**Designation: D6526 – 12**

# Standard Test Method for
# Analysis of Toluene by Capillary Column Gas Chromatography[1]

This standard is issued under the fixed designation D6526; 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 ($\varepsilon$) indicates an editorial change since the last revision or reapproval.

## 1. Scope*

1.1 This test method covers the determination of hydrocarbon impurities typically found in, and the purity of, samples containing 98 wt % and greater toluene. This test method is applicable to impurity concentrations in the range of 0.0005 to 1.6 wt %.

1.2 Monocyclic aromatic hydrocarbons containing 6 through 8 carbon atoms, cumene, 1,4–dioxane, and nonaromatic aliphatic hydrocarbons containing up to 12 carbon atoms can be detected by this test method. The nonaromatic compounds are determined as a composite.

1.3 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 E29.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 statements, see Section 9.

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1555M Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons and Cyclohexane [Metric]
D3437 Practice for Sampling and Handling Liquid Cyclic Products
D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
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
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 A portion of the sample is injected into a gas chromatograph using a microlitre syringe at the specified conditions of the test method. The toluene and other components are separated as they are transported through the column by an inert carrier gas. The components in the effluent are measured by a flame ionization detector (FID). The area of the impurity peaks and toluene are electronically integrated. The peak areas are corrected with effective carbon number (ECN)[4] response factors and normalized to 100.0000 %.

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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.

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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.

[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.

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

## 5. Significance and Use

5.1 This test method is suitable for determining the concentrations of known impurities in refined toluene and for use as an integral quality control tool where toluene is produced or used in manufacturing.

5.2 Toluene purity is reported, but a chromatographic analysis cannot determine absolute purity if unknown or undetected components are present in the sample.

## 6. Interferences

6.1 If present, nonaromatic hydrocarbons of 13 carbons or greater, alcohols, ethers, and other similar organic compounds can interfere with this test method by co-eluting with the aromatic hydrocarbons.

6.2 Compounds not detected by a FID are not determined by this test method.

6.3 Nonvolatile material is not determined.

## 7. Apparatus

7.1 *Gas Chromatograph (GC)*—any GC built for capillary column chromatography. The system shall have sufficient sensitivity, linearity, and range to obtain a minimum peak height response for 0.0010 wt % impurity of twice the height of the signal background noise, 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.

**TABLE 1 Typical Instrumental Parameters**

| Detector: | Flame ionization |
|---|---|
| Detector temperature, °C | 150°C |
| Column: | 50 m by 0.25 mm |
| Tubing | Fused silica |
| Stationary phase | TCEP |
| Film thickness, μm | 0.40 |
| Column temperature, °C | 70 |
| Carrier Gas | Helium |
| Linear velocity at 70°C, cm/s | 25 |
| Inlet: | Split |
| Injection port temperature, °C | 150°C |
| Split ratio | 40 |
| Split flow, mL/min | 55 |
| Sample size, μL | 1.0 |

7.2 *Recorder*—electronic integration is recommended.

7.3 *Capillary Column*—fused silica capillary column with 1,2,3-tris-2-cyano-ethoxypropane (TCEP) phase is recommended. Polyethylene glycol (PEG) columns have been successfully used. Other columns may be used after it has been established that such a column is capable of separating all major impurities under operating conditions appropriate for the column.

7.4 *Microsyringe*—capable of delivering 1 μL of sample.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[5] where such specifications are available, unless otherwise indicated. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Carrier Gas*—Helium, 99.99 mole % minimum, is recommended.

8.3 *FID Detector Gases:*

8.3.1 *Hydrogen*—99.99 mole % minimum.

8.3.2 *Air*—less than 10 ppm each of total hydrocarbons and water.

## 9. Hazards

9.1 Consult current OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials used in this test method.

## 10. Sample Handling

10.1 Collect the samples in accordance with Practice D3437.

10.2 To preserve sample integrity (consistency) and prevent the loss of volatile components, which may be in some samples, do not uncover samples any longer than necessary.

## 11. Preparation of Apparatus

11.1 Follow the manufacturer's instructions for mounting and conditioning the column in the chromatograph.

11.2 Adjust the instrument to the conditions as described in Table 1 to give the proper separations. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable baseline. See Practices E355 and E1510 for additional information on gas chromatography practices and terminology.

## 12. Procedure

12.1 Inject an appropriate amount of specimen, typically 1.0 μL, into the chromatograph. A low purity toluene sample chromatogram, which shows the relative retention time of components typically found in commercial toluene, is illustrated in Fig. 1.

NOTE 1—Since TCEP is a nonbonded phase, significant retention time shifts can occur with column condition.

12.2 Measure the area of all peaks. The nonaromatics fraction includes all peaks eluting before benzene. Sum together all nonaromatic peaks and report as a total area.

