



Designation: D 1319 – 99

An American National Standard



Designation: 156/97

## Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption<sup>1</sup>

This standard is issued under the fixed designation D 1319; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This test method has been approved by the sponsoring committees and accepted by the cooperating societies in accordance with established procedures.*

*This standard has been approved for use by agencies of the Department of Defense. This test method replaces Method 3703 of Federal Test Method Standard No. 791b.*

### 1. Scope

1.1 This test method covers the determination of hydrocarbon types over the concentration ranges from 5 to 99 volume % aromatics, 0.3 to 55 volume % olefins, and 1 to 95 volume % saturates in petroleum fractions that distill below 315°C. This test method may apply to concentrations outside these ranges, but the precision has not been determined. Samples containing dark-colored components that interfere in reading the chromatographic bands cannot be analyzed.

1.2 This test method is intended for use with full boiling range products. Cooperative data have established that the precision statement does not apply to narrow boiling petroleum fractions near the 315°C limit. Such samples are not eluted properly, and results are erratic.

1.3 The applicability of this test method to products derived from fossil fuels other than petroleum, such as coal, shale, or tar sands, has not been determined, and the precision statement may or may not apply to such products.

1.4 The precision statement for this test method has been determined with unleaded fuels that do not contain oxygenated blending components. It may or may not apply to automotive gasolines containing lead antiknock mixtures or oxygenated gasoline blending components, or both.

1.5 The oxygenated blending components, methanol, ethanol, methyl-*tert*-butylether (MTBE), methyl-*tert*-amylmethyl (TAME), and ethyl-*tert*-butylether (ETBE), do not interfere with the determination of hydrocarbon types at concentrations normally found in commercial blends. These oxygenated components are not detected since they elute with the alcohol

desorbent. Other oxygenated compounds shall be individually verified. When samples containing oxygenated blending components are analyzed, correct the results to a total-sample basis.

1.6 The values stated in SI units are to be regarded as standard.

NOTE 1—For the determination of olefins below 0.3 volume %, other test methods are available, such as Test Method D 2710.

1.7 *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 hazard statements, see Section 8, 9.1, and 12.5.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 770 Specification for Isopropyl Alcohol<sup>2</sup>
- D 1655 Specification for Aviation Turbine Fuels<sup>3</sup>
- D 2001 Test Method for Depentanization of Gasoline and Naphthas<sup>3</sup>
- D 2427 Test Method for Determination of C<sub>2</sub> through C<sub>5</sub> Hydrocarbons in Gasolines by Gas Chromatography<sup>3</sup>
- D 2710 Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration<sup>4</sup>
- D 3663 Test Method for Surface Area of Catalysts<sup>5</sup>
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>4</sup>
- D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tertiary*-Amyl Alcohol and C<sub>1</sub> to C<sub>4</sub> Alcohols in Gasoline by Gas Chromatography<sup>5</sup>
- D 5599 Test Method for Determination of Oxygenates in

<sup>1</sup> 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.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.04.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 05.03.

Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection<sup>5</sup>

E 11 Specification for Wire-Cloth Sieves for Testing Purposes<sup>6</sup>

### 3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aromatics*—the volume % of monocyclic and polycyclic aromatics, plus aromatic olefins, some dienes, compounds containing sulfur and nitrogen, or higher boiling oxygenated compounds (excluding those listed in 1.5).

3.1.2 *olefins*—the volume % of alkenes, plus cycloalkenes, and some dienes.

3.1.3 *saturates*—the volume % of alkanes, plus cycloalkanes.

### 4. Summary of Test Method

4.1 Approximately 0.75 mL of sample is introduced into a special glass adsorption column packed with activated silica gel. A small layer of the silica gel contains a mixture of fluorescent dyes. When all the sample has been adsorbed on the gel, alcohol is added to desorb the sample down the column. The hydrocarbons are separated in accordance with their adsorption affinities into aromatics, olefins, and saturates. The fluorescent dyes are also separated selectively, with the hydrocarbon types, and make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

### 5. Significance and Use

5.1 The determination of the total volume % of saturates, olefins, and aromatics in petroleum fractions is important in characterizing the quality of petroleum fractions as gasoline blending components and as feeds to catalytic reforming processes. This information is also important in characterizing petroleum fractions and products from catalytic reforming and from thermal and catalytic cracking as blending components for motor and aviation fuels. This information is also important as a measure of the quality of fuels, such as specified in Specification D 1655.

