# Standard Test Method for
## Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D7096; 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 the boiling range distribution of gasoline and liquid gasoline blending components. It is applicable to petroleum products and fractions with a final boiling point of 280°C (536°F) or lower, as measured by this test method.

1.2 This test method is designed to measure the entire boiling range of gasoline and gasoline components with either high or low vapor pressure and is commonly referred to as Simulated Distillation (SimDis) by gas chromatographers.

1.3 This test method has been validated for gasoline containing ethanol. Gasolines containing other oxygenates are not specifically excluded, but they were not used in the development of this test method.

1.4 This test method can estimate the concentration of *n*-pentane and lighter saturated hydrocarbons in gasoline.

1.5 The values stated in SI units (degrees Celsius) are to be regarded as the standard. Results in degrees Fahrenheit can be obtained by simply substituting Fahrenheit boiling points in the calculation of the boiling point-retention time correlation.

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]

D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D2421 Practice for Interconversion of Analysis of $C_5$ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D4814 Specification for Automotive Spark-Ignition Engine Fuel

D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and $C_1$ to $C_4$ Alcohols in Gasoline by Gas Chromatography

D5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

## 3. Terminology

3.1 *Definitions:*

3.1.1 *area slice*, *n*—area under a chromatogram within a specified retention time interval.

3.1.2 *final boiling point (FBP)*, *n*—the point at which a cumulative volume count equal to 99.5 % of the total volume counts under the chromatogram is obtained.

3.1.3 *initial boiling point (IBP)*, *n*—the point at which a cumulative volume count equal to 0.5 % of the total volume counts under the chromatogram is obtained.

3.1.4 *relative volume response factor (RVRF)*, *n*—the volume response factor (see 3.1.8) of a component *i* relative to the volume response factor of *n*-heptane.

3.1.5 *slice time*, *n*—the retention time at the end of a given area slice.

3.1.6 *slice width*, *n*—the fixed duration (1 s, or less) of the retention time intervals into which the chromatogram is divided. It is determined from the reciprocal of the frequency used in the acquisition of data.

3.1.7 *volume count, n*—the product of a slice area (or an area under a peak) and a volume response factor.

3.1.8 *volume response factor, n*—a constant of proportionality that relates the area under a chromatogram to liquid volume.

## 4. Summary of Test Method

4.1 The sample is vaporized and transported by carrier gas into a non-polar, wide-bore capillary gas chromatographic column. The column temperature is raised at a reproducible, linear rate so as to elute the hydrocarbon components in boiling point order for measurement by a flame ionization detector. Conditions are selected such that *n*-pentane and lighter saturated hydrocarbons in the calibration mixture are resolved discretely. Linear correlation between hydrocarbon boiling point and retention time is established using a known mixture of hydrocarbons covering the boiling range expected in the sample. Area slices are converted to volume using *theoretical* hydrocarbon volume response factors. Oxygenated samples require experimental determination of oxygenate response factors.

## 5. Significance and Use

5.1 The determination of the boiling range distribution of gasoline by gas chromatographic simulated distillation provides an insight into the composition of the components from which the gasoline has been blended. Knowledge of the boiling range distribution of gasoline blending components is useful for the control of refinery processes and for the blending of finished gasoline.

5.2 The determination of the boiling range distribution of light hydrocarbon mixtures by gas chromatographic simulated distillation has better precision than the conventional distillation by Test Method D86. Additionally, this test method provides more accurate and detailed information about the composition of the light ends. The distillation data produced by this test method are similar to that which would be obtained from a cryogenic, true boiling point (15 theoretical plates) distillation.

## 6. Interferences

6.1 Ethanol or other oxygenates may coelute with hydrocarbons present in the sample. Since the response of oxygenates is substantially different from the response of hydrocarbons, response factors are used to correct the area slice for the elution interval of oxygenates.

6.2 Concentrations of *n*-pentane and lighter saturated compounds may be estimated from the analysis. However, early eluting olefins present in the gasoline samples may coelute with these compounds.

## 7. Apparatus

7.1 *Gas Chromatograph*—Any gas chromatograph (GC) designed for use with wide-bore (0.53 mm inside diameter) capillary columns, that meets the performance criteria specified in Section 11, and has the following features may be used. Typical operating conditions are shown in Table 1.

**TABLE 1 Typical Operating Conditions for Wide Bore Column Inlets**

| | | |
|---|---|---|
| Column length (m) | 30 | 15 |
| Column I.D. (mm) | 0.53 | 0.53 |
| Stationary phase | 100 % poly-dimethylsiloxane | 100 % poly-dimethylsiloxane |
| Film thickness (μm) | 5 | 5 |
| Carrier gas | helium | helium |
| Carrier flow (mL/min) | 20 | 15 |
| Auxiliary flow (mL/min) | 10 | 10 |
| Column initial temperature (°C) | 40 | 40 |
| Initial time (min) | 1 | 1 |
| Program rate (°C/min) | 25 | 20 |
| Final temperature (°C) | 265 | 230 |
| Final hold (min) | 4.00 | 2.50 |
| Injection inlet | purged-packed | purged-packed |
| Sample introduction | auto syringe injection | auto syringe injection |
| Injector temperature (°C) | 250 | 250 |
| Detector temperature (°C) | 280 | 300 |
| Hydrogen flow (mL/min) | 45 | 30 |
| Air flow (mL/min) | 450 | 300 |
| Sample size (μL) | 0.1 – 0.2 | 0.2 |
| Area slice width (s) | 0.5 – 0.2 | 0.5 – 0.2 |
| Data rate (Hz) | 2 – 5 | 2 – 5 |

**TABLE 2 Typical Operating Conditions for Capillary Column Inlet**

| | |
|---|---|
| Column length (m) | 30 |
| Column I.D. (mm) | 0.53 |
| Stationary phase | 100 % polydimethylsiloxane |
| Film thickness | 5 μm |
| Carrier gas | helium (ramped flow) |
| Carrier flow (mL/min) | 5mL/min (0.5 min) to 20mL/min @ 60mL/min |
| Column initial temperature (°C) | 40 |
| Initial time (min) | 1 |
| Program rate (°C/min) | 25 |
| Final temperature (°C) | 245 |
| Final hold (min) | 4 |
| Injection port | split |
| Sample introduction | automatic syringe injection |
| Injector temperature (°C) | 250 |
| Detector temperature (°C) | 250 |
| Hydrogen flow (mL/min) | 30 |
| Air flow (mL/min) | 300 |
| Sample size (μL) | 1 uL |
| Split ratio | 1:50 |
| Data rate | 5 Hz |

7.1.1 *Column Oven Temperature Programming*—The gas chromatograph shall be capable of linear temperature-programmed operation from –40 to 280°C at rates up to 25°C/min.

7.1.2 *Injection Port*—The injection port shall be capable of operation at temperatures required to completely volatize and transfer the sample to the GC column. Non-splitting or split/splitless vaporizing sample ports optimized for use with wide-bore capillary columns are acceptable. If using a split inlet port, it should be designed to provide a linear sample split injection.

7.1.3 *Flame Ionization Detector*—The detector shall be optimized for the use of wide-bore capillary gas chromatographic columns and shall conform to the specifications as described in Practice E594.

7.1.4 *Carrier Gas Controls*—The associated carrier gas controls shall be of sufficient precision to produce reproducible column flows in order to maintain analytical integrity.

7.1.5 *Baseline Correction*—The gas chromatograph (or another component of the gas chromatographic system) shall be

capable of subtracting the area slice of a blank run from the corresponding area slice of a sample run. This can be done internally on some gas chromatographs (baseline compensation) or externally by subtracting a stored, digitized signal from a blank run.

7.2 *Sample Introduction*—Sample introduction may be by means of a constant volume liquid sample valve or by injection with a micro syringe through a septum. An automatic sample introduction device is essential to the reproducibility of the analysis. Manual injections are not recommended. Poor injection technique can result in poor resolution. If column overload occurs, peak skewing may result, leading to variation in retention times.

