Designation: D7398 – 11 (Reapproved 2016)

Standard Test Method for Boiling Range Distribution of Fatty Acid Methyl Esters (FAME) in the Boiling Range from 100 °C to 615 °C by Gas Chromatography[1]

This standard is issued under the fixed designation D7398; 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 fatty acid methyl esters (FAME). This test method is applicable to FAMES (biodiesel, B100) having an initial boiling point greater than 100 °C and a final boiling point less than 615 °C at atmospheric pressure as measured by this test method.

1.2 The test method can also be applicable to blends of diesel and biodiesel (B1 through B100), however precision for these samples types has not been evaluated.

1.3 The test method is not applicable for analysis of petroleum containing low molecular weight components (for example naphthas, reformates, gasolines, crude oils).

1.4 Boiling range distributions obtained by this test method are not equivalent to results from low efficiency distillation such as those obtained with Test Method D86 or D1160, especially the initial and final boiling points.

1.5 This test method uses the principles of simulated distillation methodology. See Test Methods D2887, D6352, and D7213.

1.6 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D1160 Test Method for Distillation of Petroleum Products at Reduced Pressure

D2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

D2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D6352 Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 °C to 700 °C by Gas Chromatography

D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels

D7213 Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 °C to 615 °C by Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

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

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

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355, E594, and E1510.

[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.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.2 *biodiesel, n*—fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *area slice, n*—area resulting from the integration of the chromatographic detector signal within a specified retention time interval. In area slice mode (6.4.2), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

3.2.2 *atmospheric equivalent temperature (AET), n*—temperature converted from the measured vapor temperature obtained at sub-ambient pressure to atmospheric equivalent temperature (AET) corresponding to the equivalent boiling point at atmospheric pressure, 101.3 kPa (760 mm Hg), The AET is the expected distillate temperature if the distillation was performed at atmospheric pressure and there was no thermal decomposition.

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

3.2.4 *cumulative corrected area, n*—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).

3.2.5 *initial boiling point (IBP), n*—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 *final boiling point (FBP), n*—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.

3.2.7 *slice rate, n*—frequency of data sampling or the frequency of data bunching provided that the frequency of data acquisition is larger than the frequency of bunching. The unit of frequency is points/seconds or Hz.

3.2.8 *slice time, n*—cumulative slice rate (analysis time) associated with each area slice throughout the chromatographic analysis. The slice time is the time at the end of each contiguous area slice.

3.2.9 *total sample area, n*—cumulative corrected area, from the initial point to the final area point.

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}; *iso*-tetradecane = *i*-C_{14}).

3.3.2 A common abbreviation for FAME compounds is to designate the number of carbon atoms and number of double bonds in the compound. The number of carbon atoms is denoted by a number after the "C" and the number following a colon indicates the number of double bonds (for example, C16:2 ; FAME with 16 carbon atoms and 2 double bonds).

4. Summary of Test Method

4.1 The boiling range distribution by distillation is simulated by the use of gas chromatography. A non-polar open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon and FAME components of the sample in order of increasing boiling point.

4.2 A sample aliquot is diluted with a viscosity reducing solvent and introduced into the chromatographic system. The solvent shall be apolar and not interfere with measurement of the sample in the 100 °C to 615 °C range. Sample vaporization is provided by separate heating of the point of injection or in conjunction with column oven heating.

4.3 The column oven temperature is raised at a reproducible linear rate to effect separation of the FAME components in order of increasing boiling point relative to a *n*-paraffin calibration mixture. The elution of sample components is quantitatively determined using a flame ionization detector. The detector signal integral is recorded as area slices for consecutive retention time intervals during the analysis.

4.4 Retention times of known normal paraffin hydrocarbons, spanning the scope of the test method ($C_5 – C_{60}$), are determined and correlated to their boiling point temperatures. The normalized cumulative corrected sample areas for each consecutive recorded time interval are used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment is calculated from the retention time calibration.

4.5 The retention time versus boiling point curve is calibrated with normal paraffin hydrocarbons since these boiling points are well defined. A mixture of FAMEs is analyzed to check column resolution. A triglyceride is analyzed to verify the system's ability to detect unreacted oil.

5. Significance and Use

5.1 The boiling range distribution of FAMES provides an insight into the composition of product related to the transesterification process. This gas chromatographic determination of boiling range can be used to replace conventional distillation methods for product specification testing with the mutual agreement of interested parties.

5.2 Biodiesel (FAMES) exhibits a boiling point rather than a distillation curve. The fatty acid chains in the raw oils and fats from which biodiesel is produced are mainly comprised of straight chain hydrocarbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 °C to 357 °C. The Specification D6751 value of 360 °C max at 90 % off by Test Method D1160 was incorporated as an precaution to ensure the fuel has not been adulterated with high boiling contaminants.

6. Apparatus

6.1 *Chromatograph*—The following gas chromatographic system performance characteristics are required:

6.1.1 *Column Oven*—Capable of sustained and linear programmed temperature operation from near ambient (for example 35 °C to 50 °C) up to 400 °C.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed temperature operation up to 400 °C at selectable linear rates up to 20 °C/min. The programming rate must be sufficiently reproducible to obtain the retention time repeatability of 0.03 min (3 s) for each component in the calibration mixture described in 7.3.

6.1.3 *Detector*—This test method requires a flame ionization detector (FID). The detector must meet or exceed the following specifications as detailed in Practice E594. The specification of flame jet orifice is approximately 0.45 mm (0.018 in.).

6.1.3.1 *Operating Temperature,* 400 °C.

6.1.3.2 *Sensitivity,* >0.005 coulombs/g carbon.

6.1.3.3 *Minimum Detectability,* 1×10^{-11} g carbon / *s*.

6.1.3.4 *Linear Range,* $>10^6$

6.1.3.5 Connection of the column to the detector must be such that no temperature below the column temperature exists. Refer to Practice E1510 for proper installation and conditioning of the capillary column.

6.1.4 *Sample Inlet System*—Any sample inlet system capable of meeting the performance specification in 6.1.5 and 7.3 may be used. Programmed temperature vaporization (PTV) and programmable cool on-column injection systems have been used successfully.

6.1.5 *Carrier Gas Flow Control*—The chromatograph shall be equipped with carrier flow control capable of maintaining constant carrier gas flow control through the column throughout the column temperature program cycle as measured with the use of flow a sensor. Flow rate must be maintained within 1 % through out the temperature program.

6.2 *Microsyringe*—A microsyringe with a 23 gauge or smaller stainless steel needle is used for on-column sample introduction. Syringes of 0.1 µL to 10 µL capacity are available.

