StandardTest Method for
Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number[1]

This standard is issued under the fixed designation D7504; 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, *p*-xylene, *o*-xylene, ethylbenzene, benzene, and styrene by gas chromatography. The purity of toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene, benzene, and stryene can also be calculated. Similar test methods, using the internal standard calibration technique and the external standard calibration technique, are Test Methods D2360, D3797, D4492, D5060, D5135, D5917, and D6563 respectively.

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 0.0001 to 2.5000 weight %.

1.2.1 A small amount of benzene in toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene, or styrene may not be distinguished from the non-aromatics 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 0.0001 to 2.5000 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 applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D841 Specification for Nitration Grade Toluene
D1555M Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons and Cyclohexane [Metric]
D2360 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography
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
D5060 Test Method for Determining Impurities in High-Purity Ethylbenzene by Gas Chromatography
D5135 Test Method for Analysis of Styrene by Capillary Gas Chromatography
D5136 Specification for High Purity *p*-Xylene
D5211 Specification for Xylenes for *p*-Xylene Feedstock
D5917 Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and External Calibration
D6229 Test Method for Trace Benzene in Hydrocarbon Solvents by Capillary 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

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[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.

Current edition approved March 15, 2012. Published March 2012. Originally approved in 2009. Last previous edition approved in 2011 as D7504 - 11. DOI: 10.1520/D7504-12.

[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.

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

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

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.

4. Summary of Test Method

4.1 The specimen to be analyzed is injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column. The peak area of each component is measured and adjusted using effective carbon number (ECN)[4] response factors. The concentration of each component is calculated based on its relative percentages of total adjusted peak area and normalized to 100.0000 %.

5. Significance and Use

5.1 Determining the type and amount of hydrocarbon impurities remaining from the manufacture of toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene, benzene, and styrene 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 or more.

5.2 This method may not detect all components and there may be unknown components that would be assigned inappropriate response factors and thus, the results may not be absolute.

6. Interferences

6.1 In some cases for toluene, mixed xylenes, *p*-xylene, *o*-xylene, ethylbenzene and styrene, 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 D6229 must be selected to ensure an accurate assessment of the benzene concentration.

6.2 The complete separation of *p*-xylene from ethylbenzene, or ethylbenzene and *m*-xylene from *p*-xylene can be difficult when either ethylbenzene or *p*-xylene is analyzed, respecively. The separation can be considered adequate if the distance from the baseline to the valley between the two peaks is not greater than 50 % of the peak height of lower of the two peaks.

7. Apparatus

7.1 Chromatographic data system is required.

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 *Gas Chromatograph*—Any instrument having a flame ionization detector and a splitter injector suitable for use with a fused silica capillary column may be used, provided the system has sufficient sensitivity, linearity, and range to determine 0.0001 wt %, while not exceeding the full scale of either the detector or the electronic integration for the major component. It shall have a split injection system that will not discriminate over the boiling range of the samples analyzed. The system should be capable of operating at conditions given in Table 1.

7.4 *Injector*—The specimen must be precisely and repeatably injected into the gas chromatograph. An automatic sample injection devise is highly recommended.

7.5 *Syringe,* chromatographic, capable of delivering appropriate µL volumes.

8. Reagents and Materials

8.1 *Purity of Reagent*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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[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] Scanlon, J. T. and Willis, D. E., "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept," *Journal of Chromatographic Science*, Vol. 23, August 1985, pp. 333–339.

TABLE 1 Recommended 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 or hydrogen
Linear velocity, cm/s at 145°C	20 helium or 45 hydrogen
Split ratio	100:1
Sample size, µL	0.6
Detector:	flame ionization
Temperature, °C	300
Analysis time, min	38

TABLE 2 Effective Carbon Number Response Factors and Density

Component	ECN Response Factor[A]	Density at 20°C
Non Aromatics	1.0000	0.7255 (average)[B]
Benzene	0.9100	0.8780[C]
Toluene	0.9200	0.8658[C]
Ethylbenzene	0.9275	0.8658[C]
p-Xylene	0.9275	0.8597[C]
m-Xylene	0.9275	0.8630[C]
o-Xylene	0.9275	0.8786[C]
Cumene	0.9333	0.8605[C]
1,4-Dioxane	3.0800	1.0329[D]
C$_{9+}$ Aromatics	0.9333	0.8715[E] average
Styrene	0.91	0.9048[C]
C$_{10}$ Aromatics	0.938	0.8694[E] average
p-diethylbenzene (PDEB)	0.938	0.8620[E]

[A] Response factors are relative to *n*-heptane.
[B] DS # 4A *Physical Constants of Hydrocarbons C$_1$ through C$_{10}$*, ASTM, 1971. Average of hexane, methylcyclopentane, methylcyclohexane, heptane, and ethylcyclopentane.
[C] Test Method D1555M.
[D] Keith, L. H., Walters, D B., Compendium of Safety Data Sheets for Research and Industrial Chemicals, Part II, VCH Publishers, Deerfield Beach, p. 726, 1985.
[E] CRC Handbook of Chemistry and Physics, David R. Lide, 88th Ed., 2007–2008.

