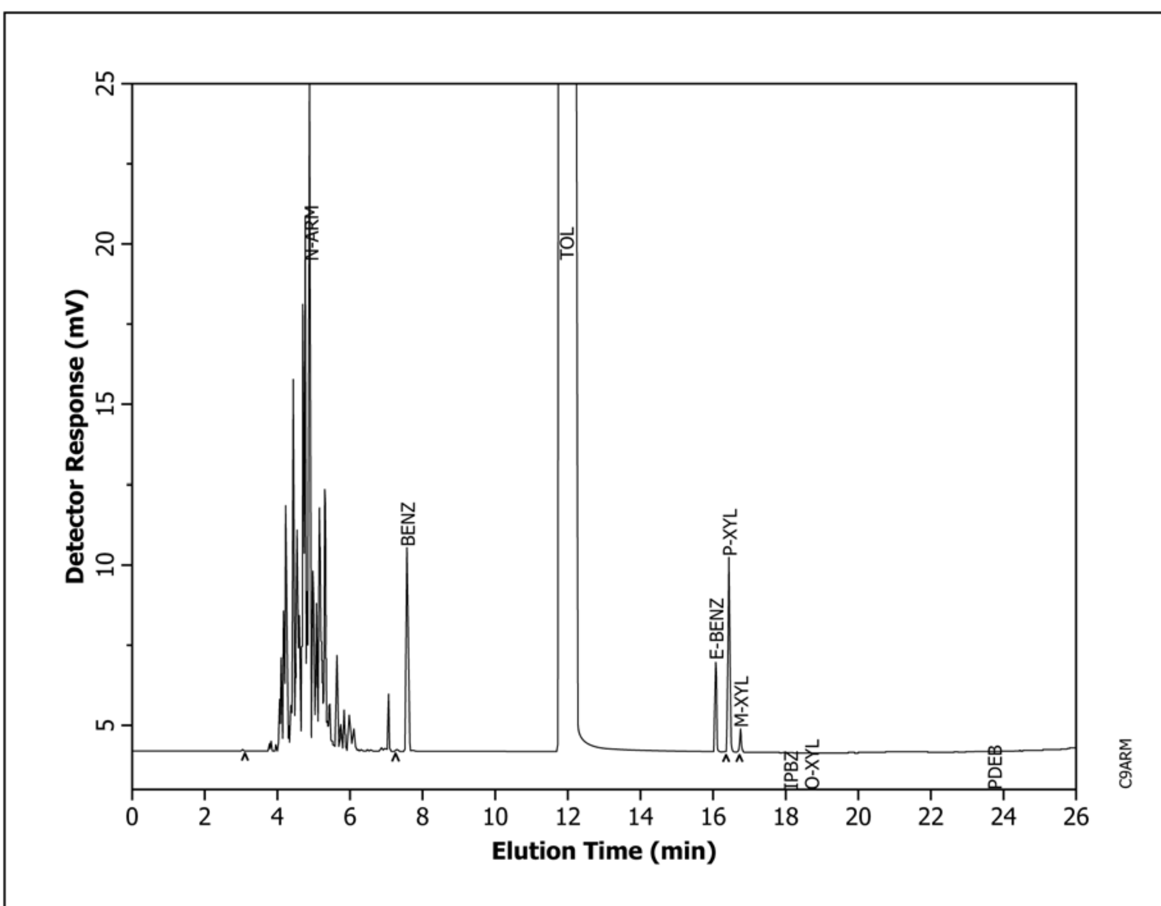

FIG. 2 Typical Chromatogram of Specification D841, Toluene

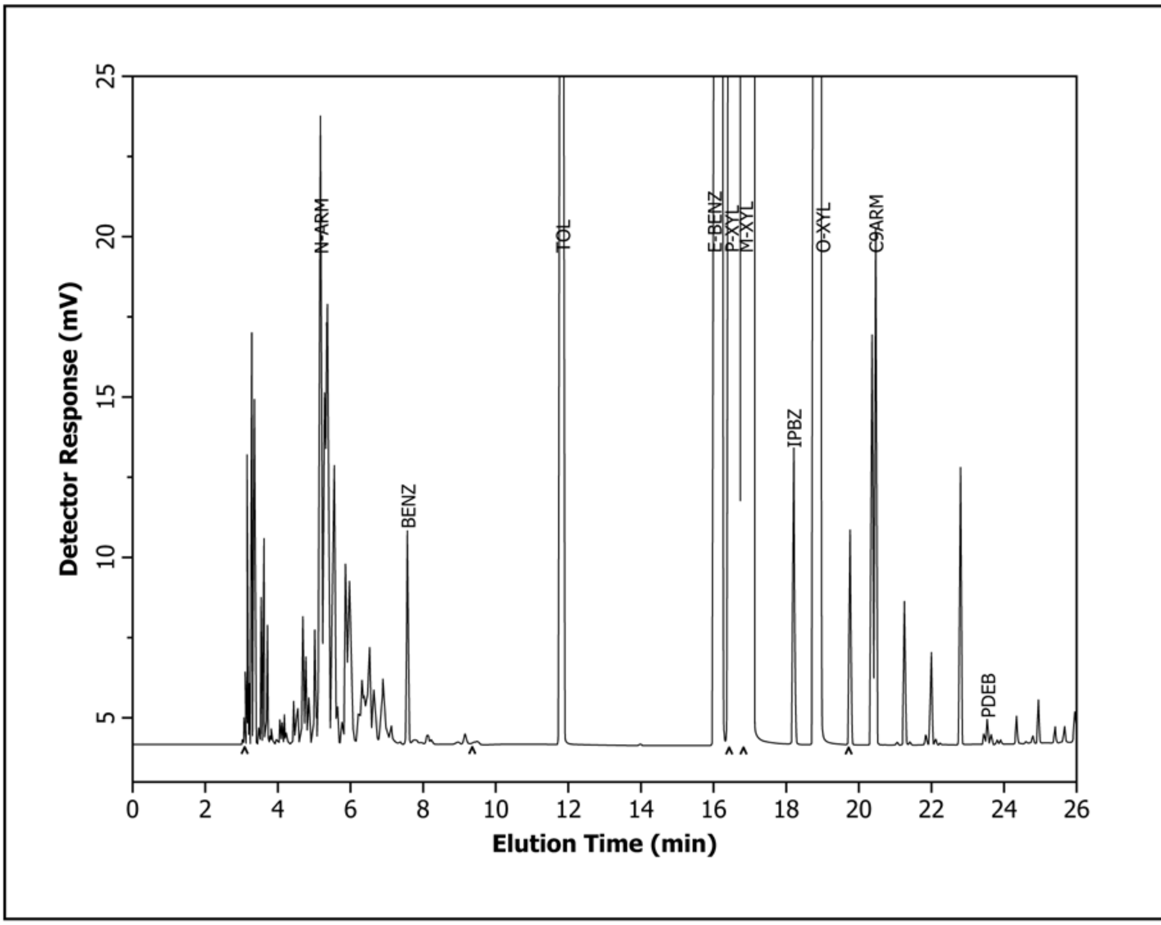

FIG. 3 Typical Chromatogram of Specification D5211, Xylenes

16. Precision and Bias

16.1 *Precision for Mixed Xylenes and Toluene:*

16.1.1 An ILS was conducted which included six laboratories analyzing one sample of mixed xylenes and one sample of toluene. Each lab was provided with two calibration standards. Each sample was analyzed twice in two days by two different operators. Results of the interlaboratory study were calculated using Practice E691. The details are given in ASTM Research Report RR:D16-1020.[5] This ILS does not meet the minimum requirements of Practice E691.

16.1.2 *Intermediate Precision*—Duplicate results by the same operator should not be considered suspect unless they differ by more than ±*r* in Table 3. Results differing by less than *r* have a 95 % probability of being correct.

16.1.3 *Reproducibility*—Results between two laboratories should not be considered suspect unless they differ by more than ±*R* in Table 3. Results differing by less than *R* have a 95 % probability of being correct.

16.2 *Precision for Para-xylene:*

16.2.1 An ILS was conducted which included eight laboratories analyzing four samples three times. One laboratory was dropped from the data analysis. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D16-1055.[6]

16.2.2 *Repeatability*—Duplicate results by the same operator should not be suspect unless they differ by more than *r* in Table 4. Results differing by less than *r* have a 95 % probability of being correct.

16.2.3 *Reproducibility*—Results submitted by two labs should not be considered suspect unless they differ by more than *R* in Table 4. Results differing by less than *R* have a 95 % probability of being correct.

16.3 *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.

17. Quality Guidelines

17.1 Refer to Guide D6809 for suggested QA/QC activities that can be used as part of this method. It is recommended that

[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.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1055. Contact ASTM Customer Service at service@astm.org.

