Designation: D3257 – 06 (Reapproved 2012)

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

---

[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.

Current edition approved June 1, 2012. Published August 2012. Originally approved in 1973. Last previous edition approved in 2006 as D3257 – 06. DOI: 10.1520/D3257-06R12.

[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**

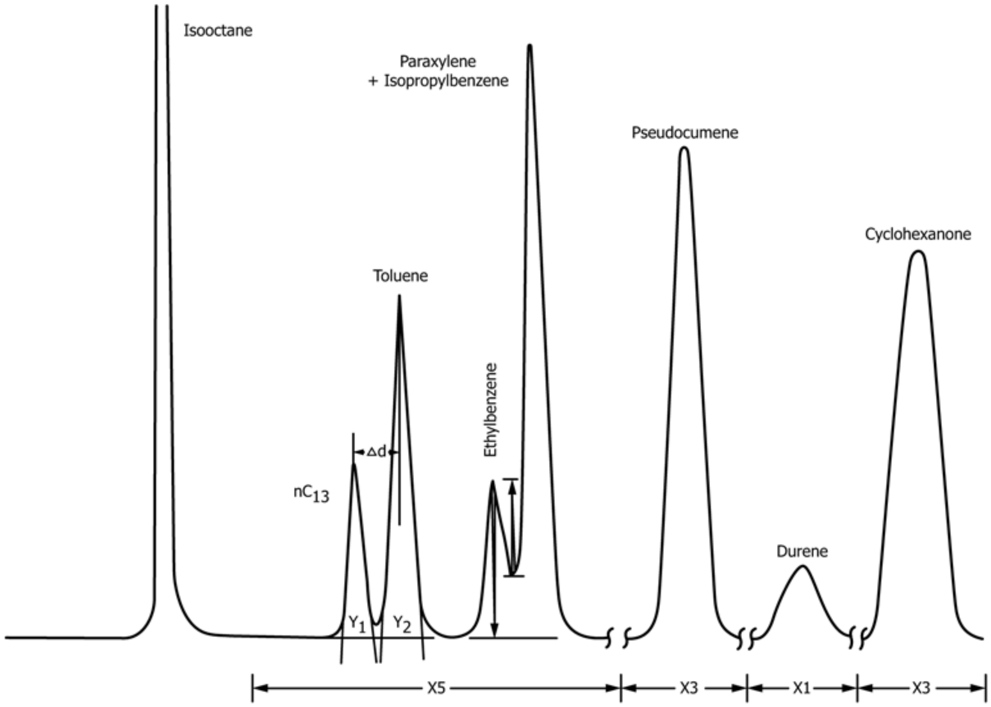

FIG. 1 Typical Resolution of Test Blend Using Packed Column

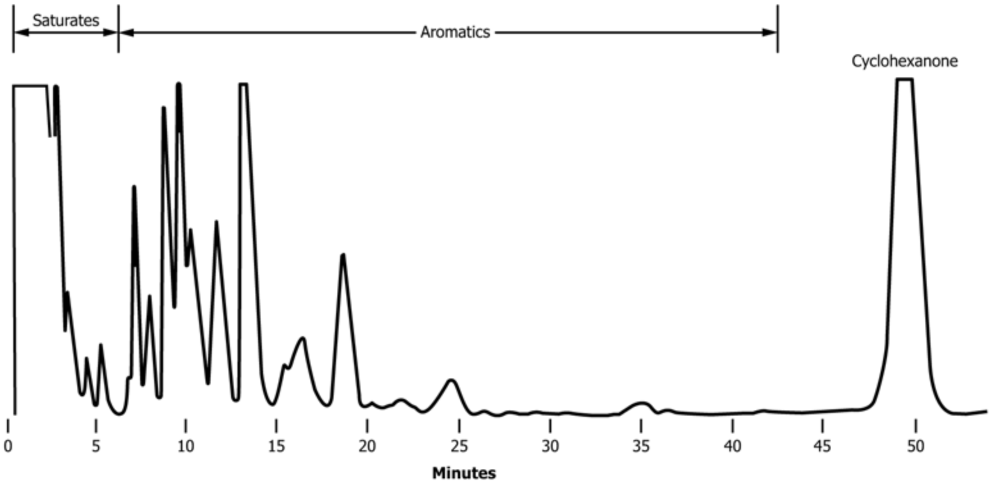

FIG. 2 Typical Packed Column Chromatogram of Mineral Spirits (Column and Conditions Described in Table 2)