6.2.1 Automatic syringe injection is recommended to achieve best precision.

6.3 *Column*—This test method is limited to the use of non-polar wall coated open tubular (WCOT) columns of high thermal stability. Glass, fused silica, and stainless steel columns, with a 0.53 mm diameter have been successfully used. Cross-linked or bonded 100 % dimethyl-polysiloxane stationary phases with film thickness of 0.5 µm to 1.0 µm have been used. The column length and liquid phase film thickness shall allow the elution of at least C_{60} *n*-paraffin (BP = 615°C) and triolein. The column and conditions shall provide separation of typical petroleum hydrocarbons and saturated FAMES in order of increasing boiling point and meet the column resolution requirements of 8.2.1. The column shall provide a resolution between five (5) and fifteen (15) using the test method operating conditions.

6.4 *Data Acquisition System:*

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

6.4.2 *Integrator*—Means shall 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 shall have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). In addition, the system shall be capable of converting the continuously integrated detector signal into area slices of fixed duration (area slice mode). 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) shall be operated within the linear range of the detector/electrometer system used.

NOTE 1—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 runs to compensate for the column bleed. Some integration systems also store and automatically subtract a blank analysis from subsequent analytical determinations.

7. Reagents and Materials

7.1 *Gases*—The following compressed gases are utilized for the operation of the gas chromatograph.

7.1.1 *Helium,* 99.999 %. (**Warning—**Compressed gas under high pressure.) This gas can be used as carrier gas. Ensure sufficient pressure for a constant carrier gas flow rate. It is not to contain more than 5 mL/m^3 of oxygen and the total amount of impurities are not to exceed 10 mL/m^3 .

7.1.2 *Nitrogen,* 99.999 %. (**Warning—**Compressed gas under high pressure.) This gas can be used as carrier gas. Ensure sufficient pressure for a constant carrier gas flow rate. It is not to contain more than 5 mL/m^3 of oxygen and the total amount of impurities are not to exceed 10 mL/m^3.

7.1.3 *Hydrogen,* 99.999 %. (**Warning—**Extremely flammable gas under high pressure.) The total impurities are not to exceed 10 mL/m^3. This gas can be used as carrier gas. Ensure sufficient pressure for a constant carrier gas flow rate. It is also used as fuel for the flame ionization detector (FID).

7.1.4 *Air,* 99.999 %. (**Warning—**Compressed gas under high pressure and supports combustion.) Total impurities are not to exceed 10 mL/m^3. This gas is used to sustain combustion in the flame ionization detector (FID).

7.2 *Solvents*—Unless otherwise indicated, it is intended that all solvents conform to the specifications of the committee on analytical Reagents of the American Chemical Society where such specifications are available.[3] Other grades may be used provided it is first ascertained that the solvent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2.1 *Carbon Disulfide* (CS_2), 99+ % pure. (**Warning—**Extremely flammable and toxic liquid.) Used as a viscosity reducing solvent and as a means of reducing mass of sample introduced onto the column to ensure linear detector response and reduced peak skewness. It is miscible with FAMES and

[3] *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.

provides a relatively small response with the FID. The quality (hydrocarbon content) is determined by this test method prior to use as a sample diluent.

7.2.2 *Cyclohexane* (C_6H_{12}), (99+ % pure) (**Warning—** Flammable. Health hazard.) Used as a viscosity reducing solvent. It is miscible with asphaltic hydrocarbons, however, it responds well to the FID. Cyclohexane will interfere with the elution of lower boiling normal paraffins. The quality (hydrocarbon content) is determined by this test method prior to use as a sample diluent.

7.3 *Calibration Mixture*—A qualitative mixture of *n*-paraffins (nominally C_5 to C_{60}) dissolved in a suitable solvent. A final concentration of approximately one part of *n*-paraffin mixture to one hundred parts of solvent is required. At least one compound in the mixture must have a boiling point lower than the initial boiling point of the sample being analyzed, as defined in the scope of this test method (1.1). The calibration mixture must contain at least 13 known *n*-paraffins (for example, C_6, C_7, C_8, C_9, C_{10}, C_{12}, C_{16}, C_{20}, C_{30}, C_{40}, C_{50}, C_{52}, C_{60}). Boiling points of *n*-paraffins are listed in Table 1.

NOTE 2—A suitable calibration mixture can be obtained by dissolving a polyolefin wax in a volatile solvent (for example, carbon disulfide or cyclohexane). Solutions of one part polyolefin wax to one hundred parts solvent can be prepared. Lower boiling point paraffins will have to be added to ensure conformance with 7.3. Fig. 1 illustrates a typical calibration mixture chromatogram.

7.3.1 *Qualitative FAME Mixture*—A qualitative mixture of FAMES (nominally C8:0 to C24:0) dissolved in a suitable solvent. A final concentration of approximately one part of FAME mixture to one hundred parts of solvent is required. The qualitative mixture contains at least 9 known FAMES (for example, C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C20:0, C22:0, C24:0). Boiling points of FAMES are listed in Table 2. This FAME qualitative mixture is used to calculate resolution of C16:0 and C18:0 (see 8.2.1). It may also be used to insure that retention time shifts as column ages does not exceed ±0.15 min (to be determined from the experimental BP versus RT curve).

7.3.2 *Quantitative Triglyceride Mixture*—A quantative mixture of triglyceride (triolein) dissolved in a suitable solvent. A final concentration of approximately 10 mass ppm is required. One qualitative mixture meeting the requirement of 7.3.1 and 7.3.2 may be used. This triglyceride reponse mixture is used to verify response to unreacted oils (see 8.2.2.1).

7.4 *Response Linearity Mixture*—Prepare a quantitatively weighed mixture of at least ten individual paraffins (>99 % purity), covering the boiling range of the test method. The highest boiling point component shall be at least *n*-C60. The mixture shall contain *n*-C40. Use a suitable solvent to provide a solution of each component at approximately 0.5 % to 2.0 % by mass.