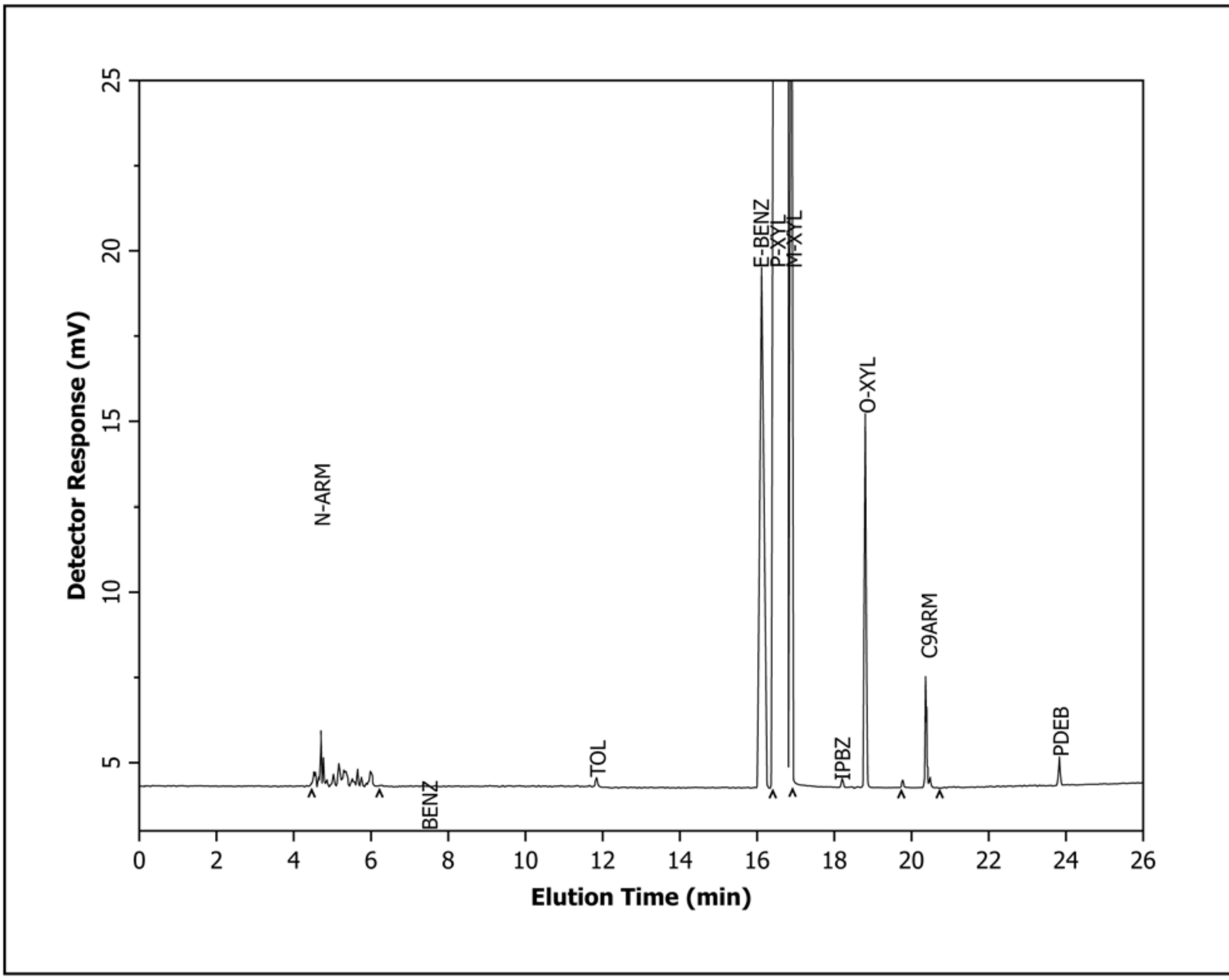

FIG. 4 Typical Chromatogram of Specification D5136, *p*-Xylene

TABLE 3 Intermediate Precision and Reproducibility (wt. %)

Toluene	Average	Intermediate Precision	Reproducibility
Nonaromatics	0.017	0.0040	0.0083
Ethylbenzene	0.017	0.0014	0.0030
p-Xylene	0.009	0.0025	0.0027
m-Xylene	0.013	0.0013	0.0025
o-Xylene	0.001	0.0003	0.0005
Toluene	99.94	0.016	0.021
Mixed Xylenes		Intermediate Precision	Reproducibility
Nonaromatics	2.286	0.1039	0.3688
Toluene	0.675	0.0244	0.1580
Cumene	0.010	0.0006	0.0020
Xylenes	96.93	0.128	0.369

the operator of this method select and perform relevant QA/QC activities like the ones in Guide D6809 to help ensure the quality of the data generated by this method.

18. Keywords

18.1 aromatics; external standard; gas chromatography; impurities; purity; *p*-xylene; toluene; xylenes

TABLE 4 Repeatability and Reproducibility (wt. %)

P-Xylene	Average[A] $\bar{X}$	Repeatability Limit[A]	Reproducibility Limit[B]
Nonaromatics	0.0032	0.0050	0.0073
Benzene	0.0015	0.0013	0.0023
Toluene	0.0318	0.0111	0.0144
Ethylbenzene	0.0080	0.0005	0.0017
Para-Xylene	99.7988	0.0315	0.0424
Meta-Xylene	0.1216	0.0261	0.0397
Ortho-Xylene	0.0247	0.0011	0.0315
C9+ aromatics	0.0098	0.0018	0.0211

[A] The average of the *r*'s for the four different levels.
[B] The average of the *R*'s for the four different levels.

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D5917–12) that may impact the use of this standard. (Approved February 1, 2015.)

(1) Section 16, Precision, was completely revised to update the mixed xylenes and toluene precision to current D16 editorial guidelines and to include the repeatability and reproducibility of para-xylene based on a new ILS.