



Designation: **D7096—16 D7096 – 19**

Standard Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography¹

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 (ϵ) 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 are to be regarded as standard. No other units of measurement are included in this standard.

1.5.1 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

- 2.1 *ASTM Standards:*²
- D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
 - D2421 Practice for Interconversion of Analysis of C₅ 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 C₁ to C₄ Alcohols in Gasoline by Gas Chromatography
 - D5191 Test Method for Vapor Pressure of Petroleum Products and Liquid Fuels (Mini Method)
 - D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection
 - D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
 - E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0H on Chromatographic Distribution Methods.

Current edition approved Jan. 1, 2016; May 1, 2019. Published February 2016; June 2019. Originally approved in 2005. Last previous edition approved in 2010 as D7096—10; D7096 – 16. DOI: 10.1520/D7096-16; 10.1520/D7096-19.

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.

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

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.

6.3 For samples containing ethanol, this test method will determine the hydrocarbon distribution. It will not simulate the azeotrope observed during physical distillation.

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.

7.1.1 *Column Oven Temperature Programming*—The gas chromatograph shall be capable of linear temperature-programmed operation from $-40\text{ }^{\circ}\text{C}$ to $280\text{ }^{\circ}\text{C}$ at rates up to $25\text{ }^{\circ}\text{C}/\text{min}$.

7.1.2 *Injection Port*—The injection port shall be capable of operation at temperatures required to completely volatilize 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.

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)	5 mL/min (0.5 min) to 20 mL/min @ 60 mL/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 µL
Split ratio	1:50
Data rate	5 Hz

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 psia 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 [Section 11.3.11](#) may be used. Columns of ~~15 metre~~ 15 m to ~~30 metre~~ 30 m 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 Hz 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 volume % 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—Warning Extremely—Extremely** flammable gases.) into a quantitative mixture of isopentane and heavier components.

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.

ASTM D7096-19

<https://standards.globalspec.com/stdn/ASTM/D07096-19> **TABLE 3 Typical Calibration Mixture Composition and Properties of Hydrocarbons** [16/astm-d7096-19](https://standards.globalspec.com/stdn/ASTM/D07096-19)

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
<i>n</i> -Butane ^D	-0.51	31.1	0.5840	—	—	1.196
Isopentane	27.8	82.1	0.6247	2.5	3.1	1.111
<i>n</i> -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
<i>n</i> -Hexane	68.7	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
<i>n</i> -Heptane	98.4	209.2	0.6882	7.5	8.4	1.000
Toluene	110.6	231.1	0.8743	15.5	13.7	0.724
<i>n</i> -Octane	125.7	258.2	0.7070	7.0	7.6	0.971
<i>p</i> -Xylene	138.4	281.1	0.8666	16.0	14.2	0.736
<i>n</i> -Propylbenzene	159.2	318.6	0.8683	6.5	5.8	0.739
<i>n</i> -Decane	174.1	345.5	0.7342	4.5	4.7	0.932
<i>n</i> -Butylbenzene	183.3	361.9	0.8660	6.0	5.3	0.745
<i>n</i> -Dodecane	216.3	421.4	0.7527	3.5	3.6	0.907
<i>n</i> -Tridecane	235.5	455.8	0.7617	4.5	4.6	0.895
<i>n</i> -Tetradecane	253.6	488.4	0.7633	3.0	3.0	0.893
<i>n</i> -Pentadecane	270.7	519.2	0.7722	5.0	5.0	0.882
<i>n</i> -Hexadecane	286.9	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. The Fahrenheit values have been rounded to the nearest 0.1 °F. The Centigrade column has been converted from the °F values prior to rounding as listed in ASTM Data Series DS 4B.

^B Volume percent is calculated as mass percent divided by specific gravity, then normalized to 100 volume percent.

^C FID volume response factors, as 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	2.37	2.93
Isopentane	2.27	2.80	<i>n</i> -Pentane	2.84	3.47
<i>n</i> -Pentane	2.72	3.33	MTBE	9.17	9.50
2-Methylpentane	3.63	4.25	<i>n</i> -Hexane	2.84	3.30
<i>n</i> -Hexane	2.72	3.16	2,4-Dimethylpentane	5.20	5.94
2,4-Dimethylpentane	4.99	5.68	<i>n</i> -Heptane	7.10	7.97
<i>n</i> -Heptane	6.80	7.63	Toluene	14.67	13.00
Toluene	14.05	12.44	<i>n</i> -Octane	6.62	7.24
<i>n</i> -Octane	6.35	6.93	<i>p</i> -Xylene	15.14	13.51
<i>p</i> -Xylene	14.50	12.93	<i>n</i> -Propylbenzene	6.15	5.48
<i>n</i> -Propylbenzene	5.89	5.25	<i>n</i> -Decane	4.26	4.48
<i>n</i> -Decane	4.08	4.29	Butylbenzene	5.68	5.07
Butylbenzene	5.44	4.86	<i>n</i> -Dodecane	3.31	3.40
<i>n</i> -Dodecane	3.17	3.25	<i>n</i> -Tridecane	4.26	4.33
<i>n</i> -Tridecane	4.08	4.14	<i>n</i> -Tetradecane	2.84	2.86
<i>n</i> -Tetradecane	2.72	2.74	<i>n</i> -Pentadecane	4.73	4.73
<i>n</i> -Pentadecane	4.53	4.53	<i>n</i> -Hexadecane	2.84	2.82
<i>n</i> -Hexadecane	2.72	2.70			

