Standard Test Method for
Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography[1]

This standard is issued under the fixed designation D 3710; 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.

ϵ^1 Note—Warning statements were made part of the text in November 1999.

1. Scope

1.1 This test method covers the determination of the boiling range distribution of gasoline and gasoline components. This test method is applicable to petroleum products and fractions with a final boiling point of 500°F (260°C) 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 Reid vapor pressure and is commonly referred to as gas chromatography (GC) distillation (GCD).

1.3 This test method has not been validated for gasolines containing oxygenated compounds (for example, alcohols or ethers).

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

1.5 *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.* For specific hazard statements, see Note 9 and 7.2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure[2]

D 323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)[2]

D 1265 Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method)[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

3. Terminology

3.1 *Definitions:*

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

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

3.1.3 *relative molar response*—the measured area of a compound divided by the moles present in the synthetic mixture relative to an arbitrarily chosen component.

3.1.4 *response factor*—a constant of proportionality that converts area to liquid volume.

3.1.5 *system noise*—the difference between the maximum and minimum area readings per second for the first 20 area readings in the blank run.

3.1.6 *volume count*—the product of the area under a peak and a response factor.

4. Summary of Test Method

4.1 The sample is introduced into a gas chromatographic column which separates hydrocarbons in boiling point order. Conditions are selected so as to measure isopentane and lighter saturates discretely. Normal pentane and heavier compounds are not completely resolved but are measured as pseudo components of narrow boiling range. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data the boiling range distribution of the sample is obtained.

5. Significance and Use

5.1 The determination of the boiling range distribution of gasoline by GC distillation provides an insight into the composition of the components from which the gasoline has been blended. This insight also provides essential data necessary to calculate the vapor pressure of gasoline, which has been traditionally determined by Test Method D 323. In addition, the

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0H on Chromatographic Methods.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

Test Method D 86 distillation curve can be predicted using GCD data. See Annex A1.

5.2 The GCD method facilitates on-line controls at the refinery, and its results offer improved means of describing several car performance parameters. These parameters include: (*1*) car-starting index, (*2*) vapor-lock index or vapor-liquid ratio, and (*3*) warm-up index. The car-starting and vapor-lock indexes have been found to be mostly affected by the front end of the Test Method D 86 distillation curve (up to about 200°F (93°C)). The warm-up index is affected by the middle and to a lesser extent by the back end of the Test Method D 86 curve, that is, the temperatures corresponding to the 50 to 90 % off range. Since the boiling range distribution provides fundamental information on composition, an improved expression for the above performance parameters may be worked out, even when the boiling range distribution curve is not smooth. Currently, car performance cannot be assessed accurately under such conditions.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph may be used that meets the performance requirements in Section 8. Place in service in accordance with manufacturer's instructions. Typical operating conditions are shown in Table 1.

6.1.1 *Detector*—Either a thermal conductivity or a flame ionization detector may be used. Detector stability must be such that the sensitivity and baseline drift requirements as defined in Section 8 are met. The detector also must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed, and it must be connected to the column so as to avoid any cold spots.

Note 1—Care must be taken that the sample size chosen does not allow some peaks to exceed the linear range of the detector. This is especially critical with the flame ionization detector. With thermal conductivity detectors, sample sizes of the order of 1 to 5 μL generally are satisfactory. With flame ionization detectors, the sample size should not exceed 1 μL.

Note 2—It is not desirable to operate the detector at temperatures much higher than the maximum column temperature employed. Operation at higher temperatures only serves to shorten the useful life of the detector, and generally contributes to higher noise levels and greater drift.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of program temperature operation over a range sufficient to establish a retention time of at least 15 s for propane and of allowing elution of the entire sample within a reasonable time period. Subambient capability may be required. The programming rate must be sufficiently reproducible to meet the requirements of 8.7.

Note 3—If the column is operated at subambient temperature, 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 this test method.

6.1.3 *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 on-column injection with some means of programming the entire column, including point of sample introduction up to the maximum temperature required. The sample inlet system must be connected to the chromatographic column so as to avoid any cold spots.

6.1.4 *Flow Controllers*—Chromatographs must be equipped with constant-flow controllers capable of holding carrier gas flow constant to ±1 % over the full operating temperature range.

6.2 *Sample Introduction*—Sample introduction may be either by means of a constant-volume liquid sample valve or by injection with a microsyringe through a septum. If the sample is injected manually, cool the syringe to 0 to 4°C (32 to 40°F) before taking the sample from the sample vial.

Note 4—Automatic liquid-sampling devices or other sampling means, such as sealed septum-capped vials, may be used, provided no loss of light ends occurs. The system must be operated at a temperature sufficiently

TABLE 1 Gas Chromatography Column and Conditions

Column:					
Liquid phase, material	UCW-982	Supelco 2100	UCW-98	OV-101	UCW-98
weight %	10	20	10	10	10
Solid support, material	Chromosorb P	Chromosorb W	Chromosorb G	Chromosorb P	Supelcoport
mesh size	80/100	80/100	60/80	60/80	80/100
Length, m (ft)	0.5 (1.5)	1.5 (5)	0.9 (3)	1.2 (4)	1.5 (5)
Outside diameter, mm (in.)	6.4 (1/4)	3.2 (1/5)	6.4 (1/4)	3.2 (1/8)	3.2 (1/8)
Temperatures:					
Initial column temperature, °C	−30	40	−20	0	0
Final column temperature, °C	250	250	200	250	230
Detector temperature, °C	250	250	345	250	250
Injection zone temperature, °C	250	300	345	250	230
Operating Variables:					
Program rate, °C/min	10.6	16	10	15	16
Carrier gas	He	He	He	He	He
flow rate, cm³/min	50	30	60	29	30
Sample size, μL	3	2	3	2	1
Detector voltage (or mA)	150 mA	160 mA	135 mA	...	175 mA
Instrument:					
Detector type	TC	TC	TC	TC	TC
Sampling system	automatic syringe	syringe	syringe	valve	valve
Area measurement method	integrating A/D	integrating A/D	integrating A/D	time slice	time slice
Time slices per second	2	1/2	5	5	1/2

high to vaporize completely hydrocarbons with an atmospheric boiling point of 500°F (260°C), and the sampling system must be connected to the chromatographic column so as to avoid any cold spots.

