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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption[1]

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 (ε) 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 is for determining 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 following oxygenated blending components: methanol, ethanol, methyl-*tert*-butylether, *tert*-amylmethylether and ethyl-*tert*-butylether 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 must be individually verified. When samples containing oxygenated blending components are analyzed, the results must be corrected 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 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 Notes 3-7, and Note 10.

2. Referenced Documents

2.1 *ASTM Standards:*

D 770 Specification for Isopropyl Alcohol[2]
D 1655 Specification for Aviation Turbine Fuels[3]
D 2001 Test Method for Dependentanization of Gasoline and Naphthas[3]
D 2427 Test Method for Determination of C_2 through C_5 Hydrocarbons in Gasolines by Gas Chromatography[3]
D 2710 Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration[4]
D 3663 Test Method for Surface Area of Catalysts[5]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]
D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tertiary*-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography[5]

[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 Analyses.

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

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[2] *Annual Book of ASTM Standards*, Vol 06.04.
[3] *Annual Book of ASTM Standards*, Vol 05.01.
[4] *Annual Book of ASTM Standards*, Vol 05.02.
[5] *Annual Book of ASTM Standards*, Vol 05.03.

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

2.2 *Other Standards:*

GC/OFID EPA Test Method–Oxygen and Oxygenate Content Analysis[7]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *saturates*—the volume % of alkanes plus cycloalkanes.

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

3.1.3 *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).

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 according to 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 contains significant amounts of C_5 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

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] Code of Federal Regulations, Part 80 of Title 40, 80.46(g); also published in the Federal Register, Vol 59, No. 32, Feb. 16, 1994, p 7828. Available from Library of Congress.

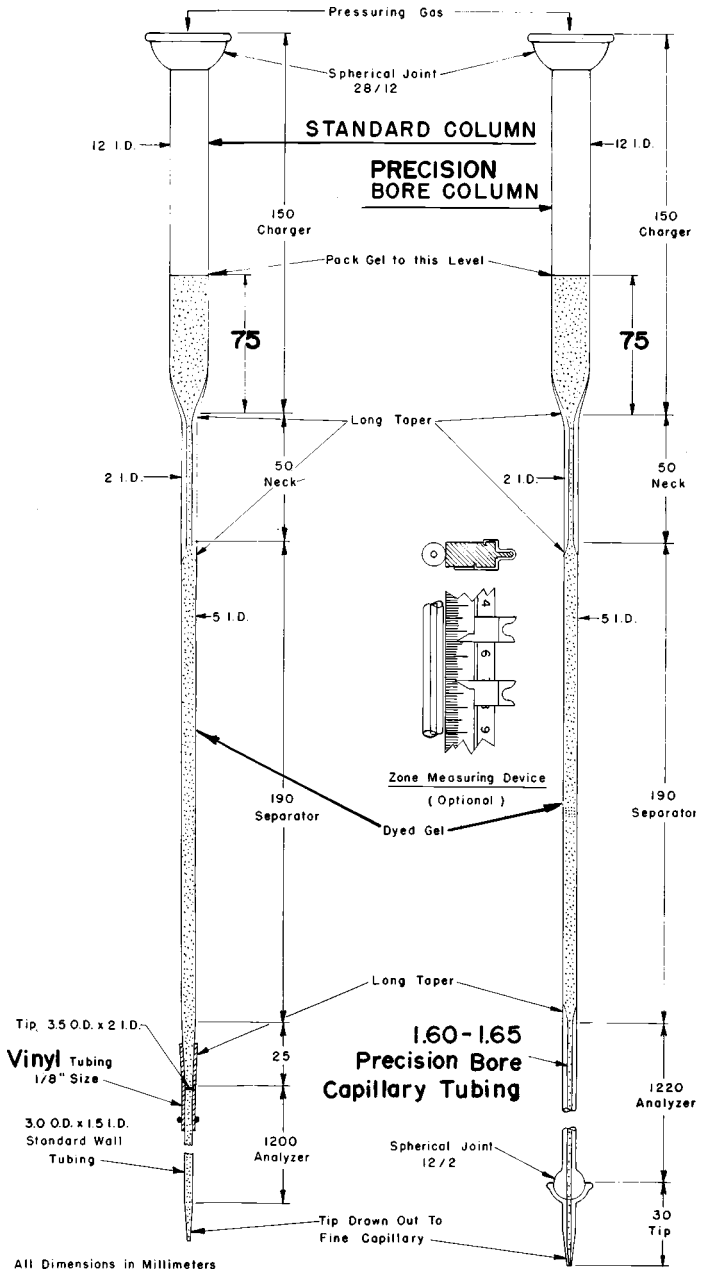

FIG. 1 Adsorption Columns with Standard Wall (left) and Precision Bore (right) Tubing in Analyzer Section

