ASTM INTERNATIONAL

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Standard Test Methods for
Aromatics in Mineral Spirits by Gas Chromatography[1]

This standard is issued under the fixed designation D3257; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 These test methods cover the determination of ethylbenzene and total eight-carbon (C_8) and heavier aromatics in the concentration range from 0.1 to 30 % in mineral spirits having a distillation range from 149 to 210°C (300 to 410°F) as determined by Test Method D86. The procedures permit the identification and calculation of concentrations of aromatic components to 0.1 volume %.

1.2 It is recognized by analytical chemists that a single column gas chromatography analysis of an unknown sample is risky. In such cases, multiple and different analytical techniques must be used for absolutely positive identification, for example, several different gas chromatography columns, gas chromatography/mass spectrometer, or gas chromatography/infrared, etc. In these test methods the material is known and is clearly defined.

1.3 Oxygenated compounds, if present, may interfere and cause erroneous results. Such oxygenated compounds are not normally present in mineral spirits.

1.4 Three test methods are covered as follows:

1.4.1 *Test Method A,* measurement of ethylbenzene content, C_8 plus higher aromatics (except ethylbenzene), and total aromatics by means of a single packed column gas chromatographic analysis.

1.4.2 *Test Method B,* measurement of ethylbenzene content by means of a rapid packed column gas chromatographic analysis.

1.4.3 *Test Method C,* measurement of ethylbenzene content, C_8 plus higher aromatics (except ethylbenzene) and total aromatics by means of a capillary column gas chromatographic analysis.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 For purposes of determining conformance of an observed or a calculated value using this test method to relevant specifications, test result(s) 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.

1.7 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

1.8 *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]

D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E260 Practice for Packed Column Gas Chromatography

2.2 *ASTM Adjuncts:*

D2PP Determination of Precision and Bias Data[4]

3. Summary of Test Methods

3.1 The material, with an internal standard, is introduced into a gas chromatographic column containing a strongly polar liquid phase. The polar phase has very little affinity for saturated and olefinic hydrocarbons while exhibiting a pronounced retention of aromatics. This selectivity, which is illustrated in Fig. 1 results in the elution of all saturated and

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[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from ASTM International Headquarters. Order Adjunct No. ADJD6300.

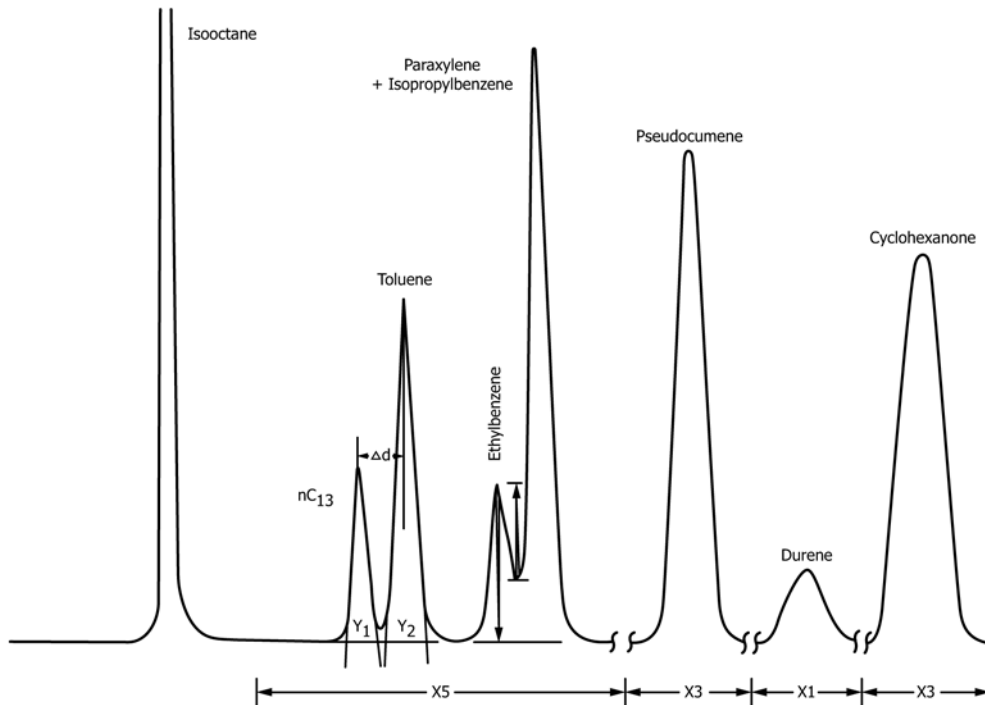***A Summary of Changes section appears at the end of this standard**