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

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~~—~~WarningCompressed~~—~~Compressed~~ gas under high pressure.)

8.4 *Detector Gasses*:

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

8.4.2 *Oxidant*—Air, 99.999 % free of hydrocarbons and water. (~~Warning~~—~~WarningCompressed~~—~~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~~—~~WarningExtremely~~—~~Extremely~~ flammable liquid. Vapors are harmful if inhaled.)

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.

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	1.90
<i>tert</i> -Butanol	74.1	0.7922	1.298	1.128
Methyl- <i>tert</i> -butyl ether (MTBE)	88.2	0.7460	1.528	1.410
Ethyl- <i>tert</i> -butyl ether (ETBE)	102.2	0.7452	1.385	1.279
<i>tert</i> -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. RVRFs from the precision study ranged from 1.86-1.92 for ethanol.

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 °C 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 °C 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 C₁₂ to C₁₆ 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 6 and 10 when calculated according to Eq 1 (also see Fig. 1).

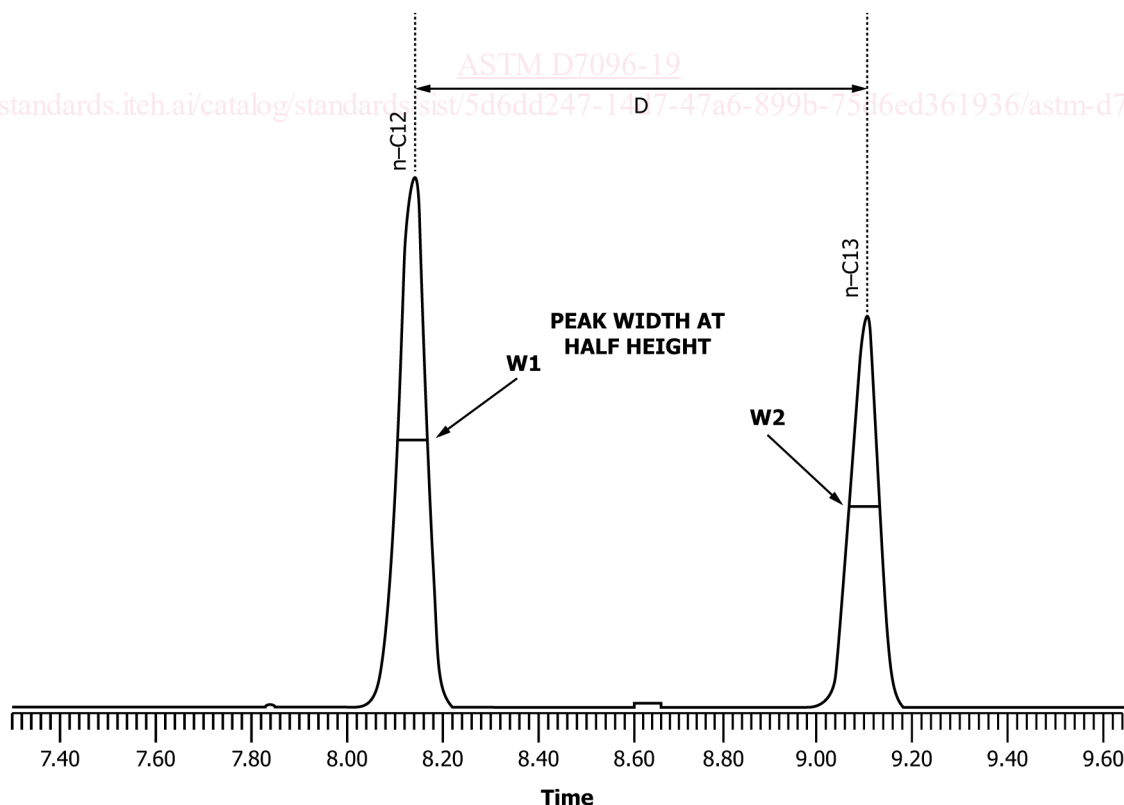


FIG. 1 Parameters for Resolution Calculation