



Standard Test Method for Engine Oil Volatility by Gas Chromatography¹

This standard is issued under the fixed designation D 5480; 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.

^{ε1} NOTE—Warning statements were made part of the text in November 1999.

1. Scope

1.1 This test method provides for the determination of the amount of engine oil volatilized at 371°C (700°F). This test method is applicable to engine oils containing high molecular weight components that need not elute from a gas chromatographic column.

1.1.1 This test method can also be used to determine the amount of oil volatilized at any temperature between 238 and 371°C, if so desired.

1.2 This test method is limited to samples having an initial boiling point (IBP) greater than 238°C (460°F).

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 6.2, 6.3, and 6.4

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

2.2 DIN Standard:

DIN 51.581 Noack Evaporative Test³

3. Summary of Test Method

3.1 The sample is mixed with an internal standard and a dilute tetracosane solution, and injected into a gas chromatograph. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout

the run. The retention time (RT) at 371°C (700°F) is calculated using linear regression, utilizing the *n*-paraffins comprising the internal standard and the tetracosane retention time/boiling point data. The area response (area/g) of the internal standard is related to the area of the sample determined to the 371°C RT to obtain the mass percentage of oil volatilized at 371°C.

4. Significance and Use

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

4.2 This test method is intended to give a more precise measurement of oil volatility than that obtainable using the Noack method.⁴

4.3 This test method can be used on lubricant products not within the scope of Test Method D 2887.

5. Apparatus

5.1 *Chromatograph*, any gas chromatograph can be used that has the following characteristics:

5.1.1 *Oven*, a column oven having high-temperature (400°C/752°F) capability is required.

5.1.2 *Detector*, a flame ionization detector capable of continuous operation at temperatures of 405°C (761°F) is required.

5.1.3 *Column Temperature Programmer*—The chromatograph must be capable of reproducible linear temperature programming over the temperature range required for the test method.

5.1.4 *Sample Inlet System*—The sample inlet system must provide for on-column injection or equivalent such as programmable splitless injection.

5.1.5 *Column*, 12 m by 0.53 mm by 0.15 μ m nonpolar, carborane modified polydimethylsiloxane bonded phase column or equivalent that can withstand the high column oven temperature employed, and meets the resolution requirements stipulated in 7.3 must be used.

5.1.6 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of a computer or electronic integrator. A timing

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

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

³ DIN 51.581, Prüfung von Schmierstoffen: Bestimmung des Verdampfungsverlustes von Schmierölen nach Noack [Testing of Lubricants: Determination of Noack Volatility of Lubricating Oils] (1958).

⁴ The samples used in the ASTM cooperative study for this test method conducted by ASTM Subcommittee D02.04 were also used for a round-robin study of a proposed Standard Test Method for Evaporation Loss of Lubricating Oils by the Noack Method conducted in 1992 by ASTM Subcommittee D02.06. Refer to the minutes of the December 1992 Subcommittee D02.06 meeting for information on the differences between the methods.

device can be used to record the area at set time intervals. The same basis for measuring time must be used to determine the retention times of the internal standard components and the tetracosane. The maximum signal measured must be within the linear range of the measuring system used.

5.1.7 *Pressure/Flow Controller*—The chromatograph must be equipped with a constant pressure/constant flow device capable of maintaining the carrier gas at a constant flow rate throughout the temperature program.

5.1.8 *Microsyringe*, required for the introduction of sample to the gas chromatograph. A 10- μ L syringe is recommended.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Carbon Disulfide (CS₂)*: (**Warning**—Carbon disulfide is extremely flammable. Also, breathing of its vapor and skin contact should be avoided.)

6.3 *Carrier Gas*—Helium (high purity). Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons (**Warning**—Helium is a compressed gas under high pressure).

6.4 *Detector Gases*—Air, hydrogen (**Warning**—Air and hydrogen are compressed gases under high pressure. Hydrogen is an extremely flammable gas).

6.5 *Decane* [CH₃(CH₂)₈CH₃].

6.6 *Dodecane* [CH₃(CH₂)₁₀CH₃].

6.7 *Hexadecane* [CH₃(CH₂)₁₄CH₃].

6.8 *Octadecane* [CH₃(CH₂)₁₆CH₃].

6.9 *Tetracosane* [CH₃(CH₂)₂₂CH₃].

6.10 *Undecane* [CH₃(CH₂)₉CH₃].

7. Preparation of Apparatus

7.1 *Column Preparation*—The column must be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of column substrate. The column can be conditioned using the following procedure:

7.1.1 Disconnect the column from the detector.

7.1.2 Purge the column at ambient temperature for at least 30 min.

7.1.3 With carrier gas flowing through the column, raise the column oven temperature to the maximum temperature that will be used and maintain the temperature at this level for 12 to 16 h.

⁵ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.1.4 Cool the column to ambient temperatures.