6.3 *Recorder*—A recording potentiometer or equivalent with a full-scale response time of 2 s or less may be used.

6.4 *Column*—Any column and conditions may be used, provided, under the conditions of the test method, separations are in order of boiling points and the column meets the performance requirements in Section 8. See Table 1 for columns and conditions that have been used successfully. Since a stable baseline is an essential requirement of this test method, provisions must be made to compensate for column bleed. Traditionally this is done by using matching dual columns and detectors. At best, this procedure is only marginally successful. An even more satisfactory procedure is to record the area profile of the column bleed during a blank run, and subtract this profile from subsequent sample runs, as outlined in 11.1.

6.4.1 *Column Preparation*—Any satisfactory method, used in the practice of the art, that will produce a column meeting the requirements of Section 8, may be used. The column must be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of column substrate.

NOTE 5—The column can be conditioned very rapidly and effectively by the following procedure:

(*1*) Disconnect column from detector.

(*2*) Purge the column thoroughly at ambient temperature with carrier gas.

(*3*) Turn off the carrier gas and allow the column to depressurize completely.

(*4*) Raise the column temperature to the maximum operating temperature and hold at this temperature for at least 1 h with no flow through the column.

(*5*) Cool the column to at least 100°C before turning on carrier gas again.

(*6*) Program the column temperature up to the maximum several times with normal carrier gas flow. The column then should be ready for use.

NOTE 6—An alternative method of column conditioning, which 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 maximum operating temperature for 12 to 16 h.

6.5 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of a computer, or automatic operation can be achieved with electronic integration. A timing device is used to record the accumulated area at set time intervals. The same basis for measuring time must be used to determine retention times in the calibration, the blank, and the sample. If an electronic integrator is used, the maximum area measurement must be within the linear range of the integrator.

6.6 *Sample Containers*—Pressure cylinders or vials with septums should be provided for the calibration mixture and samples to avoid loss of light ends.

6.7 *System*—Any satisfactory combination of the above components that will meet the performance requirements of Section 8.

7. Reagents and Materials

7.1 *Calibration Mixture*—A synthetic mixture of pure liquid hydrocarbons of known boiling point covering the boiling range of the sample. At least one compound in the mixture must have a boiling point equal to or lower than the initial boiling point of the sample, and one compound must have a retention time greater than any component in the sample. The concentration of all compounds heavier than *n*-butane must be known within 0.1 %. The synthetic composition shown in Table 1 should be used for gasoline analysis. Compounds necessary for evaluation of system performance are noted in Table 2.

NOTE 7—If the sample contains significant quantities of compounds that can be identified on the chromatogram, these peaks may be used as internal boiling point calibrations.

NOTE 8—Two calibration mixtures can be used for convenience. One that contains known concentrations of isopentane and heavier compounds

TABLE 2 Calibration Mixture

Peak Number	Compound Identification	NBP, °F	Relative Density,[A] 60/60°F	Approximate Volume, %	Typical Thermal Conductivity Response Factors
1[B]	nC$_3$	−44	0.5077	1	1.15
2[B]	isoC$_4$	11	0.5631	3	1.14
3[B]	nC$_4$	31	0.5844	10	1.07
4[B]	isoC$_5$	82	0.6248	9	1.08
5	nC$_5$	97	0.6312	7	1.03
6	2-MeC$_5$	140	0.6579	5	1.03
7[C]	nC$_6$	156	0.6640	5	1.01
8[D]	2,4-DiMeC$_5$	177	0.6772	5	1.07
9	nC$_7$	209	0.6882	9	1.00
10[C]	Toluene	231	0.8719	10	0.89
11	nC$_8$	258	0.7068	5	0.98
12[C]	p-Xylene	281	0.8657	12	0.90
13[C]	n-Propylbenzene	319	0.8666	4	0.94
14	nC$_{10}$	345	0.7341	3	0.99
15[C]	n-Butylbenzene	362	0.8646	3	0.93
16[C]	nC$_{12}$	421	0.7526	3	1.00
17[C]	nC$_{13}$	456	0.7601	2	1.02
18	nC$_{14}$	486	0.7667	2	1.04
19	nC$_{15}$	519	0.7721	2	1.05

[A]"Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Project 44, Table 23-2, April 1956.
[B]Necessary if sample contains isopentane and lighter compounds.
[C]Necessary for system evaluation.
[D]Replace 2-methylhexane (2-MeC$_6$) or benzene if the sample contains more than 5 % benzene.

can be used for determining response factors, sensitivity, and concentration repeatability. The other would contain a complete boiling range of compounds including propane, butane, and isobutane, whose concentrations are known only approximately. It would be used for measuring resolution, skewness, retention time repeatability, polarity, and retention time-boiling point relationship.

NOTE 9—If the sample is known to contain more than 5 % benzene, 2,4 dimethylpentane should be replaced with benzene in the calibration mixture. (**Warning**—Benzene is poisonous and carcinogenic, harmful or fatal if swallowed.)