[5] *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.
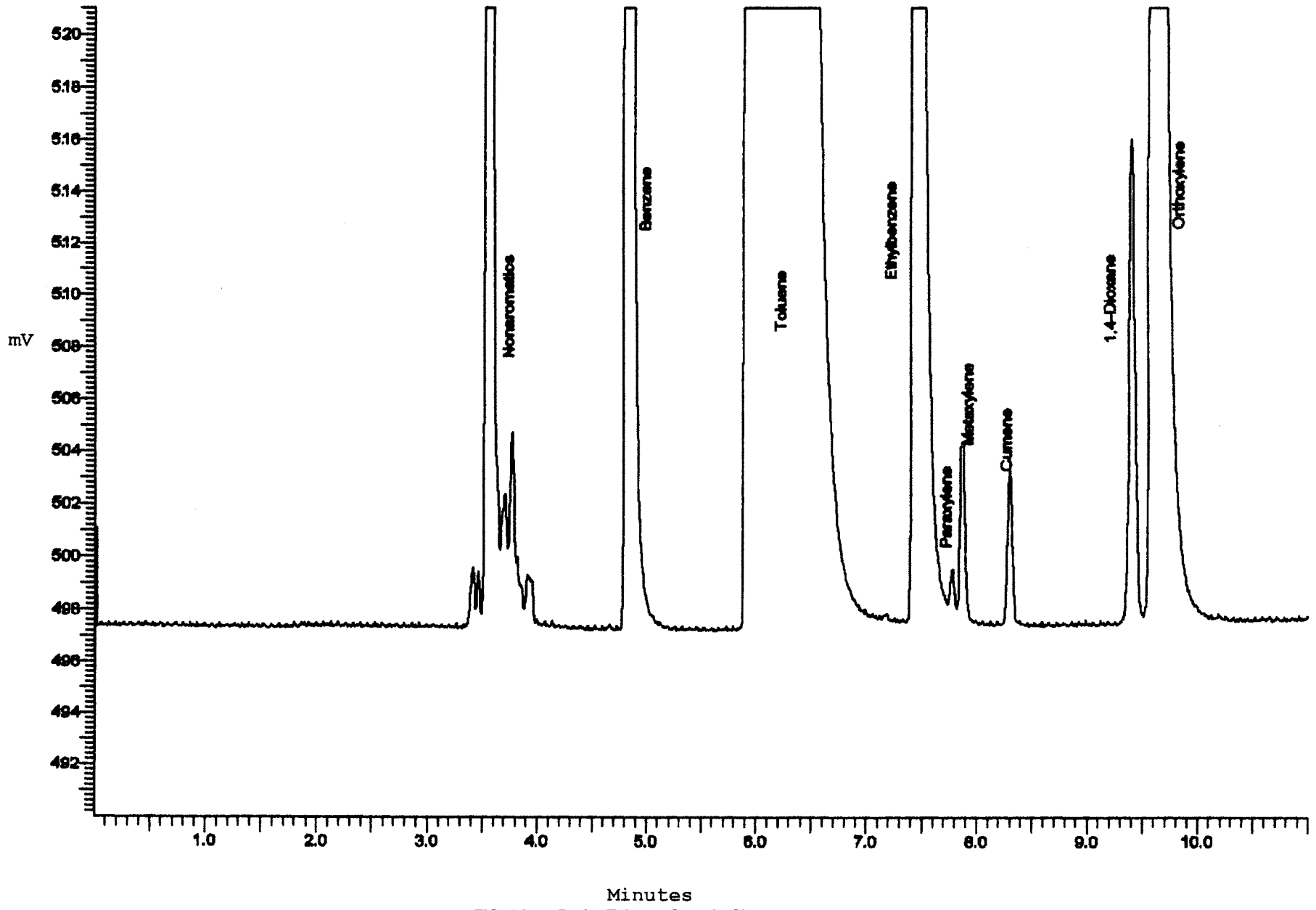
FIG. 1 Low Purity Toluene Sample Chromatogram

**TABLE 2 Effective Carbon Number Response Factors and Density**

| Component | ECN Response Factor[A,B] | Density at 20°C |
|---|---|---|
| Non Aromatics | 1.0000 | 0.7255 (average)[C] |
| Benzene | 0.9100 | 0.8780[D] |
| Toluene | 0.9200 | 0.8658[D] |
| Ethylbenzene | 0.9275 | 0.8658[D] |
| p-Xylene | 0.9275 | 0.8597[D] |
| m-Xylene | 0.9275 | 0.8630[D] |
| o-Xylene | 0.9275 | 0.8786[D] |
| Cumene | 0.9333 | 0.8605[D] |
| 1,4-Dioxane | 3.0800 | 1.0329[E] |

[A] 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.
[B] Response factors are relative to *n*-heptane.
[C] DS #4, *Physical Constants of Hydrocarbons $C_i$ through $C_{10}$*, ASTM, 1971, Average of hexane, methylcyclopentane, methycyclohexane, heptane, and ethylcyclopentane.
[D] Test Method D1555M.
[E] Keith, L. H. and Walters, D. B., Compendium of Safety Data Sheets for Research and Industrial Chemicals, Part II, VCH Publishers, 1985, Deerfield Beach, p. 726.