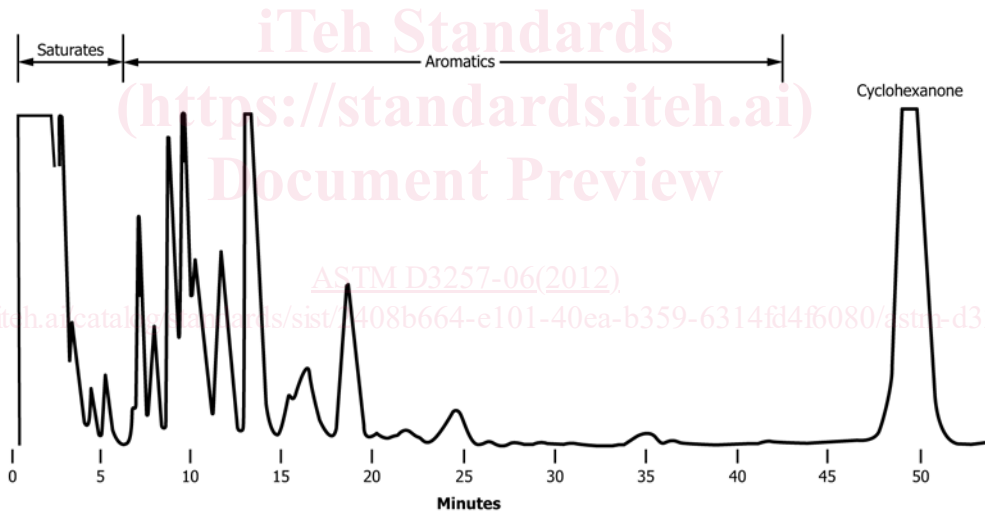**FIG. 1 Typical Resolution of Test Blend Using Packed Column**

FIG. 2 Typical Packed Column Chromatogram of Mineral Spirits (Column and Conditions Described in Table 2)

olefinic hydrocarbons in the products described above prior to the elution of toluene. Either a thermal conductivity or flame ionization detector may be used. Calibration is obtained in Test Method A and C from a synthetic blend of the most important aromatic compounds. Internal standards are used in all three test methods. Typical chromatograms are shown in Fig. 2 and Fig. 3.

NOTE 1—Refer to Practice E260 for additional information on gas chromatography techniques.

4. Significance and Use

4.1 These test methods were developed to measure the types and amounts of aromatics in mineral spirits to determine compliance with air pollution regulations that restrict the
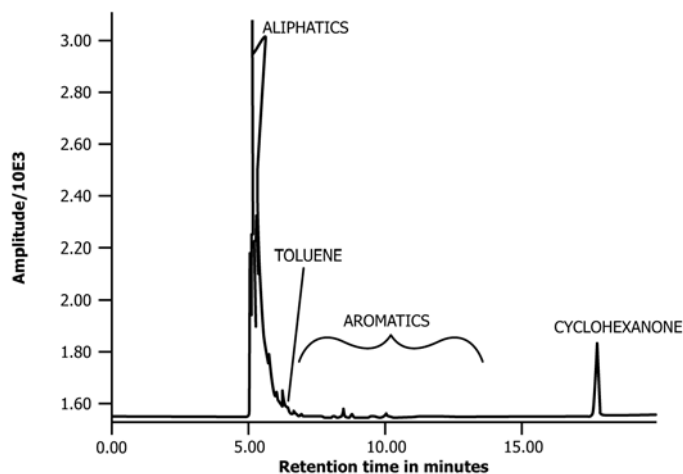
FIG. 3 Typical Capillary Chromatogram of Mineral Spirits (Column and Conditions Described in Table 3)

aromatic content of solvents. They have been demonstrated to be workable and to produce accurate results. However, due to the sensitivity of the tests to operating variables, some laboratories having limited experience with gas chromatographic analyses of hydrocarbons may experience difficulty in performing the tests.

