



Standard Test Method for Estimation of Engine Oil Volatility by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D 6417; 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 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, non-volatile 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 non-volatile additives, and the results might be biased high relative to Test Method D 5480, which uses an internal standard to account for the uneluted material. 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:

D 2887 Test Method for Boiling Range Distribution of

Petroleum Fractions by Gas Chromatography²

D 4626 Practice for Calculation of Gas Chromatographic Response Factors²

D 5480 Test Method for Motor Oil Volatility by Gas Chromatography³

D 5800 Test Method for Evaporation Loss of Lubricating Oils by the Noack Method³

E 355 Practice for Gas Chromatographic Terms and Relationships⁴

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography⁴

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs⁴

2.2 DIN Standard:

DIN 51.581 Noack Evaporative Test⁵

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E 355, E 594, and E 1510.

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.

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).

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved April 10, 1999. Published June 1999.

² *Annual Book of ASTM Standards*, Vol 05.02.

³ *Annual Book of ASTM Standards*, Vol 05.03.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ Published by Deutsches Institut für Normung and available from Beuth Verlag, GmbH, Burggrafenstrasse 6, 1000 Berlin 30, Germany.

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 *Abbreviation*—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-C₁₀; iso-tetradecane = i-C₁₄).

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 (C₈-C₆₀) 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 D 5800 and D 5480 and the Noack method for the determination of engine oil volatility (see DIN 51.581). The data obtained from this test method are not directly equivalent to Test Method D 5800. 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 D 2887.

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 E 594.

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 E 1510 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**—See Notes 2 and 3.) 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.

NOTE 2—**Warning:** Helium and nitrogen are compressed gases under high pressure.

NOTE 3—**Warning:** Hydrogen is an extremely flammable gas under high pressure.

7.2 Hydrogen—Hydrogen of high purity (for example, hydrocarbon free) is used as fuel for the FID. (**Warning**—See Note 3.)

7.3 Air—High purity (for example, hydrocarbon free) compressed air is used as the oxidant for the FID. (**Warning**—See Note 4.)

NOTE 4—**Warning:** Compressed air is a gas under high pressure and supports combustion.

7.4 Carbon Disulfide (CS₂) (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**—See Note 5.)

NOTE 5—**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**—See Note 6.)

NOTE 6—**Warning:** Cyclohexane is flammable.

7.6 Calibration Mixture—A qualitative mixture of n-paraffins (nominally C₈ to C₆₀) 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, C₈, C₉, C₁₀, C₁₂, C₁₆, C₂₀, C₃₀, C₄₀, C₅₀, C₅₂ and C₆₀). Boiling points of n-paraffins are listed in Table 1.

NOTE 7—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-C₆₀. The mixture must 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

Carbon Number	Boiling Point °C	Boiling Point °F	Carbon Number	Boiling Point °C	Boiling Point °F
2	-89	-128	52	584	1083
3	-42	-44	53	588	1090
4	0	32	54	592	1098
5	36	97	55	596	1105
6	69	156	56	600	1112
7	98	209	57	604	1119
8	126	259	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	455	63	625	1157
14	254	489	64	629	1164
15	271	520	65	632	1170
16	287	549	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	401	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	871	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			

^ABoiling points from API Project 44, 72-10-31.

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 E 1510.

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 E 1510.

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 C₅₀ and C₅₂ paraffins from a calibration mixture analysis (see 7.6). A resolution (*R*) of at least one and not more than twelve, using the identical conditions employed for sample analyses, has been found to be acceptable.

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

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

where:

R = resolution,

*t*₁ = time (s) for the n-C₅₀ peak maximum,

*t*₂ = time (s) for the n-C₅₂ peak maximum,

*w*₁ = peak width (s), at half height, of the n-C₅₀ peak, and

*w*₂ = peak width (s), at half height, of the n-C₅₂ 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 D 4626 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 = concentration 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-C₈) in the calibration mixture and the maximum boiling point (615°C) n-paraffin (n-C₆₀) 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