7.2.1 Samples with a vapor pressure (VP) of less than 16 psia as measured by Test Method D5191, or equivalent, may be introduced into the gas chromatograph by syringe injection into a heated, vaporizing inlet. Samples with vapor pressures between 12 and 16 psia should be kept chilled (refrigerated or in a cooled sample tray) and may require injection with a cooled syringe. Samples with a vapor pressure above 16 psia should be introduced by way of a constant volume liquid sampling valve. Refer to 9.1 for sampling practices.

7.3 *Column*—Any wide bore (0.53 mm inside diameter) open tubular (capillary) column, coated with a non-polar (100 % polydimethylsiloxane) phase that meets the performance criteria of 11.3 may be used. Columns of 15 to 30 metre lengths with a stationary phase film thickness of 5.0 μm have been successfully used. With either of these columns, initial cryogenic temperatures are not necessary.

7.4 *Data Acquisition System*—A computer provided with a monitor, printer, and data acquisition software is necessary to carry out this analysis. The computer should have sufficient hardware capacity and random access memory in order to run the data acquisition program while acquiring data at a frequency of 2 to 5 Hz. The software should also be able to store the data for future recall, inspection, and analysis. The data acquisition software should be capable of presenting a real time plot. It may also be capable of controlling the operating variables of the gas chromatograph. Specialized software is necessary to obtain the boiling point distribution.

7.5 *Bulk Sample Containers*, floating piston cylinders (see 9.1.1); epoxy phenolic-lined metal cans; glass bottles with polytetrafluoroethylene-lined screw caps.

## 8. Reagents and Materials

8.1 *Calibration Mixture*—A synthetic mixture of pure liquid hydrocarbons with boiling points that encompass the boiling range of the sample shall be used for retention time determination and response factor validation. Response factors for propane, isobutane, and *n*-butane are extrapolated from the relative molar response of the *n*-paraffins. An example of a relative response factor mixture with suggested nominal composition is given in Table 3. This mixture shall be accurately prepared on a mass basis using Practice D4307 or equivalent.

8.1.1 A single calibration standard may be used for retention time-boiling point determination and response factor validation provided isopentane and heavier components are known quantitatively. Gaseous components propane, isobutane, and *n*-butane are added in small quantities (< 0.2 vol% each). These small quantities do not significantly change the concentrations of the remaining hydrocarbons. This standard would also be used for measuring performance criteria in Section 11. It may be practical to generate this standard by bubbling a small amount of gaseous propane, isobutane, and *n*-butane (**Warning**—Extremely flammable gases.) into a quantitative mixture of isopentane and heavier components.

**TABLE 3 Typical Calibration Mixture Composition and Properties of Hydrocarbons**

| Compound | BP[A] | | Relative Density[A] 15.6/15.6°C (60/60°F) | Nominal Mass% | Approx.[B] Vol% | FID[C] RVRF |
|---|---|---|---|---|---|---|
| | °C | °F | | | | |
| Propane[D] | -42.1 | -43.8 | 0.5070 | – | – | 1.394 |
| Isobutane[D] | -11.8 | 10.8 | 0.5629 | – | – | 1.241 |
| *n*-Butane[D] | -0.5 | 31.1 | 0.5840 | – | – | 1.196 |
| Isopentane | 27.8 | 82.1 | 0.6247 | 2.5 | 3.1 | 1.111 |
| *n*-Pentane | 36.1 | 96.9 | 0.6311 | 3.0 | 3.7 | 1.099 |
| 2-Methylpentane | 60.3 | 140.5 | 0.6578 | 4.0 | 4.7 | 1.050 |
| *n*-Hexane | 68.9 | 155.7 | 0.6638 | 3.0 | 3.5 | 1.040 |
| 2,4-Dimethylpentane | 80.5 | 176.9 | 0.6764 | 5.5 | 6.3 | 1.017 |
| *n*-Heptane | 99.2 | 209.2 | 0.6882 | 7.5 | 8.4 | 1.000 |
| Toluene | 110.6 | 231.1 | 0.8743 | 15.5 | 13.7 | 0.724 |
| *n*-Octane | 126.1 | 258.2 | 0.7070 | 7.0 | 7.6 | 0.971 |
| *p*-Xylene | 138.3 | 281.1 | 0.8666 | 16.0 | 14.2 | 0.736 |
| *n*-Propylbenzene | 159.2 | 318.6 | 0.8683 | 6.5 | 5.8 | 0.739 |
| *n*-Decane | 174.1 | 345.5 | 0.7342 | 4.5 | 4.7 | 0.932 |
| *n*-Butylbenzene | 183.3 | 361.9 | 0.8660 | 6.0 | 5.3 | 0.745 |
| *n*-Dodecane | 216.3 | 421.4 | 0.7527 | 3.5 | 3.6 | 0.907 |
| *n*-Tridecane | 235.5 | 455.8 | 0.7617 | 4.5 | 4.6 | 0.895 |
| *n*-Tetradecane | 253.6 | 488.4 | 0.7633 | 3.0 | 3.0 | 0.893 |
| *n*-Pentadecane | 271.1 | 519.2 | 0.7722 | 5.0 | 5.0 | 0.882 |
| *n*-Hexadecane | 287.2 | 548.3 | 0.7772 | 3.0 | 3.0 | 0.876 |

[A] Normal boiling points and relative densities (15.6/15.6°C) obtained from *Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds*, ASTM Data Series DS 4B, 1988.
[B] Volume percent is calculated as mass percent divided by specific gravity, then normalized to 100 volume percent.
[C] FID volume response factors, specified for use with this test method, are calculated from theoretical mass response factors and are relative to *n*-heptane (*RVRF* = 1).
[D] Necessary if sample is expected to contain components boiling lower than isopentane. These gases are added non-quantitatively to the liquid calibration mixture.

**TABLE 4 Typical Composition of Relative Response Mixtures Containing Oxygenates**

| Component | Mass% | Vol%[A] | Component | Mass% | Vol%* |
|---|---|---|---|---|---|
| Ethanol | 9.35 | 9.09 | | | |
| Isopentane | 2.27 | 2.80 | Isopentane | 2.37 | 2.93 |
| n-Pentane | 2.72 | 3.33 | n-Pentane | 2.84 | 3.47 |
| 2-Methylpentane | 3.63 | 4.25 | MTBE | 9.17 | 9.50 |
| n-Hexane | 2.72 | 3.16 | n-Hexane | 2.84 | 3.30 |
| 2,4-Dimethylpentane | 4.99 | 5.68 | 2,4-Dimethylpentane | 5.20 | 5.94 |
| n-Heptane | 6.80 | 7.63 | n-Heptane | 7.10 | 7.97 |
| Toluene | 14.05 | 12.44 | Toluene | 14.67 | 13.00 |
| n-Octane | 6.35 | 6.93 | n-Octane | 6.62 | 7.24 |
| p-Xylene | 14.50 | 12.93 | p-Xylene | 15.14 | 13.51 |
| n-Propylbenzene | 5.89 | 5.25 | n-Propylbenzene | 6.15 | 5.48 |
| n-Decane | 4.08 | 4.29 | n-Decane | 4.26 | 4.48 |
| Butylbenzene | 5.44 | 4.86 | Butylbenzene | 5.68 | 5.07 |
| n-Dodecane | 3.17 | 3.25 | n-Dodecane | 3.31 | 3.40 |
| n-Tridecane | 4.08 | 4.14 | n-Tridecane | 4.26 | 4.33 |
| n-Tetradecane | 2.72 | 2.74 | n-Tetradecane | 2.84 | 2.86 |
| n-Pentadecane | 4.53 | 4.53 | n-Pentadecane | 4.73 | 4.73 |
| n-Hexadecane | 2.72 | 2.70 | n-Hexadecane | 2.84 | 2.82 |

[A] Volume percent is calculated from the weight percent using specific gravity.