TABLE 1 Boiling Points of *n*-Paraffins[A,B]

Carbon Number	Boiling Point °C	Boiling Point °F	Carbon Number	Boiling Point °C	Boiling Point °F
5	36	97	33	474	885
6	69	156	34	481	898
7	98	209	35	489	912
8	126	258	36	496	925
9	151	303	37	503	937
10	174	345	38	509	948
11	196	385	39	516	961
12	216	421	40	522	972
13	235	456	41	528	982
14	254	488	42	534	993
15	271	519	43	540	1004
16	287	548	44	545	1013
17	302	576	45	550	1022
18	316	601	46	556	1033
19	330	626	47	561	1042
20	344	651	48	566	1051
21	356	674	49	570	1058
22	369	695	50	575	1067
23	380	716	51	579	1074
24	391	736	52	584	1083
25	402	755	53	588	1090
26	412	774	54	592	1098
27	422	791	55	596	1105
28	431	808	56	600	1112
29	440	825	57	604	1119
30	449	840	58	608	1126
31	458	856	59	612	1134
32	466	870	60	615	1139

[A] API Project 44, 72-10-31, is believed to have provided the original normal paraffin boiling point data that are listed in Table 1. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D7398 have changed, and they are no longer equivalent. Table 1 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 D7398 has traditionally used *n*-paraffin boiling points rounded to the nearest whole degree for calibration. The boiling points listed in Table 1 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 results will not agree with the table values 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 208 °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.

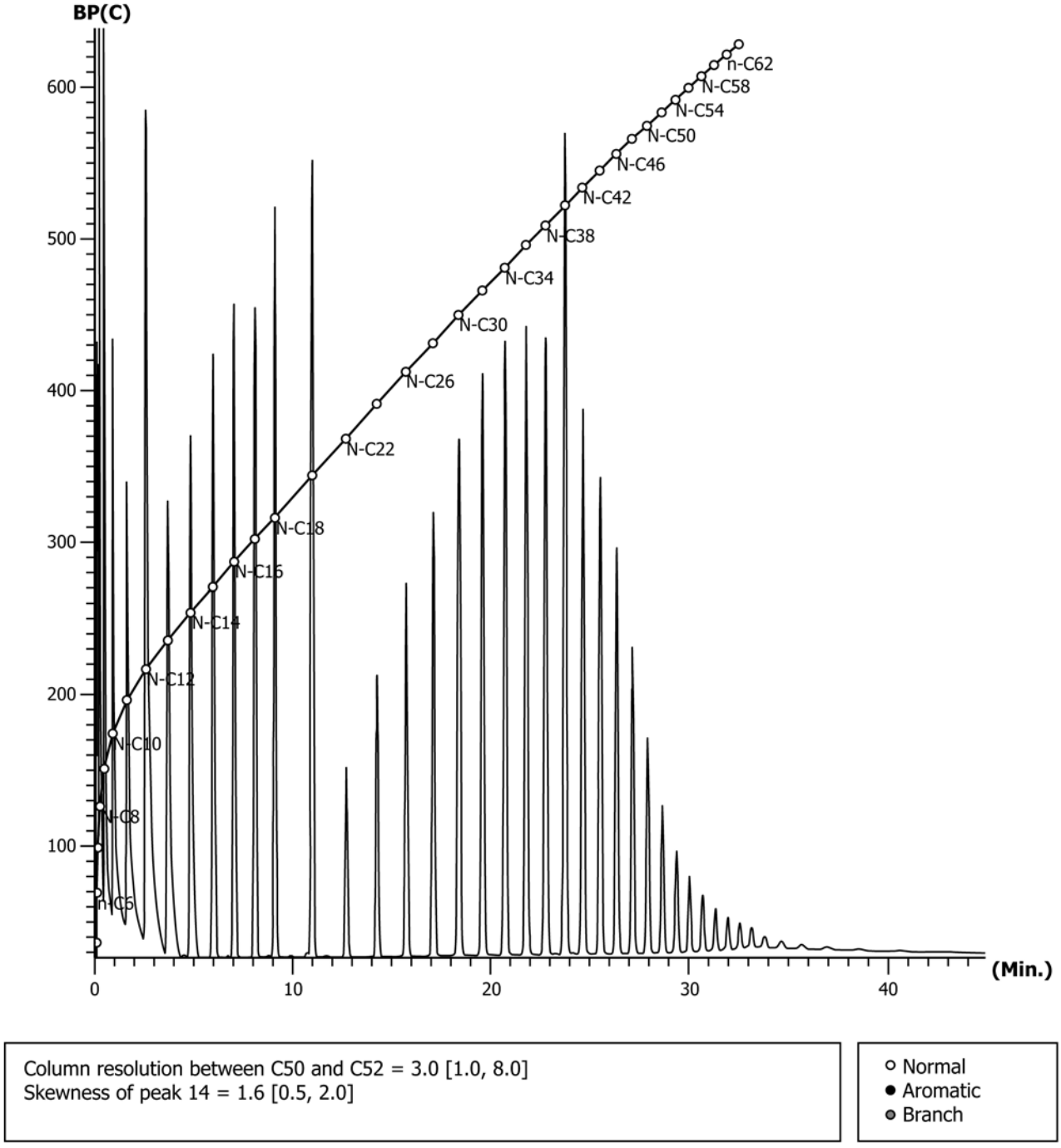

FIG. 1 Typical Calibration Curve with Plot

7.5 *Reference Material*—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 is being determined.

8. Preparation of Apparatus

8.1 *Gas Chromatograph Setup:*

8.1.1 Place the gas chromatograph and ancillary equipment into operation in accordance with the manufacturers instructions. Recommended operating conditions are shown in Table 3.

8.1.2 When attaching the column to the detector inlet, ensure that the end of the column terminates as close as possible to the FID jet. Follow the instructions in Practice E1510.

8.1.3 Periodically inspect the FID and, if necessary, remove any foreign deposits formed in the detector from combustion of silicone liquid phase or other materials. Such deposits will change the response characteristics of the detector.

8.1.4 The inlet liner and initial portion of the column must be periodically inspected and replaced if necessary to remove extraneous deposits or sample residue.

TABLE 2 FAME and Triglyceride Boiling Point Table

NOTE 1—Boiling points of FAMEs and triglycerides are normally published in the literature at reduced pressure. This table compares the converted to AET literature BP values from one source to the BP values as determined by extrapolating the retention time of the FAME from the retention time/BP of the preceding and the following *n*-paraffin from a chromatographic run using the conditions of this method.

