Designation: D 2887 – 04

An American National Standard

Designation: 406

# Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography[1,2]

This standard is issued under the fixed designation D 2887; 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 Department of Defense.*

## 1. Scope*

1.1 This test method covers the determination of the boiling range distribution of petroleum products. The test method is applicable to petroleum products and fractions having a final boiling point of 538°C (1000°F) or lower at atmospheric pressure as measured by this test method. This test method is limited to samples having a boiling range greater than 55°C (100°F), and having a vapor pressure sufficiently low to permit sampling at ambient temperature.

1.2 This test method is not to be used for the analysis of gasoline samples or gasoline components. These types of samples must be analyzed by Test Method D 3710.

1.3 The values stated in SI units are to be regarded as standard. The inch-pound units given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
D 1160 Test Method for Distillation of Petroleum Products at Reduced Pressure
D 2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)
D 3710 Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4626 Practice for Calculation of Gas Chromatographic Response Factors
E 260 Practice for Packed Column Gas Chromatography
E 355 Practice for Gas Chromatography Terms and Relationships
E 516 Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography
E 594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography



## 3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E 260, E 355, and E 594.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *area slice*—the area, resulting from the integration of the chromatographic detector signal, within a specified retention time interval. In area slice mode (see 6.3.2), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

3.2.2 *corrected area slice*—an area slice corrected for baseline offset, by subtraction of the exactly corresponding area slice in a previously recorded blank (non-sample) analysis.

3.2.3 *cumulative corrected area*—the accumulated sum of corrected area slices from the beginning of the analysis through a given retention time, ignoring any non-sample area (for example, solvent).

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved May 1, 2004. Published June 2004. Originally approved in 1973. Last previous edition approved in 2003 as D 2887–03.

[2] This standard as been developed through the cooperative effort between ASTM and the Institute of Petroleum, London. The IP and ASTM logos imply that the ASTM and IP standards are technically equivalent, but their use does not imply that both standards are editorially identical.

[3] 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.**

3.2.4 *final boiling point (FBP)*—the temperature (corresponding to the retention time) at which a cumulative corrected area count equal to 99.5 % of the total sample area under the chromatogram is obtained.

3.2.5 *initial boiling point (IBP)*—the temperature (corresponding to the retention time) at which a cumulative corrected area count equal to 0.5 % of the total sample area under the chromatogram is obtained.

3.2.6 *slice rate*—the time interval used to integrate the continuous (analog) chromatographic detector response during an analysis. The slice rate is expressed in hertz (for example, integrations or slices per second).

3.2.7 *slice time*—the time associated with the end of each contiguous area slice. The slice time is equal to the slice number divided by the slice rate.

3.2.8 *total sample area*—the cumulative corrected area, from the initial area point to the final area point, where the chromatographic signal is considered to have returned to baseline after complete sample elution.

3.3 *Abbreviations:*

3.3.1 A common abbreviation of hydrocarbon compounds is to designate the number of carbon atoms in the compound. A prefix is used to indicate the carbon chain form, while a subscripted suffix denotes the number of carbon atoms (for example, normal decane = $n$-$C_{10}$; isotetradecane = $i$-$C_{14}$).

## 4. Summary of Test Method

4.1 The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A nonpolar packed or open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution can be obtained.

## 5. Significance and Use

5.1 The boiling range distribution of petroleum fractions provides an insight into the composition of feedstocks and products related to petroleum refining processes. The gas chromatographic simulation of this determination can be used to replace conventional distillation methods for control of refining operations. This test method can be used for product specification testing with the mutual agreement of interested parties.

5.2 Boiling range distributions obtained by this test method are essentially equivalent to those obtained by true boiling point (TBP) distillation (see Test Method D 2892). They are not equivalent to results from low efficiency distillations such as those obtained with Test Method D 86 or D 1160.

## 6. Apparatus

6.1 *Chromatograph*—The gas chromatograph used must have the following performance characteristics:

6.1.1 *Detector*—Either a flame ionization or a thermal conductivity detector may be used. The detector must have sufficient sensitivity to detect 1.0 % dodecane with a peak height of at least 10 % of full scale on the recorder under conditions prescribed in this test method and without loss of resolution as defined in 9.3.1. When operating at this sensitivity level, detector stability must be such that a baseline drift of not more than 1 % of full scale per hour is obtained. The detector must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. Connection of the column to the detector must be such that no temperature below the column temperature exists.