### 6. Interferences

6.1 Errors in the direction of high saturate values and low aromatic and low olefin values can result if the sample containing significant amounts of C<sub>5</sub> and lighter hydrocarbons. Such samples are to be depentanized by Test Method D 2001.

### 7. Apparatus

7.1 *Adsorption Columns*, with precision bore (“true bore” IP designation) tubing, as shown on the right in Fig. 1, made of glass and consisting of a charger section with a capillary neck, a separator section, and an analyzer section; or with standard wall tubing, as shown on the left in Fig. 1.

7.1.1 The inner diameter of the analyzer section for the precision bore tubing shall be 1.60 to 1.65 mm. In addition the

length of an approximately 100-mm thread of mercury shall not vary by more than 0.3 mm in any part of the analyzer section. In glass-sealing the various sections to each other, long-taper connections shall be made instead of shouldered connections. Support the silica gel with a small piece of glass wool located between the ball and socket of the 12/2 spherical joint and covering the analyzer outlet. The column tip attached to the 12/2 socket shall have a 2-mm internal diameter. Clamp the ball and socket together and ensure that the tip does not tend to slide from a position in a direct line with the analyzer section during the packing and subsequent use of the column.

7.1.2 For convenience, adsorption columns with standard wall tubing, as shown on the left in Fig. 1, can be used. When using standard wall tubing for the analyzer section, it is necessary to select tubing of uniform bore and to provide a leakproof connection between the separator and the analyzer sections. Calibrations of standard wall tubing would be impractical; however, any variations of 0.5 mm or greater, as measured by ordinary calipers, in the outside diameter along the tube can be taken as an indication of irregularities in the inner diameter and such tubing should not be used. Draw out one end of the tubing selected for the analyzer section to a fine capillary to retain the gel. Connect the other end of the analyzer section to the separator section with a 30-mm length of vinyl tubing, making certain that the two glass sections touch. To ensure a leakproof glass-to-vinyl seal with the analyzer section, it is necessary to heat the upper end of the analyzer section until it is just hot enough to melt the vinyl, then insert the upper end of the analyzer section into the vinyl sleeve. Alternatively, this seal can be made by securing the vinyl sleeve to the analyzer section by wrapping it tightly with soft wire.

7.2 *Zone-Measuring Device*—The zones may be marked with a glass-writing pencil and the distances measured with a meter rule, with the analyzer section lying horizontally. Alternatively, the meter rule may be fastened adjacent to the column. In this case, it is convenient to have each rule fitted with four movable metal index clips (Fig. 1) for marking zone boundaries and measuring the length of each zone.

7.3 *Ultraviolet Light Source*, with radiation predominantly at 365 nm is required. A convenient arrangement consists of one or two 915 or 1220-mm units mounted vertically along the apparatus. Adjust to give the best fluorescence.

7.4 *Electric Vibrator*, for vibrating individual columns or the frame supporting multiple columns.

7.5 *Hypodermic Syringe*, 1 mL, graduated to 0.01 or 0.02 mL, with needle 102 mm in length. Needles of No. 18, 20, or 22 gage are satisfactory.

7.6 *Regulator*, 2-stage, 0 to 103 kPa gage delivery range.

### 8. Reagents and Materials

8.1 *Silica Gel*,<sup>7</sup> manufactured to conform to the specifications shown in Table 1. Determine the surface area of the gel by Test Method D 3663. Determine the pH of the silica gel as follows: Calibrate a pH meter with standard pH 4 and pH 7 buffer solutions. Place 5 g of the gel sample in a 250-mL

<sup>6</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>7</sup> Available from W. R. Grace and Co., Davison Chemical Div., Baltimore, MD 21203 by specifying Code 923.