8.1.2 A combination of two calibration standards may also be used. A quantitative standard, containing known concentrations of isopentane and heavier compounds, is used to determine response factors. A qualitative standard, containing a wide boiling range of compounds including propane, n-butane, and isobutane is used for measuring the retention time-boiling point relationship and establishing the performance criteria outlined in Section 11.

8.2 *Calibration Mixture with Oxygenates*—When samples to be measured contain oxygenates, the calibration mixture (see 8.1) shall also contain the oxygenates. Therefore, the identity of the oxygenate(s) shall be known prior to analysis of the sample. Oxygenate content may be determined by Test Method D4815, Test Method D5599, or equivalent. Oxygenates, such as ethanol, should be added to the calibration mixture at an approximate concentration as that in the samples. This mixture is used to define the retention time boundary and relative volume response of the oxygenate to be applied to this region. For gasoline containing other oxygenates, determine if the oxygenate coelutes with any of the hydrocarbons listed in Table 3. If a coelution occurs, the coeluting hydrocarbon should not be included in the blend. Typical compositions of oxygenated blends are given in Table 4. Typical relative volume response factors, molecular weights, and densities for various oxygenated compounds are provided in Table 5.

8.3 *Carrier Gas*—Helium, 99.999 mol% pure. (**Warning**—Compressed gas under high pressure.)

8.4 *Detector Gasses*:

8.4.1 *Fuel*—Hydrogen, 99.999 mol% pure. (**Warning**—Extremely flammable gas under pressure.)

8.4.2 *Oxidant*—Air, 99.999 % free of hydrocarbons and water. (**Warning**—Compressed gas under high pressure. Supports combustion.)

8.5 *Reference Gasoline*—A gasoline sample that has been analyzed by laboratories participating in a test method cooperative study. (**Warning**—Extremely flammable liquid. Vapors are harmful if inhaled.)

**TABLE 5 Typical Relative Response Factors by Weight and Volume, Molecular Weights (MW), and Densities for Oxygenated Compounds[A]**

| Compound | MW | Relative Density[A] 15.6/15.6°C (60/60°F) | RWRF[B] | RVRF[C] |
|---|---|---|---|---|
| Methanol | 32.0 | 0.7963 | 3.008 | 2.600 |
| Ethanol | 46.1 | 0.7939 | 2.188 | 1.896 |
| tert-Butanol | 74.1 | 0.7922 | 1.298 | 1.128 |
| Methyl-tert-butyl ether (MTBE) | 88.2 | 0.7460 | 1.528 | 1.410 |
| Ethyl-tert-butyl ether (ETBE) | 102.2 | 0.7452 | 1.385 | 1.279 |
| tert-Amyl methyl ether (TAME) | 102.2 | 0.7758 | 1.339 | 1.188 |

[A] Relative densities from Test Method D4814.
[B] Weight response factors, relative to n-heptane and to be determined experimentally.
[C] Volume response factors, relative to n-heptane and to be determined experimentally.

## 9. Sampling

9.1 *Sampling from Bulk Storage*—Hydrocarbon liquids with vapor pressures of 16 psia or less may be sampled either into a floating piston cylinder or into an open container.

9.1.1 *Piston Cylinder Sampling*—Refer to Practice D3700 for instructions on transferring a representative sample of a hydrocarbon fluid from a source into a floating piston cylinder.

9.1.2 *Open Container Sampling*—Refer to Practice D4057 for instructions on manual sampling from bulk storage into open containers. Seal containers immediately after sampling and preserve the samples by storing at 0 to 4°C and maintaining that temperature until prior to analysis.

9.2 *Aliquoting Samples for Test*:

9.2.1 *Sampling from an Open Container*—Cooled samples are transferred to a pre-cooled septum vial and sealed immediately. Obtain the test specimen for analysis directly from the sealed septum vial for automatic injection.

9.2.2 *Sampling from a Floating Piston Cylinder*—Samples contained in floating piston cylinders are transferred directly to a liquid sampling valve in the gas chromatograph by means of the ballast pressure in the cylinders. Before injection, verify that ballast pressure is sufficiently high to completely liquefy the sample.

9.3 *Calibration Mixture*—The calibration mixture should be stored in the refrigerator (0 to 4°C) until ready for use. The calibration mixture shall be warmed to room temperature before sub-sampling (or analysis) to ensure that all components, particularly the $C_{12}$ to $C_{16}$ paraffins, are completely dissolved.

## 10. Preparation of Apparatus

10.1 *Chromatographic Operating Conditions*—Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Tables 1 and 2. Other conditions may be used provided they meet the criteria outlined in Section 11. Ensure that all components in the calibration mixture elute completely before the maximum oven temperature is reached.

10.2 *Column Preparation*—Follow Practice E1510 for recommended installation and conditioning procedures.

## 11. System Performance

11.1 Conformance with the performance criteria shall be established upon initial set-up of this test method and whenever any changes are made to the apparatus or the operating conditions. To check system performance, analyze in duplicate the calibration mixture (see 8.1 or 8.2), following the procedure described in Section 13. Using these results, confirm that the following criteria have been met.

11.2 *Resolution*—The system shall be able to identify the beginning and end of the elution of *n*-pentane and lighter saturated hydrocarbons from the column. The resolution (*R*) of dodecane and tridecane shall be between 7 and 15 when calculated according to Eq 1 (also see Fig. 1).

$$R = \frac{2d}{1.699\,(W_1 + W_2)} \tag{1}$$

where:
$d$ = time between the peak maxima of dodecane and tridecane, s,
$W_1$ = peak width at half height of dodecane, s, and
$W_2$ = peak width at half height of tridecane, s.

11.3 *Column Selectivity*—Using a linear least squares fit of the data for only the *n*-paraffins ($C_5$ through $C_{16}$), establish the boiling point versus retention time relationship (see 12.1.1). From this relationship, calculate the apparent boiling point of each of the aromatics in the calibration mixture from their observed retention times. The apparent boiling point of each aromatic shall not differ from its actual boiling point by more than 2°C (3°F).