7.2 *Carrier Gas*—Helium or hydrogen for use with thermal conductivity detectors. Nitrogen, argon, or helium for use with flame ionization detectors. (**Warning**—Helium, nitrogen, and argon are compressed gases under high pressure.) (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

7.3 *Liquid Phase for Columns*:

NOTE 10—The following materials have been used successfully as liquid phases:

  Silicone gum rubber GE-SE-30[4]
  Silicone gum rubber OV-1[5]
  Silicone gum rubber OV-101[5]
  Silicone gum rubber Supelco 2100[6]
  Silicone gum rubber UC-W98[7]

7.4 *Solid Support*—Usually crushed fire brick or inert diatomaceous earth such as Chromosorb P, G, or W,[8] acid-washed, dimethyl silanized. Sieve size and support loading should be such that it will give optimum resolution and analysis time. In general, support loadings of 3 to 10 % have been found most satisfactory but higher ones have been used as shown in Table 1.

8. System Performance

8.1 *Resolution*—For samples containing isopentane and lighter materials, the system must be able to identify the beginning and end of isopentane and lighter saturated compounds as they elute from the column. Individual peaks must be resolved from adjacent peaks so that the height at the valley above the baseline is not more than 5 % of the height of the smaller peak adjacent to it. The resolution, R, between nC_{12} and nC_{13} must be between 2 and 4 when calculated in accordance with the following equation as shown in Fig. 1:

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[4] Registered trademark of General Electric Co.
[5] Registered trademark of Ohio Valley Specialty Chemical Co.
[6] Registered trademark of Supelco, Inc.
[7] Registered trademark of Union Carbide Co.
[8] Registered trademark of Johns-Manville Co.

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

where:
D = time, s, between nC_{12} and nC_{13} apexes,
Y_1 = peak width of nC_{12}, s, and
Y_2 = peak width of nC_{13}, s.

8.2 *Sensitivity and Noise*—These criteria test the sensitivity and noise of the total system. From the first 20 readings or time intervals of the blank run, calculate the noise as the difference between the maximum area reading per second minus the minimum reading per second. From the measurements on the calibration mixture, calculate the signal/noise ratio, as follows:

$$A/(N \times S) \qquad (2)$$

where:
A = total area of the hexane peak,
N = noise, and
S = width of the hexane peak in seconds.

This value must not be less than 10 for each 0.05 volume % of hexane in the calibration mixture, for example, 200 for 1 %. If the noise is undetectable, assume the noise to be 1 count per second.

8.3 *Drift*—From the blank run, calculate by the following test procedure, a total area measured after the start of the run until the end of the run. Adjust the apparatus so that all measurements can be read whether positive or negative. On some equipment such as integrators, readings will need to be positive and increasing in value. Obtain the absolute difference between the average area reading in the first five time intervals and the individual readings in each time interval from the start of the blank run until the end. Sum these differences to obtain the total area for the blank. The total area measurement from the blank run must not be greater than 2.0 % of the total area measurement of the calibration mixture.

8.4 *Skewing of Peaks*—Calculate the ratio A/B on peaks in the calibration mixture as shown on Fig. 2. A is the width in seconds of the part of the peak ahead of the time of the apex at 5 % of peak height, and B equals the width in seconds of the part of the peak after the time of the apex at 5 % of peak height. This ratio must not be less than 0.5 nor more than 2.0.
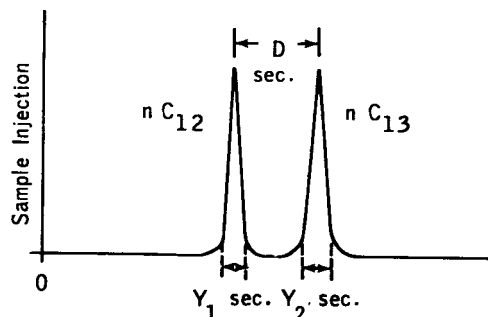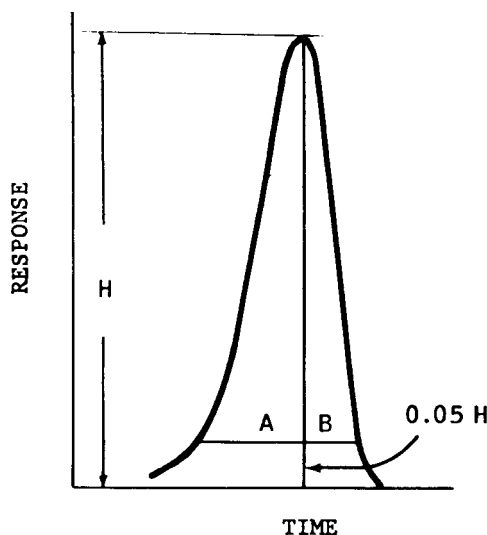

FIG. 1 Column Resolution

FIG. 2 Peak Skewness

NOTE 11—A ratio of more than 2.0 is probably due to overloading of the column. This can be corrected by smaller sample size, higher loading of the liquid phase on the packing, or larger diameter column. A ratio of less than 0.5 probably indicates tailing, overloading the detector, or loss of liquid substrate. The column must be changed when tailing becomes excessive. It is possible that the peak shape can be distorted due to a combination of these reasons.

8.5 *Retention Time*—The system must be sufficiently repeatable when testing the calibration mixture to obtain peak maxima retention time repeatability (maximum difference between duplicate results) of 3 s for isopentane and lighter compounds, if present. The maximum difference between duplicate results of retention times of the normal pentane and heavier compounds must not be greater than a time equivalent to 3°C (2°F). In addition, the retention time of the apex of the first peak in the calibration mixture should be at least 15 s.