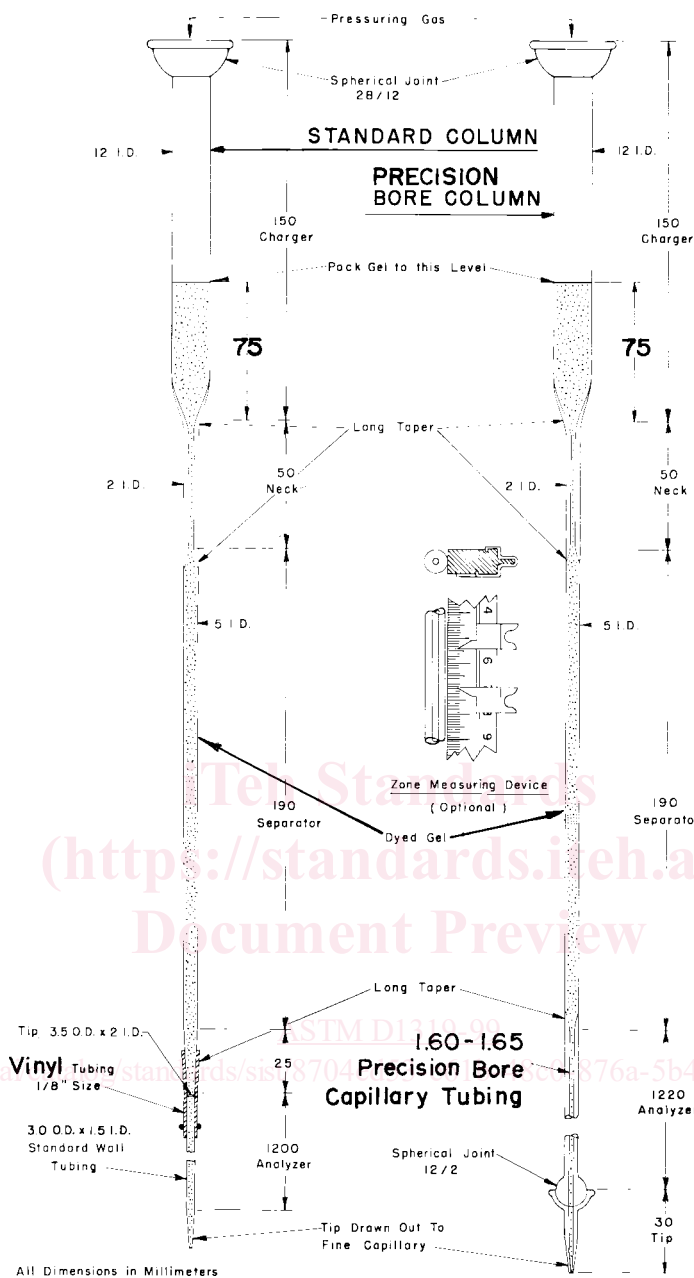


FIG. 1 Adsorption Columns with Standard Wall (left) and Precision Bore (right) Tubing in Analyzer Section

TABLE 1 Silica Gel Specifications

Surface area, m <sup>2</sup> /g	430 to 530	
pH of 5 % water slurry	5.5 to 7.0	
Loss on ignition at 955°C, mass-%	4.5 to 10.0	
Iron as Fe <sub>2</sub> O <sub>3</sub> , dry basis, mass-ppm	50 max	
Particle Size		
Sieve Number <sup>A</sup>	µm	Mass-%
on 60	250	0.0 max
on 80	180	1.2 max
on 100	150	5.0 max
through 200	75	15.0 max

<sup>A</sup> Detailed requirements for these sieves are given in Specification E 11, and BS410: 1943.

vessel at 175°C for 3 h. Transfer the dried gel to an air tight container while still hot, and protect it thereafter from atmospheric moisture.

NOTE 2—Some batches of silica gel that otherwise meet specifications have been found to produce olefin boundary fading. The exact reason for this phenomenon is unknown but will affect accuracy and precision.

8.2 *Fluorescent Indicator Dyed Gel*— A standard dyed gel,<sup>8</sup> consisting of a mixture of recrystallized Petrol Red AB4 and purified portions of the olefin and aromatic dyes obtained by chromatographic adsorption, following a definite, uniform

<sup>8</sup> Available from UOP LLC, Finished Product Technologies Dept., 25 E. Algonquin Rd., Des Plaines, IL 60017-5017, by requesting "FIA Standard Dyed Gel," UOP LLC Product No. 80675.