FAME	Name	Alternate Name	BP °C[A]	AET BP °C[B]	Extrapolated BP °C[C]
C8:0	Octanoic Acid, Methyl Ester	Methyl caprylate	83 [15]	200	197
C10:0	Decanoic Acid, Methyl Ester	Methyl caprate	114 [15]	237	237
C12:0	Dodecanoic Acid, Methyl Ester	Methyl laurate	141 [15]	270	272
C14:0	Tetradecanoic Acid, Methyl Ester	Methyl Myristate	155-7 [7]	308	304
C16:0	Hexadecanoic Acid, Methyl Ester	Methyl palmitate	148 [2]	330	332
C18:0	Octadecanoic Acid, Methyl Ester	Methyl stearate	215 [15]	357	358
C20:0	Eicosanoic Acid, Methyl Ester	Methyl arachidate	215-16 [10]	369	382
C22:0	Docosanoic Acid, Methyl Ester	Methyl behenate	224-5 [12]	375	404
C24:0	Tetracosanoic Acid, Methyl Ester			413	425
C18			235-40 [15 18]		
Triglyceride	Triolein			375	
C18					606
Triglyceride	Triolein				

[A] Reduced pressure boiling points in degrees Celsius and mm Hg as published in *CRC Handbook of Chemistry & Physics*, 61st Edition.
[B] Atmospheric equivalent temperature calculated as per Test Method D2892 equations. At present there is insufficient evidence that TBP (Test Method D2892) yields distillation curves equivalent to those that may be obtained by classical vacuum distillations.
[C] Boiling point extropolated from retention time of *n*-paraffins under the condition of this chromatographic method. The relative good agreement with the boiling point determined by using *n*-paraffins to calibrate the retention time indicates the validity of such calibration.

TABLE 3 Recommended Operating Conditions

Injector	cool on-column or PTV
Injection temperature	oven-track mode or programmed; initial temperature 100 °C initial hold 0 minutes program rate 10 °C/min final temperature 385 °C
Auto sampler	required for best precision
Data collection	data is collected as independent area slices (average data collection rate is 1.0 Hz or one sample/s)
Column	capillary, 4 m × 0.53 mm ID film thickness; 1.0 microns (polydimethylsiloxane)
Flow conditions	UHP helium at 10 mL/min (constant flow) (make-up gas helium)
Detector	Flame Ionization; Temperature: 390 °C
Oven program	initial oven temperature 35 °C, initial hold 0 min., program rate 10 °C/min., final oven temperature 385 °C,
Sample size	0.5 microliter
Sample dilution	2 % by mass in carbon disulfide
Calibration dilution	1 % by mass in carbon disulfide

8.1.5 *Column Conditioning*—A new column will require conditioning at the upper test method operating temperature to reduce or eliminate significant liquid phase bleed, resulting in a stable chromatographic baseline. Follow the guidelines outlined in Practice E1510.

8.2 *System Performance Specification:*

8.2.1 *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 C16:0 and C18:0 FAMES from a calibration mixture analysis (or a retention time boiling point mixture) (see 7.3.1). Resolution (R) shall be at least five (5) and not more than fifteen (15), 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 for the C16:0 peak maximum,
t_2 = time for the C18:0 peak maximum,
w_1 = peak width, at half height, of the C16:0 peak and,
w_2 = peak width, at half height, of the C18:0 peak.

8.2.2 *Detector Response Calibration*—This test method assumes that the FID response to petroleum hydrocarbons is proportional to the mass of individual components. This shall be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the response linearity mixture (7.4) using the identical procedure to be used for the analysis of samples (Section 9). Calculate the relative response factor for each *n*-paraffin (relative to *n*-tetracontane) as per Practice D4626 and Eq 2:

$$F_n = (M_n/A_n)/(M_{40}/A_{40}) \quad (2)$$

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_{40} = mass of the *n*-tetracontane in the mixture and,
A_{40} = peak area of the *n*-tetracontane in the mixture.

The relative response factor (F_n) of each *n*-paraffin must not deviate from unity by more than ±5 %.

8.2.2.1 *Unreacted Oil Response Calibration*—Ensure that the system can detect unreacted oil in concentrations that may be found in biodiesel. This shall be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the quantitative triolein standard (7.3.2) using the identical procedure to be used for the analysis of samples (Section 9).

8.2.3 *Column Temperature*—The column temperature program profile is selected such that the C8:0 peak can be differentiated from the solvent and that the maximum boiling point triolein is eluted from the column before reaching the end

of the temperature program. The actual program rate used will be influenced by other operating variables such as column dimensions, liquid phase film thickness, carrier gas and flow rate, and sample size.

8.2.4 *Column Elution Characteristics*—The recommended column liquid phase is a non-polar phase such as 100 % polydimethylsiloxane.

9. Procedure

9.1 *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 and injector to the initial starting temperature, equilibration time, sample injection and system start, analysis, and final temperature hold time.

9.1.1 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.

9.1.2 During the cool down and equilibration time, ready the integrator/computer system. If a retention time calibration is being performed, use the peak detection mode. For samples and baseline compensation (with or without solvent injection), use the area slice mode operation. The recommended slice rate for this test method is 1.0 Hz (1 sample per second). Faster 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.

9.1.3 At the exact time set by the schedule, inject either the calibration mixture, solvent, 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 protocol for all subsequent repetitive analyses or calibrations. Since complete resolution of sample peaks is not expected, do not change the sensitivity setting during the analysis.

9.2 *Baseline Blank*—Perform a blank analysis (baseline blank) at least once per day. The blank analysis may be without injection or by injection of an equivalent solvent volume as used with sample injections, depending upon the subsequent data handling capabilities for baseline/solvent compensation. 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 carry over from previous sample analyses.

NOTE 3—If automatic baseline correction (see Note 1) 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 which 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.

9.3 *Retention Time versus Boiling Point Calibration*—A retention time versus boiling point calibration shall be performed on the same day that analyses are performed. Inject an appropriate aliquot (0.2 µL to 2.0 µL) of the calibration mixture (7.3) 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. Fig. 1 illustrates a graphical plot of a calibration analysis.

9.3.1 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 of the column, which will result in displacement of the peak apex relative to non-overloaded peaks. Distortion in retention time measurement and hence errors in boiling point temperature calibration will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on acceptable sample size. Reanalyze the calibration mixture using a smaller sample size or a more dilute solution to avoid peak distortion.

9.3.1.1 *Skewness Calculation*—Calculate the ratio *A/B* on specified peaks in the calibration mixture as indicated by the designations in Fig. 2. *A* is the width in seconds of the portion of the peak eluting prior to the time of the peak apex and measured at 5 % of peak height (0.10-H), and *B* is the width in seconds of the portion of the peak eluting after the time of the peak apex at 10 % of peak height (0.10-H). This ratio for C18:0 FAME peak in the calibration mixture shall not be less than 0.5 or more than 2.0.

9.3.2 Prepare a calibration table based upon the results of the analysis of the calibration mixture by recording the time of each peak maximum and the boiling point temperature in degrees Celsius (or Fahrenheit) for every component in the mixture. *n*-Paraffin boiling point temperatures (atmospheric equivalent temperatures) are listed in Table 1. An example of a typical calibration report, showing retention times and boiling points for each *n*-paraffin, is found in Table 4.