**TABLE 3 Intermediate Precision and Reproducibility**

| | Actual (Weight %) | Intermediate Precision | Reproducibility |
|---|---|---|---|
| **Non Aromatic** | | | |
| Std #1 | 1.6314 | 0.0078 | 0.2024 |
| Std #2 | 0.9718 | 0.0039 | 0.1243 |
| Std #3 | 0.0207 | 0.0022 | 0.0081 |
| **Benzene** | | | |
| Std #1 | 0.0006 | 0.0001 | 0.0002 |
| Std #2 | 0.0010 | 0.0002 | 0.0003 |
| Std #3 | 0.0301 | 0.0008 | 0.0070 |
| **Toluene** | | | |
| Std #1 | 98.2688 | 0.0084 | 0.2142 |
| Std #2 | 98.9756 | 0.0042 | 0.1327 |
| Std #3 | 99.8967 | 0.0025 | 0.0272 |
| **EthylBenzene** | | | |
| Std #1 | 0.0987 | 0.0015 | 0.0185 |
| Std #2 | 0.0506 | 0.0007 | 0.0116 |
| Std #3 | 0.0203 | 0.0007 | 0.0051 |
| **1,4–dioxane** | | | |
| Std #1 | 0.0005 | 0.0004 | 0.0008 |
| Std #2 | 0.0010 | 0.0007 | 0.0008 |
| Std #3 | 0.0302 | 0.0012 | 0.0079 |

## 13. Calculation

13.1 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 results for component(s) $i$, weight %,
$A_i$ = peak area of component(s) $i$, and
$R_i$ = ECN response factor for component(s) $i$.

13.2 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 13.1, and
$D_i$ = density of component $i$.

## 14. Report

14.1 Report the following information:

14.1.1 Report impurity concentrations less than 0.0005 % as <0.0005 %.

14.1.2 Report greater than 0.0005 % each of the nonaromatics, benzene, ethylbenzene, xylenes, and cumene to the nearest 0.0001 %.

14.1.3 Report toluene purity to the nearest 0.01 %.

## 15. Precision and Bias

15.1 *Precision*—The following criteria should be used to judge the acceptability of results obtained by this test method (95 % confidence level). The precision criteria were derived from six laboratories performing three analyses on three standards over a two-day period. The results of the precision study were calculated using Practice E691.

15.1.1 *Intermediate Precision (formerly called Repeatability)*—Duplicated results obtained on the same sample in the same laboratory by the same operator on the same instrument should not be considered suspect unless they differ by more than the intermediate precision value shown in Table 3.

15.1.2 *Reproducibility*—Duplicated results obtained on the same sample by different laboratories, with different operators, different instruments, and at different times should not differ by more than the reproducibility value listed in Table 3.

15.1.3 *Bias*—Systematic deviation of the method average value or the measured value from an accepted reference value. Since the absolute purity of the toluene solvent could not be

**TABLE 4 Estimated Bias**

| | Actual (weight %) | Mean | Difference |
|---|---|---|---|
| **NonAromatic** | | | |
| Std #1 | 1.6314 | 1.6404 | −0.0090 |
| Std #2 | 0.9718 | 0.9854 | −0.0136 |
| Std #3 | 0.0207 | 0.0254 | −0.0047 |
| **Benzene** | | | |
| Std #1 | 0.0006 | 0.0006 | 0.0000 |
| Std #2 | 0.0010 | 0.0011 | −0.0001 |
| Std #3 | 0.0301 | 0.0286 | 0.0015 |
| **Toluene** | | | |
| Std #1 | 98.2688 | 98.2603 | 0.0085 |
| Std #2 | 98.9756 | 98.9615 | 0.0141 |
| Std #3 | 99.8967 | 99.8905 | 0.0062 |
| **EthylBenzene** | | | |
| Std #1 | 0.0987 | 0.0984 | 0.0003 |
| Std #2 | 0.0506 | 0.0509 | −0.0003 |
| Std #3 | 0.0203 | 0.0204 | −0.0001 |
| **1,4–dioxane** | | | |
| Std #1 | 0.0005 | 0.0005 | 0.0000 |
| Std #2 | 0.0010 | 0.0012 | −0.0002 |
| Std #3 | 0.0302 | 0.0321 | −0.0019 |

determined, an absolute statement of bias could not be determined from this study. An estimate of bias was made by preparing three gravimetric standards with three different concentrations of impurities. The standards were then analyzed as unknowns in the interlaboratory study (see Table 4).

## 16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.

16.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

16.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

16.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

16.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

## 17. Keywords

17.1 benzene; gas chromatography; impurities; toluene purity; 1,4-dioxane

## SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D6526 - 10) that may impact the use of this standard. (Approved March 15, 2012.)

*(1)* Added section 13.2 to calculate volume %.

*(2)* Modified Table 2 to include density.