11.4 *Peak Skewing*—Peak skewing can result in retention time variance. Check skewness by calculating the ratio of the segments *A/B* as shown in Eq 2, on peaks in the calibration mixture. The ratio should be between 0.8 to 1.3. A graphical example of skew is given in Fig. 2.
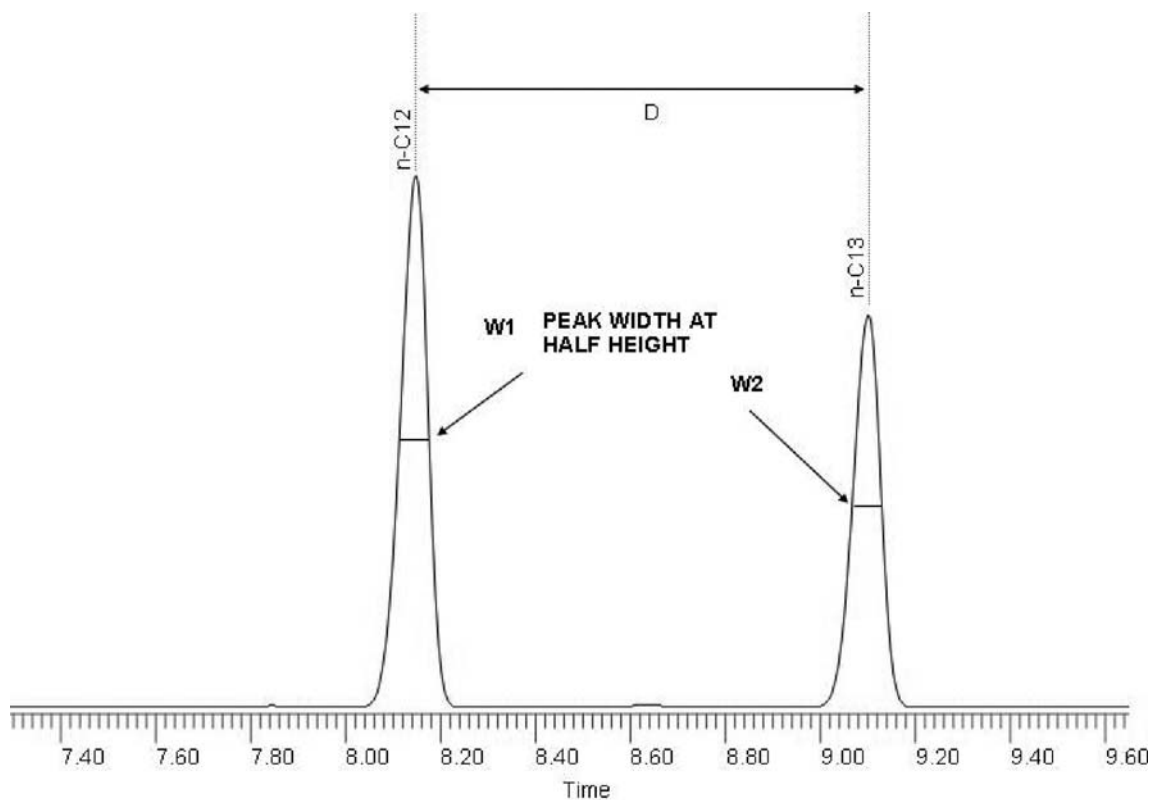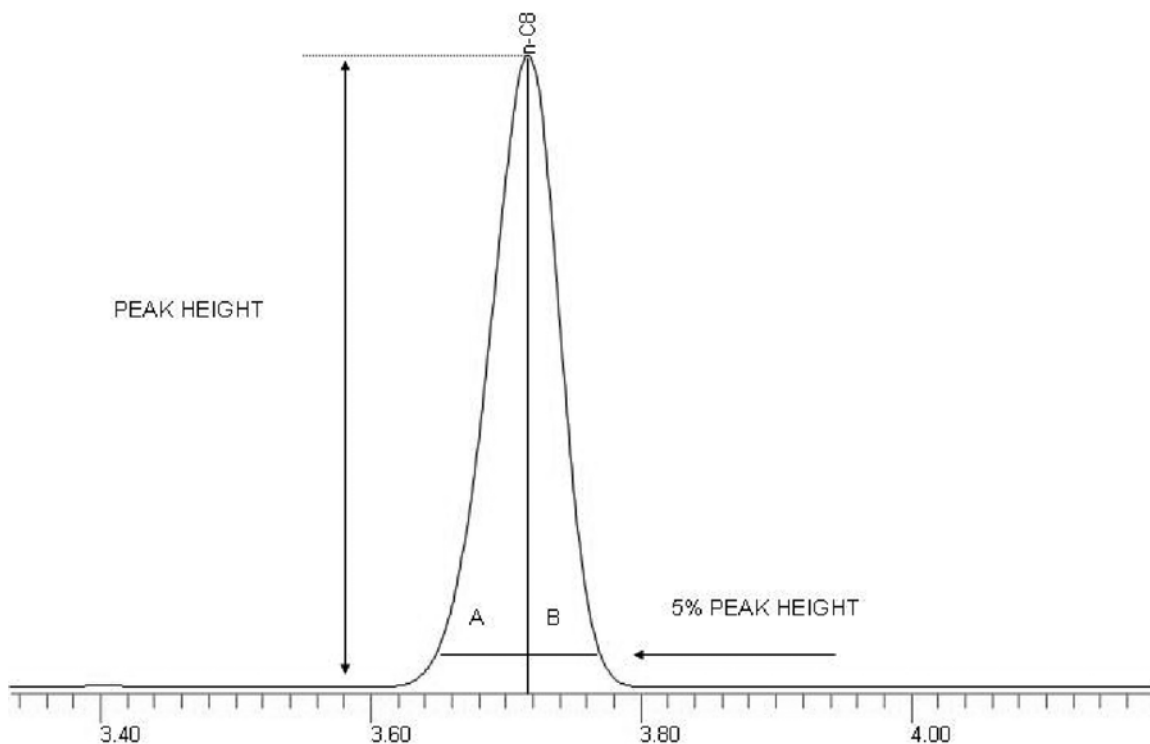


**FIG. 1 Parameters for Resolution Calculation**

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**FIG. 2 Peak Skewness**

$$S = \frac{A}{B} \quad (2)$$

where:
$A$ = segment of the peak width (at 5 % of peak height) before the peak apex, and
$B$ = segment of the peak width (at 5 % of peak height) after the peak apex.

11.5 *Retention Time Repeatability*—For consecutive analyses of the retention time mixture, the maximum difference in retention time for any component shall be 3 s (0.05 min), or less.

11.6 *Minimum Propane Retention*—Selection of column length and instrument operating conditions shall be such as to provide a minimum retention time for propane of at least 10 s (0.167 min).

11.7 *Response Factor Validation*—Refer to Practice D4626 for calculation of gas chromatographic response factors. To validate the experimental response factors, it is necessary to know the concentrations of the response factor standard components in both volume and mole percents. If conversion from one basis to another is required, a review of Practice D2421 is recommended. Appendix X4 provides sample calculations for response factor validation.

11.7.1 Volume response factors for each hydrocarbon component in the calibration mixture (not including the gaseous components) are calculated according to Eq 3. The values obtained shall agree within ±10 % of the theoretical volume response factors listed in Table 3.

$$RVRF_i = (V_i \times A_{C7}) / (V_{C7} \times A_i) \quad (3)$$

where:
$RVRF_i$ = volume response factor of component $i$, relative to the volume response factor of $n$-heptane,
$A_{C7}$ = area of $n$-heptane peak,
$V_{C7}$ = volume percent $n$-heptane,
$A_i$ = area of component $i$, and
$V_i$ = volume percent component $i$.

This same equation is used for the determination of the response factors of the oxygenate components that may be present in the gasoline.

11.7.2 The relative volume response factors of the gases are obtained by first determining the relative molar response factors of the $C_5 - C_{16}$ $n$-paraffins as calculated by Eq 4.

$$RMR_i = (A_i \times M_{C7}) / (A_{C7} \times M_i) \quad (4)$$

where:
$RMR_i$ = molar response factor of component $i$, relative to molar response factor of $n$-heptane,
$A_{C7}$ = area of $n$-heptane peak,
$M_{C7}$ = molar percent $n$-heptane,
$A_i$ = area of component $i$, and
$M_i$ = molar percent component $i$.

11.7.3 The relative molar response factor (*RMR*) is a linear function of the molecular weight for the $n$-paraffins. Thus, the $RMR_i$ is plotted versus the molecular weight. The data for the linear plot is subjected to a least squares fit. The plot should have a minimum least square fit ($r^2$) of 0.99. By extrapolation, the $RMR_i$ for propane and $n$-butane are calculated from the resulting equation. Since the molecular weight of isobutane is the same as that of $n$-butane, both compounds have the same *RMR*; however, since their densities are not the same, their

relative volume response factors will be different. Because of the low boiling point of isopentane and the difficulty in handling it on a balance, this compound is sometimes considered a gaseous component.

11.7.4 Convert the relative molar response factors of the gases to relative volume response factors utilizing the following equation (Eq 5):

$$RVR_i = (MW_i \times RMR_{C7} \times D_{C7}) / (MW_{C7} \times RMR_i \times D_i) \quad (5)$$

where:
$RVR_i$ = relative volume response factor for the gas $i$,
$MW_i$ = the molecular weight of $i$th gas,
$MW_{C7}$ = the molecular weight $n$-heptane,
$D_i$ = the density of the $i$th gas, and
$D_{C7}$ = the density of $n$-heptane.

$RMR_i$ and $RMR_{C7}$ are the relative molar response factors for $i$th gas and for $n$-heptane, respectively, as determined by Eq 4.

