Designation: D6417 – 15

Standard Test Method for Estimation of Engine Oil Volatility by Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D6417; 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 an estimation of the amount of engine oil volatilized at 371 °C (700 °F).

1.1.1 This test method can also be used to estimate the amount of oil volatilized at any temperature between 126 °C and 371 °C, if so desired.

1.2 This test method is limited to samples having an initial boiling point (IBP) greater than 126 °C (259 °F) or the first calibration point and to samples containing lubricant base oils with end points less than 615 °C (1139 °F) or the last n-paraffins in the calibration mixture. By using some instruments and columns, it is possible to extend the useful range of the test method.

1.3 This test method uses the principles of simulated distillation methodology.

1.4 This test method may be applied to both lubricant oil base stocks and finished lubricants containing additive packages. These additive packages generally contain high molecular weight, nonvolatile components that do not elute from the chromatographic column under the test conditions. The calculation procedure used in this test method assumes that all of the sample elutes from the column and is detected with uniform response. This assumption is not true for samples with nonvolatile additives, and application of this test method under such conditions will yield results higher than expected. For this reason, results by this test method are reported as area percent of oil.

1.5 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are provided for information only.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D5800 Test Method for Evaporation Loss of Lubricating Oils by the Noack Method

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

2.2 *Coordinating European Council Standard:*

CEC L-40–93 Evaporation Loss of Lubricating Oils (NOACK Evaporative Tester)[3]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *area slice*—the area resulting from the integration of the chromatographic detector signal within a specified retention time interval. In area slice mode (see 6.5.2), peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time intervals.

[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] Available from Coordinating European Council (CEC), C/o Interlynk Administrative Services, Ltd., P.O. Box 6475, Earl Shilton, Leicester, LE9 9ZB, U.K., http://www.cectests.org.

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

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

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

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

3.2.5 *slice time*—the 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.

3.2.6 *total sample area*—the cumulative corrected area from the initial point to the final area point.

3.3 *Abbreviations*—A common way to abbreviate 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 subscript suffix denotes the number of carbon atoms (for example, normal decane n-C_{10}; iso-tetradecane = i-C_{14}).

4. Summary of Test Method

4.1 A nonpolar open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon 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. At least one laboratory analyzed samples using neat injection without solvent dilution. The precision of the method was calculated on diluted samples. If a laboratory chooses to use neat injection, it should first confirm that it is obtaining similar results. 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 hydrocarbon components in order of increasing boiling point. The elution of sample components is quantitatively determined by a flame ionization detector (FID). The detector signal integral is recorded as area slices for consecutive RT intervals during the analysis.

4.4 RTs of known hydrocarbons spanning the scope of the test method (C_8-C_{60}) are determined and correlated to their boiling point temperatures. The RT at 371 °C (700 °F) is calculated using linear regression, utilizing the calibration developed from the n-paraffins. The cumulative corrected area of the sample determined to the 371 °C RT is used to calculate the percentage of oil volatilized at 371 °C.

5. Significance and Use

5.1 The determination of engine oil volatility at 371 °C (700 °F) is a requirement in some lubricant specifications.

5.2 This test method is intended as an alternative to Test Methods D5800 and the Noack method for the determination of engine oil volatility (CEC L-40–93). The data obtained from this test method are not directly equivalent to Test Method D5800. The calculated results of the oil volatility estimation by this test method can be biased by the presence of additives (polymeric materials), which may not completely elute from the gas chromatographic column, or by heavier base oils not completely eluting from the column. The results of this test method may also not correlate with other oil volatility methods for nonhydrocarbon synthetic oils.

5.3 This test method can be used on lubricant products not within the scope of other test methods using simulated distillation methodologies, such as Test Method D6352.

6. Apparatus

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

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 RT repeatability of 0.1 min (6 s) for each component in the calibration mixture described in 7.6.

6.1.3 *Detector*—This test method requires a FID. The detector must meet or exceed the following specifications as detailed in Practice E594.

6.1.3.1 *Operating Temperature,* up to 400 °C.

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

6.1.3.3 *Minimum Detectability,* carbon, 1×10^{-11} g/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 7.6 may be used. Programmed temperature vaporization (PTV) and programmable cool on-column injection systems have been used successfully.