8.6 *Polarity*—Calculate the boiling point retention time relationship specified in 10.2.2, using only the *n*-paraffins. Using the observed retention time of the aromatic compounds, calculate their apparent boiling points. Compare the apparent boiling points of the aromatics with their known boiling points. The apparent boiling point of the aromatic compounds must not deviate more than 10°F (6°C) from linearity or normal paraffins in the calibration mixture.

8.7 *Area Measurement*—The area measurement may be made by an electronic integrator or an analog-to-digital converter in conjunction with a computer. As the run progresses, the amount of material eluted from the column is measured from time zero in time slice areas or counts at specified time intervals. The counts are summed continuously, and the time intervals are equated to equivalent temperatures using the calibration curve generated in 10.2.2. Continue measurement for 2 min after the apex of the last peak or until the chromatogram returns to a constant baseline at the end of the run. Duplicate results on consecutive runs on the area percent of the compounds in the calibration mixture must not differ by more than 0.1 %.

8.7.1 Time intervals need not be uniform throughout the run. However, it is important that all measurement be on the same basis for the blank, calibration, and sample. No interval shall be greater than 0.5 % of the total length of the run. In addition, in order to facilitate the measurement of light ends, the size of the time intervals for the isopentane and lighter compounds should be small enough to allow measurement of their areas and times to peak maxima.

NOTE 12—The end of the run can be defined by using the following algorithm: find the time where the rate of change of the chromatographic signal is less than or equal to a specified value (0.05 mV/min and 0.001 % of the total area under the chromatogram have been used successfully). Then search for 1 min before and after that time. The point where the number of counts per slice is at a minimum in that 2-min period is defined as the end of the run.

8.8 *Difference from Calibration Mixture*—Multiply the area of each peak in the calibration mixture by the liquid volume response factor calculated in 11.2, and normalize the volume percent of each compound so that the volumes of all compounds heavier than *n*-butane add up to 100.0. Compare the volume percent of each compound heavier than *n*-butane with the known percent. The difference between the calculated and

known percentages must not be greater than 0.5.

9. Sampling

9.1 *Sampling from Bulk Storage:*

9.1.1 *Cylinder* Refer to Practice D 1265 for instructions on introducing samples into a cylinder from bulk storage. The cylinder should be pressurized with carrier gas to a pressure of at least 345 kPa (50 psi) above the vapor pressure of the sample (**Warning**—Gasoline is extremely flammable. Vapors are harmful if inhaled.). If the sample is to be transferred to another vessel such as a vial with septum, the cylinder must be cooled to a temperature between 32 and 40°F (0 and 4°C).

9.1.2 *Open Containers*—Refer to Practice D 4057 for instructions on introducing samples into open-type containers from bulk storage. Cool the container and its contents to 32 to 40°F (0 to 4°C) before removing any sample from it.

9.2 *Sampling from Open-Type Containers*—Follow the instructions in Test Method D 323 for transferring material from an open-type container.

10. Procedure

10.1 *Blank*—After conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used. Following a rigorously standardized schedule, cool the column to the selected starting temperature. At the exact time set by the schedule, without injecting a sample, start the column temperature program. Measure and record the area in each time interval from the start of the run until the end of the run as specified in 8.7. Make a blank run at least daily.

10.1.1 In order for the blank run to be valid, it must meet the drift requirement specified in 8.3. In addition, no peaks must be found such that the difference in area readings per second in consecutive time intervals be greater than five times the noise. If the noise is not detectable, assume it to be 1 count per second.

NOTE 13—The identification of a constant baseline at the end of the run is critical to this test method. Constant attention must be given to all factors that influence baseline stability, such as substrate bleed.

NOTE 14—Some gas chromatographs have an algorithm built into their operating software, which causes a mathematical model of the column bleed profile to be stored in memory. This profile is subtracted automatically from the detector signal on subsequent runs to compensate for the column bleed.

10.2 *Calibration*:

10.2.1 Using the same conditions described in 10.1, inject the calibration mixture into the chromatograph. Record the data in such a manner that retention time of peak maxima and peak area of the individual components are obtained. As noted in 8.7, this can be done by means of a computer or integrator.

NOTE 15—When determination of peak maxima and peak area is done by the time slice technique, the following algorithms can be used to verify the start of peak, end of peak, and peak maxima: A peak is defined as starting in that time slice in which the rate of change of the chromatographic signal is greater than a specified value (0.05 mV/min and 0.001 %/s have been used successfully). This criterion must be confirmed for two consecutive time segments in order to be valid. Once a peak is detected, the end is determined by one of two criteria. The first applies when there is good resolution between peaks. The peak can be defined as ending when the rate of change of the chromatographic signal is less than

the value specified above. The second criterion applies when resolution between peaks is not complete. The first peak ends when, after the apex has passed, the area per time segment reaches a minimum and starts to increase. The retention time of peak maxima can be determined by the following equation, as shown in Fig. 3:

$$t_{max} = t_i + (t_{i+1} - t_i) A_{i+1}/(A_{i-1} + A_{i+1}) \tag{3}$$

where:

t_{max} = retention time of peak maxima,
t_i = time to start of segment i,
t_{i+1} = time to start of segment $i + 1$,
A_{i+1} = area of segment that starts at t_{i+1}, and
A_{i-1} = area of segment that starts at t_{i-1}.

For systems in which the output is in units other than millivolts, an equivalent measure of the slope may be used.

10.2.2 Plot the retention time of the maxima of each peak versus the corresponding normal boiling point in degrees Celsius (or Fahrenheit) as shown in Fig. 4. If the sample is known to contain less than 5.0 % aromatics, do not include aromatic compounds in the retention time calibration curve.