TEST METHOD A—ETHYLBENZENE AND TOTAL AROMATICS CONTENTS BY MEANS OF A SINGLE PACKED COLUMN GAS CHROMATOGRAPHIC ANALYSIS

5. Apparatus

5.1 *Chromatograph,* any gas chromatographic instrument that has the following performance and characteristics:

5.1.1 *Sensitivity*—The overall sensitivity must be sufficient to detect 0.1 volume % of any aromatic compound of interest with a peak height of at least 10 % of full-scale chart deflection without loss of resolution as defined in 5.1.2, or 10 times the noise level.

5.1.2 *Column*—Any column and conditions may be used provided the system meets all the following criteria when the test blend is injected into the chromatograph and the chromatogram recorded in accordance with 7.2, is analyzed as follows:

5.1.2.1 Construct tangents to the peak to intersect the baseline for the *n*-tridecane (nC_{13}) and toluene peaks. Measure the distance between the two peaks and the width of each peak as the distance along the baseline under the peak between the points of intersection (see Fig. 1).

5.1.2.2 Calculate the peak resolution,

$$R = 2\Delta d/\left(Y_1 + Y_2\right) \qquad (1)$$

where:

Δd = distance between nC_{13} and toluene peaks,
Y_1 = width of nC_{13} peak along the baseline, and
Y_2 = width of the toluene peak along the baseline.

The peak resolution, R, must be not less than 0.9, otherwise the resolution of ethylbenzene may be lost.

NOTE 2—The selectivity of the column (separation of the nonaromatics from aromatics) can be increased by increasing the concentration of liquid

phase or by increasing the temperature of the chromatographic column. The resolution of the aromatic compounds can be improved by increasing the length of the column or by decreasing the oven temperature or inlet pressure of the carrier gas.

5.1.2.3 Ethylbenzene must be separated from paraxylene and isopropylbenzene or from paraxylene plus isopropylbenzene with the depth of the valley after ethylbenzene not less than 50 % of the ethylbenzene peak height.

5.1.2.4 The system must measure durene with a peak height of at least 10 % of full scale chart deflection or at least 10 times the noise level.

NOTE 3—A combination of column materials and conditions that has been found to be particularly suitable for this test method is listed in Table 1. Such column may be obtained from most chromatography supply houses that offer packed GC columns.

5.2 *Strip Chart Recorder Integrator*—A recording potentiometer with a fullscale deflection of 10 mV or less should be used. If manual integration, such as triangulation, paper cut-out or planimeter, is employed the chart speed should be at least 1.5 m/h (60 in./h) in order to minimize errors in peak area measurement. This is not necessary where a ball-and-disk or an electronic integrator is employed.

5.3 *Electronic Integration*—Any electronic data processing system or integration device, or both, may be used to determine the areas of the chromatographic peaks.

5.4 *Micro Syringe*—A 10-µL micro syringe for specimen introduction.

6. Reagents and Materials

6.1 *Aromatic Hydrocarbons*—Toluene, ethylbenzene, paraxylene, isopropylbenzene (cumene), 1,2,4-trimethylbenzene (pseudocumene), and 1,2,4,5-tetramethylbenzene (durene) 99.5 mol % minimum.

6.2 *Carrier Gas* (Note 3).

TABLE 1 Typical Column and Conditions

Length, m	3.7 (12 ft)
Diameter, mm:	
Inside	...
Outside	3.2 (⅛ in.)
Liquid phase	CEF[A]
Weight % liquid	25
Solid support:	calcined pink, diatomaceous silica[B]
Mesh	80–100
Treatment	none
Inlet, °C	250
Detector, °C	250
Column, °C	110
Carrier gas	helium
Inlet pressure, KPa	550 (80 psi)
Flow rate, mL/min	35
Detector	flame ionization
Recorder, mV	1
Specimen, µL	2
Sample split	(30 to 1)

[A] N,N-bis (2-cyanoethyl) formamide.
[B] The sole source of supply of the material Chromosorb-P known to the committee at this time is Celite Corp. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

6.3 *Internal Standard*—Cyclohexanone, 99.5 mol % minimum (see 1.7).