9.4 *Sample Preparation*—Sample aliquots are introduced into the gas chromatograph as solutions in a suitable solvent (for example carbon disulfide or cyclohexane).

9.4.1 Dilute the sample to approximately 2 weight % with the solvent.

9.4.2 Seal (cap) the vial and mix the contents thoroughly to provide a homogeneous mixture. It may be necessary to warm the mixture initially to effect complete solution of the sample. However, the sample shall be in stable solution at room temperature prior to injection.

9.5 *Sample Analysis*—Using the analysis sequence protocol, inject a diluted sample aliquot into the gas chromatograph. Collect a contiguous time slice record of the entire analysis (area slice mode).

9.5.1 Be careful that the injection size chosen does not exceed the linear range of the detector. The typical sample size ranges from 0.2 µL to 2.0 µL of the diluted sample. The

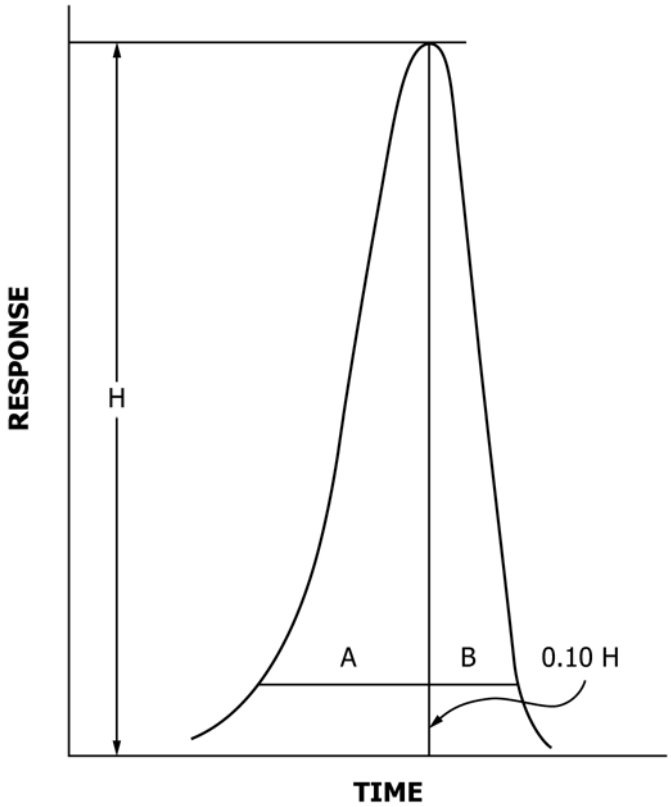

FIG. 2 Designation of Parameters for Calculation of Peak Skewness

maximum sample signal amplitude shall not exceed the maximum calibration signal amplitude. A sample chromatogram is found in Fig. 3.

10. Calculations

10.1 Load the sample chromatogram slices into a table.

10.2 Perform a slice offset.

10.2.1 Calculate the average slice offset at start of chromatogram as follows: Calculate the average and standard deviation of the average of the first five area slices of the chromatogram. Throw out any of the first five slices that are not within one standard deviation of the average and recompute the average. This eliminates any area that is due to possible baseline upset from injection.

10.2.2 Subtract the average slice offset from all the slices of the sample chromatogram. This will zero the chromatogram.

10.3 Load the blank run chromatogram slices into a table.

NOTE 4—For instruments that compensate the baseline directly at the detector producing an electronically corrected baseline, either process the sample chromatogram directly or do a baseline subtraction. If the compensation is made by the instrument 10.4, 10.5, 10.6 and 10.7 may be eliminated and proceed to 10.8.

10.4 Repeat 10.2 using the blank run table.

10.5 Verify that the slice width used to acquire the sample chromatogram is the same used to acquire the blank run chromatogram.

10.6 Subtract from each slice in the sample chromatogram table with its correspondent slice in the blank run chromatogram table.

10.7 Offset the corrected slices of the sample chromatogram by taking the smallest slice and subtracting it from all the slices. Set any negative values to zero. This will zero the chromatogram.

10.8 Verify the extent of baseline drift.

10.8.1 Calculate the average and standard deviation of the first five area slices of the chromatogram.

10.8.2 Eliminate any of the first five slices that are not within one standard deviation of the average and recompute the average. This eliminates any area that is due to possible baseline upset from injection.

10.8.3 Record the average area slice as *Initial Baseline Signal*.

10.8.4 Repeat 10.8.1 and 10.8.2 using the last five area slices of the chromatogram.

10.8.5 Record the average area slice as *Final Baseline Signal*.

10.8.6 Compare and report the *Initial* and *Final* Baseline Signals. These numbers should be similar.

10.9 Determine the start of sample elution time.

10.9.1 Calculate the total area. Add all the corrected slices in the table. If the sample to be analyzed has a solvent peak, start counting area from the point at which the solvent peak has eluted completely. Otherwise, start at the first corrected slice.

10.9.2 Calculate the rate of change between each two consecutive area slices, beginning at the slice set in 10.9.1 and working forward. The rate of change is obtained by subtraction the area of a slice from the area of the immediately preceding slice and dividing by the slice width. The time where the rate

TABLE 4 Typical Calibration Report

Calibration Table			
Number	Name	RT(min)	BPI(C)
1	n-C5	0.11	36.1
2	n-C6	0.14	68.7
3	N-C7	0.21	98.4
4	N-C8	0.34	125.7
5	N-C9	0.81	150.8
6	N-C10	1.11	174.1
7	N-C11	1.89	195.9
8	N-C12	2.91	216.3
9	N-C13	4.02	235.4
10	N-C14	5.17	253.9
11	N-C15	6.30	270.6
12	N-C16	7.39	287.2
13	N-C17	8.42	301.9
14	N-C18	9.42	316.1
15	N-C20	11.27	343.9
16	N-C22	12.94	368.3
17	N-C24	14.51	391.1
18	N-C26	15.97	412.2
19	N-C28	17.33	431.1
20	N-C30	18.60	449.7
21	N-C32	19.79	466.1
22	N-C34	20.92	481.1
23	N-C36	21.98	496.1
24	N-C38	22.98	508.9
25	N-C40	23.98	522.2
26	N-C42	24.84	533.9
27	N-C44	25.70	545.0
28	N-C46	26.52	556.1
29	N-C48	27.30	566.1
30	N-C50	28.06	575.0
31	N-C52	28.78	583.9
32	N-C54	29.48	592.2
33	N-C56	30.15	600.0
34	N-C58	30.81	607.8
35	N-C60	31.47	615.0
36	n-C62	32.06	622.2
37	n-C84	32.65	628.9

of change first exceed 0.0001 % per second of the total area (see 10.9.1) is defined as the start of the sample elution time.