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-mm 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*,[8] 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 beaker. Add 100 mL of water and a stirring bar. Stir the slurry on a magnetic stirrer for 20 min and then determine the pH with the calibrated meter. Before use, dry the gel in a shallow 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,[9] 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 procedure, and deposited on silica gel. The dyed gel shall be stored in a dark place under an atmosphere of nitrogen. When stored under these conditions, the dyed gel can have a shelf life of at least five years. It is recommended that portions of the dyed gel be transferred as required to a smaller working vial from which the dyed gel is routinely taken for analyses.

8.3 *Isoamyl Alcohol*, (3-methyl-1-butanol) 99 %.

NOTE 3—**Warning:** Flammable. Health hazard.

8.4 *Isopropyl Alcohol*, (2-propanol) 99 %, conforming to Specification D 770.

NOTE 4—**Warning:** Flammable. Health hazard.

8.5 *Pressuring Gas*—Air (or nitrogen) delivered to the top of the column at pressures controllable over the range from 0 to 103 kPa gage.

NOTE 5—**Warning:** Compressed gas under high pressure.

8.6 *Acetone*, reagent grade, residue free.

NOTE 6—**Warning:** Flammable. Health hazard.

8.7 *Buffer Solutions*, pH 4 and 7.

9. Sampling

9.1 Obtain a representative sample according to sampling procedures in Practice D 4057. Store the sample until ready for analysis at 2 to 4°C.

NOTE 7—**Warning:** Flammable. Health hazard.

10. Preparation of Sample

10.1 Samples containing C_3 or lighter hydrocarbons, more than 5 % C_4 hydrocarbons, or more than 10 % C_4 and C_5 hydrocarbons can be depentanized in accordance with Test Method D 2001.

11. Preparation of Apparatus

11.1 Mount the apparatus assembly in a darkened room or area to facilitate observation of zone boundaries. For multiple determinations, assemble an apparatus that includes the ultraviolet light source, a rack to hold the columns, and a gas manifold system with spherical joints to connect to the desired number of columns.

[8] Available from W. R. Grace and Co., Davison Chemical Div., Baltimore, MD 21203 by specifying Code 923.

TABLE 1 Silica Gel Specifications

Surface area, m^2/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_2O_3, dry basis, mass-ppm		50 max
Particle Size		
Sieve Number[A]	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

[A] Detailed requirements for these sieves are given in Specification E 11, and BS410: 1943.

[9] Available from UOP, Refining Chemicals Dept., 25 E. Algonquin Rd., Des Plaines, IL 60017-5017, by requesting "FIA Standard Dyed Gel," UOP Product No. 675.

12. Procedure

12.1 Freely suspend the column from a loose-fitting clamp placed immediately below the spherical joint of the charger section. While vibrating the column along its entire length, add small increments of silica gel through a glass funnel into the charger section until the separator section is half full. Stop the vibrator and add a 3 to 5-mm layer of dyed gel. Start the vibrator and vibrate the column while adding additional silica gel. Continue to add silica gel until the tightly packed gel extends 75 mm into the charger section. Wipe the length of the column with a damp cloth while vibrating the column. This aids in packing the column by removing static electricity. Vibrate the column for about 4 min after filling is completed.

NOTE 8—More than one column can be prepared simultaneously by mounting several on a frame or rack to which an electric vibrator is attached.

12.2 Attach the filled column to the apparatus assembly in the darkened room or area, and when a permanently mounted meter rule is used, fasten the lower end of the column to the fixed rule with a rubber band.

12.3 Chill the sample and a hypodermic syringe to 2 to 4°C. Draw 0.75 ± 0.03-mL of sample into the syringe and inject the sample 30 mm below the surface of the gel in the charger section.

12.4 Fill the charger section to the spherical joint with isopropyl alcohol. Connect the column to the gas manifold and apply 14 kPa gas pressure for 2.5 min to move the liquid front down the column. Increase the pressure to 34 kPa gage for another 2.5 min and then adjust the pressure required to give a transit time of about 1 h. Usually a gas pressure of 28 to 69 kPa gage is needed for gasoline-type samples and 69 to 103 kPa gage for jet fuels. The pressure required will depend on the tightness of packing of the gel and the molecular weight of the sample. A transit time of 1 h is optimum; however, high-molecular weight samples may require longer transit times.