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[5] where such specifications are available. Reagents with an establish purity greater than ACS reagent grade may be used.

8.2 *Carrier Gas, Makeup Gas and Detector Gases 99.999 % pure.* Oxygen in carrier gas 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 for the FID should contain less than 0.1 ppm total hydrocarbon.

8.4 *Calibration Check Standard.* This standard may be purchased if desired.

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

12. Calibration

12.1 Prior to implementation of the ECN method, a laboratory should demonstrate that acceptable precision and bias can be obtained using a synthetic mixture of known composition (Calibration check sample).

13. Procedure

13.1 Bring the sample to room temperature.

13.2 Check the chromatography performance to make sure that the column is properly resolving peaks.

13.3 Inject an appropriate amount of sample into the instrument.

13.4 Review the chromatographic data system result. Measure the area of all peaks. The non-aromatics fraction includes all peaks up to ethylbenzene except for the peaks assigned to benzene and toluene. Sum together all the non-aromatic peaks as a total area. When either benzene or toluene is analyzed and 1,4-dioxane is required to be reported, the non-aromatic fraction does not include the peak assigned to 1,4-dioxane.

NOTE 1—A poorly resolved peak, such as *p*-xylene from high purity ethylbenzene or *m*-xylene from high purity *p*-xylene, will often require a tangent skim from the neighboring peak.

13.5 See Figs. 1-8 for representative chromatograms.

14. Calculation or Interpretation of Results

14.1 Using the ECN weight response factors listed in Table 2, calculate the concentration of each component as follows:

$$C_i = 100 \times (A_i \times R_i) / \sum_{i=1}^{n} (A_i \times R_i) \qquad (1)$$

where:
C_i = concentration for component i, weight %,
A_i = peak area of component i, and
R_i = ECN response factor for component i.

14.2 Calculate the volume percent concentration of each component using the density in Table 2 as follows:

$$V_i = 100 \times (C_i / D_i) / \sum_{i=1}^{n} (C_i / D_i) \qquad (2)$$

where:
V_i = calculated vol % concentration of component i,
C_i = calculated wt % concentration of component i from 14.1, and
D_i = density of component i.

15. Report

15.1 Report individual impurities and total non-aromatics, to the nearest 0.0001 %.

15.1.1 If required, report total C$_9^+$ aromatics to the nearest 0.0001 %. It is the sum of cumene and all peaks emerging after *o*-xylene.

15.1.2 If required, report total xylenes to the nearest 0.0001 %. It is the sum of *m*-xylene, *o*-xylene, *p*-xylene, and ethylbenzene by industry convention.