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 have been used.

6.2.1 Automatic syringe injection is recommended to achieve best precision.

6.3 *Column*—This test method is limited to the use of nonpolar 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 methyl silicone liquid phases with film thickness from 0.10 µm to 1.0 µm have been used. The column length and liquid phase film thickness must allow the elution of at least C60 n-paraffin (boiling point = 615 °C). The column and conditions must provide separation of typical petroleum

hydrocarbons in order of increasing boiling point and meet the column resolution requirements of 8.2.1.

6.4 *Carrier Gas Flow/Pressure Control*—The optimum carrier gas flow for the column and chromatographic system should be used. It is recommended that the system be equipped with a constant pressure/constant flow device capable of maintaining the carrier gas at a constant flow rate throughout the temperature program.

6.5 *Data Acquisition System:*

6.5.1 *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.

6.5.2 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of an electronic integrator or computer based chromatography data system. The integrator/computer system must have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). In addition, the system must be capable of converting the continuously integrated detector signal into area slices of fixed duration (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) must be 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 *Carrier Gas*—Helium, nitrogen, or hydrogen of high purity. (**Warning**—Helium and nitrogen are compressed gases under high pressure. Hydrogen is an extremely flammable gas under high pressure.) Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure must be sufficient to ensure a constant carrier gas flow rate.

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

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

7.4 *Carbon Disulfide (CS_2)* (99+ % pure), may be used as a viscosity reducing solvent. It is miscible with asphaltic hydrocarbons and provides relatively little response with the FID. The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning**—Carbon disulfide is extremely flammable and toxic.)

7.5 *Cyclohexane*—(99+ % pure), may be used as a viscosity reducing solvent. It is miscible with asphaltic hydrocarbons; however, it responds well to the FID. The quality (hydrocarbon content) should be determined by this test method prior to use as a sample diluent. (**Warning**—Cyclohexane is flammable.)

7.6 *Calibration Mixture*—A qualitative mixture of n-paraffins (nominally C_8 to C_{60}) dissolved in a suitable solvent. The final concentration should be approximately 1 part of n-paraffin mixture to 100 parts of solvent. It is recommended that at least one compound in the mixture have a boiling point lower than the IBP of the sample being analyzed, as defined in the scope of this test method (see 1.1). It is recommended that the calibration mixture contain at least eleven known n-paraffins (for example, C_8, C_9, C_{10}, C_{12}, C_{16}, C_{20}, C_{30}, C_{40}, C_{50}, C_{52} and C_{60}). Boiling points of n-paraffins are listed in Table 1.

NOTE 2—A suitable calibration mixture can be obtained by dissolving a synthetic wax in a volatile solvent (for example, carbon disulfide or cyclohexane). Solutions of 1 part synthetic wax to 200 parts solvent can be prepared. Lower boiling point paraffins will have to be added to ensure conformance with 7.5. The synthetic wax can be obtained from the Petrolite Company as well as from chromatography suppliers under the name of Polywax 500 or Polywax 655. This mixture is used for measuring the resolution (see 8.2.1).

7.7 *Response Linearity Mixture*—Prepare a quantitatively weighed mixture of about ten individual paraffins (>99 % purity), covering the boiling range of the test method. The highest boiling point component should be at least n-C_{60}. The mixture must contain n-C_{40}. Use a suitable solvent to provide a solution of each component at approximately 0.5 % to 2.0 % by mass.

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 manufacturer's instructions. Recommended operating conditions are shown in Table 2.

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 The FID should be periodically inspected 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.