10.9.3 To reduce the possibility of noise or an electronic spike falsely indicating the start of sample elution time, a 3 s slice average can be used instead of a single slice. For noisier baselines, a slice average larger than 3 s may be required.

10.10 Calculate the sample total area. Add all the corrected slices in the table stating from the slice corresponding to the start of sample elution time.

10.10.1 Calculate the rate of change between each two consecutive area slices, beginning at the end of run and working backward. The rate of change is obtained by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width. The time where the rate of change first exceeds 0.0001 % per second of the total area (see 10.9.1) is defined as the end of sample elution time.

10.10.2 To reduce the possibility of noise or an electronic spike falsely indicating the end of sample elution a 3 s slice average can be used instead of a single slice. For noisier baselines a slice average larger than 3 s may be required.

10.11 Calculate the sample total area. Add all the slices from the slice corresponding to the start of sample elution time to the slice corresponding to the end of sample elution time.

10.12 Normalize to area percent. Divide each slice in the sample chromatogram table by the total area (see 10.11) and multiply it by 100.

10.13 *Calculate the Boiling Point Distribution Table:*

10.13.1 *Initial Boiling Point*—Add slices in the sample chromatogram until the sum is equal to or greater than 0.5 %. If the sum is greater than 0.5 %, interpolate (refer to the algorithm in 10.15.1) to determine the time that will generate the exact 0.5 % of the area. Calculate the boiling point temperature corresponding to this slice time using the calibration table. Use interpolation when required (refer to the algorithm in 10.15.2).

10.13.2 *Final Boiling Point*—Add slices in the sample chromatogram until the sum is equal to or greater than 99.5 %. If the sum is greater than 99.5 %, interpolate (refer to the algorithm in 10.15.1) to determine the time that will generate the exact 99.5 % of the area. Calculate the boiling point temperature corresponding to this slice time using the calibration table. Use interpolation when required (refer to the algorithm in 10.15.2).

10.13.3 *Intermediate Boiling Point*—For each point between 1 % and 99 %, find the time where the accumulative sum is equal to or greater than the area percent being analyzed. As in 10.13.1 and 10.13.2, use interpolation when the accumulated sum exceeds the area percent to be estimated (refer to the algorithm in 10.15.1). Use the calibration table to assign the boiling point.

10.14 *Report Results*—Print the boiling point distribution table.

10.15 *Calculation Algorithms:*

10.15.1 Calculations to determine the exact point in time that will generate the X percent of total area, where X = 0.5, 1, 2,...., 99.5 %.

10.15.1.1 Record the time of the slice just prior to the slice that will generate an accumulative slice area larger than the X percent of the total area. Let us call this time, T_s, and the accumulative area at this point, A_c.

10.15.1.2 Calculate the fraction of the slice required to produce the exact X percent of the total area:

$$A_x = \frac{X - A_c}{A_{c+1} - A_c} \tag{3}$$

10.15.1.3 Calculate the time required to generate the fraction of area A_x:

$$T_f = A_x \cdot W \tag{4}$$

where:

W = slice width.

10.15.1.4 Record the exact time where the accumulative area is equal to the X percent of the total area:

$$T_t = T_s + T_f \tag{5}$$

10.15.2 Interpolate to determine the exact boiling point given the retention time corresponding to the cumulative slice area.

10.15.2.1 Compare the given time against each retention time in the calibration table. Select the nearest standard having

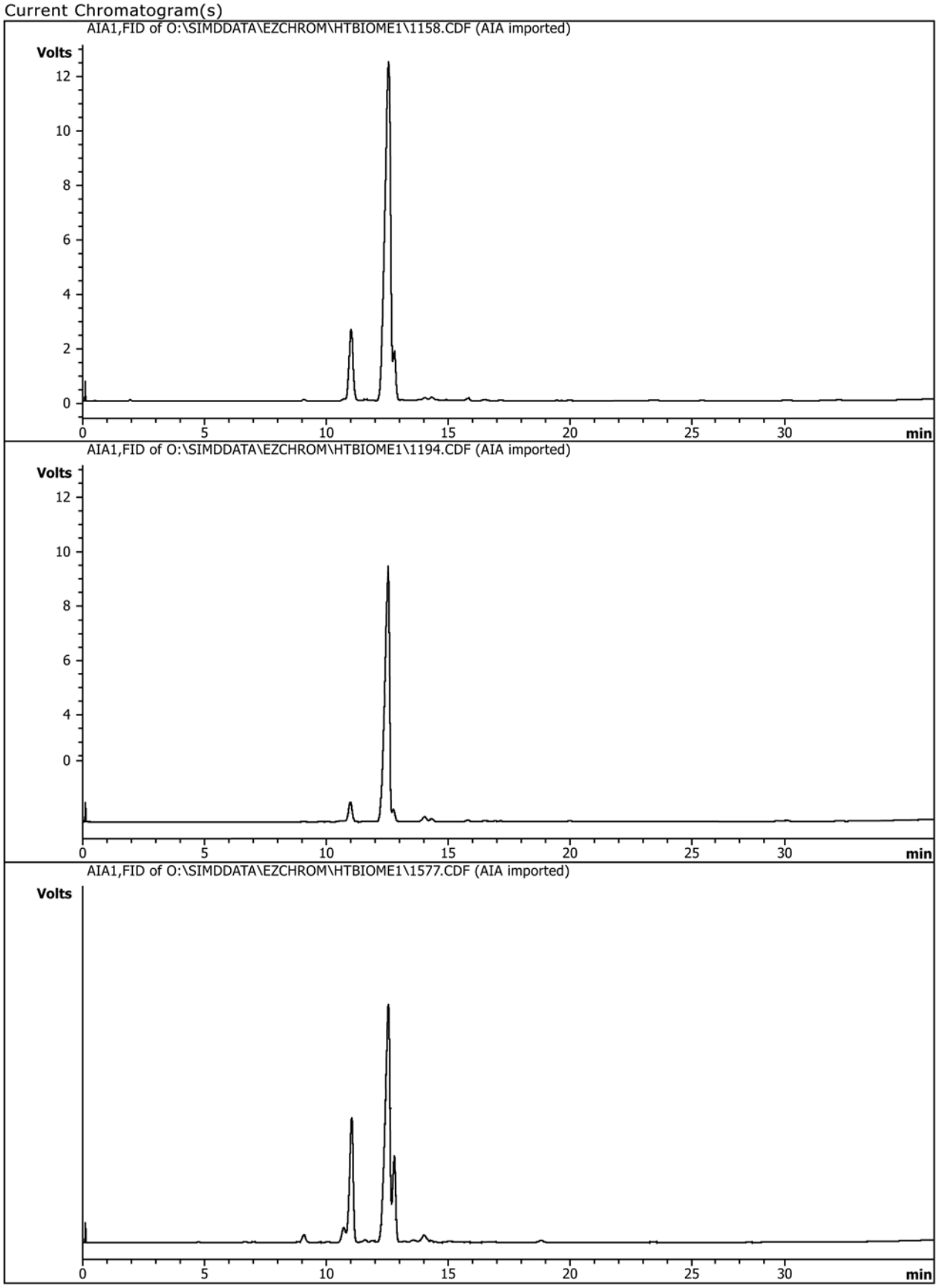

FIG. 3 Examples of Biodiesel Chromatograms

a retention time equal to or larger than the interpolation time. Sort the retention time table in ascending order.