## 12. Calibration and Standardization

12.1 *Non-oxygenated Gasoline*—Prior to the analysis of samples, the analyzer should be calibrated to establish the boiling point versus retention time relationship. Calibration is carried out by analyzing the retention time and qualitative calibration mix(es) (see 8.1) using the procedure outlined in Section 13. Results from the calibration analyses are used to determine the following:

12.1.1 *Boiling Point—Retention Time Correlation*—Tabulate the retention time of each peak maximum and atmospheric boiling point in degrees Celsius (or Fahrenheit) of each component in the calibration mixture. Plot the retention times of the hydrocarbon components versus the corresponding atmospheric boiling point temperatures, as shown in Fig. 3. Visually verify that the calibration curve is essentially a straight line with slight curvature for the lowest boiling components.

12.1.2 *Relative Volume Response Factors Calibration*—Tabulate, for all components in the calibration mix, the retention time, area, and volume percent for each component. Utilize Eq 3 to calculate the relative volume response factor of each hydrocarbon heavier than $n$-butane. Calculate the molar percent composition of each $n$-paraffin in the mix. Plot the

molar percent of each component versus the molecular weight, as described in 11.7. Fig. 4 shows a relative molar response plot. Using Eq 4 and 5, calculate the relative volume response factors for propane, isobutane, and $n$-butane. Tabulate the relative volume response factors and compare them to the theoretical volume response factors listed in Table 3. If agreement between experimental and theoretical response factors is within 10 %, the theoretical values should be used to determine the distillation results.

NOTE 1—If the concentrations of propane, $n$-butane, and isobutane in the calibration mixture are known, differences noted between the observed and calculated molar response factors (MRF) indicate loss of light components. If a fresh calibration mixture is used, these differences can be indicative of sampling problems. Deviation of the molar response factors of the heavier components from the linear relationship could indicate problems in volatilizing the sample. Possible reasons include injection port temperature being too low, insufficient carrier gas flow, or lack of homogeneity during sampling. Fig. 4 illustrates these effects.

12.2 *Oxygenated Gasoline*—To measure gasoline blends containing oxygenates, the oxygenate shall be accounted for in the calibration. Calibration is carried out by analyzing the retention time and qualitative calibration mix(es) (see 8.2) using the procedure outlined in Section 13. Example chromatograms are presented in Figs. 5 and 6. Results from the calibration analyses are used to determine the following:

12.2.1 *Boiling Point—Retention Time Correlation*—Follow 12.1.1, omitting the oxygenate from the boiling point-retention time plot.

12.2.2 *Relative Volume Response Factor Calibration*—Follow 12.1.2, to calculate the experimental relative volume response factors of all components in the calibration mixture. Verify that the hydrocarbon response factors are within 10 % of theoretical. The oxygenate response factors should be similar to those listed in Table 5. Theoretical hydrocarbon response factors and experimental oxygenate response factors should be used for determining the distillation results.

12.3 *Control Standard Analysis*—A reference gasoline sample is used to verify both the chromatography and calculation process involved in this test method. Reference material should be analyzed daily to validate the distillation results. Following the procedures described in Section 13, analyze the
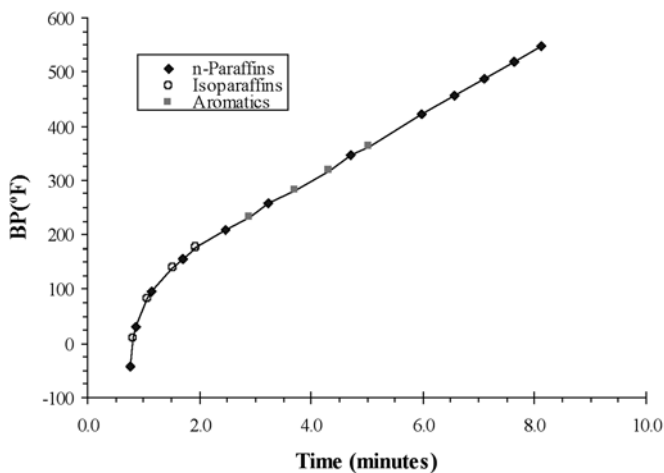


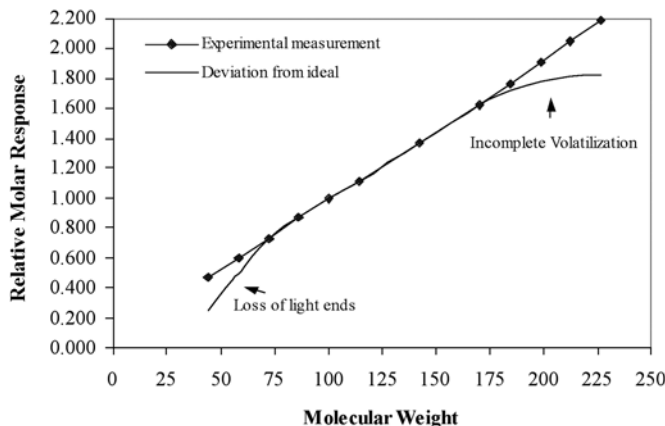FIG. 3 Boiling Point Calibration Curve



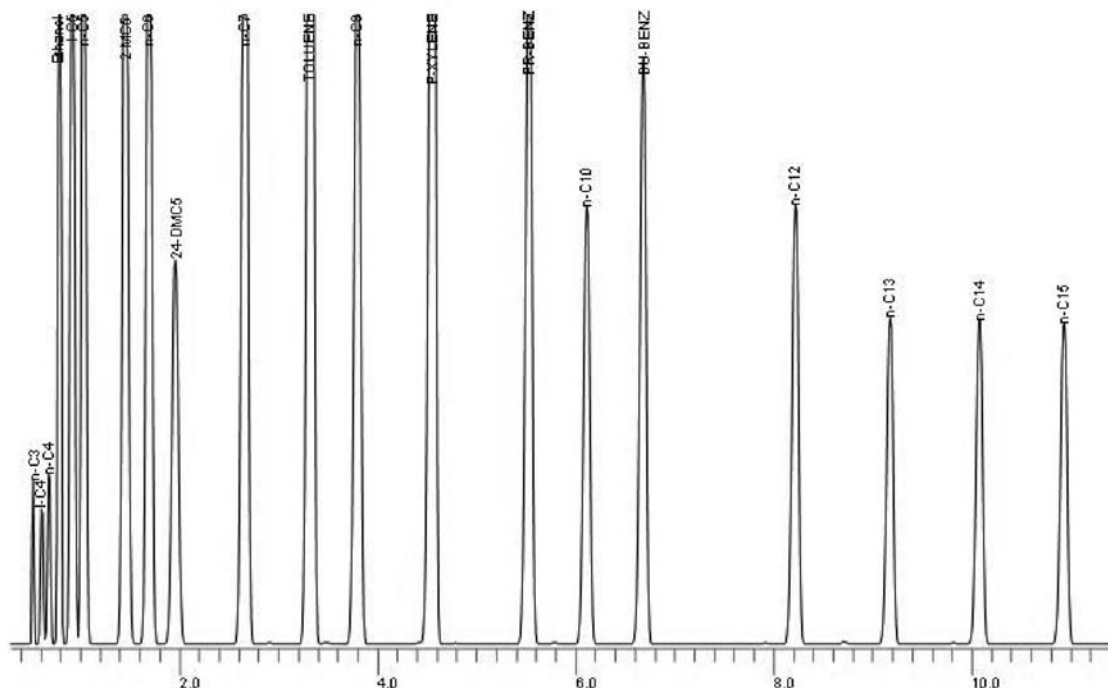FIG. 4 Relative Molar Response versus Molecular Weight for *n*-Paraffins

FIG. 5 Retention Time Standard for Gasoline Containing Ethanol

reference gasoline (see 8.5). The boiling range distribution of the reference gasoline is calculated using the algorithm specified in Section 14. Consensus values will be available after the round robin is performed.

## 13. Procedure

13.1 *Gas Chromatographic Analysis*—Set the data acquisition system in a mode that provides continuous integration of the detector signal and storage of the integral as area slices. The data acquisition rate should be between 2 to 5Hz so that the slice width is 0.5 to 0.2 s, respectively, and remains fixed throughout the analysis. Program the column to the maximum temperature to be used and perform the gas chromatographic analysis by following the sequence described below.