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

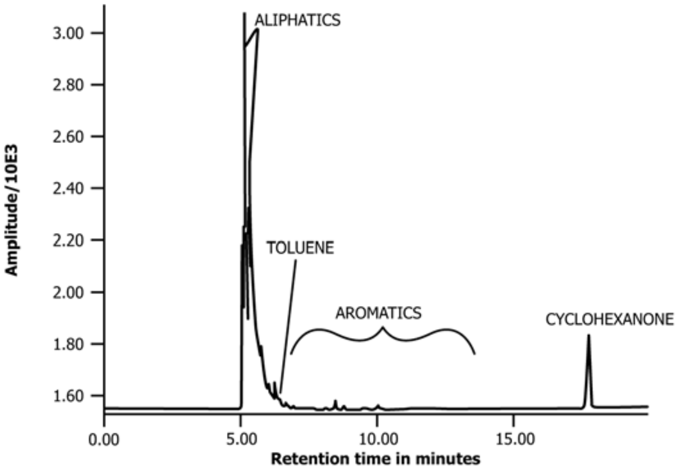

FIG. 3 Typical Capillary Chromatogram of Mineral Spirits (Column and Conditions Described in Table 3)

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,

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

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 (1⁄8 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:

$$r = \frac{A_{\mathrm{IS}}}{V_{\mathrm{IS}}} \times \frac{V_{\mathrm{a}}}{A_{\mathrm{a}}} \qquad (2)$$

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:

$$V_{\mathrm{a}} = (A_{\mathrm{a}} \times r \times 10)/(A_{\mathrm{IS}} \times 0.9) \qquad (4)$$

$$= \frac{A_{\mathrm{a}}}{A_{\mathrm{IS}}} \times r \times 11.11$$

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.

10. Report

10.1 Report the following information: concentrations of ethylbenzene, total aromatics, and C_8 plus higher aromatics (except ethylbenzene) in volume percent to the nearest 0.1 %.

11. Precision and Bias[5]

11.1 The precision estimates are based on an interlaboratory study on four samples, containing approximately 6.5, 8.5, 11.8, and 16.5 % total aromatics and 0.0, 1.0, 4.0, and 0.3 % ethylbenzene. One analyst in each of six laboratories performed duplicate determinations on different days, for a total of 48 determinations of total aromatics content and 48 determinations of ethylbenzene content. The within-laboratory coefficient of variation was found to be 1.7 % relative with 23 df, and the between-laboratories coefficient of variation was 4.4 % relative with 5 df. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

11.1.1 *Repeatability*—Two results obtained by the same operator on different days should be considered suspect if they differ by more than 5 % relative.

11.1.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 16 % relative.

11.2 *Bias*—There was no statistically significant bias of the results compared with expected values for quantitatively prepared standards. Hence, the determination of total aromatics in mineral spirits by packed column gas chromatography as described in this test method has no bias.

TEST METHOD B—ETHYLBENZENE CONTENT BY MEANS OF A RAPID PACKED COLUMN GAS CHROMATOGRAPHIC ANALYSIS

12. Apparatus

12.1 *Chromatograph*—Any gas chromatographic instrument complying with the sensitivity described in 5.1, and equipped with a thermal conductivity detector may be used.

12.2 *Column*—Any column and conditions may be used provided the system meets all the requirements of 14.3 and Section 17. The following column was used to establish the precision found in Section 17: 5.5-m (18-ft) of 6.3-mm (¼-in.) copper, aluminum, or stainless steel tubing packed with 35 % by weight of *N,N-bis* (2-cyanoethyl) formamide on 60 to 80 mesh untreated, calcined, pink diatomaceous silica (see Footnote B in Table 1).

NOTE 6—The column may be prepared in two 2.7-m (9-ft) sections and joined together, if preferred. Such columns may be obtained from most chromatography supply houses that offer packed GC columns.

12.3 *Strip Chart Recorder*—See 5.2 and 5.3.

12.4 *Micro Syringe*—See 5.4.

13. Reagents and Materials

13.1 *Aromatic Hydrocarbons*—Benzene, toluene and ethylbenzene of 99.5 mol % minimum purity (see 1.7).