6.4 *Chromatographic Column* (Note 3).

6.5 *Normal Paraffin*—*n*–Tridecane, 99.5 mol % minimum.

6.6 *Solid Support* (Note 3).

6.7 *Paraffin Solvent for Test Blend*—*n*-Hexane, *n*-heptane, or *iso*-octane 99 mol % minimum.

7. Calibration

7.1 *Preparation of Test Blend*—Prepare a test blend to evaluate the sensitivity and resolution of the equipment and test procedure. To do this, pipet the exact volume of each hydrocarbon indicated in Table 2 into a 100-mL volumetric flask. Fill to the 100-mL mark with one of the solvents listed in 6.7 and mix by inverting several times. See 1.7.

Note 4—Durene is a solid. In preparing the test blend, the quantity of durene required should be weighed, using as its density 0.8875 g/mL.

7.2 Select the instrument conditions and specimen size so as to give the necessary sensitivity and resolution. Inject the test blend into the column at these conditions. Change the attenuation, if necessary, so that the internal standard and aromatic peaks are measured with a chart deflection of not less than 25 % nor more than 95 % of full scale for attenuated peaks. Check the column performance against the requirements given in 5.1.2.

7.3 *Response Factor*—Assume that the aromatics in the sample have the same relative response as pseudocumene in the test blend. Using the results from the test blend, calculate the response factor as follows:

$$r = \frac{A_{IS}}{V_{IS}} \times \frac{V_a}{A_a} \qquad (2)$$

where:
r = relative response factor for aromatics,
A_{IS} = area of the internal standard peak in arbitrary units corrected for attenuation,
V_{IS} = volume % of the internal standard in the blend,
A_a = area of the pseudocumene peak in arbitrary units corrected for attenuation, and
V_a = volume % of pseudocumene in the blend.

TABLE 2 Composition of Test Blend

	Volume, mL
Normal tridecane from 6.5	1
Toluene	2
Ethylbenzene	1
Paraxylene	2
Isopropylbenzene	2
Durene (Note 4)	0.1
Cyclohexanone from 6.3	2
Pseudocumene	2
Paraffin Solvent from 6.5	87.9

8. Procedure

8.1 Using the exact instrument conditions as were used in the calibration, inject the test material. Inspect the chromatogram to determine that there is complete resolution between the saturated and the aromatic peaks.

8.2 Pipet exactly 1.0 mL of cyclohexanone internal standard into a 10-mL volumetric flask. Fill to the mark with the sample and mix by inverting several times.

8.3 With the exact instrumental conditions used in the calibration, inject the same volume of sample containing the internal standard. Change the attenuation, if necessary, so as to measure the area of the internal standard and aromatic peaks with not less than 25 % nor more than 95 % chart deflection on attenuated peaks.

9. Calculation

9.1 Measure the areas of all aromatic and internal standard peaks. Use of an electronic integrator is recommended to obtain the best accuracy and precision.

Note 5—Because the C_8 and heavier aromatic compounds may not be completely resolved, peak height multiplied by one half width or retention time must not be used as a means of measuring the area.

9.2 If a different attenuation is used for part of the chromatogram, correct to a constant attenuation basis by multiplying the area of the aromatic peaks by the ratio:

$$S_a/S_s \qquad (3)$$

where:
S_s = attenuation sensitivity used for the internal standard peak and
S_a = attenuation sensitivity used for the aromatic peak.

9.3 Calculate the concentrations of ethylbenzene and C_8 and heavier aromatics as follows:

$$V_a = (A_a \times r \times 10)/(A_{IS} \times 0.9) \qquad (4)$$

$$= \frac{A_a}{A_{IS}} \times r \times 11.11$$

where:
V_a = volume % of the aromatic compound(s),
A_a = area of the aromatic peak(s) corrected to a constant attenuation,
r = relative response factor for the aromatic compounds,
10 = volume % of internal standard,
A_{IS} = area of the internal standard peak, and
0.9 = factor to correct for the dilution by the internal standard.

9.4 *Total Aromatics*—Add the amounts of the aromatic compounds found to obtain the volume percent of total aromatics in the sample.