NOTE 1—It is not desirable to operate a thermal conductivity detector at a temperature higher than the maximum column temperature employed. Operation at higher temperature generally contributes to higher noise levels and greater drift and can shorten the useful life of the detector.

6.1.2 *Column Temperature Programmer*— The chromatograph must be capable of linear programmed temperature operation over a range sufficient to establish a retention time of at least 1 min for the IBP and to elute compounds up to a boiling temperature of 538°C (1000°F) before reaching the upper end of the temperature program. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.1 min (6 s) for each component in the calibration mixture described in 7.8.

6.1.3 *Cryogenic Column Cooling*—Column starting temperatures below ambient will be required if samples with IBPs of less than 93°C (200°F) are to be analyzed. This is typically provided by adding a source of either liquid carbon dioxide or liquid nitrogen, controlled through the oven temperature circuitry. Excessively low initial column temperature must be avoided to ensure that the stationary phase remains liquid. The initial temperature of the column should be only low enough to obtain a calibration curve meeting the specifications of the method.

6.1.4 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed, or provide for on-column injection with some means of programming the entire column, including the point of sample introduction, up to the maximum temperature required. Connection of the column to the sample inlet system must be such that no temperature below the column temperature exists.

6.1.5 *Flow Controllers*—The gas chromatograph must be equipped with mass flow controllers capable of maintaining carrier gas flow constant to ±1 % over the full operating temperature range of the column. The inlet pressure of the carrier gas supplied to the gas chromatograph must be sufficiently high to compensate for the increase in column backpressure as the column temperature is raised. An inlet pressure of 550 kPa (80 psig) has been found satisfactory with the packed columns described in Table 1. For open tubular columns, inlet pressures from 10 to 70 kPa (1.5 to 10 psig) have been found to be suitable.

6.1.6 *Microsyringe*—A microsyringe is needed for sample introduction.

NOTE 2—Automatic sampling devices or other sampling means, such as indium encapsulation, can be used provided: the system can be operated

**TABLE 1 Typical Operating Conditions**

| Packed Columns | 1 | 2 | 3 | 4 | Open Tabular Columns | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| Column length, m (ft) | 1.2 (4) | 1.5 (5) | 0.5 (1.5) | 0.6 (2) | Column length (m) | 7.5 | 5 | 10 |
| Column outside diameter, mm (in.) | 6.4 (1/4) | 3.2 (1/8) | 3.2 (1/8) | 6.4 (1/8) | Column inner diameter (mm) | 0.53 | 0.53 | 0.53 |
| Liquid phase | OV-1 | SE-30 | UC-W98 | SE-30 | Stationary phase | DB-1 | HP-1 | HP-1 |
| Percent liquid phase | 3 | 5 | 10 | 10 | Stationary phase thickness (m) | 1.5 | 0.88 | 2.65 |
| Support material | S[A] | G[B] | P[C] | P[C] | Carrier gas | nitrogen | helium | helium |
| Support mesh size | 60/80 | 60/80 | 80/100 | 60/80 | Carrier gas flow rate, mL/min | 30 | 12 | 12 |
| Initial column temperature, °C | −20 | −40 | −30 | −50 | Initial column temperature, °C | 40 | 35 | 35 |
| Final column temperature, °C | 360 | 350 | 360 | 390 | Final column temperature, °C | 340 | 350 | 350 |
| Programming rate,° C/min | 10 | 6.5 | 10 | 7.5 | Programming rate, °C/min | 10 | 10 | 20 |
| Carrier gas | helium | helium | $N_2$ | helium | Detector | FID | FID | FID |
| Carrier gas flow, mL/min | 40 | 30 | 25 | 60 | Detector temperature, °C | 350 | 380 | 370 |
| Detector | TC | FID | FID | TC | Injector temperature, °C | 340 | cool on-column | cool on-column |
| Detector temperature, °C | 360 | 370 | 360 | 390 | Sample size, µL | 0.5 | 1 | 0.1–0.2 |
| Injection port temperature, °C | 360 | 370 | 350 | 390 | Sample concentration mass % | 25 | 2 | neat |
| Sample size, µ | 4 | 0.3 | 1 | 5 | | | | |

[A] Diatoport S; silane treated.
[B] Chromosorb G (AW-DMS).
[C] Chromosorb P, acid washed.

at a temperature sufficiently high to completely vaporize hydrocarbons with atmospheric boiling points of 538°C (1000°F), and the sampling system is connected to the chromatographic column avoiding any cold temperature zones.