NOTE 16—For best precision, the calibration curve should be essentially a linear plot of boiling point versus retention time. In general, the lower the initial boiling point of the sample, the lower will be the starting temperature of the chromatographic column. If the starting temperature is too high, there will be considerable curvature at the lower end of the curve, and loss of precision in that boiling range. Since it is impractical to operate the column so as to eliminate curvature completely at the lower end of the curve where initial boiling points below ambient temperature are encountered, at least one point on the curve should have a boiling point lower than or equal to the initial boiling point of the sample. Extrapolation of the curve at the upper end is more accurate, but for best accuracy, calibration points should bracket the boiling range of the sample at both the low and high ends.

10.2.3 The boiling point retention time calibration curve must be checked at least daily by either the calibration mixture or a secondary standard of known boiling point characteristics.

NOTE 17—If peaks in the sample are used as boiling point calibration marks, the calibration mixture need not be run. However, it may prove helpful in establishing identity of peaks in the sample to run the calibration mixture once. Furthermore, precision may be improved in some cases by adding to the sample an n-paraffin, selected so as to be resolved completely from the sample, to serve as an additional boiling point calibration. Plot the retention times of the peaks versus the corresponding atmospheric boiling points to obtain the calibration curve.
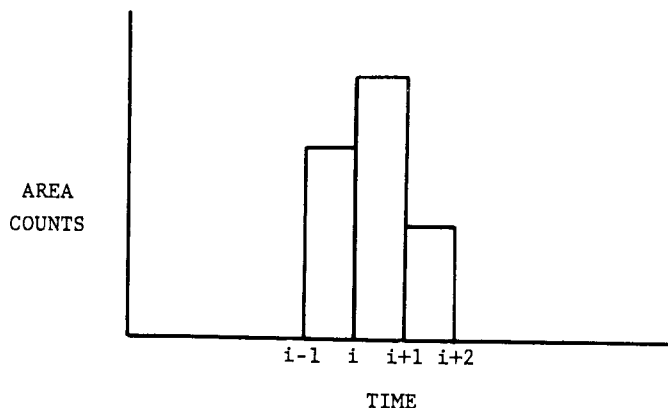
10.3 *Sampling*:

AREA
COUNTS

i-1   i   i+1   i+2

TIME

FIG. 3 Determination of Time to Peak Maxima

10.3.1 Using the exact conditions and time basis as were used in the blank and calibration, inject the sample into the chromatograph. Disregarding peaks (if any) before propane, measure and record the area of each time segment at time intervals as specified in 8.7.

11. Calculation

11.1 *Drift Correction*—Drift correction is not necessary if the drift is less than 0.5 % as calculated in 8.3.

11.1.1 Correct the blank, calibration, and sample runs for initial offset from zero by subtracting from each time interval the average area of the first five time intervals in the corresponding run. Omit from the average any readings (extraneous peaks) that are more than three times the noise as defined in 8.2.

11.1.2 Correct the calibration and sample for drift by subtracting the corrected area of each time segment of the blank from the corresponding segment of the sample

NOTE 18—The corrected area for each time segment is calculated as follows:

$$A_{Ci} = A_i - A_{B/i} - (O - O_B) \tag{4}$$

where:

A_{Ci} = corrected area of segment i, sample or calibration,
A_i = uncorrected area of segment i,
A_{Bi} = area of corresponding segment of blank,
O = offset from run, sample or calibration, and
O_B = offset from blank.

11.1.3 An alternative procedure of correcting for drift and offset is by subtracting a triangular segment of area based on the sample itself as illustrated in Fig. 5.

NOTE 19—For the scheme shown in Fig. 5, the corrected area for each time segment is calculated as follows:

$$A_{Ci} = A_i - \left[A_o + (A_f - A_o)\left(\frac{t_i - t_o}{t_f - t_o}\right) \right] \tag{5}$$

where:

A_{Ci} = corrected area of segment i, sample or calibration,
A_i = uncorrected area of segment i,
A_o = average area of last five segments before start of first peak,
A_f = area of first segment after end of last peak,
t_i = time to segment i from beginning of run,
t_o = time to last segment before start of first peak, and
t_f = time to first segment after end of last peak.

11.1.4 In cases where the calibration is peak-integrated instead of time-sliced, the drift corrections need not be applied.

11.2 *Response Factors:*

11.2.1 Using the corrected areas from the calibration run and composition of the calibration mixture, calculate the response factor relative to the factor for nC_7 for all compounds iC_5 and heavier:

$$\text{Response factor, } F_i = (V_i \times A_c)/(V_o \times A_{c_i}) \tag{6}$$

where:

F_i = response factor of the compound,
A_{ci} = corrected area for each pure compound,
V_i = volume percent from the calibration mixture,
A_{Co} = corrected area of nC_7, and
V_o = volume percent of nC_7 in the calibration mixture.

