Designation: D 6526 – 03$^{\epsilon 1}$

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

ϵ^1 NOTE—Editorial change was made in 14.1.2 in June 2003.

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 E 29.

1.4 *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:*

D 3437 Practice for Sampling and Handling Liquid Cyclic Products[2]

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

E 355 Practice for Gas Chromatography Terms and Relationships[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

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 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)[6] response factors and normalized to 100.0000 %.

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

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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] *Annual Book of ASTM Standards*, Vol 06.04.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

[5] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

[6] Scanlon, J. T., and Willis, D. E., "Calculation of Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept", *Journal of Chromatographic Science*, Vol 35, August, 1985, pp. 333-339.

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

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[7], 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 D 3437.

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 E 355 and E 1510 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.

13. Calculation

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

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

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[7] *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.

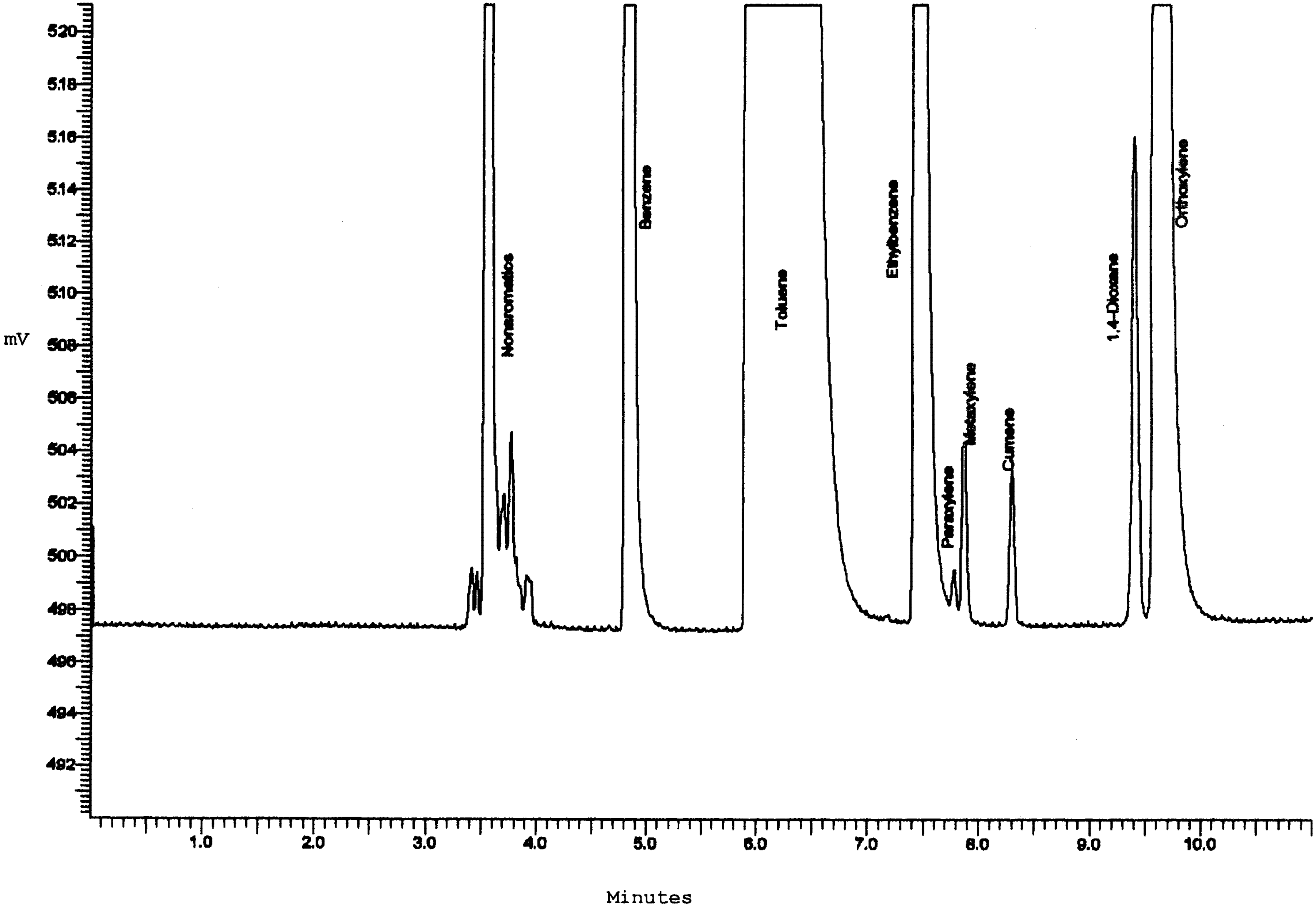

FIG. 1 Low Purity Toluene Sample Chromatogram

TABLE 2 Effective Carbon Number Response Factors

Component	Response Factor (Weight)
Nonaromatics:	0.9975
Benzene	0.9100
Toluene	0.9200
Ethylbenzene	0.9275
p-Xylene	0.9275
m-Xylene	0.9275
o-Xylene	0.9275
Cumene	0.9333
1,4-Dioxane	3.0800

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.

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 E 691.

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 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. Keywords

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

TABLE 3 Intermediate Precision and Reproducibility

	Actual (Weight %)	Intermediate Precision	Reproducibility
NonAromatic			
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

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

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D 6526 - 00) that may impact the use of this standard.

(1) Section 1.1 of the Scope was expanded to reflect the results of the interlaboratory study.

(2) The statement “Polyethylene glycol columns have been successfully used” was added to Section 7.3.

(3) The detection of impurities was lowered from 0.0010 to 0.0005 % in Section14.1.1

(4) The statement indicating to report “greater than 0.0010 to 0.0005 % was changed to “greater than 0.0005 % in 14.1.2.

(5) The Precision and Bias section was rewritten to include the interlaboratory data.

(6) A bias statement was added in Section 15.1.3.

(7) Table 4 was added for estimated bias.

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