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's physical parameters and operating conditions, affects the overall determination of boiling range distribution. Resolution is therefore specified to maintain

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
2	–89	–127	52	584	1083
3	–42	–44	53	588	1090
4	0	31	54	592	1098
5	36	97	55	596	1105
6	69	156	56	600	1112
7	98	209	57	604	1119
8	126	258	58	608	1126
9	151	303	59	612	1134
10	174	345	60	615	1139
11	196	385	61	619	1146
12	216	421	62	622	1152
13	235	456	63	625	1157
14	254	488	64	629	1164
15	271	519	65	632	1170
16	287	548	66	635	1175
17	302	576	67	638	1180
18	316	601	68	641	1186
19	330	625	69	644	1191
20	344	651	70	647	1197
21	356	675	71	650	1202
22	369	696	72	653	1207
23	380	716	73	655	1211
24	391	736	74	658	1216
25	402	755	75	661	1222
26	412	774	76	664	1227
27	422	791	77	667	1233
28	431	808	78	670	1238
29	440	824	79	673	1243
30	449	840	80	675	1247
31	458	856	81	678	1252
32	466	870	82	681	1258
33	474	885	83	683	1261
34	481	898	84	686	1267
35	489	912	85	688	1270
36	496	925	86	691	1276
37	503	937	87	693	1279
38	509	948	88	695	1283
39	516	961	89	697	1287
40	522	972	90	700	1292
41	528	982	91	702	1296
42	534	993	92	704	1299
43	540	1004	93	706	1303
44	545	1013	94	708	1306
45	550	1022	95	710	1310
46	556	1033	96	712	1314
47	561	1042	97	714	1317
48	566	1051	98	716	1321
49	570	1058	99	718	1324
50	575	1067	100	720	1328
51	579	1074			

[A] API Project 44, October 31, 1972 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 D6417 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] D6417 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 209 °F, while converting 98 °C gives 208.4 °F, which rounds to 208 °F. Carbon numbers 2, 4, 7, 8, 9, 13, 14, 15, 16, 25, 27, and 32 are affected by rounding.

equivalence between different systems (laboratories) employing this test method. Resolution is determined using Eq 1 and the C_{50} and C_{52} paraffins from a calibration mixture analysis

TABLE 2 Recommended Operating Conditions

Injector	Cool on-column or equivalent
Injection temperature	oven-track mode
Auto sampler	required for best precision
Data collection	data is collected as independent area slices (average slice data collection rate is 3/s)
Column	Capillary, 5 m × 0.53 mm id film thickness; 0.1 µm to 1.0 µm (polymethylsiloxane)
Flow conditions	UHP helium at 12 mL/min (constant flow) or optimized for the column (make-up gas helium at 18 mL/min)
Detector	Flame Ionization; Temperature: 390 °C
Oven program	initial oven temperature 50 °C, initial hold 0 min, program rate 10 °C/min, final oven temperature 380 °C, final hold 12 min, equilibration time 2 min
Sample size	0.1 µL to 0.5 µL
Sample dilution	2 % by mass in carbon disulfide
Calibration dilution	1 % by mass in carbon disulfide

(see 7.6 and Note 2). Resolution (R) should be at least one, using the identical conditions employed for sample analyses.

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

where:

R = resolution,
t_1 = time (s) for the n-C_{50} peak maximum,
t_2 = time (s) for the n-C_{52} peak maximum,
w_1 = peak width (s), at half height, of the n-C_{50} peak, and
w_2 = peak width (s), at half height, of the n-C_{52} 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 must 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 (see 7.7), using the identical procedure to be used for the analysis of samples (see 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 F_n of each n-paraffin should not deviate from unity by more than ±5 %.

8.2.3 *Column Temperature*—The column temperature program profile is selected such that there is separation between the solvent and the first n-paraffin peak (n-C_8) in the calibration

mixture and the maximum boiling point (615 °C) n-paraffin (n-C_{60}) 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, carrier gas and flow rate, and sample size.

8.2.4 *Column Elution Characteristics*—The recommended column liquid phase is a nonpolar phase, such as 100 % methyl silicone.

9. Procedure

9.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. Include in the schedule: cooling the column oven and injector to the initial starting temperature, equilibration time, sample injection and system start, analysis, and final temperature hold time. See Table 2 for typical conditions.

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 RT 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. This is not necessary if the calculations are done using peak integration software as in 10.3.2. The recommended slice rate for this test method is 5.0 Hz (slices, 5/s). Other slice rates may be used if within the limits of 0.02 and 0.2 % of the RT of the final calibration component (C_{60}). Other 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. A detailed description on the use of the slice mode is given in Appendix X1.

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 batch of samples. 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.