15.2 For concentrations of impurities less than 0.0001 %, report as <0.0001 %, and consider as 0.0000 in summation of impurities.
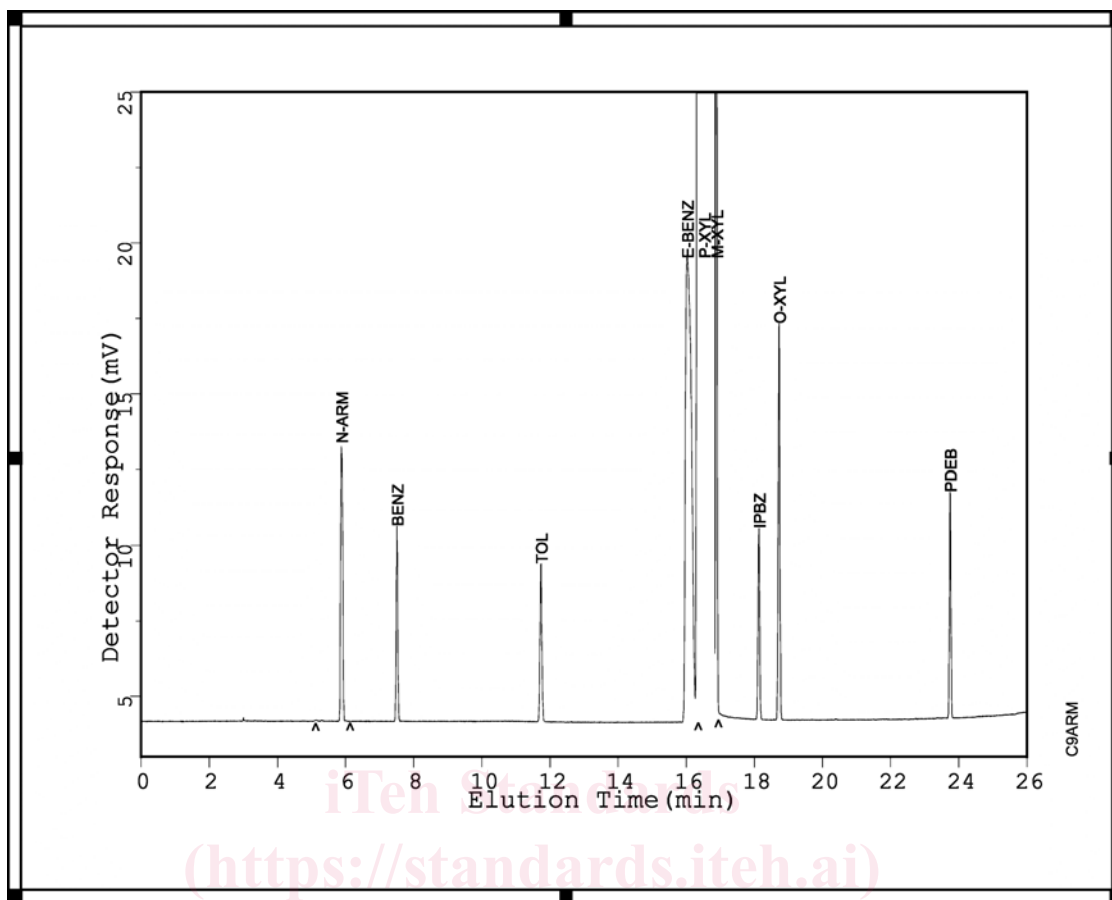
FIG. 1 Typical Chromatogram of Synthetic Blend

15.3 Report the total impurities to the nearest 0.01 %.

15.4 Report purity as "purity (by *GC*)" to the nearest 0.01 %.

16. Precision and Bias[6, 7,8]

16.1 The precision of this test method is based on an intralaboratory study of Test Method D7504 conducted in 2008 and 2010. One laboratory tested thirteen different materials (two samples of *p*-xylene, two samples of mixed xylene, and a single toluene, two samples of *o*-xylene, two samples of ethylbenzene, and two samples of benzene, and two samples of styrene) for a number of impurities. Every test result represents an individual determination. The laboratory reported 20 replicate results for each analysis/material combination in order to estimate the repeatability limits of the standard. Practice E691 was followed for the design and analysis of the repeatability data; the details are given in Research Report No. D16–1036, D16–1040, and D16–1043.

16.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

16.1.1.1 Repeatability limits are listed in Tables 3-15.

16.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

16.1.2.1 Reproducibility limits cannot be determined from the current study.

16.1.3 The above terms (repeatability and reproducibility limit) are used as specified in Practice E177.

16.1.4 Any judgment in accordance with statements 16.1.1 would have an approximate 95 % probability of being correct.

16.2 *Bias*—At the time of the study, the test specimens chosen for analysis were not accepted reference materials suitable for determining the bias for this test method, therefore no statement on bias is being made.
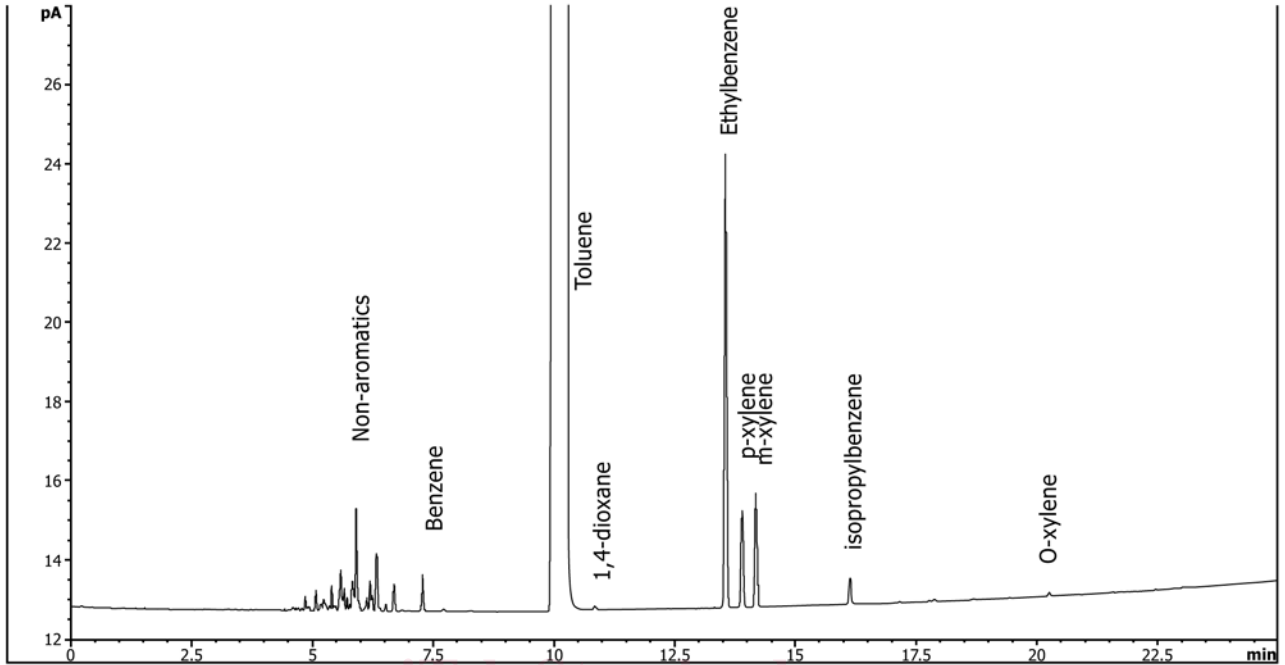
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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1036.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1040.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1043.