6.2 *Column*—Any column and conditions may be used that provide separation of typical petroleum hydrocarbons in order of increasing boiling point and meet the column performance requirements of 9.3.1 and 9.3.3. Successfully used columns and conditions are given in Table 1.

6.3 *Data Acquisition System*:

6.3.1 *Recorder*—A 0 to 1 mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less may be used.

6.3.2 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of an electronic integrator or computer based chromatography data system. The integrator/computer system must have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). In addition, the system must be capable of converting the continuously integrated detector signal into area slices of fixed duration. These contiguous area slices, collected for the entire analysis, are stored for later processing. The electronic range of the integrator/computer (for example, 1 V, 10 V) must be within the linear range of the detector/electrometer system used. The system must be capable of subtracting the area slice of a blank run from the corresponding area slice of a sample run.

NOTE 3—Some gas chromatographs have an algorithm built into their operating software that allows a mathematical model of the baseline profile to be stored in memory. This profile is automatically subtracted from the detector signal on subsequent sample analyses to compensate for any baseline offset. Some integration systems also store and automatically subtract a blank analysis from subsequent analytical determinations.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Liquid Phase for Columns*—Methyl silicone gums and liquids provide the proper chromatographic hydrocarbon elution characteristics for this test method.

7.3 *Solid Support for Packed Columns*— Chromatographic grade diatomaceous earth solid support material within a particle size range from 60 to 100 sieve mesh size is recommended.

7.4 *Carrier Gas*—Helium or nitrogen of high purity. (**Warning**—Helium and nitrogen are compressed gases under high pressure.) Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure must be sufficient to ensure a constant carrier gas flow rate (see 6.1.5).

7.5 *Hydrogen*—Hydrogen of high purity (for example, hydrocarbon free) is used as fuel for the flame ionization detector (FID). (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

7.6 *Air*—High purity (for example, hydrocarbon free) compressed air is used as the oxidant for the flame ionization detector (FID). (**Warning**—Compressed air is a gas under high pressure and supports combustion.)

7.7 *Column Resolution Test Mixture*—For packed columns, a nominal mixture of 1 mass % each of *n*-$C_{16}$ and *n*-$C_{18}$ paraffin in a suitable solvent, such as *n*-octane, for use in testing the column resolution. (**Warning**—*n*-octane is flammable and harmful if inhaled.) The calibration mixture specified in 7.8.2 may be used as a suitable alternative, provided the



[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Boiling Points of Normal Paraffins[A,B]

| Carbon Number | Boiling Point, °C | Boiling Point, °F | Carbon Number | Boiling Point, °C | Boiling Point, °F |
|---|---|---|---|---|---|
| 1 | −162 | −259 | 23 | 380 | 716 |
| 2 | −89 | −127 | 24 | 391 | 736 |
| 3 | −42 | −44 | 25 | 402 | 755 |
| 4 | 0 | 31 | 26 | 412 | 774 |
| 5 | 36 | 97 | 27 | 422 | 791 |
| 6 | 69 | 156 | 28 | 431 | 808 |
| 7 | 98 | 209 | 29 | 440 | 825 |
| 8 | 126 | 258 | 30 | 449 | 840 |
| 9 | 151 | 303 | 31 | 458 | 856 |
| 10 | 174 | 345 | 32 | 466 | 870 |
| 11 | 196 | 385 | 33 | 474 | 885 |
| 12 | 216 | 421 | 34 | 481 | 898 |
| 13 | 235 | 456 | 35 | 489 | 912 |
| 14 | 254 | 488 | 36 | 496 | 925 |
| 15 | 271 | 519 | 37 | 503 | 937 |
| 16 | 287 | 548 | 38 | 509 | 948 |
| 17 | 302 | 576 | 39 | 516 | 961 |
| 18 | 316 | 601 | 40 | 522 | 972 |
| 19 | 330 | 626 | 41 | 528 | 982 |
| 20 | 344 | 651 | 42 | 534 | 993 |
| 21 | 356 | 674 | 43 | 540 | 1004 |
| 22 | 369 | 695 | 44 | 545 | 1013 |

[A] API Project 44, October 31, 1972 is believed to have provided the original normal paraffin boiling point data that are listed in Table 2. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D 2887 have changed, and they are no longer equivalent. Table 2 represents the current normal paraffin boiling point values accepted by Subcommittee D02.04 and found in all test methods under the jurisdiction of Section D02.04.0H.