11.2.2 Determine the response factors for propane, isobutane, and n-butane in the following manner. Calculate the
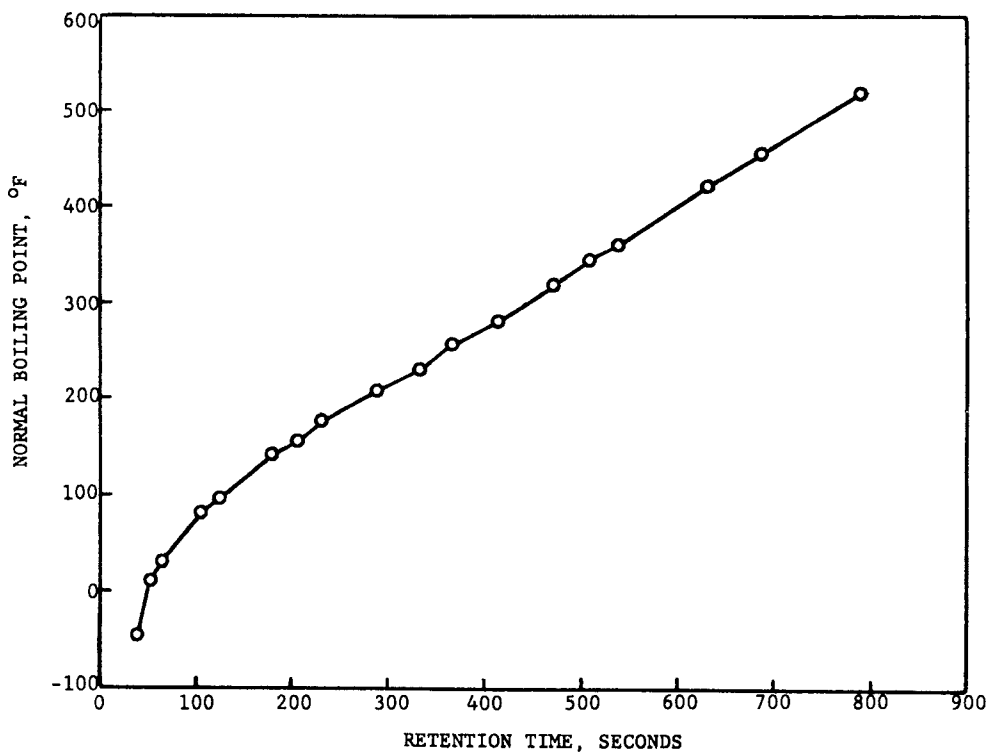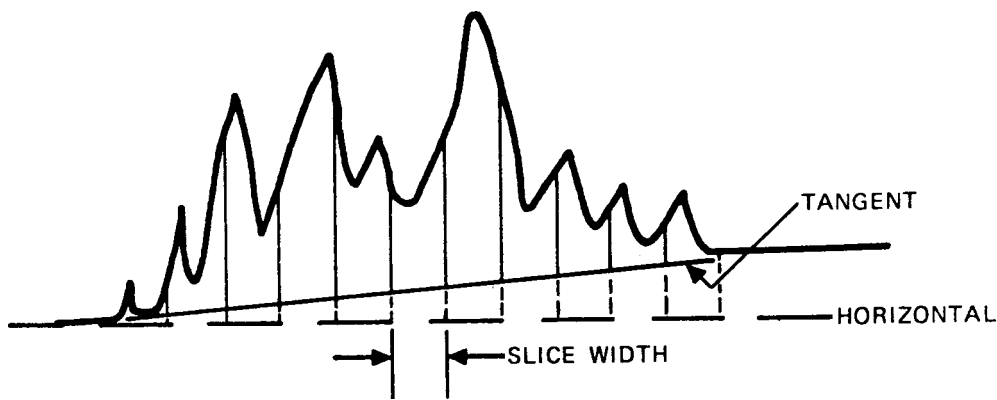
FIG. 4 Typical Calibration Curve

FIG. 5 GCD Drift Correction

relative molar response, RMR, for each of the normal paraffins starting with nC_5 as follows:

$$RMR_i = (A_{c_i} \times m_o)/(A_{c_o} \times m_i) \qquad (7)$$

where:
RMR$_i$ = relative molar response for the compound,
m_i = mole percent of the compound in the calibration mixture, and
m_o = mole percent of nC_7 in the calibration mixture.

The RMR is a linear function of molecular weight.[9] The measured RMR's are fit to the linear equation RMR = a MW + b employing the least squares technique. The RMR for

propane and n-butane is calculated using the resulting equation. For isobutane, use the RMR measured for n-butane. Calculate response factors for these three components as follows:

$$\text{Response factor, } F_i = (MW_i \times RMR_o \\ \times \text{Den}_o)/(MW_o \times RMR_i \times \text{Den}_i) \qquad (8)$$

where:
MW_i = molecular weight of the compound,
MW_o = molecular weight of nC_7,
RMR_i = relative molar response of the compound,
RMR_o = relative molar response of nC_7,
Den_i = relative density of the compound, and
Den_o = relative density of nC_7.

[9] Messner, A. E., et al, "Correlation of Thermal Conductivity Cell Response with Molecular Weight and Structure," *Analytical Chemistry,* ANCHA, Vol 31, No. 2, February 1959, pp. 230–233.

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Typical response factors along with relative densities are shown in Table 2.

NOTE 20—If the concentrations of propane and butane in the calibration mixture are known, differences noted between the observed and calculated response factors indicate loss of front-end components. If a fresh calibration mixture is used, these differences can be indicative of sampling problems. Deviation of the response factors of the heavier components from the straight-line 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 in sampling. Fig. 6 illustrates these effects.

11.2.3 Apply the response factor for each compound in the calibration mixture to the corrected areas of all time intervals in the sample that falls between a point (*a*) that is halfway between the observed apex of that compound and the observed apex of that compound and the observed apex of the preceding compound, and a point (*b*) that is halfway between the observed apex of that compound and the observed apex of the succeeding compound. The response factors used may differ according to sample type. For commercial gasolines, typical response factors are shown in Table 2. For gasoline blending components containing small amounts of aromatics, such as alkylates, the aromatic response factors should be omitted and only paraffin response factors used. The response factors measured are used until such time as the detectors or columns are changed or there is some reason to suspect that their values are no longer applicable.

11.3 *Calculation of Sample*:

11.3.1 For each time segment between the beginning of the first peak and the end of the last peak, multiply the area by the suitable response factor to get volume counts. Divide the cumulative volume counts at the end of each interval by the total volume counts and multiply by 100. This will give the cumulative percent of sample recovered at each interval.

