

Designation: D1840 - 22

# Standard Test Method for Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry<sup>1</sup>

This standard is issued under the fixed designation D1840; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

# 1. Scope\*

- 1.1 This test method covers the determination, by ultraviolet spectrophotometry, of the total concentration of naphthalene, acenaphthene, and alkylated derivatives of these hydrocarbons in jet fuels. This test method is designed to analyze fuels containing not more than 5 % of such components and having end points below 315 °C (600 °F). The range of concentrations used in the interlaboratory test programs which established the precision statements for this test method was 0.08 % to 5.6 % by volume. This test method determines the maximum amount of naphthalenes that could be present.
- 1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.3 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific warning statements, see 8.1 and 8.2.
- 1.4 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

# 2. Referenced Documents

2.1 ASTM Standards:<sup>2</sup>

E131 Terminology Relating to Molecular Spectroscopy

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

**E275** Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

# 3. Terminology

- 3.1 Definitions:
- 3.1.1 Definitions of terms and symbols relating to absorption spectroscopy in this test method shall conform to Terminology E131. Terms of particular significance are the following:
- 3.1.2 *radiant energy, n*—energy transmitted as electromagnetic waves.
- 3.1.3 *radiant power, P, n*—rate at which energy is transported in a beam of radiant energy.
  - 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 *absorbance*, *A*, *n*—the molecular property of a substance that determines its ability to take up radiant power, expressed by

$$1000 - 4 dc0 - ba5f - A = \log_{10}(1/T) = -\log_{10}T \cdot 1840 - 22 \tag{1}$$

where:

T = transmittance as defined in 3.2.5.

- 3.2.1.1 *Discussion*—It may be necessary to correct the observed transmittance (indicated by the spectrophotometer) by compensating for reflectance losses, solvent absorption losses, or refraction effects.
- 3.2.2 *absorptivity, a, n*—the specific property of a substance to absorb radiant power per unit sample concentration and path length, expressed by

$$a = A/bc (2)$$

where:

A = absorbance defined in 3.2.1,

b = sample cell path length, and

c = quantity of absorbing substance contained in a unit volume of solvent.

3.2.2.1 *Discussion*—Quantitative ultraviolet analyses are based upon the absorption law, known as Beer's law. The law

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<sup>&</sup>lt;sup>2</sup> 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.

states that the absorbance of a homogeneous sample containing an absorbing substance is directly proportional to the concentration of the absorbing substance at a single wavelength, expressed by

$$A = abc (3)$$

where:

- A = absorbance as defined in 3.2.1,
- a = absorptivity as defined in 3.2.2,
- b = sample cell path length, and
- c = quantity of absorbing substance contained in a unit volume of solvent.
- 3.2.3 *concentration, c, n*—the quantity of naphthalene hydrocarbons in grams per litre of *iso*octane.
- 3.2.4 sample cell path length, b, n—the distance, in centimetres, measured in the direction of propagation of the beam of radiant energy, between the surfaces of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.
- 3.2.4.1 *Discussion*—This distance does not include the thickness of the cell in which the specimen is contained.
- 3.2.5 *transmittance*, *T*, *n*—the molecular property of a substance that determines its transportability of radiant power expressed by

$$T = P/P_o \tag{4}$$

where:

P = radiant power passing through the sample, and  $P_o$  = radiant power incident upon the sample.

# 4. Summary of Test Method

4.1 The total concentration of naphthalenes in jet fuels is determined by measurement of the absorbance at 285 nm of a solution of the fuel at known concentration.

#### 5. Significance and Use

5.1 This test method for naphthalene hydrocarbons is one of a group of tests used to assess the combustion characteristics of aviation turbine fuels of the kerosene boiling range. The naphthalene hydrocarbon content is determined because naphthalenes, when burned, tend to have a relatively larger contribution to a sooty flame, smoke, and thermal radiation than single ring aromatics.

# 6. Interferences

- 6.1 Interferences add to the apparent naphthalene content. Phenanthrenes, dibenzothiophenes, biphenyls, benzothiophenes, and anthracenes interfere if present. The end point limitation of 315 °C will minimize this interference except for benzothiophenes and biphenyls. The contribution to measured naphthalene content by the presence of 1 % of such interfering compounds can be estimated from Table 1.
- 6.2 Saturated hydrocarbons, olefins, thiophenes, and alkyl or cycloalkyl derivatives of benzene will not interfere.