12.5 After the red, alcohol-aromatic boundary has advanced 350 mm into the analyzer section, make a set of readings by quickly marking the boundary of each hydrocarbon zone (see Note 9) observed in ultraviolet light (see Note 10) in the following sequence. Refer to Fig. 2 as an aid in identifying the boundaries. For the noninfluorescent saturate zone, mark the front of the charge and the point where the yellow fluorescence first reaches its maximum intensity; for the upper end of the second, or olefin zone, mark the point where the first intense blue fluorescence occurs; finally, for the upper end of the third, or aromatic zone, mark the upper end of a reddish or brown zone. With colorless distillates, the alcohol-aromatic boundary is clearly defined by a red ring of dye. However, impurities in cracked fuels often obscure this red ring and give a brown coloration, which varies in length, but which shall be counted as a part of the aromatic zone, except that when no blue fluorescence is present, the brown or reddish ring shall be considered as part of the next distinguishable zone below it in the column. If the boundaries have been marked off with index clips, record the measurements.

NOTE 9—**Precaution:** Avoid touching the column with the hands during this operation.

NOTE 10—**Precaution:** Direct exposure to ultraviolet light can be harmful, and operators should avoid this as far as possible, particularly with regard to their eyes.

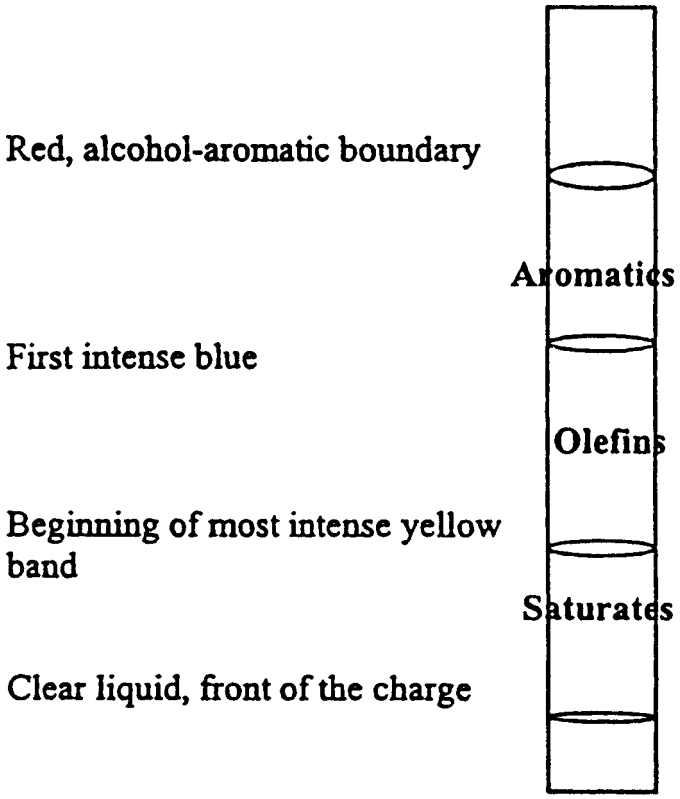

FIG. 2

12.6 When the sample has advanced another 50 mm down the column, make a second set of readings by marking the zones in the reverse order as described in 12.5 so as to minimize errors due to the advancement of boundary positions during readings. If the marking has been made with a glass-writing pencil, two colors can be used to mark off each set of measurements and the distances measured at the end of the test with the analyzer section lying horizontally on the bench top. If the boundaries have been marked off with index clips, record the measurements.

12.7 Erroneous results can be caused by improper packing of the gel or incomplete elution of hydrocarbons by the alcohol. With precision bore columns, incomplete elution can be detected from the total length of the several zones, which must be at least 500 mm for a satisfactory analysis. With standard wall tubing, this criterion of total sample length is not strictly applicable because the inside diameter of the analyzer section is not the same in all columns.

NOTE 11—For samples containing substantial amounts of material boiling above 204°C, the use of isoamyl alcohol instead of isopropyl alcohol may improve elution.

12.8 Release the gas pressure and disconnect the column. To remove used gel from the precision bore column, invert it above a sink and insert through the wide end a long piece of No. 19-gage hypodermic tubing with a 45° angle tip. By means of 6-mm outside diameter copper tubing at the opposite end for attaching a rubber tube, connect to a water tap and flush with a rapid stream of water. Rinse with residue-free acetone and dry by evacuation.