11.3.2 Tabulate the cumulative volume percent recovered at each interval and the retention time at the end of the interval. Using linear interpolation where necessary, determine the retention time associated with 0.5 and 99.5 volume % recovered. These are respectively the initial and final boiling points. Determine the retention time for each volume percent off between 1 and 99.

11.3.3 For each volume percent and its associated retention time, determine the corresponding temperature from the calibration curve (10.2.2). Use linear interpolation between all calibration points.

11.3.4 Identify individually the propane through isopentane peaks by comparing the retention time of each peak to the corresponding retention time in the calibration run. Check to see that the retention time of the apex of the propane, iso-, and normal butane and isopentane peaks is within a time equivalent to 5°F (3°C) of the calibration run. Note any isopentane or lighter component that is apparently absent. Calculate the volume percent of the individual compounds by using the suitable response factors. Include any peaks between normal butane and isopentane with the normal butane peak.

12. Report

12.1 Report the temperature to the nearest 1°F (0.5°C) at 1 % intervals between 1 and 99 %, and at 0.5 % and 99.5 %. The report format is shown in Table 3. Other formats based on users' needs may also be employed.

12.2 Report volume percent of isopentane and lighter compounds individually. This provides a more absolute basis for describing commercial gasolines than the IBP.

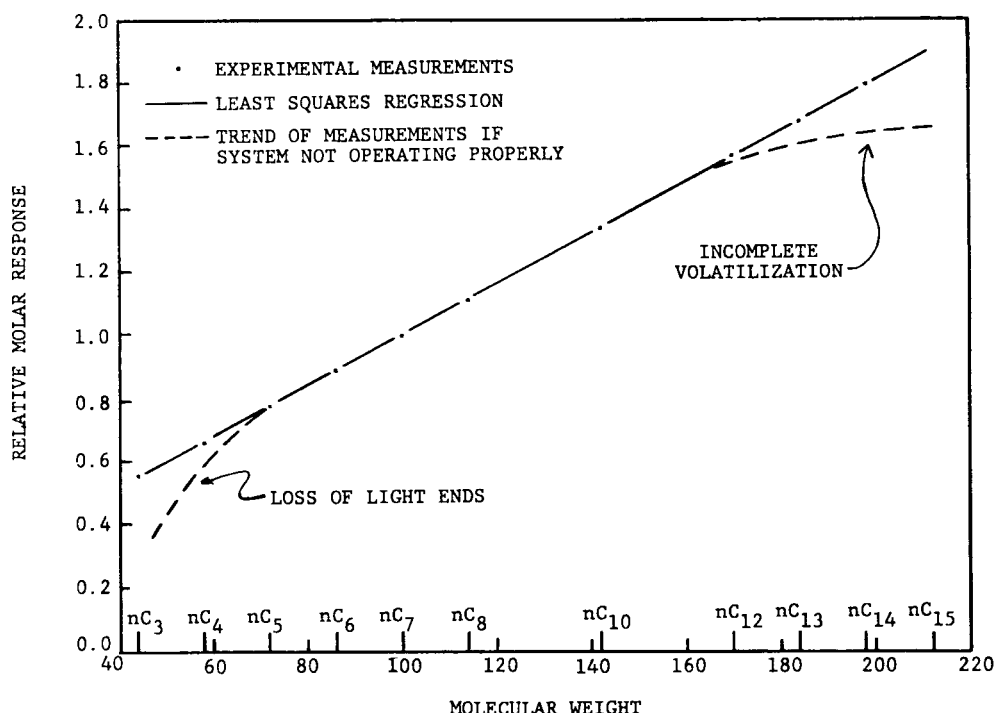NOTE 21—Some olefins will be measured with butane and isopentane. See 11.3.4.

FIG. 6 Relative Molar Response versus Molecular Weight for n-Paraffins

TABLE 3 Report Format

Percent Off	°F	Percent Off	°F
0.5 (IBP)		51	
1		52	
2		53	
3		54	
4		55	
5		56	
6		57	
7		58	
8		59	
9		60	
10		61	
11		62	
12		63	
13		64	
14		65	
15		66	
16		67	
17		68	
18		69	
19		70	
20		71	
21		72	
22		73	
23		74	
24		75	
25		76	
26		77	
27		78	
28		79	
29		80	
30		81	
31		82	
32		83	
33		84	
34		85	
35		86	
36		87	
37		88	
38		89	
39		90	
40		91	
41		92	
42		93	
43		94	
44		95	
45		96	
46		97	
47		98	
48		99	
49		99.5 (FBP)	
50			

Component	Volume Percent
n-C$_3$	
iso-C$_4$	
n-C$_4$	
iso-C$_5$	

13. Precision and Bias

13.1 The precision of this test method depends upon the shape of the boiling range distribution curve. Both the repeat- ability and reproducibility vary with percent recovered and the rate of change of temperature with percent recovered:

$$dT/dV \qquad (9)$$

where:
T = temperature, and
V = percent recovered.

The slopes, dT/dV, are computed from points adjacent to the selected percent recovered points, for example, for 60 %, the temperatures at 58, 59, 61, and 62 %.

13.2 The following criteria should be used for judging acceptability of results. These data were generated from cooperative analyses of gasolines with a wide range of vola- tilities.

13.2.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 4 only in one case in twenty.

13.2.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators work- ing in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 5 only in one case in twenty.

13.3 *Bias*—Bias cannot be determined since there is no acceptable reference material suitable for determining the bias for the procedure in this test method.