9.3 *Solvent Blank Run*—Since not all of the material contained in fully formulated engine oil sample elute from the column, it is recommended that base oil samples without an additive package not be run in the sample batch as engine oils. Run a solvent blank after each batch of engine oil samples.

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, examine the slice area data to determine if further correction is necessary. Determine if any offset has been added to the compensated signal by examining the corrected area slices of those time slices that precede the elution of any chromatographic unretained substance. If these corrected area slices (representing the true baseline) deviate from zero, subtract the average of these corrected area slices from each corrected area slice in the analysis.

9.4 *Retention Time Versus Boiling Point Calibration*—A RT versus boiling point calibration must be performed with each batch of samples analyzed. Inject an appropriate aliquot (0.1 µL to 0.5 µL) of the calibration mixture (7.6) into the chromatograph, using the analysis sequence protocol. Obtain a normal (peak detection) data record to determine the peak RTs 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.

9.4.1 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. Fig. 4 shows the two segments resulting from drawing a perpendicular from the peak apex to the time axis (A and B). Ideally, the ratio taken at 1/10 of the peak height should be a value of 1.0. Distortion in RT 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. Acceptable range of skewness is 0.8 to 1.5.

9.4.2 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 are listed in Table 1. An example of a typical calibration report, showing RTs and boiling points for each n-paraffin, is found in Table 3.

9.5 *Sample Preparation*—Introduce sample aliquots into the gas chromatograph as a solution in a suitable solvent (for example, CS_2 or cyclohexane).

9.5.1 Place approximately 0.1 g to 1 g of the sample aliquot into a screw-capped or crimp-cap vial.

9.5.2 Dilute the sample aliquot to approximately 2 % by mass with the solvent.

9.5.3 Seal (cap) the vial, and mix the contents thoroughly to provide a homogeneous mixture.

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

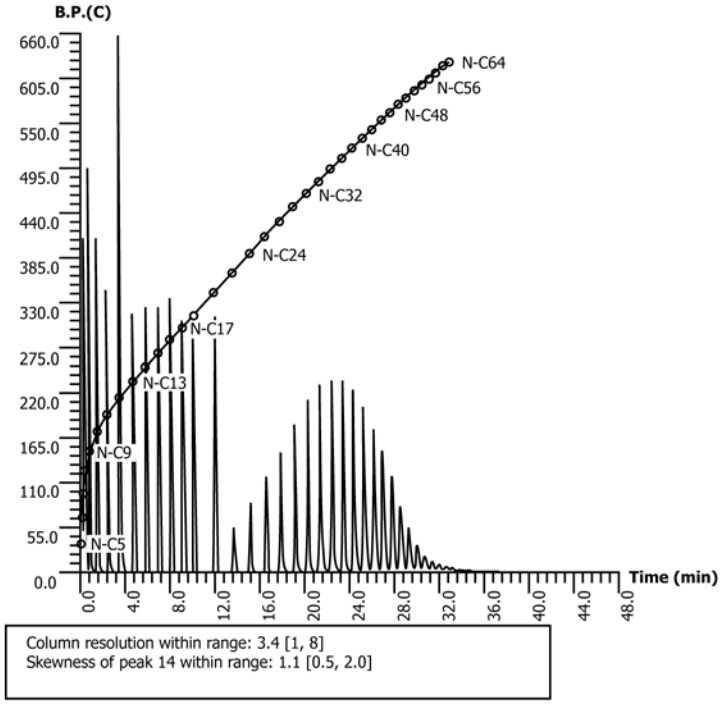

FIG. 1 Typical Calibration Curve with Plot

9.6.1 Be careful that the injection size chosen does not exceed the linear range of the detector. The typical sample size ranges from 0.1 µL to 0.5 µL of the diluted sample. The maximum sample signal amplitude should not exceed the maximum calibration signal amplitude found in 9.4.1.

10. Calculation

10.1 Tabulate the RTs observed for the calibration standard (n-paraffin blend) versus their respective boiling points. Calculate the RT equivalent to 371 °C (700 °F), using linear regression and interpolation.

10.1.1 Descriptions of how to apply linear regression can be found in many mathematical textbooks. Scientific hand calculators and software programs may also be used to perform the calculations.