13.1.1 Cool the column oven to the starting temperature and allow it to equilibrate for a defined period of time (at least 2 min).

13.1.2 Inject an appropriate volume (0.1 to 0.5 μL) of the sample into the inlet of the gas chromatograph and immediately begin the temperature program. The data acquisition system shall start recording data immediately upon sample injection and, therefore, must be synchronized with the injection. Continue acquiring data until the temperature program cycle is completed and the oven begins to cool.

13.1.3 For each additional analysis, repeat 13.1.1 and 13.1.2.

13.2 *Sequence Protocol*—A recommended sequence of analyses follows. The same run conditions should be used for each sequence event.

| Event | Purpose |
|---|---|
| Bake | Remove any impurities from column. |
| Blank | Ensure successful bake-out. |
| Baseline Correction | Internal or external column compensation by by storing a blank analysis. |
| Calibration | Determine retention time versus boiling point relationship. Verify response factors. |
| Reference Gasoline Analysis | Verify that distillation results are within established acceptance criteria. |
| Sample Analyses | Determine distillation results. |
| Reference Gasoline Analysis | Verify instrument performance. |

13.3 *Baseline Correction*—A baseline compensation analysis, or baseline blank, is performed exactly like an analysis, except that no injection is made. A blank analysis shall be performed at least once per day. The blank analysis is necessary due to the usual occurrence of chromatographic baseline instability and is subtracted from sample analyses to remove any non-sample slice area from the chromatographic data. The blank analysis is typically performed prior to sample analyses, but may be useful if determined between samples or at the end of a sample sequence, to provide additional data regarding instrument operation or residual carry-over from previous sample analyses. Attention shall be given to all factors that influence baseline stability, such as column bleed, septum bleed, detector temperature control, constancy of carrier gas flow, leaks, instrument drift, and so forth. Periodic baseline blank analyses should be made, following the analysis sequence protocol, to give an indication of baseline stability.

NOTE 2—If automatic baseline correction is provided by the gas chromatograph, further correction of area slices may not be required.
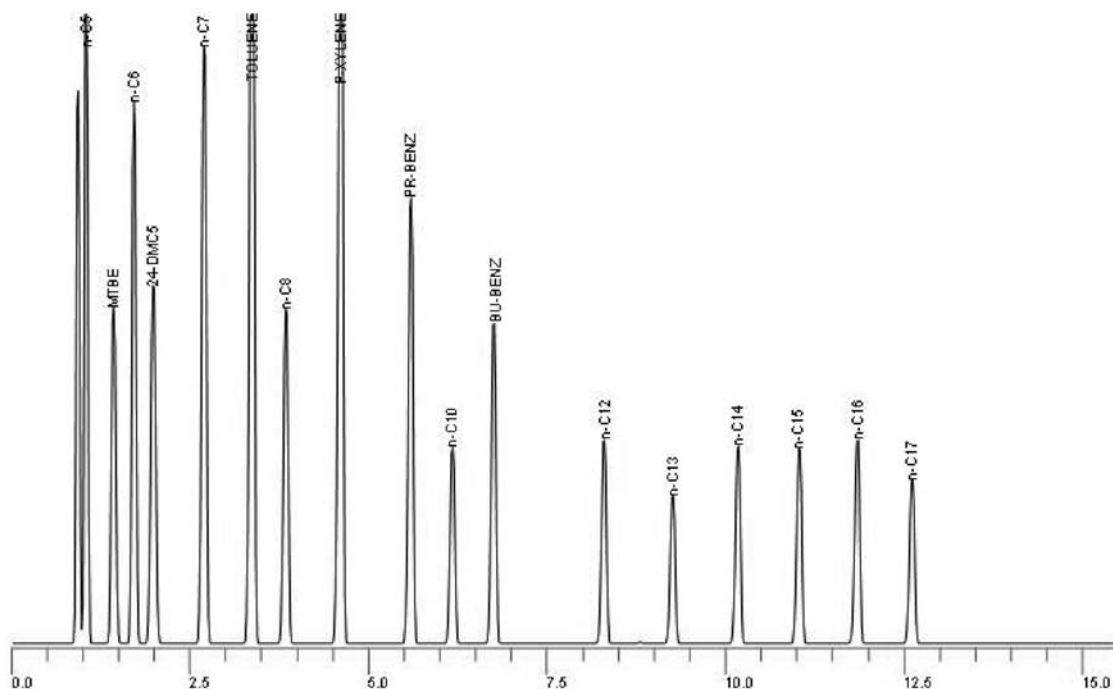
FIG. 6 Response Factor Standard for Gasoline Containing MTBE

However, if an electronic offset is added to the signal after baseline compensation, additional area slice correction may be required in the form of offset subtraction. Consult the specific instrumentation instructions to determine if an offset is applied to the signal. If the algorithm used is unclear, the slice area data can be examined to determine if further correction is necessary. Determine if any offset has been added to the compensated signal by examining the corrected area slices of those time slices that precede the elution of any chromatographic unretained substance. If these corrected area slices (representing the true baseline) deviate from zero, subtract the average of these corrected area slices from each corrected area slice in the analysis.

## 14. Calculations

14.1 *Offset Correction*—Create a sample chromatogram table consisting of the area slices and associated slice times in chronological order. Correct area slices for electronic offset as follows:

14.1.1 Throw out any of the first five area slices that are not within one standard deviation of the average and recalculate the average. This eliminates any area that is due to possible baseline upset from injection.

14.1.2 Subtract the recalculated average from every slice in the table and replace the original area slice with this offset-corrected area slice. Set any negative values to zero. If the sample chromatogram was obtained with a valid, instrument-compensated baseline (see Note 2), do not perform the baseline subtraction described in 14.2.

14.2 *Reference Baseline Subtraction*—Create a reference baseline table consisting of the area slices and associated slice times from the blank baseline run. Verify that the slice width

used to acquire the area slices of the sample chromatogram is the same as was used to acquire the area slices of the reference baseline chromatogram.

14.2.1 Correct area slices in the reference baseline table for electronic offset as directed in 14.1.

14.2.2 Subtract from each offset-corrected area slice in the sample chromatogram table the corresponding offset-corrected area slice in the reference baseline chromatogram table. Replace each entry in the sample chromatogram table with the baseline corrected value.

14.2.3 If, in the previous step, there are negative slices, set them to zero.

14.2.4 Determine the total corrected area by summing all baseline-corrected area slices in the chromatogram.

NOTE 3—See Appendix X1 for the recommended calculation algorithms for 14.3 and 14.4.

14.3 *Start of Sample Determination*—Using the baseline-corrected area slices of the sample chromatogram (14.2), determine the time at which the chromatogram first begins to deviate from the baseline.

14.4 *End of Sample Determination*—Using the baseline-corrected area slices of the sample chromatogram (14.2), determine the time at which the sample has been completely eluted and the detector signal has returned to baseline (end of sample).

14.5 *Conversion of Area to Volume Percent*—Determine the volume percent represented by each area slice through the time corresponding to the end of sample as follows:

14.5.1 Convert each corrected area slice to a volume count by multiplying by the appropriate assigned volume response factor. Use the response factor assigned to the calibration component whose retention time is closest to the slice time, as described in Appendix X3. In reformulated gasoline, the oxygenate is typically much higher in concentration than corresponding hydrocarbons that elute near the same retention time (specifically in the case of ethanol). Therefore, when an oxygenate is present, the oxygenate response factor shall be used for that time slice, even if hydrocarbons are coeluting.

14.5.2 Determine the total volume count by summing the volume counts from beginning of run to the time corresponding to the end of sample. Calculate volume percent (to the nearest 0.01 %) by dividing each individual volume count by the total volume count and multiplying by 100.

14.5.3 For each slice time, determine the *cumulative* volume percent eluted by totaling the volume percent for all slices through that time.