13.2 *Carrier Gas*—Helium.

14. Procedure

14.1 Set the gas chromatograph instrument conditions as follows:

Detector cell temperature, °C	300
Detector cell current, mA	150
Injection port temperature, °C	300
Helium flow at exit, mL/min	110
Column temperature, °C	100

14.2 Pipet exactly 1.0 mL of toluene internal standard into a 10-mL volumetric flask. Fill to the mark with the mineral spirits sample, and mix thoroughly by inverting several times. See 1.7.

NOTE 7—Both ethyl benzene and toluene contents may be determined, if present, by using benzene as the internal standard.

14.3 Inject 3 µL of sample containing the internal standard, and chromatograph under the prescribed operating conditions. Change attenuation, if necessary, so as to measure the area of the internal standard with not less than 25 % nor more than 95 % chart deflection. Ethylbenzene will emerge in about 11 min.

14.4 Purge the column of high-boiling aromatics by raising the temperature to 130°C. After the high-boiling components emerge, reset the column temperature to 100°C.

15. Calculation

15.1 Measure the areas of the ethylbenzene and toluene internal standard peaks. See 8.1.

15.2 If different attenuations are used for the ethylbenzene and internal standard peaks, correct to a constant attenuation basis, as in 9.2.

15.3 Calculate the concentration of ethylbenzene as follows:

$$V_e = (Ae \times 10 \times 1.036)/A_{IS}$$

where:

V_e = volume % of ethylbenzene,
A_e = area of the ethylbenzene peak corrected to a constant attenuation,
10 = volume % of internal standard added,
1.036 = relative response factor for ethylbenzene, and
A_{IS} = area of the internal standard peak.

Duplicate results may be averaged, at the 95 % confidence level, if they differ by no more than 0.2 %, absolute.

NOTE 8—The suggested response factor for ethylbenzene should be verified for the particular instrument used, in accordance with the procedure described in 7.3, and with the internal standard (toluene or benzene) used for the analysis. The response factor actually determined should be used in the ethylbenzene content calculation.

16. Report

16.1 Report the following information: concentration of ethylbenzene in volume percent to the nearest 0.1 %.

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1015. Contact ASTM Customer Service at service@astm.org.

17. Precision and Bias[6]

17.1 The precision estimates are based on an interlaboratory study in which one operator in eight different laboratories analyzed two samples of mineral spirits in duplicate on two different days. The samples contained 1.0 and 8.0 % ethylbenzene, and were prepared by adding ethylbenzene to dearomatized mineral spirits. The results were analyzed in accordance with Practice E180. The within-laboratory and between-laboratories standard deviations were found at different levels of ethylbenzene content to be as follows:

	Within Laboratories		Between Laboratories	
Actual ethylbenzene content, %	1.0	8.0	1.0	8.0
Degrees of freedom	16	16	7	7
Standard deviation	0.05	0.10	0.21	0.25

Based upon these standard deviations, the following criteria should be used for judging the acceptability of results at a 95 % confidence level.

17.2 *Repeatability*—Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 0.2 % absolute at the 1 % ethylbenzene level, or by more than 0.3 % absolute at the 8 % ethylbenzene level.

17.3 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.7 % absolute at the 1 % ethylbenzene level, or by more than 0.9 % absolute at the 8 % ethylbenzene level.

17.4 *Bias*—There was no statistically significant bias of the results compared with expected values for quantitatively prepared standards. Hence, the determination of ethylbenzene in mineral spirits by packed column gas chromatography as described in this test method has no bias.

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

18. Apparatus

18.1 *Gas Chromatograph*—Any gas chromatograph equipped with a split/splitless capillary injector and flame ionization detector capable of operating at the conditions listed in Table 3 may be employed.

18.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection may be employed. Devices capable of delivering between 0.1 to 1 µL are suitable.

18.3 *Sensitivity*—The overall sensitivity of the detector shall be sufficient to detect 0.1 volume % of any aromatic compound of interest with a peak height of at least 5 times the height of the noise level.

18.4 *Column*—A 60 m × 0.25 mm inside diameter by 0.4-µm film thickness, fused silica capillary column coated with triscyanoethoxypropane (TCEP) has been found to be acceptable. Calculate the resolution in accordance with 5.1.2.2. The resolution, *R*, shall be no less than 2.0. Other columns may be used provided they meet the specified performance criteria.