[B] Test Method D 2887 has traditionally used *n*-paraffin boiling points rounded to the nearest whole degree for calibration. The boiling points listed in Table 2 are correct to the nearest whole number in both degrees Celsius and degrees Fahrenheit. However, if a conversion is made from one unit to the other and then rounded to a whole number, the result will not agree with the table value for a few carbon numbers. For example, the boiling point of *n*-heptane is 98.425°C, which is correctly rounded to 98°C in the table. However, converting 98.425°C gives 209.165°F, which rounds to 209°F, while converting 98°C gives 208.4°F, which rounds to 208°F. Carbon numbers 2, 4, 7, 8, 9, 13, 14, 15, 16, 25, 27, and 32 are affected by rounding.



concentrations of the *n*-$C_{16}$ and *n*-$C_{18}$ components are nominally 1.0 mass % each. For open tubular columns, use the mixture specified in 7.8.3.

7.8 *Calibration Mixture*—An accurately weighed mixture of approximately equal mass quantities of *n*-hydrocarbons dissolved in carbon disulfide ($CS_2$). (**Warning**—Carbon disulfide is extremely volatile, flammable, and toxic.) The mixture shall cover the boiling range from *n*-$C_5$ to *n*-$C_{44}$, but does not need to include every carbon number (see Note 4).

7.8.1 At least one compound in the mixture must have a boiling point lower than the IBP of the sample and at least one compound in the mixture must have a boiling point higher than the FBP of the sample. Boiling points of *n*-paraffins are listed in Table 2.

7.8.1.1 If necessary, for the calibration mixture to have a compound with a boiling point below the IBP of the sample, propane or butane can be added to the calibration mixture, non-quantitatively, by bubbling the gaseous compound into the calibration mixture in a septum sealed vial using a gas syringe.

NOTE 4—Calibration mixtures containing normal paraffins with the carbon numbers 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 20, 24, 28, 32, 36, 40, and 44 have been found to provide a sufficient number of points to generate a reliable calibration curve.

7.8.2 *Packed Columns*—The final concentration should be approximately ten parts of the *n*-paraffin mixture to one hundred parts of $CS_2$.

7.8.3 *Open Tubular Columns*—The final concentration should be approximately one part of the *n*-paraffin mixture to one hundred parts of $CS_2$.

7.9 *Reference Gas Oil No. 1*—A reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in Table 3.

## 8. Sampling

8.1 Samples to be analyzed by this test method must be obtained using the procedures outlined in Practice D 4057.

8.2 The test specimen to be analyzed must be homogeneous and free of dust or undissolved material.

## 9. Preparation of Apparatus

9.1 *Chromatograph*—Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1.

9.1.1 When a FID is used, regularly remove the deposits formed in the detector from combustion of the silicone liquid phase decomposition products. These deposits will change the response characteristics of the detector.

9.1.2 If the sample inlet system is heated above 300°C (572°F), a blank analysis must be made after a new septum is installed to ensure that no extraneous detector response is produced by septum bleed. At the sensitivity levels commonly employed in this test method, conditioning of the septum at the operating temperature of the sample inlet system for several hours will minimize this problem. A recommended practice is to change the septum at the end of a series of analyses rather than at the beginning of the series.

9.2 *Column Preparation*:

9.2.1 *Packed Columns*—Any satisfactory method that will produce a column meeting the requirements of 9.3.1 and 9.3.3 can be used. In general, use liquid phase loadings of 3 to 10 %. Condition the column at the maximum operating temperature to reduce baseline shifts due to bleeding of the column substrate. The column can be conditioned very rapidly and effectively using the following procedure:

9.2.1.1 Connect the column to the inlet but leave the detector end free.

9.2.1.2 Purge the column thoroughly at ambient temperature with carrier gas.

9.2.1.3 Turn off the carrier gas and allow the column to depressurize completely.

9.2.1.4 Seal off the open end (detector) of the column with an appropriate fitting.

9.2.1.5 Raise the column temperature to the maximum operating temperature.

9.2.1.6 Hold the column at this temperature for at least 1 h with no flow through the column.

9.2.1.7 Cool the column to ambient temperature.

9.2.1.8 Remove the cap from the detector end of the column and turn the carrier gas back on.

TABLE 3 Test Method D 2887 Reference Gas Oil No. 1[A]