7.1.5 Reconnect the column to the detector.

7.1.6 Set the detector temperature at least 5°C higher than the maximum column temperature to be used.

7.1.7 Program the column temperature up to the maximum several times with normal carrier gas flow until a stable baseline is obtained.

7.2 *Performance Standard*—To test column resolution and linearity of response, a performance standard is prepared as follows: Prepare a stock solution by accurately weighing 0.1 g (to the nearest 0.1 mg) of decane, dodecane, hexadecane, octadecane and tetracosane (all 99+ % purity) into a 100-mL volumetric flask. Dilute to the mark with carbon disulfide and mix well until each hydrocarbon is completely dissolved and the solution is uniform. The performance standard is prepared by pipetting 0.1 mL of the stock solution into a 10-mL volumetric flask, diluting to the mark with carbon disulfide and mixing well.

7.3 *Column Resolution*—To test column resolution, inject the same volume of performance standard as is used in the analysis of samples and obtain a chromatogram using the procedure described in Section 8. Referring to Fig. 1, calculate resolution using the following equation:

$$R = [2(d_2 - d_1)]/[1.699(Y_1 + Y_2)] \quad (1)$$

where:

R = column resolution,

d_2 = retention time for octadecane at peak maximum, s,

d_1 = retention time for hexadecane at peak maximum, s,

Y_1 = peak width of hexadecane at half height, s, and

Y_2 = peak width of octadecane at half height, s.

The column resolution must be between 19 and 26 to be acceptable.

7.4 *Linearity of Response*—The relative response factor for each component in the performance standard (relative to octadecane) should be within 5 % of unity. After obtaining the chromatogram of the performance standard, calculate the relative response factor for each n -paraffin in the mixture, in accordance with Test Method D 4626, by relating the mass of each component to its respective peak area. Calculate the relative response factor for each component as follows:

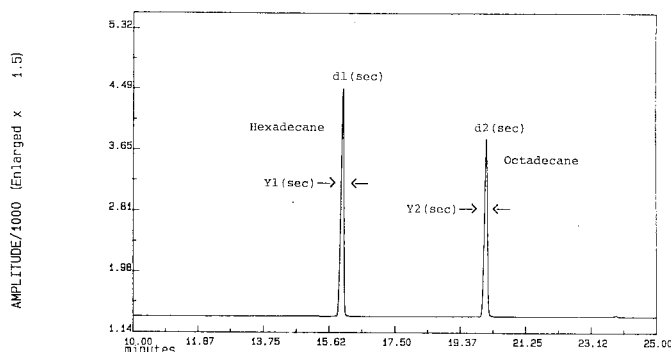


FIG. 1 A Portion of the Performance Standard Chromatogram Showing the Hexadecane and Octadecane Peaks Used to Determine Column Resolution

$$RRF = (Mn/An)/(M_{18}/A_{18}) \quad (2)$$

where:

- RRF = relative response factor,
- Mn = mass of the component in the mixture,
- An = area of the component in the mixture,
- M_{18} = mass of octadecane in the mixture, and
- A_{18} = area of octadecane in the mixture.

Also, examine the peak shape of the components in the performance standard. If peak distortion is evident, a smaller sample size may need to be used or the column may need to be replaced.

8. Procedure

8.1 Prepare the internal standard mixture by adding 10 mL each of decane, undecane, and dodecane to a stoppered flask, and mix well.

8.2 Prepare the tetracosane solution by adding 0.2 g tetracosane to a 100-mL volumetric flask and diluting to the mark with carbon disulfide (Solution A).

8.3 Weigh 2.0 g engine oil and 0.1 g of internal standard mixture (each to the nearest 0.1 mg) into a 25-mL volumetric flask and dilute to the mark with carbon disulfide (Solution B).

8.4 Using a pipet, add 1 mL of Solution A and 1 mL of Solution B to a 10-mL volumetric flask and dilute to the mark with carbon disulfide (Solution C).

8.5 Inject an aliquot of Solution C into the gas chromatograph using the instrument parameters given in 8.6. An injection technique should be chosen which does not cause distortion of the peak shapes associated with the performance standard prepared in 7.2. They can vary depending upon the instrument and column utilized. The final column temperature should not exceed the recommendations of the manufacturer, but should be high enough to ensure elution of the oil. A typical chromatogram is shown in Fig. 2.