### 7. Apparatus

7.1 Spectrophotometer, equipped to measure the absorbance of solutions in the spectral region 240 nm to 300 nm with a

**TABLE 1 Interfering Compounds** 

Type of Interfering Compound	Error in Percentage of Naphthalenes Caused by 1 % Interfering Compound
Phenanthrenes	2
Dibenzothiophenes	2
Biphenyls	1
Benzothiophenes	0.6
Anthracenes	0.1

spectral slit width of 1 nm or less. Wavelength measurements shall be repeatable and known to be accurate within 0.1 nm or less as measured by mercury emission line at 253.65 nm or the absorption spectrum of either holmium oxide glass at 287.5 nm or holmium oxide solution at 287.1 nm. At the 0.4 absorbance level in the spectral region between 240 nm and 300 nm, absorbance measurements shall be repeatable within  $\pm 0.5\,\%$  or better. In the absorbance range encompassing 0.2 to 0.8, the photometric accuracy shall not differ by more than  $\pm 0.5\,\%$  of samples whose absorbance has been established by a standardizing laboratory.

- 7.1.1 *Discussion*—Many manufacturers provide secondary standards, traceable to NIST primary standards, for checking the wavelength accuracy and photometric accuracy of spectrophotometers. These materials may be used to verify spectrophotometer performance provided that they have been recalibrated periodically as recommended by the manufacturer.
- 7.2 It shall be initially and thereafter periodically demonstrated that an instrument can be operated in a manner to give test results equivalent to those described in 7.1.

Note 1—For recommended methods of testing spectrophotometers to be used in this test method, refer to Practice E275. Other preferred alternatives to those in 7.1 are potassium dichromate in perchloric acid (NIST SRM 935 series as described in Practice E275) for photometric accuracy and a 20 mg/L high (>99 %) purity naphthalene in spectroscopic grade *iso*octane for wavelength accuracy. The latter has a minor maximum at 285.7 nm. The naphthalene solution shall not be used for photometric accuracy.

- 7.3 Vitreous Silica Cells, two, having path lengths of  $1.00~\rm{cm} \pm 0.005~\rm{cm}$ .
  - 7.4 Pipets, Class A.
  - 7.5 Lens Paper.
- 7.6 *Balance*, capable of taring or weighing 100 g to the nearest 0.0001 g. The balance shall be accurate to  $\pm 0.0002$  g at a 100 g load.

#### 8. Solvents

8.1 Spectroscopic 2,2,4 Trimethylpentane (Isooctane). (Warning—Isooctane is extremely flammable, harmful if inhaled.)

Note 2—Spectroscopic-grade *iso* octane is available commercially. Technical-grade *iso* octane is a satisfactory base stock for the preparation of spectroscopic solvent. Allow about 4 L or 5 L of this material to percolate through a column of activated silica gel (74  $\mu m$ ) 50.8 mm to 76.2 mm in diameter and 0.6 m to 0.9 m in depth. Collect only the portion of the solvent that has a transmission compared to distilled water greater than 90 % over the entire spectral range from 240 nm to 300 nm. Store in scrupulously clean glass-stoppered bottles and always keep covered. In general it will be best to use a fresh portion of silica gel in preparing a new

batch of solvent. However the gel can be reactivated by pouring 500 mL of acetone through the column, draining, drying by suction, and heating the gel in thin layers in an oven at 400  $^{\circ}$ C until white color is restored. Activated silica gel is stored in closed containers.

8.2 Solvents for Cleaning Cells—Acetone or ethyl alcohol (Warning—Acetone and ethyl alcohol are extremely flammable and can be harmful if inhaled), with residue after evaporation no greater than 10 mg/kg.

Note 3—The  $10 \, \text{mg/kg}$  is the American Chemical Society (ACS) reagent grade maximum specification. An ACS reagent grade solvent may be used without further testing.

#### 9. Calibration and Standardization

9.1 Instead of direct calibration of the spectrophotometer with known naphthalenes, the average absorptivity of the  $C_{10}$  to  $C_{13}$  naphthalenes at 285 nm can be taken at 33.7 L/g·cm. The data used to calculate this average are given in Table 2.