10.15.2.2 If the interpolation time is equal to the retention time of the standard, record the corresponding boiling point.

10.15.2.3 If the retention time is not equal to a retention time of the standards (see 9.3), interpolate the boiling point temperature as follows:

10.15.2.4 If the interpolation time is less than the first retention time in the calibration table, then extrapolate using the first two components in the table:

$$BP_x = m_1 \cdot (RT_x - RT_1) + BP_1 \quad (6)$$

where:

m_1 = $(BP_2–BP_1)$ / $(RT_2–RT_1)$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_1 = retention time of the first component in the calibration table,
BP_1 = boiling point of the first component in the calibration table,
RT_2 = retention time of the second component in the calibration table, and
BP_2 = boiling point of the second component in the calibration table.

10.15.2.5 IF the interpolation time is between two retention times in the calibration table, then interpolate using the upper and lower standard components:

$$BP_x = m_u \cdot (RT_x - RT_1) + BP_1 \quad (7)$$

where:

m_u = $(BP_u–BP_1)$ / $(RT_u–RT_1)$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_1 = retention time of the lower bound component in the calibration table,
BP_1 = boiling point of the lower bound component in the calibration table,
RT_u = retention time of the upper bound component in the calibration table, and
BP_u = boiling point of the upper bound component in the calibration table.

10.15.2.6 If the interpolation time is larger than the last retention time in the calibration table, then extrapolate using the last two standard components in the table:

$$BP_x = m_n \cdot (RT_x - RT_{n-1}) + BP_{n-1} \quad (8)$$

where:

m_n = $(BP_n–BP_{n-1})$ / $(RT_n–RT_{n-1})$,
BP_x = boiling point extrapolated,
RT_x = retention time to be extrapolated,
RT_{n-1} = retention time of the standard component eluting prior to the last component in the calibration table,
BP_{n-1} = boiling point of the standard component eluting prior to the last component in the calibration table,
RT_n = retention time of the last component in the calibration table, and
BP_n = boiling point of the standard component in the calibration table.

11. Report

11.1 Report the temperature to the nearest 0.5 °C (1 °F) at 1 % intervals between 1 % and 99 % and at the IBP (0.5 %) and the FBP (99.5 %). Other report formats based upon users' needs may be employed.

NOTE 5—If a plot of the boiling point distribution curve is desired, use graph paper with uniform subdivisions and use either retention time or temperature as the horizontal axis. The vertical axis will represent the sample boiling range distribution from 0 to 100 %. Plot each boiling point temperature against its corresponding accumulated percent slice area. Draw a smooth curve connecting the points.

12. Precision and Bias[4]

12.1 *Precision:*

12.1.1 *Repeatability*—The difference between two 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 following values only in one case in twenty:

T90 Repeatability 0.8°C

12.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

T90 Reproducibility 6.8°C

NOTE 6—This test method requires further standardization. The current degrees of freedom for reproducibility are too low. Coordinating Subcommittee D02.94 does not recommend the use of this test method for commerce.

12.2 *Bias*—Because the boiling point distribution can be defined only in terms of a test method, no bias for these procedures in Test Method D7398 for determining the boiling range distribution of light and middle petroleum fractions by gas chromatography have been determined.

12.2.1 A rigorous, theoretical definition of the boiling range distribution of FAME is not possible due to the complexity of the mixture as well as the unquantifiable interactions amongst the components (for example, azeotropic behavior). Any other means used to define the distribution would require the use of a physical process, such as conventional physical distillation or gas chromatographic characterization. This would therefore result in a method-dependent definition and would not constitute a true value from which bias can be calculated.

13. Keywords

13.1 biodiesel; boiling range distribution; distillation; FAME; gas chromatography; petroleum; simulated distillation

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1729.

APPENDIX

(Nonmandatory Information)

X1. BOILING POINTS OF NONPARAFFINIC HYDROCARBONS

X1.1 There is an apparent discrepancy in the boiling point of multiple ring-type compounds. When the retention time of these compounds are compared to *n*-paraffins of equivalent atmospheric boiling point, these ring compounds appear to be eluted early from methyl silicone columns. A plot showing 36 compounds other than *n*-paraffins plotted along the calibration curve for *n*-paraffins alone is shown in Fig. X1.1. The numbered dots are identified in Table X1.1. In this figure the atmospheric boiling points are plotted against the observed retention times. If columns contained different percentages of stationary phase or different temperature programming rates are used, the slope and curvature on the *n*-paraffin curve (solid line) would change, but the relative relationships would remain essentially the same. Deviations of simulated distillation boiling points, as estimated from the curve, from actual boiling points for a few compounds are shown in Table X1.2. The deviations obtained by plotting boiling points at 10 mm Hg rather than 76 mm Hg are tabulated also. It is apparent that the deviation is much less at 10 mm Hg pressure. This indicates that the distillation data produced by gas chromatography closely approximates those obtained in reduced pressure distillations. Since the vapor-pressure-temperature curves for multiple-ring type compounds do not have the same slope or curvature as those of *n*-paraffins, an apparent discrepancy would exist when *n*-paraffin boiling points at atmospheric pressure are used.

X1.2 However, this discrepancy does not introduce any significant error when comparing with laboratory distillation because the pressure must be reduced in such procedures when overhead temperature reach approximately 260 °C (500 °F) to prevent cracking of the sample. Thus, distillation data are subject to the same deviations experienced in simulated distillation by gas chromatography.