| % Off | Batch 1 | | Batch 2 | | Allowable Difference | |
|---|---|---|---|---|---|---|
| | °C | °F | °C | °F | °C | °F |
| IBP | 114 | 238 | 115 | 240 | 7.6 | 13.7 |
| 5 | 143 | 289 | 151 | 304 | 3.8 | 6.8 |
| 10 | 169 | 336 | 176 | 348 | 4.1 | 7.4 |
| 15 | 196 | 384 | 201 | 393 | 4.5 | 8.1 |
| 20 | 221 | 429 | 224 | 435 | 4.9 | 8.7 |
| 25 | | | 243 | 470 | | |
| 30 | 258 | 496 | 259 | 499 | 4.7 | 8.4 |
| 35 | | | 275 | 527 | | |
| 40 | 287 | 548 | 289 | 552 | 4.3 | 7.7 |
| 45 | | | 302 | 576 | | |
| 50 | 312 | 594 | 312 | 594 | 4.3 | 7.7 |
| 55 | | | 321 | 611 | | |
| 60 | 332 | 629 | 332 | 629 | 4.3 | 7.7 |
| 65 | 343 | 649 | 343 | 649 | | |
| 70 | 354 | 669 | 354 | 668 | 4.3 | 7.7 |
| 75 | 364 | 688 | 365 | 690 | | |
| 80 | 376 | 709 | 378 | 712 | 4.3 | 7.7 |
| 85 | 389 | 732 | 391 | 736 | | |
| 90 | 404 | 759 | 407 | 764 | 4.3 | 7.7 |
| 95 | 425 | 797 | 428 | 803 | 5.0 | 9.0 |
| FBP | 475 | 887 | 475 | 888 | 11.8 | 21.2 |

[A] Consensus results for Batch 2 obtained from 30 laboratories in 1995.[10]

9.2.1.9 Program the column temperature up to the maximum several times with normal carrier gas flow. Connect the free end of the column to the detector.

9.2.1.10 An alternative method of column conditioning that has been found effective for columns with an initial loading of 10 % liquid phase consists of purging the column with carrier gas at the normal flow rate while holding the column at the maximum operating temperature for 12 to 16 h, while detached from the detector.

9.2.2 *Open Tubular Columns*—Open tubular columns with cross-linked and bonded stationary phases are available from many manufacturers and are usually pre-conditioned. These columns have much lower column bleed than packed columns. Column conditioning is less critical with these columns but some conditioning may be necessary. The column can be conditioned very rapidly and effectively using the following procedure.

9.2.2.1 Once the open tubular column has been properly installed into the gas chromatograph and tested to be leak free, set the column and detector gas flows. Before heating the column, allow the system to purge with carrier gas at ambient temperature for at least 30 min.

9.2.2.2 Increase the oven temperature about 5 to 10°C per minute to the final operating temperature and hold for about 30 min.

9.2.2.3 Cycle the gas chromatograph several times through its temperature program until a stable baseline is obtained.

9.3 *System Performance Specification*:

9.3.1 *Column Resolution*—The column resolution, influenced by both the column physical parameters and operating conditions, affects the overall determination of boiling range distribution. Resolution is therefore specified to maintain equivalence between different systems (laboratories) employing this test method. Resolution is determined using Eq 1 and the $C_{16}$ and $C_{18}$ paraffins from a column resolution test mixture analysis (see 7.7 and Section 10), and is illustrated in Fig. 1. Resolution ($R$) should be at least three, using the identical conditions employed for sample analyses:

$$R = 2(t_2 - t_1) / [1.699(w_2 + w_1)] \quad (1)$$

where:
$R$ = resolution,
$t_1$ = time(s) for the $n$-$C_{16}$ peak maximum,
$t_2$ = time(s) for the $n$-$C_{18}$ peak maximum,
$w_1$ = peak width(s), at half height, of the $n$-$C_{16}$ peak, and
$w_2$ = peak width(s), at half height, of the $n$-$C_{18}$ peak.

9.3.2 *Detector Response Calibration*— This test method assumes that the detector response to petroleum hydrocarbons is proportional to the mass of individual components. This must be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the calibration mixture using the identical procedure to be used for the analysis of samples (see Section 10). Calculate the relative response factor for each *n*-paraffin (relative to *n*-decane) in accordance with Practice D 4626 and Eq 2:

$$F_n = (M_n / A_n) / (M_{10} / A_{10}) \quad (2)$$

where:
$F_n$ = relative response factor,
$M_n$ = mass of the *n*-paraffin in the mixture,
$A_n$ = peak area of the *n*-paraffin in the mixture,
$M_{10}$ = mass of the *n*-decane in the mixture, and
$A_{10}$ = peak area of the *n*-decane in the mixture.

The relative response factor ($F_n$) of each *n*-paraffin must not deviate from unity (1) by more than ±10 %.