14.6 *Conversion of Slice Times to Boiling Points*— Determine the boiling temperature (to the nearest 0.1°C) equivalent to each slice time using linear interpolation between adjacent calibration components as directed in Appendix X2. The resultant table of cumulative volume percents versus boiling temperatures comprises the full boiling range distribution of the material analyzed and is used to produce reports in the desired format.

## 15. Report

15.1 Boiling range distribution may be reported in two formats: boiling temperature as a function of volume percent distilled or volume percent distilled as a function of boiling temperature. The former is in a format similar to conventional (pot) distillations, while the latter presents data useful for gasoline blending applications.

15.1.1 *Boiling Temperature at 1 Vol% Increments (Distillation Format)*—Search the table of cumulative volume percents (see 14.6) for the first occurrence of a volume percent equal to or greater than 0.5 %. Report the boiling temperature (to the nearest 1°C) associated with this percent as the IBP. Repeat for each increment from 1 through 99 %, and for 99.5 % (FBP).

15.1.2 *Volume Percent at 10°C Increments (Blending Format)*—Search the table of cumulative volume percents (see 14.6) for the first occurrence of a boiling temperature equal to or greater than 0°C. Report the cumulative volume percent (to the nearest 0.1 %) associated with that temperature as the volume percent distilled through 0°C. Repeat for each 10°C increment from 10°C through 280°C.

15.2 If desired, report the estimated volume percent of propane, isobutane, butane, isopentane, and pentane individually. This provides a more detailed description of the volatile components in gasoline. Propylene, butenes, and some pentenes will coelute with the above-mentioned compounds.

15.2.1 The volume percent propane is arbitrarily defined as the cumulative volume percent through a slice time half way between the propane and isobutane retention times.

15.2.2 The volume percent isobutane is determined by subtracting the volume percent propane from the cumulative volume percent through a slice time half way between the isobutane and *n*-butane retention times.

15.2.3 The volume percent *n*-butane is determined by subtracting the volume percents of propane and isobutane from the cumulative volume percent through a slice time half way between the *n*-butane and isopentane retention times.

15.2.4 The volume percent isopentane is determined by subtracting the volume percents of propane, isobutane, and *n*-butane from the cumulative volume percent through a slice time half way between the isopentane and *n*-pentane retention times.

15.2.5 The volume percent *n*-pentane is determined by subtracting the volume percent propane, isobutane, *n*-butane, and isopentane from the cumulative volume percent through a slice time half way between the *n*-pentane and 2-methylpentane retention times.

NOTE 4—Some commercial simulated distillation software reports the slice width, total area, and retention time corresponding to the end of sample for diagnostic purposes.

NOTE 5—When reporting data, specification that the boiling point distribution is calculated by this test method is recommended. This is done to distinguish the data from that of other distillation methods.

## 16. Precision and Bias

16.1 The precision of this test method is determined by the statistical examination of limited interlaboratory test results. The precision data are provisional, and further data are to be developed in an interlaboratory cooperative test program before the five-year reapproval required by the society.

16.1.1 *Repeatability*—The repeatability standard deviation was calculated from results of three laboratories analyzing the same sample. The results of the final round robin will replace the temporary data shown here:

|  | °F | °C |
|---|---|---|
| IBP | 2.3 | 1.3 |
| 2 % | 2.3 | 1.3 |
| 5 % | 2.3 | 1.3 |
| 10 % | 2.5 | 1.4 |
| 20 % | 2.4 | 1.3 |
| 30 % | 2.1 | 1.2 |
| 40 % | 2.4 | 1.3 |
| 50 % | 2.4 | 1.3 |
| 60 % | 2.7 | 1.5 |
| 70 % | 3.0 | 1.7 |
| 75 % | 3.4 | 1.9 |
| 80 % | 3.0 | 1.7 |
| 85 % | 3.1 | 1.7 |
| 90 % | 3.3 | 1.8 |
| 95 % | 4.3 | 2.4 |
| 98 % | 5.7 | 3.2 |
| FBP | 7.8 | 4.3 |

For the gases, the repeatability values are as follows:

|  | Vol% Gas |
|---|---|
| $C_3$ | 0.05 |
| $i\text{-}C_4$ | 0.04 |
| $n\text{-}C_4$ | 0.15 |
| $i\text{-}C_5$ | 0.20 |

16.1.2 *Reproducibility*—The reproducibility of this test method is being determined and will be available on or before December 2009.

16.2 *Bias*—The bias in results of this test method cannot be determined because the boiling range distribution is defined by the test method.

## 17. Keywords

17.1 blending streams; boiling range distribution; capillary gas chromatography; gas chromatography; gasoline; oxygenate

## APPENDIXES

### (Nonmandatory Information)

### X1. CALCULATION ALGORITHM

X1.1 *Required Starting Elements*:

X1.1.1 *Sample Data Array, N Area Slices*—The data shall be collected at a sampling frequency of 2 to 5 Hz. In addition, the slice width shall be such that no sample or solvent elutes in the first five slices.

X1.1.2 *Blank Data Array, N Area Slices*—The slice width for the blank and sample runs shall be identical. (A blank data array is not necessary if electronic baseline compensation is used.) The analysis conditions for blank and sample shall be identical through the point where sample analysis is terminated.

X1.1.2.1 The number of slices in the blank array shall be equal to or greater than the number of slices in the sample chromatogram. If the number of slices in the blank array is greater than the number of slices inn the sample array, then drop the extra slices in the blank array. This situation could occur if a blank run extended beyond the point where the sample analysis was terminated.

X1.1.2.2 *Retention Times of Calibration Components*—The retention time of each component in the calibration mixture shall be obtained from a processed (peak) data file form the analysis of the calibration mixture, run under identical conditions as the samples and blank.

X1.2 *Subtract Blank from Sample*:

X1.2.1 Subtract each blank area slice from the exactly corresponding sample area slice. This corrects the sample area slices for the blank. (Automatic baseline compensation is available on many instruments and is allowed by this test method. However, automatic baseline compensation may not give the same results as slice-by-slice blank subtraction.)

NOTE X1.1—If the data was acquired on an instrument using automatic baseline compensation, X1.2 shall be skipped. In this case, the zeroed and bunched sample data array contains the corrected area slices to be used in subsequent calculations.

X1.3 *Determine Start of Sample Elution Time*:

X1.3.1 Starting at the slice corresponding to the solvent exclusion time (or the first slice if no solvent was used) and working towards the end of the data array, determine where the ate of change per second between two consecutive bunched slices first exceeds 0.00001 % of the total chromatogram area.

X1.3.1.1 For determining start of sample elution, the rate of change is calculated by subtracting the area of a slice from the area of the immediately following slice and dividing by the bunched slice width in seconds.

X1.3.1.2 If (<slice>*N*+1 – <slice>*N*)/(bunched slice width) > 1E-7 · total chromatogram area, then take slice *N*+1 as the start of sample slice.

X1.3.2 Store the retention time corresponding to the start of sample elution.

X1.4 *Determine End of Sample Elution Time*:

X1.4.1 Beginning with the baseline-corrected area slices at the end of the chromatogram and working backwards, calculate the rate of change between consecutive moving averages of 3 slices using Eq X1.1:

$$\bar{O} = \frac{(\mu_{i-1} - \mu_i) \times 100}{(W)(A_{tot})} \tag{X1.1}$$

where:

$\bar{O}$ = rate of change between two consecutive moving averages of three area slices, %/s,

$\mu_{i-1}$ = average area of slices $i$-3, $i$-2, and $i$-1,

$\mu_i$ = average area of slices $i$-2, $i$-1, and $i$,

$W$ = slice width, s, and

$A_{tot}$ = total of all baseline corrected area slices in chromatogram.

X1.4.2 The slice time of the area slice ($\mu_{i-1}$) at which the rate of change of the moving averages first exceeds 0.0001 % per second is defined as the end of sample.

## X2. CALCULATION OF BOILING POINT FROM RETENTION TIME

X2.1 Use linear interpolation between adjacent entries in the calibration table (see Table 3) to determine the exact boiling point corresponding to a given retention time.