FIG. 2 Typical Chromatogram of Toluene
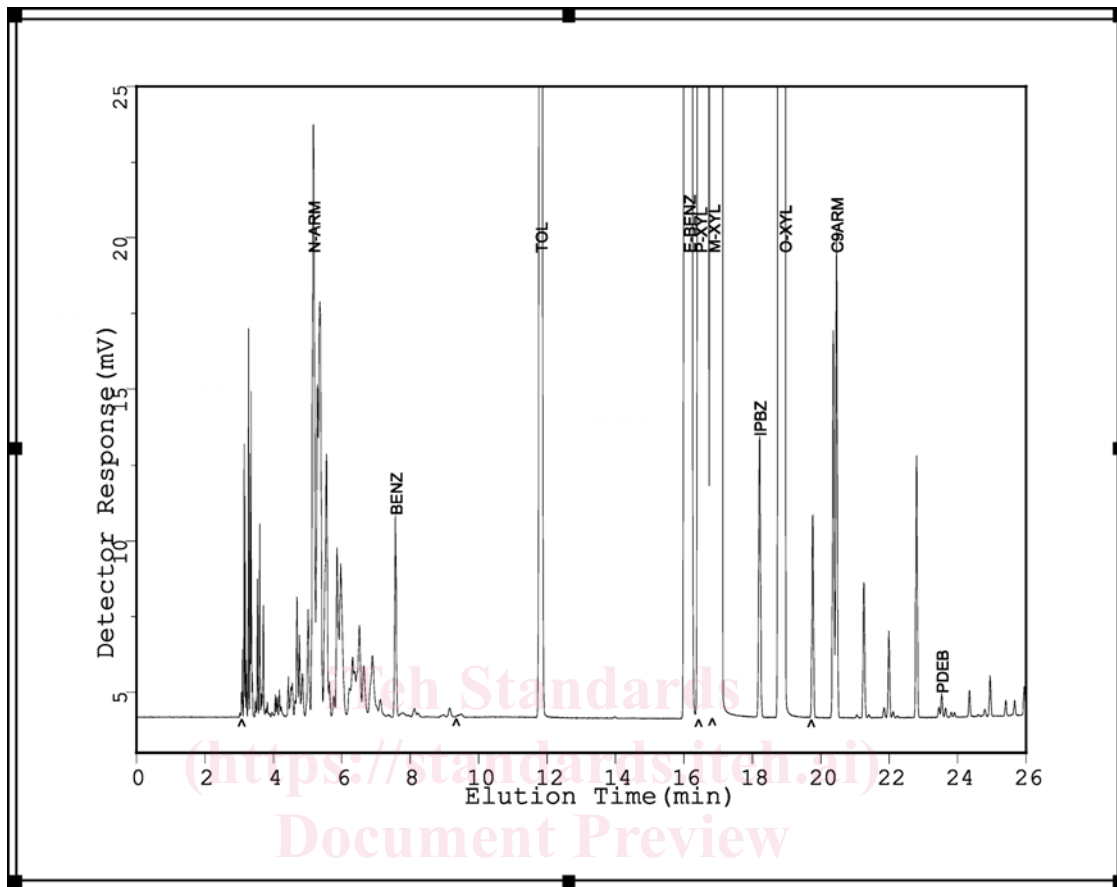
FIG. 3 Typical Chromatogram of Specification D5211, Xylenes