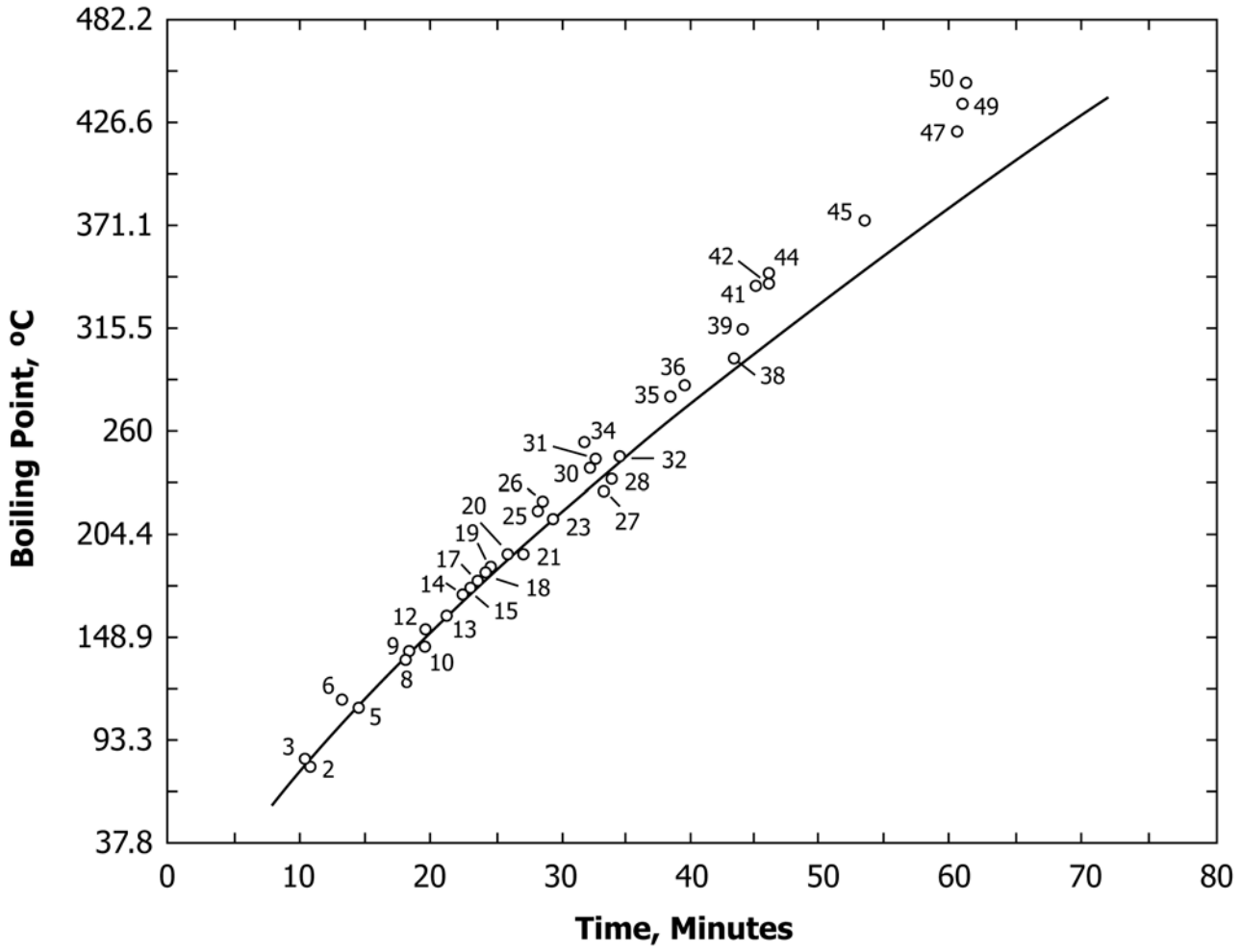

FIG. X1.1 Boiling Point—Retention Time Relationships for Several High-Boiling Multiple-Ring Type Compounds (see Table X1.1)

TABLE X1.1 Compound Identification—Number Dots (see Fig. X1.1)

Number	Boiling Point, °C (°F)	Compound	Number	Boiling Point, °C (°F)	Compound
2	80 (176)	benzene	27	227 (441)	di-*n*-amylsilfide
3	84 (183)	thiophene	28	234 (453)	tri-isopropylbenzene
5	111 (231)	toluene	30	241 (466)	2-methlynaphthalene
6	116 (240)	pyridine	31	295 (473)	1-methlynaphthalene
8	136 (277)	2,5-dimethlythiophene			
9	139 (282)	*p*-xylene	34	254 (894)	indole
10	143 (289)	di-*n*-propylsulfide	35	279 (534)	acenaphthene
12	152 (306)	cumene			
13	159 (319)	1-hexahydroindan	38	298 (568)	*n*-decylbenzene
14	171 (339)	1-decene	39	314 (598)	1-octadecene
15	173 (344)	*sec*-butylbenzene			
17	178 (352)	2,3-dihydroindene	41	339 (642)	phenanthrene
18	183 (361)	*n*-butylbenzene	42	342 (647)	anthracene
19	186 (366)	trans-decalin			
20	194 (382)	cis-decalin	44	346 (655)	acridine
21	195 (383)	di-*n*-propyldisulfide	45	395 (743)	pyrene
23	231 (416)	1-dodecene	47	404 (496)	triphenylene
25	218 (424)	naphthalene	49	438 (820)	naphthacene
26	221 (430)	2,3-benzothiophene	50	447 (837)	chrysene

TABLE X1.2 Deviations of Simulated Distillation Boiling Points from Actual Boiling Points

Compound	Boiling Point, °C (°F) (760 mm)	Deviation from Actual Boiling Point, °C (°F) (760 mm)	Deviation from Actual Boiling Point, °C (°F) (10 mm)
benzene	80 (176)	+3 (+6)	-2 (-4)
thiophene	84 (183)	+4 (+7)	+1 (+2)
toluene	111 (231)	+2 (+3)	-1 (-2)
p-xylene	139 (282)	0 (0)	+2 (+4)
1-dodecene	213 (416)	0 (0)	0 (0)
naththalene	218 (424)	-11 (-20)	-4 (-8)
2,3-benzothiophene	221 (430)	-13 (-23)	0 (0)
2-methylnaphthalene	241 (466)	-12 (-21)	-2 (-3)
1-methylnaphthalene	245 (473)	-12 (-21)	-1 (-1)
dibenzothiophene	332 (630)	-32 (-58)	-6 (-10)
phenanthrene	339 (642)	-35 (-63)	-9 (-16)
athracene	342 (647)	-36 (-64)	-8 (-15)
pyrene	395 (743)	-48 (-87)	-16 (-29)
chrysene	447 (837)	-60 (-108)	[A]

[A] No data at 10 mm for chrysene.