10.2 Subtract the blank analysis (see 9.3) from the sample analysis (see 9.6). If automatic baseline compensation (see Note 3) has been used, skip this step.

10.3 Determine total sample area and area up to the retention time corresponding to 371 °C (700 °F). This may be done using either area slice summation or peak integration routines in commercial chromatography data systems. See Fig. 2 for baseline definition of fully formulated engine oil sample.

10.3.1 If using area slice summation, first prepare the signal as outlined in Appendix X1 by applying X1.1.1 through X1.1.3. Secondly, use the procedure in X1.4 to find the start of elution and use the procedure described in X1.5 to find the end of elution.

10.3.1.1 Sum the area slices from start of sample elution to the last area slice found at the end of the run using a horizontal forward baseline. This is the total sample area, *C*.

10.3.1.2 Sum the area slices from start of sample to the slice corresponding to the RT corresponding to 371 °C (700 °F) found in 10.1. This is the area of sample up to 371 °C, *B*.

10.3.2 If using peak integration software, set integration parameters to determine total sample area, *C*.

10.3.2.1 Set integration parameters to determine the total area from the start of sample elution to the RT corresponding to 371 °C found in 10.1, using a horizontal forward baseline. This is the area of sample up to 371 °C, *B* .

10.4 Determine the percentage of engine oil volatilized to 371 °C, using Eq 3 as follows:

$$A = 100 \times B/C \tag{3}$$

where:

A = engine oil volatilized to 371 °C, area %,
B = area of the engine oil up to 371 °C,
C = area of total engine oil sample, and
100 = factor to convert area/area to %.

10.5 Report results as the area percent oil volatilized to 371 °C (700 °F) to the nearest 0.1 %. Fig. 3 shows typical report showing calculated volatility and chromatogram of a fully formulated engine oil.

11. Reference Materials

11.1 The performance of this test method should be monitored by analyzing a reference material with each batch of samples. The accepted value of the reference material shall be established by round robin testing. The precision of the value established by the round robin testing shall meet the precision