14. Keywords

14.1 boiling range distribution; gas chromatography; gaso- line; gasoline blending component

TABLE 4 Repeatability as a Function of Percent Recovered and dT/dV

	Repeatability, r, °F (°C)										
Volume Percent Recovered, dT/dV:	0	2(1)	4(2)	6(3)	8(4)	10(6)	12(7)	14(8)	20(11)	30(17)	40(22)
IBP	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)
1	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	—	—	—
5	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	—	—	—
10	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	2(1)	—	—	—
20	2(1)	3(2)	4(2)	5(3)	7(4)	10(6)	—	—	—	—	—
30 to 90	2(1)	3(2)	4(2)	5(3)	7(4)	10(6)	14(8)	19(10)	—	—	—
95	—[A]	—	2(1)	3(2)	5(3)	7(4)	9(6)	13(7)	—	—	—
99	—	—	—	—	—	—	—	6(3)	6(3)	6(3)	6(3)
FBP	—	—	—	—	—	—	—	—	6(3)	6(3)	6(3)

CONCENTRATION				
Component	Repeatability, r,			
	C3	iC4	nC4	iC5
Volume %				
0.10	—	0.02	—	—
0.15	0.02	0.02	—	—
0.20	0.02	0.03	—	—
0.4		0.03	—	—
0.6	—	0.04	—	—
0.8	—	0.05	—	—
1.0	—	0.05	—	—
1.2	—	0.06	—	—
1.4	—	0.07	—	—
1.6	—	0.07	—	—
2	—		0.11	
4	—		0.22	0.25
6	—		0.32	0.28
8	—		0.43	0.30
10	—		0.54	0.32
12	—		0.65	0.34
14	—		0.76	0.36
16	—		0.86	0.39
18	—		—	0.41
20	—		—	0.43
22	—		—[A]	0.45

[A](–) Outside the range observed in the cooperative study

TABLE 5 Reproducibility as a Function of Percent Recovered and dT/dv

	Reproducibility, R, °F (°C)										
Volume Percent Recovered, dt/dv:	0	2(1)	4(2)	6(3)	8(4)	10(6)	12(7)	14(8)	20(11)	30(17)	40(22)
IBP	7(4)	7(4)	8(4)	8(4)	8(4)	8(4)	8(4)	8(4)	9(5)	10(6)	12(7)
1	5(3)	5(3)	5(3)	6(3)	6(3)	6(3)	6(3)	6(3)	—	—	—
5	5(3)	5(3)	5(3)	5(3)	5(3)	5(3)	5(3)	6(3)	—	—	—
10	6(3)	6(3)	6(3)	6(3)	6(3)	6(3)	3(7)	—	—	—	—
20	5(3)	7(4)	11(6)	16(9)	23(13)	30(17)	—	—	—	—	—
30 to 90	6(3)	9(5)	13(7)	20(11)	27(15)	36(20)	46(26)	55(31)	—	—	—
95	—	—	11(6)	16(9)	23(13)	30(17)	38(21)	46(26)	—	—	—
99	—	—	—	—	—	—	—	20(11)	24(13)	33(18)	36(20)
FBP	—	—	—	—	—	—	—	—	19(11)	26(14)	36(20)

	Reproducibility, R							Detector Bias (FID-TCD)			
	C3	iC4		nC4		iC5		C3	iC4	nC4	iC5
Detector	Both	TCD	FID	TCD	FID	TCD	FID				
Volume %											
0.10	—	0.10	0.09					—	0.00	—	—
0.15	0.13	0.10	0.11					0.00	0.00	—	—
0.20	0.13	0.10	0.13					0.00	0.00	—	—
0.4	—	0.12	0.20					—	−0.01	—	—
0.6	—	0.13	0.27					—	−0.03	—	—
0.8	—	0.15	0.34					—	−0.04	—	—
1.0	—	0.16	0.41					—	−0.05	—	—
1.2	—	0.18	0.48					—	−0.06	—	—
1.4	—	0.19	0.55					—	−0.07	—	—
1.6	—	0.20	0.62					—	−0.09	—	—
2	—	—	—	0.28	1.62			—	—	−0.33	—
4	—	—	—	0.57	1.91	0.79	0.29	—	—	−0.28	−0.27
6	—	—	—	0.85	2.19	0.98	0.48	—	—	−0.24	−0.14
8	—	—	—	1.14	2.48	1.16	0.66	—	—	−0.19	0.00
10	—	—	—	1.42	2.76	1.35	0.85	—	—	−0.14	+ 0.14
12	—	—	—	1.70	3.04	1.54	1.04	—	—	−0.10	+ 0.28
14	—	—	—	1.99	3.33	1.72	1.22	—	—	−0.05	+ 0.42
16	—	—	—	2.27	3.61	1.91	1.41	—	—	−0.01	+ 0.55
18	—	—	—	—	—	2.09	1.59	—	—	—	+ 0.69
20	—	—	—	—	—	2.28	1.78	—	—	—	+ 0.83
22	—	—	—	—	—	2.48	1.97	—	—	—	+ 0.97

ANNEX

(Mandatory Information)

A1. CALCULATION AND PREDICTION

A1.1   Results obtained by this test method may be used to calculate the vapor pressure of the gasoline sample, including its Reid vapor pressure (RVP) and to predict the Test Method D 86 distillation curve.

A1.2   Calculate Reid vapor pressure by the following general equation:

$$RVP = \Sigma \, aV_i \, e^{-bt_i} \qquad \text{(A1.1)}$$

where:
V_i = volume fraction eluted in cut i,
t_i = boiling point of cut i, as determined from the calibration curve, and

a,b = empirically determined constants

A1.3   Predict Test Method D 86 distillation curve from the GCD boiling range distribution curve by an empirical correlation of the general form:

$$\text{Percent off, } D\,86_i = \Sigma \, A_{ij} \times V_j \qquad \text{(A1.2)}$$

where:
A_{ij} = empirically determined constants, and
V_j = percent off by GCD at cutpoint j.

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