9.3.3 *Column Elution Characteristics*— The column material, stationary phase, or other parameters can affect the elution order of non-paraffinic sample components, resulting in deviations from a TBP versus retention time relationship. If stationary phases other than those referenced in 7.3 are used, the retention times of a few alkylbenzenes (for example, *o*-xylene, *n*-butyl-benzene, 1,3,5-triisopropylbenzene, *n*-decyl-benzene,

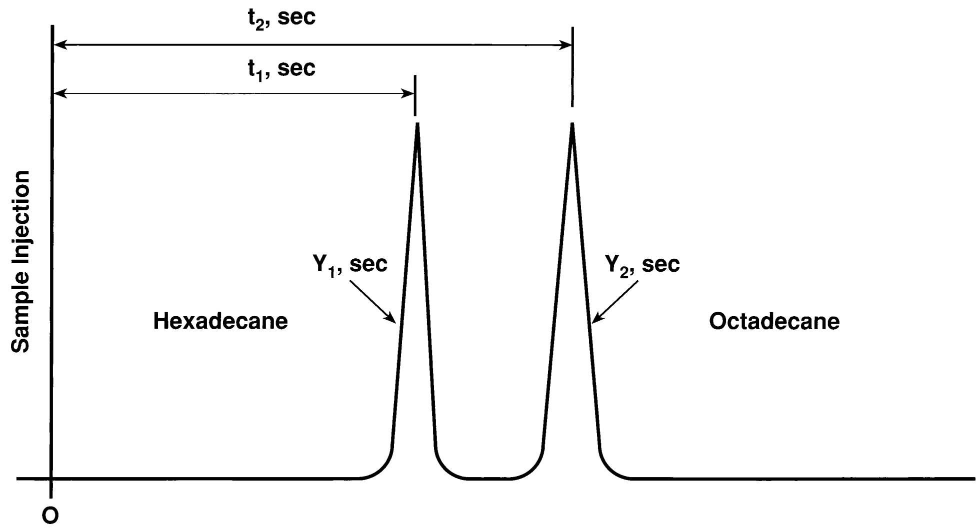


FIG. 1 Column Resolution Parameters

and tetradecylbenzene) across the boiling range should be analyzed to make certain that the column is separating in accordance with the boiling point order (see Appendix X1).

## 10. Calibration and Standardization

10.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule will include cooling the column oven to the initial starting temperature, equilibration time, sample injection and system start, analysis, and final upper temperature hold time.

10.1.1 After chromatographic conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used and hold that temperature for the selected time. Following the analysis sequence protocol, cool the column to the initial starting temperature.

10.1.2 During the cool down and equilibration time, ready the integrator/computer system. If a retention time or detector response calibration is being performed, use the peak detection mode. For samples and baseline compensation determinations, use the area slice mode of integration. The recommended slice rate for this test method is 1.0 Hz (one slice per second). Other slice rates may be used if within the limits of 0.02 and 0.2 % of the retention time of the final calibration component ($C_{44}$). Larger slice rates may be used, as may be required for other reasons, if provision is made to accumulate (bunch) the slice data to within these limits prior to determination of the boiling range distribution.

10.1.3 At the exact time set by the schedule, inject either the calibration mixture or sample into the chromatograph; or make no injection (baseline blank). At the time of injection, start the chromatograph time cycle and the integrator/computer data acquisition. Follow the analysis sequence protocol for all subsequent repetitive analyses or calibrations. Since complete resolution of sample peaks is not expected, do not change the detector sensitivity setting during the analysis.

10.2 *Baseline Compensation Analysis*—A baseline compensation analysis, or baseline blank, is performed exactly like an analysis except no injection is made. A blank analysis must 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 nonsample 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 sample carryover from previous sample analyses. Attention must 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 5—If automatic baseline correction (see Note 3) is provided by the gas chromatograph, further correction of area slices may not be required. 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.

10.3 *Retention Time Versus Boiling Point Calibration*—A retention time versus boiling point calibration must be performed on the same day that analyses are performed. Inject an appropriate aliquot (0.2 to 2.0 µL) of the calibration mixture (see 7.8) into the chromatograph, using the analysis sequence protocol. Obtain a normal (peak detection) data record in order to determine the peak retention times and the peak areas for each component. Collect a time slice area record if a boiling range distribution report is desired.

10.3.1 Inspect the chromatogram of the calibration mixture for evidence of skewed (non-Gaussian shaped) peaks. Skewness is often an indication of overloading the sample capacity