18.4.1 Ethyl benzene shall be separated from *p*-xylene with a depth of the valley after ethyl benzene not less than 75 % of the ethyl benzene peak height. *P*-xylene shall be separated from cumene with the depth of the valley after *p*-xylene not less than 75 % of the *p*-xylene peak height.

NOTE 9—TCEP is a low temperature, nonbonded stationary phase. It was observed during the interlaboratory study that with continued use, significant loss of stationary phase occurred resulting in progressively shorter retention times for all peaks. As a result, this affected proper peak identification and area integration when using automated electronic data processing. Due to the observed changes in retention times with time, it is recommended that the calibration blend be run prior to any analysis. If the retention time for toluene has shifted by more than 0.1 min, recalibrate the method to reflect the shift in retention times. To achieve the maximum useful lifetime of the column, it is suggested that the oven temperature be lowered to 50°C when the column is not in use.

18.5 *Data Acquisition:*

18.5.1 *Recorder*—A recording potentiometer or equivalent with a full-scale deflection of 5 mv or less may be used. Full-scale response time should be 1 s or less to accommodate peaks eluting from a capillary column.

18.5.2 *Electronic Integration*—Any electronic data acquisition system or integration device, or both, suitable for capillary gas chromatography may be used.

18.6 *Chromatographic Conditions*—The chromatographic conditions that have been found to be particularly suitable for this test method are listed in Table 3.

19. Reagents and Materials (See Section 6)

20. Preparation of Apparatus

20.1 Install and condition the capillary column according to the instrument and column manufacturer's recommendations.

20.2 After conditioning the column, adjust the carrier gas head pressure such that an average linear velocity of 20 cm/s, measured using methane, is obtained at a column temperature of 110°C.

20.2.1 The average linear gas velocity is calculated as follows:

$$u = L/t_m \tag{5}$$

where:

u = average linear gas velocity,
L = the length of the column in cm, and
t_m = is the retention time of methane in seconds.

20.3 After setting the specified average linear gas velocity, adjust the remaining GC parameters to conform to those listed in Table 3.

21. Calibration

21.1 *Preparation of Test Blend*—Prepare a test blend as described in 7.1.

21.2 Inject the test blend into the column using the conditions specified in Table 3. Change the attenuation, if necessary,

---

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1090. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Typical Chromatographic Conditions for the Capillary Column Method

Column length	60 m
Column ID	0.25 mm
Stationary phase	TCEP
Film thickness	0.4 µm
Carrier gas	helium
Head pressure	26 psi (approximate)
Linear velocity	20 cm/s set @ 110°C
Injector	split
Split ratio	100:1
Split vent flow	65–70 mL/min
Injector temperature	220°C
Detector	FID
Detector temperature	220°C
Make-up gas	Nitrogen @ 30 mL/min
Column temperature	110°C
Sample size	1.0 µL

so that the internal standard and aromatic peaks are measured with a chart deflection of not more than 25 % nor more than 95 % of full scale for attenuated peaks. Check the column performance against the requirements given in 5.1.2.

21.3 A typical chromatogram of the test blend analyzed under the conditions listed in Table 3 is shown in Fig. 3.

21.4 *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:

$$r = \frac{A_{IS}}{V_{IS}} \times \frac{V_a}{A_a} \qquad (6)$$

where:

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

22. Procedure (See Section 8)

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

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

22.3 Using the exact instrument conditions as were used for 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 .

23. Calculation

23.1 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 10—Aromatic peaks are assumed to be all peaks, excluding the internal standard, eluting after nC_{13} in the chromatogram. C_8 plus heavier aromatics are all peaks, excluding the internal standard, that elute after toluene. Because the C_8 plus heavier aromatic compounds may not be completely resolved from each other, peak height multiplied by one half width or retention time must not be used as a means of measuring them. A sum of the peak areas measured by electronic integration is recommended.