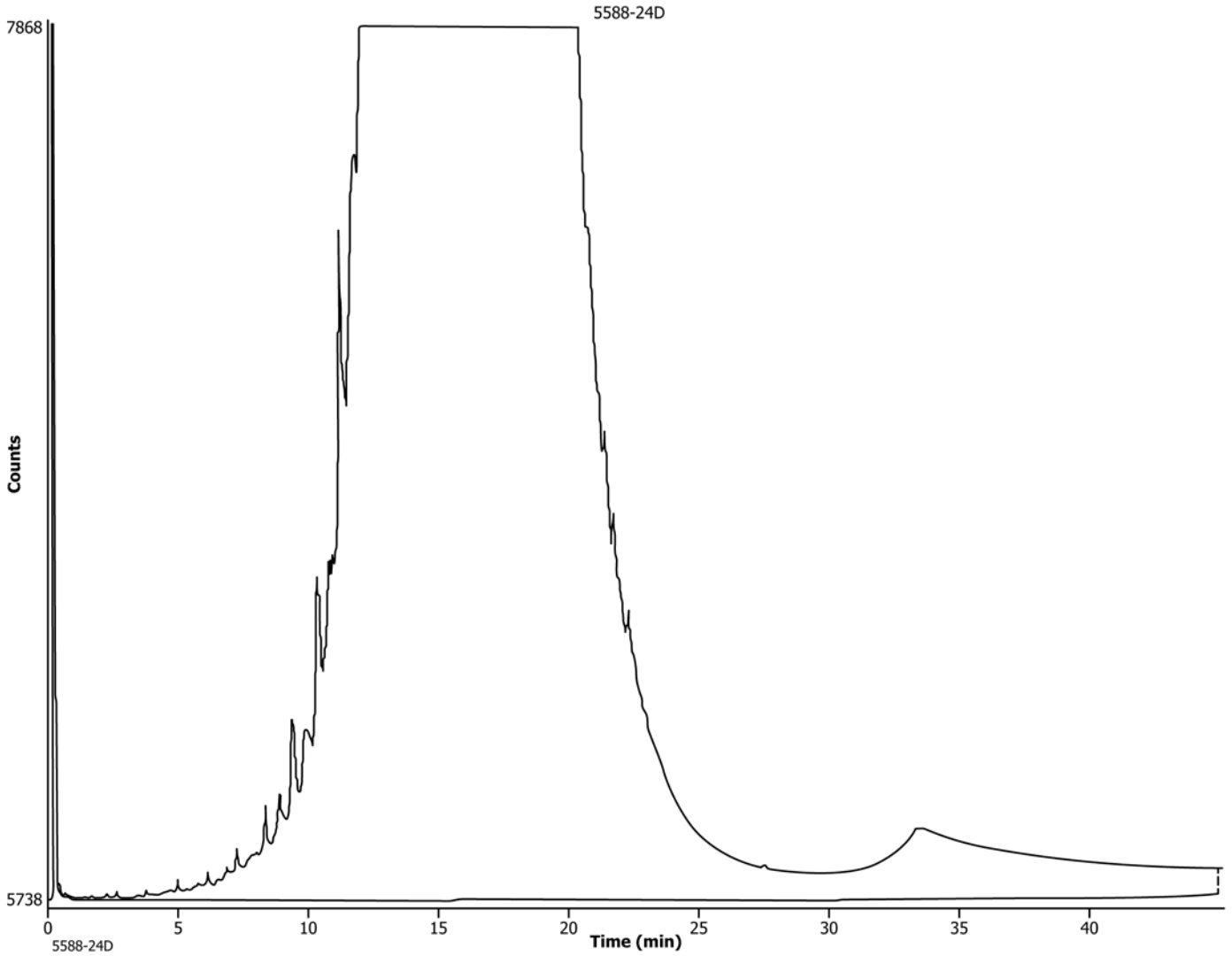

FIG. 2 Baseline Definition of Fully Formulated Engine Oil Sample

statement in Section 12 of this test method. Suitable reference materials are available from a number of suppliers of standard materials.

12. Precision and Bias[4]

12.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory test data for results between 1.8 % and 19.8 % is as follows (see Table 4):

12.1.1 *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 following values by only one case in twenty.

$$\text{Repeatability} = 0.1352X^{0.5}$$

where:

X = volatility level

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, exceed the following values only one case in twenty.

$$\text{Reproducibility} = 0.6036X^{0.5}$$

where:

X = volatility level

12.2 *Bias*—No bias can be determined since the value for the percent volatilized at 371 °C (700 °F) is defined by the test method.

13. Keywords

13.1 boiling range distribution; engine oil, volatility; gas chromatography; lubricants; petroleum; simulated distillation; volatility

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1451.

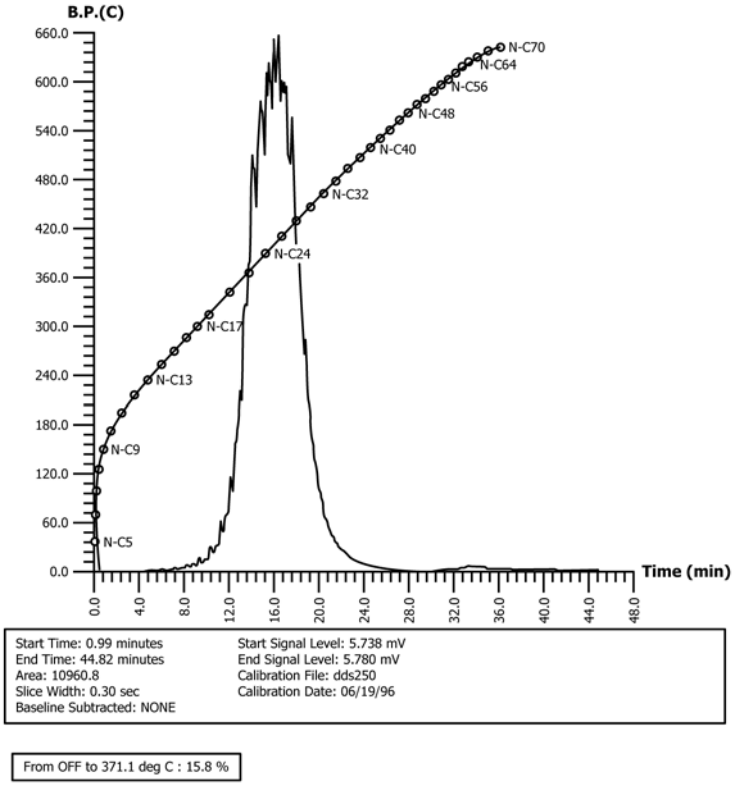

FIG. 3 Typical Report Showing Calculated Volatility and Chromatogram of a Fully Formulated Engine Oil