13. Calculation

13.1 For each set of observations calculate the hydrocarbon types to the nearest 0.1 volume % as follows:

$$\text{Aromatics, \% volume} = (L_a/L) \times 100 \quad (1)$$

$$\text{Olefins, \% volume} = (L_o/L) \times 100 \quad (2)$$

$$\text{Saturates, \% volume} = (L_s/L) \times 100 \quad (3)$$

where:

L_a = length of the aromatic zone, mm,
L_o = length of the olefin zone, mm,
L_s = length of the saturate zone, mm, and
L = sum of $L_a + L_o + L_s$.

Average the respective calculated values for each type and report as directed in 14.1. If necessary, adjust the result for the largest component so that the sum of the components is 100 %.

13.2 Eq 1, Eq 2, and Eq 3 calculate concentrations on an oxygenate-free basis and are correct only for samples that are composed exclusively of hydrocarbons. For samples that contain oxygenated blending components (see 1.5), the above results can be corrected to a total sample basis as follows:

$$C' = C \times \frac{100 - B}{100} \quad (4)$$

where:

C' = concentration of hydrocarbon type (% volume) on a total sample basis,
C = concentration of hydrocarbon type (% volume) on an oxygenate-free basis, and
B = concentration of total oxygenate blending components (% volume) in sample as determined by Test Method D 4815, or GC/OFID or equivalent.

14. Report

14.1 Report the averaged value for each hydrocarbon type (corrected to a total sample basis, if oxygenates are present) to the nearest 0.1 volume % and the total volume % oxygenates in the sample as calculated.

14.1.1 Results for samples that have been depentanized must be identified as being for the C_6 and heavier portion of the sample. Alternatively, the C_5 and lighter portion of the sample can be analyzed for olefins and saturates in accordance with Test Method D 2427. Using these values and the percentage of overhead and bottoms, the hydrocarbon type distribution in the total sample can be calculated.

15. Precision and Bias [10]

15.1 The following criteria are to be used for judging the acceptability of results (95 % probability):

[10] Data supporting the precision obtained from a round robin test for oxygenate containing samples in Table 3 has been filed in a research report at ASTM headquarters. Request RR:D02-1361.

TABLE 2 Reproducibility and Repeatability–Oxygenate Free Samples

	Volume %		
	Level	Repeatability	Reproducibility
Aromatics	5	0.7	1.5
	15	1.2	2.5
	25	1.4	3.0
	35	1.5	3.3
	45	1.6	3.5
	50	1.6	3.5
	55	1.6	3.5
	65	1.5	3.3
	75	1.4	3.0
	85	1.2	2.5
	95	0.7	1.5
	99	0.3	0.7
Olefins	1	0.4	1.7
	3	0.7	2.9
	5	0.9	3.7
	10	1.2	5.1
	15	1.5	6.1
	20	1.6	6.8
	25	1.8	7.4
	30	1.9	7.8
	35	2.0	8.2
	40	2.0	8.4
	45	2.0	8.5
	50	2.1	8.6
	55	2.0	8.5
Saturates	1	0.3	1.1
	5	0.8	2.4
	15	1.2	4.0
	25	1.5	4.8
	35	1.7	5.3
	45	1.7	5.6
	50	1.7	5.6
	55	1.7	5.6
	65	1.7	5.3
	75	1.5	4.8
	85	1.2	4.0
	95	0.3	2.4

15.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 or Table 3 only in one case in twenty.

15.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 or Table 3 only in one case in twenty.

15.1.3 Table 2 shall be used for judging repeatability and reproducibility of non-oxygenate containing samples. Table 3 shall be used for judging the repeatability and reproducibility of oxygenate-containing samples.

15.2 *Bias*—Bias cannot be determined because there are no acceptable reference materials suitable for determining the bias for the procedure in this test method.

TABLE 3 Reproducibility and Repeatability for Oxygenate Containing Samples

	Range	Repeatability, Volume %	Reproducibility
Aromatics	13 – 40	1.3	3.7
Olefins	4 – 33	$0.2578X^{0.6}$	$0.8185X^{0.6A}$
Saturates	45 – 68	1.5	4.2

[A] X = the volume % of olefins.

NOTE 12—The precision specified in Table 3 was determined for samples that were not depentanized.

16. Keywords

16.1 aromatics; fluorescent indicator absorption (FIA); hydrocarbon types; olefins; saturates