Designation: D6417 – 09

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

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 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
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.

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.

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

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 D2887.

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 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,* >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 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 gage, 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 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 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.

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

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

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.

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 data collection rate is 3 slices per s)
Column	Capillary, 5 m × 0.53 mm id film thickness; 0.1 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	1 μL
Sample dilution	2 mass % in carbon disulfide
Calibration dilution	1 mass % in carbon disulfide

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:

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

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 %.