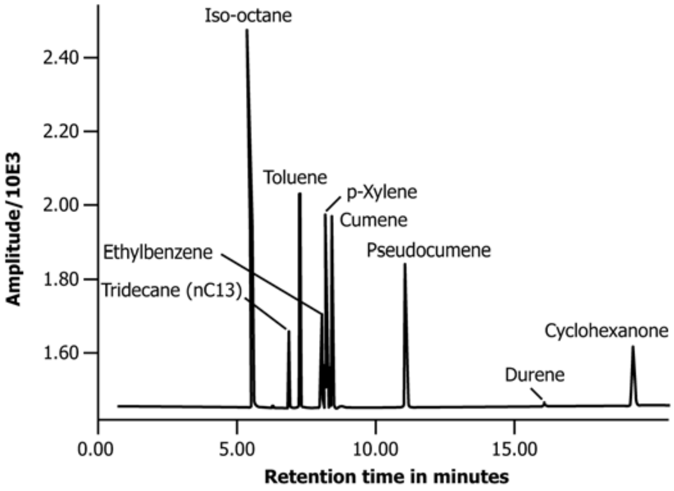

FIG. 4 Typical Capillary Chromatogram of the Calibration Test Blend (Column and Conditions Described in Table 3)

23.2 If a different attenuation is used for part of the chromatogram (strip chart recorder using manual integration techniques), correct to a constant attenuation basis by multiplying the area of the aromatic peaks by the ratio:

$$S_a/S_s \qquad (7)$$

where:

S_s = attenuation sensitivity used for the internal standard peak, and
S_a = attenuation sensitivity used for the aromatic peak area.

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

$$V_a = (A_a \times r \times 10)/(A_{IS} \times 0.9) \qquad (8)$$

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

where:

V_a = volume % of aromatic compound(s),
A_a = area of the aromatic peaks (individual, in the case of ethylbenzene, or summed, in the case of C_8 plus heavier aromatics) corrected to a constant attenuation,
r = relative response factor for the aromatic compounds,
10 = volume % of the internal standard,
A_{IS} = area of the internal standard peak, and
0.9 = factor to correct for the dilution by the internal standard.

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

24. Report

24.1 Report the following information: Concentration of ethylbenzene, total aromatics and C_8 plus heavier aromatics (except ethylbenzene) in volume percent to the nearest 0.1 %.

25. Precision and Bias[6]

25.1 *Precision*—The following criteria should be used to judge the acceptability (95 % probability level) of results obtained by this test method. The criteria were derived from a interlaboratory study among 9 laboratories utilizing a total of 8 samples, 5 of them were actual mineral spirits and three were synthetic blends used to determine bias, ranging in total aromatics content from <1 to 17 vol %. The interlaboratory study was conducted and results analyzed in accordance with the guidelines set forth in RR:D02-1007[7] and the software D2PP.[4]

25.1.1 *Ethylbenzene*—The repeatability and reproducibility values at 95 % confidence level are independent of the mean and are given as follows:

$$\text{Repeatability } (r) = 0.03 \text{ vol \%} \tag{9}$$

$$\text{Reproducibility } (R) = 0.10 \text{ vol \%}$$

25.1.2 *C_8 Aromatics (all components after ethylbenzene)*—The repeatability and reproducibility values at a 95 % confidence level are dependent on the results, and are given as follows:

$$\text{Repeatability } (r) = 0.04 \times \bar{X} \text{ vol \%} \tag{10}$$

$$\text{Reproducibility } (R) = 0.17 \times \bar{X} \text{ vol \%}$$

where $\bar{X}$ is the mean of two determinations.

25.1.3 *Total Aromatics (toluene, ethylbenzene and C_8 aromatics)*—The repeatability and reproducibility values at 95 % confidence level are dependent on the results and are given as follows:

$$\text{Repeatability } (r) = 0.02 \times \bar{X} \text{ vol \%} \tag{11}$$

$$\text{Reproducibility } (R) = 0.17 \times \bar{X} \text{ vol \%}$$

where $\bar{X}$ is the mean of two determinations.

25.2 *Bias*—There was no statistically significant bias of the results compared to expected values for quantitatively prepared standards. Hence, the determination of total aromatics in mineral spirits by capillary gas chromatography as described in this test method has no bias.

26. Keywords

26.1 aromatics in mineral spirits; ethylbenzene in mineral spirits; gas chromatography (GC); mineral spirits

---

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1007. Contact ASTM Customer Service at service@astm.org.

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D3257 – 01) that may impact the use of this standard. (Approved April 1, 2006.)

(1) Added reference to Practice E29 in the scope section.

(2) Added Practice E29 to list of Referenced Documents.