8.6 Recommended Instrument Operating Parameters:

Initial oven temperature, °C	40
Initial time, min	1
Final oven temperature, °C	400
Program rate, °C/min	5
Final time, min	5
Detector temperature, °C	405
Injection port temperature	Cold on-column
Carrier gas	Helium
Carrier gas flow rate, mL/min	7-10
Sample size, µL	1-3

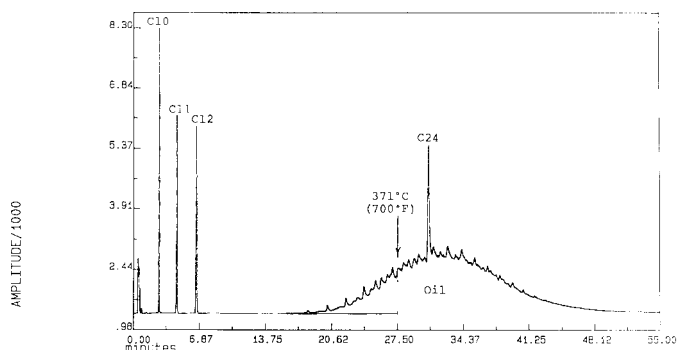


FIG. 2 Typical Chromatogram of a 5W-30 Engine Oil Showing the Positions of the Internal Standard and the Tetracosane Marker In Relation to the Oil Envelope

9. Calculation

9.1 Tabulate the retention times observed for decane, undecane, dodecane, and tetracosane versus their respective boiling points, and calculate the retention time equivalent to 371°C (700°F) using linear regression and interpolation.

9.1.1 Although descriptions of how to apply linear regression can be found in many mathematical textbooks,⁶ scientific hand calculators are readily available that will perform the operation.

9.1.2 Refer to Table 1 for boiling points of *n*-paraffins.

9.2 Determine the mass percentage of engine oil volatilized to 371°C as follows:

$$A = 100 BC/DE \quad (3)$$

where:

- A = engine oil volatilized to 371°C, mass, %,
- B = area of the engine oil up to 371°C,
- C = mass of internal standard added, g,
- D = total area of the three internal standard peaks,
- E = mass of total engine oil, g, and
- 100 = factor to convert g/g to mass, %.

10. Report

10.1 Report mass percent oil volatilized to 371°C (700°F) to the nearest 0.1 %.

11. Precision and Bias⁷

11.1 *Precision*—The precision of the procedure in this test method for determining the amount of oil volatilized at 371°C (700°F) in engine oil by gas chromatography as determined by the statistical examination of interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials

⁶ See Draper, N. R., and Smith, H., *Applied Regression Analysis*, 2nd Ed. New York: Wiley, 1981, p. 8.

⁷ The results of the cooperative test program, from which these values have been derived, are filed at ASTM Headquarters. Request Report No. RR:D02-1311.

TABLE 1 Boiling Points of *n*-Paraffins^A

Carbon Number	°C	°F
10	174	345
11	196	385
12	216	421
13	235	455
14	254	489
15	271	520
16	287	549
17	302	576
18	317	603
19	330	626
20	344	651
21	356	673
22	368	694
23	380	716
24	391	736

^AC₁₀–C₂₀ values from "Selected Values of Properties of Hydrocarbons and Related Compounds," API Project 44, p. K-1011, Oct. 31, 1970. C₂₁–C₂₄ values from "Selected Values of Properties of Hydrocarbons and Related Compounds," API Project 44, p. K-1030, Oct. 31, 1972. F values were calculated from C values.

would, in the long run, in the normal and correct operation of the test method exceed the following values only one case in twenty (see Table 2):

$$\text{Repeatability} = 0.403 * X^{0.25} \quad (4)$$

where:

X = volatility level.

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators in different laboratories on identical test materials would, in the long run, exceed the following values only in one case in twenty (see Table 2):

$$\text{Reproducibility} = 1.617 * X^{0.25} \quad (5)$$

where:

X = volatility level.

12. Keywords

12.1 gas chromatography; engine oil; lubricants; volatility

TABLE 2 Precision Estimates for Oil Volatility

Volatility at 371°C (700°F), %	Repeatability	Reproducibility
3.0	0.53	2.13
3.5	0.55	2.21
4.0	0.57	2.29
4.5	0.59	2.36
5.0	0.60	2.42
5.5	0.62	2.48
6.0	0.63	2.53
6.5	0.64	2.58
7.0	0.66	2.63
7.5	0.67	2.68
8.0	0.68	2.72
8.5	0.69	2.76
9.0	0.70	2.80
9.5	0.71	2.84
10.0	0.72	2.88
10.5	0.73	2.91
11.0	0.73	2.95
11.5	0.74	2.98
12.0	0.75	3.01
12.5	0.76	3.04
13.0	0.76	3.07
13.5	0.77	3.10
14.0	0.78	3.13
14.5	0.79	3.16
15.0	0.79	3.18
15.5	0.80	3.21
16.0	0.81	3.23
16.5	0.81	3.26
17.0	0.82	3.28
17.5	0.82	3.31
18.0	0.83	3.33
18.5	0.84	3.35
19.0	0.84	3.38
19.5	0.85	3.40
20.0	0.85	3.42
20.5	0.86	3.44
21.0	0.86	3.46

 **D 5480**

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