X2.1.1 Compare the given retention time ($t_x$) against each retention time in the the retention time calibration table.

X2.1.2 If the given retention time matches that of one of the calibration mixture components, use the boiling point of that component.

X2.1.3 If the given retention time does not match any of the calibration mixture components, record the retention time ($t_{n-1}$) and the boiling point ($T_{n-1}$) of the calibration mixture component that is closest to, but less than, the given retention time. Also record the retention time ($t_n$) and boiling point ($T_n$) of the

calibration mixture component that is closest to, but greater than, the given retention time.

X2.1.4 Use Eq X2.1 to calculate the boiling point ($T_x$) corresponding to the given retention time.

$$T_x = T_{n-1} + \left[ (T_{n-1}) \times \frac{(t_x - t_{n-1})}{(t_n - t_{n-1})} \right] \quad (X2.1)$$

X2.2 *Example*—Assume the retention times of octane and *m*-xylene are 4.354 min respectively and their boiling points are 125.7 and 139.1°C. The boiling point corresponding to a retention time of 4.500 min. is calculated as follows:

$$T_x = 125.7$$
$$= + [(13999.1 - 125.7) \times (4.500 - 4.354) / (4.896 - 4.354)]$$
$$= 129.3°C \quad (X2.2)$$

## X3. THEORETICAL RESPONSE FACTOR ASSIGNMENT

X3.1 Volume response factors for this test method are calculated on a theoretical basis and verified by actual analysis of a relative response calibration mixture. Theoretical response factors are used to improve the precision of this test method.

X3.2 Relative volume response factors (as shown in Table 3) are calculated for each of the components in the calibration mixture (combined gas and liquid mixtures) according to Eq X3.1.

$$RVR_i = \frac{0.577}{D_i} \times \frac{(12.011 \times C_n) + (1.008 \times H_n)}{(12.011 \times C_n)} \quad (X3.1)$$

where:

$RVR_i$ = volume response factor of component $i$, relative to *n*-heptane,

0.577 = factor to adjust relative volume response factor of *n*-heptane to 1.00,

$C_n$ = number of carbon atoms in component $i$,

$H_n$ = number of hydrogen atoms in component $i$, and

$D_i$ = density of component $i$, g/m$^3$ at 15°C.

X3.3 The volume response factor that is assigned to any given area slice is the theoretical response factor of the calibration mixture component whose retention time is closest to the slice time of the given area slice.

X3.4 *Example*—Assume the retention times of calibration mixture components; octane, *m*-xylene and nonane are 4.354 min and 5.249 min respectively. The response factor assigned to all area slices with slice times from 4.625 min (half way between octane and *m*-xylene) to 5.072 min (half way between *m*-xylene and nonane) is the relative volume response factor of *m*-xylene.

## X4. RESPONSE FACTOR VALIDATION

X4.1 The preliminary step required for validation of response factors involves tabulating calibration component concentrations in the format necessary for comparison. Since most standards are purchased in mass percent, conversion to volume and mole percent may be required.

X4.1.1 *Example*—Table X4.1 represents a typical conversion table. The ellipses indicate components not listed for brevity.

X4.1.2 Tabulate the mass percent of each component $i$. Determine the raw volume by dividing by the density of the component:

$$\text{Raw volume } i = \text{mass\% } i / \text{density } i \quad (X4.1)$$

For *n*-pentane, raw volume = 2.08 / 0.6311 = 3.29.

X4.1.3 Sum the raw volume of each component $i$. Normalize according to the following equation:

**TABLE X4.1 Example Conversion Table from Mass Percent to Volume or Mole Percent**

| Name | Relative Density (60/60) | Molecular Weight (MW) | Mass Percent (Mass%) | Raw Volume | Volume Percent (Vol%) | Raw moles | Mole Percent (Mol%) |
|---|---|---|---|---|---|---|---|
| Propane | 0.5070 | 44.10 | … | … | … | … | … |
| … | … | … | … | … | … | … | … |
| n-Pentane | 0.6311 | 72.15 | 2.08 | 3.29 | 2.54 | 0.029 | 3.24 |
| 2-Methylpentane | 0.6578 | 86.18 | 4.14 | 6.29 | 4.86 | 0.048 | 5.40 |
| n-Hexane | 0.6638 | 86.18 | 2.80 | 4.22 | 3.26 | 0.033 | 3.66 |
| 2,4-Dimethylpentane | 0.6764 | 100.21 | 5.42 | 8.01 | 6.19 | 0.054 | 6.08 |
| n-Heptane | 0.6882 | 100.21 | 7.44 | 10.81 | 8.35 | 0.074 | 8.36 |
| … | … | … | … | … | … | … | … |
| n-Hexadecane | 0.7772 | 226.45 | 3.02 | 3.89 | 3.00 | 0.013 | 1.50 |
| SUM | … | … | 100.00 | 129.50 | 100.00 | 0.889 | 100.00 |

$$\text{Normalized Volume Percent of component } i = \text{raw volume } i \,/\, \text{total volume} \times 100 \quad (X4.2)$$

For n-pentane, normalized vol% = 3.29 / 129.5 × 100 = 2.54 vol%.

X4.1.4 Calculate the raw moles for each component i:

$$\text{Raw moles } i = \text{mass\% } i \,/\, MW_i \quad (X4.3)$$

For n-pentane, raw moles = 2.08 / 72.15 = 0.029 mol.

X4.1.5 Sum the raw moles for each component in the mix. Then calculate normalized mole percent:

$$\text{Mole Percent } i = \text{raw moles } i \,/\, \text{total moles} \times 100 \quad (X4.4)$$

For n-pentane, mol% = 0.029 / 0.889 × 100 % = 3.24.

X4.2 Determine the relative volume response factors ($RVR_i$) for the components i in the quantitative calibration mix.

X4.2.1 *Example*—For a standard containing 3.03 vol% isopentane with a peak area of 9506 counts and 8.36 vol% n-heptane with 29 033 area counts, relative volume response is calculated according to Eq 3 (see 11.7):

$$RVR_i = (3.03 \times 29\,033) / (8.36 \times 9506) = 1.107 \quad (X4.5)$$

X4.3 To determine the relative molar response (*RMR*) for the gases propane, isobutane, and butane, it is necessary to first calculate the relative molar response (*RMR*) for each n-paraffin ($C_5 - C_{16}$).

X4.3.1 *Example*—Given 3.24 mol% n-pentane with 8204 area counts, relative to 8.36 mol% n-heptane with 29 033 area counts, the RMR is calculated using Eq 4 (see 11.2):

$$RMR_i = (8204 \times 8.36) / (29\,033 \times 3.24) = 0.729 \quad (X4.6)$$

X4.3.2 Tabulate the *RMR* values for each n-paraffin in the response factor calibration standard. Plot the component *RMR* values calculated above versus the molecular weight. A straight line should result. Determine the equation for the line.

X4.3.3 Substitute the molecular weights of propane and n-butane for *X* in the equation to determine the *RMR* for each.

X4.3.4 *Example*—For propane:

$$RMR = (0.0093 \times 44.10 \text{ g/mol}) + 0.0605 = 0.471 \quad (X4.7)$$

X4.3.5 From the *RMR* of the gases, calculate the *F* using Eq 5 (see 11.2). Relative density and molecular weights are given in the previous table (see 11.7).

X4.3.6 *Example*—For propane relative to n-heptane:

$$RVR_i = (44.10 \times 1.000 \times 0.6440) / (100.21 \times 0.471 \times 0.5077) = 1.268 \quad (X4.8)$$

X4.4 Tabulate the $RVR_i$ values determined for the liquids (see X3.1) and the gases (see X3.3) and compare them to theoretical. Values should vary by no more than 10 %.

X4.4.1 The percent difference is calculated as follows:

$$\%\text{difference} = \frac{(\text{Experimental } RVR_i - \text{Theoretical } RVR_i)}{\text{Theoretical} \times 100} \quad (X4.9)$$