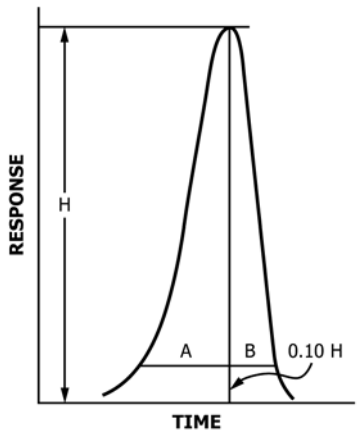

FIG. 4 Designation of Parameters for Calculation of Skewness

TABLE 3 Typical Calibration Report

Peak	Retention Time	Boiling Point (°F)	Boiling Point (°C)
N-C5	0.14	97	36
N-C6	0.20	156	69
N-C7	0.32	209	98
N-C8	0.51	258	126
N-C9	0.90	303	151
N-C10	1.56	345	174
N-C11	2.48	385	196
N-C12	3.58	421	216
N-C13	4.73	456	235
N-C14	5.88	488	254
N-C15	7.00	519	271
N-C16	8.07	548	287
N-C17	9.11	576	302
N-C18	10.09	601	316
N-C20	11.92	651	344
N-C22	13.58	696	369
N-C24	15.12	736	391
N-C26	16.55	774	412
N-C28	17.89	808	431
N-C30	19.14	840	449
N-C32	20.32	870	466
N-C34	21.42	898	481
N-C36	22.47	925	496
N-C38	23.47	948	509
N-C40	24.41	972	522
N-C42	25.31	993	534
N-C44	26.17	1013	545
N-C46	26.99	1033	556
N-C48	27.78	1051	566
N-C50	28.54	1067	575
N-C52	29.27	1083	584
N-C54	29.97	1098	592
N-C56	30.64	1112	600
N-C58	31.28	1126	608
N-C60	31.91	1139	615
N-C62	32.5	1152	622

TABLE 4 Precision of Test Method D6417

Volatility at 371 °C (700 °F), %	Repeatability	Reproducibility
2.0	0.19	0.85
3.0	0.23	1.05
4.0	0.27	1.21
5.0	0.30	1.35
6.0	0.33	1.48
7.0	0.36	1.60
8.0	0.38	1.71
9.0	0.41	1.81
10.0	0.43	1.91
11.0	0.45	2.00
12.0	0.47	2.09
13.0	0.49	2.18
14.0	0.51	2.26
15.0	0.52	2.34
16.0	0.54	2.41
17.0	0.56	2.49
18.0	0.57	2.56
19.0	0.59	2.63

APPENDIXES

(Nonmandatory Information)

X1. BOILING POINT DISTRIBUTION SOFTWARE CALCULATIONS

NOTE X1.1—This appendix has been added for the user who uses Boiling Point Distribution Software in performing the calculations of this test method. Research Report RR:D02-1451[5] showed that the majority of participants used this mode of calculation.

X1.1 *Acquisition Rate Requirements*:

X1.1.1 The number of slices required at the beginning of data acquisition depends on chromatographic variables such as the column flow, column film thickness, and initial column temperature as well as column length. In addition, the detector signal level has to be as low as possible at the initial temperature of the analysis. The detector signal level for both the sample signal and the blank at the beginning of the run has to be similar for proper zeroing of the signals.