# 10. Procedure

- 10.1 For recommended techniques, refer to Practices E169. Check carefully sections on handling and cleaning of cells and glassware, instrument adjustments, and method of absorbance measurement.
- 10.2 Sample Preparation—Add an appropriate mass of sample to a clean, dry, tared 100 mL volumetric flask. Record the mass to the nearest 0.0001 g. Dilute to the mark with spectroscopic grade *iso*octane, stopper, and mix thoroughly.
- 10.2.1 Refer to Table 3 for lists of sample masses associated with naphthalene(s) concentrations that give 0.2 to 0.8 absorbance readings as directed in Note 6. A 60 mg sample will be appropriate for typical jet fuels in the range of 0.8 % to 3.0 % by volume naphthalenes.

Note 4—The mass of the sample should be controlled so that solution absorbance readings fall within a range of 0.2 to 0.8 for maximum reproducibility of results

Note 5—A micropipette is a convenient tool for adding an appropriate volume. If the fuel density is not known at the time of sample preparation, use 0.8 as an approximation.

10.3 Determination of Cell Correction—Measure and record the absorbance of the spectroscopic *iso*octane-filled sample cell as compared to the spectroscopic *iso*octane-filled solvent cell.

TABLE 2 Data Issued by API Research Project 44

Compound	API Serial Number	L/g⋅cm
Naphthalene	605	28.5
1-methyl Naphthalene	539	32.0
2-methyl Naphthalene	572	22.9
1,2-dimethyl Naphthalene	215	37.3
1,3-dimethyl Naphthalene	216	36.4
1,4-dimethyl Naphthalene	217	43.5
1,5-dimethyl Naphthalene	218	54.0
1,6-dimethyl Naphthalene	219	36.4
1,7-dimethyl Naphthalene	220	36.0
1,8-dimethyl Naphthalene	221	46.0
2,3-dimethyl Naphthalene	222	22.0
2,6-dimethyl Naphthalene	226	21.3
2,7-dimethyl Naphthalene	224	23.5
1-isopropyl Naphthalene	203	31.7

TABLE 3 Estimated Sample Mass and Volume to Take for the Volume % Naphthalene Content of the Sample in the Single Dilution Procedure to Keep the Absorption Values Between 0.2 and 0.8 Units (Assuming a Density of 0.8)

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Sample	Sample	Volume % Naphthalenes	Volume % Naphthalenes		
Volume	Mass	for Expected	for Expected		
(mL)	(mg)	Absorbance	Absorbance		
		of 0.2 units	of 0.8 units		
0.050	40	1.2	4.8		
0.075	60	0.8	3.2		
0.100	80	0.6	2.4		
0.150	120	0.4	1.6		
0.200	160	0.3	1.2		
0.300	240	0.2	0.8		

10.4 Measurement of Absorbance—Transfer portions of the final dilution into the sample cell of the spectrophotometer. Cover the cells immediately to prevent transfer of aromatic hydrocarbons from the sample cell to the solvent cell. Check the windows of the absorption cells and make certain they are clean. Measure the absorbance as recommended in Practices E169. Record the absorbance of the sample as compared to spectroscopic isooctane at 285 nm.

### 11. Calculations

11.1 Calculate the mass percentage of naphthalenes in the sample as follows:

Naphthalenes, mass 
$$\% = [(A \times K)/(33.7 \times W)] \times 100$$
 (5)

where:

A = corrected absorbance (observed absorbance minus cell correction) of the dilution measured,

K = 0.10,

 $W_{00}$  = grams of sample used, and

33.7 = the average absorptivity of  $C_{10}$  to  $C_{13}$  naphthalenes in litres per gram-centimetre.

11.2 Calculate the volume percentage of naphthalenes as follows:

Naphthalenes, volume 
$$\% = M \times (B/C)$$
 (6)

where:

M = percentage of naphthalenes by mass,

B = relative density of the total fuel (15 °C/15 °C), and

C = relative density of the naphthalenes  $(15 \, {}^{\circ}\text{C}/15 \, {}^{\circ}\text{C}) = 1.00$ .

#### 12. Report

12.1 Report numerical values of volume percent naphthalene to the nearest 0.01 %.

# 13. Reference Spectra

13.1 Absorptivities of individual naphthalene hydrocarbons at 285 nm are derived from data in the API catalog of ultraviolet spectral data issued by Research Project 44 as given in Table 2.

Note 6—The arithmetic average of the above absorptivities is 33.7. The reliability of the average absorptivity as a measure of selected individual naphthalenes can be estimated from the above table.