X1.1.2 The sampling frequency has to be adjusted so that at least a significant number of slices are acquired prior to the start of elution of sample or solvent. For example, if the time for start of sample elution is 0.06 min (3.6 s) , a sampling rate of 5 Hz would acquire 18 slices. However, a rate of 1 Hz would only acquire 3.6 slices which would not be sufficient for zeroing the signals. Rather than specifying number of slices, it is important to select an initial time segment i.e. one or two seconds. Insure that the smallest number of slices is 5 or greater.

X1.1.3 Verify that the slice width used to acquire the sample chromatogram is the same used to acquire the blank run chromatogram.

X1.2 *Chromatograms Offset for Sample and Blank*—Perform a slice offset for the sample chromatogram and blank chromatogram. This operation is necessary so that the signal is corrected from its displacement from the origin. This is achieved by determining an average slice offset from the slices accumulated in the first segment (that is, first s) and performing a standard deviation calculation for the first N slices accumulated. It is carried out for both sample signal and baseline signal.

X1.2.1 *Sample Offset:*

X1.2.1.1 Calculate the average slice offset of sample chromatogram using the first second of acquired slices. Ensure that no sample has eluted during this time and that the number of slices acquired is at least 5. Throw out any of the first N slices selected 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.

X1.2.1.2 Subtract the average slice offset from all the slices of the sample chromatogram. Set negative slices to zero. This will zero the chromatogram.

X1.2.2 *Blank Offset:*

NOTE X1.2—If you are using electronic baseline compensation proceed to X1.4. It is strongly recommended that the offset method use the slices acquired by running a blank with or without solvent according on how the sample was prepared. Use these acquired blank slices for the offset or zero calculations.

X1.2.3 Repeat X1.2.1 using the blank run table.

X1.3 *Offset Sample Chromatogram with Blank Chromatogram*—Subtract from each slice in the sample chromatogram table with its correspondent slice in the blank run chromatogram table. Set negative slices to zero.

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

X1.4.1 *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.

X1.4.2 *Calculate Rate of Change between each Two Consecutive Area Slices*—Begin at the slice set in X1.4.1 and work forward. 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 10.4) is defined as the start of the sample elution time. To reduce the possibility of noise or an electronic spike falsely indicating the start of sample elution time, a 1 s slice average can be used instead of a single slice. For noisier baselines, a slice average larger than 1 s may be required.

X1.5 *Determine End of Sample Elution Time*:

X1.5.1 *Calculate Rate of Change between each Two Consecutive Area Slices*—Begin at the end of run and work 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 X.4.1) is defined as the end of sample elution time. To reduce the possibility of noise or an electronic spike falsely indicating the end of sample elution a 1 s slice average can be used instead of a single slice. For noisier baselines a slice average larger than 1 s may be required

X1.6 *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. This is the total sample area, C.

X1.7 *Calculate the Sample Area up to 371 °C (700 °F)*—Add all the slices from the slice corresponding to the start of sample elution time to the slice corresponding to the RT corresponding to 371 °C (700 °F). This is sample area B.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1451. Contact ASTM Customer Service at service@astm.org.

X1.8 Determine the percentage of engine oil volatilized to 371 °C, using Eq 3 in Section 10.

X2. SUMMARY OF PAST CHANGES

X2.1 A list of changes made to the D6417–99 version to create the D6417–02 (and –09) (and –15) revision follows:

(1) Corrected selected Fahrenheit boiling point values in Table 1 and added footnote explaining the derivation of the corrected values.

(2) Expanded the quality control section of this test method to include criterion for developing other suitable quality control materials.

(3) Corrected Table 1, Footnote A.

(4) Renamed Section 11 and reworded 11.1 to replace the words "quality control materials" with "reference materials."

(5) Revised Table 3 to reflect changes made in correcting selected Fahrenheit boiling point values in Table 1.

(6) Revised 1.4, Section 2, and 5.2 to remove all references to withdrawn Test Method D5480.

(7) Revised 2.2 and accompanying footnote and 5.2 to update the referenced Noack volatility method.

(8) Added Appendix X1 in order to clarify the slice mode calculation.

(9) Changes were made to subsections 9.4.1, 9.4.2, 9.6.1, 10.3.1, equation 1 (parenthesis missing), 10.3.1, and Note 2.

(10) Added new Fig. 4 since the Resolution is mentioned in the text but no figure was given.