



Designation: D6839 – 17

Standard Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography¹

This standard is issued under the fixed designation D6839; 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 the quantitative determination of saturates, olefins, aromatics, and oxygenates in spark-ignition engine fuels by multidimensional gas chromatography. Each hydrocarbon type can be reported either by carbon number (see **Note 1**) or as a total.

NOTE 1—There can be an overlap between the C₉ and C₁₀ aromatics; however, the total is accurate. Isopropyl benzene is resolved from the C₈ aromatics and is included with the other C₉ aromatics.

1.2 This test method is not intended to determine individual hydrocarbon components except benzene.

1.3 This test method is divided into two parts, Part A and Part B.

1.3.1 Part A is applicable to automotive motor gasoline for which precision (Table 9) has been obtained for total volume fraction of aromatics of up to 50 %; a total volume fraction of olefins from about 1.5 % up to 30 %; a volume fraction of oxygenates, from 0.8 % up to 15 %; a total mass fraction of oxygen from about 1.5 % to about 3.7 %; and a volume fraction of benzene of up to 2 %. Although this test method can be used to determine higher-olefin contents of up to 50 % volume fraction, the precision for olefins was tested only in the range from about 1.5 % volume fraction to about 30 % volume fraction. The method has also been tested for an ether content up to 22 % volume fraction but no precision data has been determined.

1.3.1.1 This test method is specifically developed for the analysis of automotive motor gasoline that contains oxygenates, but it also applies to other hydrocarbon streams having similar boiling ranges, such as naphthas and reformates.

1.3.2 Part B describes the procedure for the analysis of oxygenated groups (ethanol, methanol, ethers, C₃ to C₅ alcohols) in ethanol fuels containing an ethanol volume fraction between 50 % and 85 % (17 % to 29 % oxygen). The gasoline is diluted with an oxygenate-free component to lower the ethanol content to a value below 20 % before the analysis by

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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GC. The diluting solvent should not be considered in the integration, this makes it possible to report the results of the undiluted sample after normalization to 100 %.

1.4 Oxygenates as specified in Test Method D4815 have been verified not to interfere with hydrocarbons. Within the round robin sample set, the following oxygenates have been tested: MTBE, ethanol, ETBE, TAME, *iso*-propanol, isobutanol, *tert*-butanol and methanol. The derived precision data for methanol do not comply with the precision calculation as presented in this International Standard. Applicability of this test method has also been verified for the determination of *n*-propanol, acetone, and *di*-isopropyl ether (DIPE). However, no precision data have been determined for these compounds.

1.4.1 Other oxygenates can be determined and quantified using Test Method D4815 or D5599.

1.5 The method is harmonized with ISO 22854.

1.6 This test method includes a relative bias section for U.S. EPA spark-ignition engine fuel regulations for total olefins reporting based on Practice D6708 accuracy assessment between Test Method D6839 and Test Method D1319 as a possible Test Method D6839 alternative to Test Method D1319. The Practice D6708 derived correlation equation is only applicable for fuels in the total olefins concentration range from 0.2 % to 18.2 % by volume as measured by Test Method D6839. The applicable Test Method D1319 range for total olefins is from 0.6 % to 20.6 % by volume as reported by Test Method D1319.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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.*

1.9 *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.*

*A Summary of Changes section appears at the end of this standard

2. Referenced Documents

2.1 ASTM Standards:²

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

2.2 Other Documents:

ISO 4259 Petroleum Products—Determination and Application of Precision Data in Relation to Methods of Test³

ISO 22854 Liquid Petroleum Products—Determination of Hydrocarbon Types and Oxygenates in Automotive-Motor Gasoline—Multidimensional Gas Chromatography Method³

3. Terminology

3.1 Definitions:

3.1.1 *oxygenate, n*—an oxygen-containing organic compound, which may be used as a fuel or fuel supplement, for example, various alcohols and ethers.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *hydrogenation, n*—the process of adding hydrogen to olefin molecules as a result of a catalytic reaction.

3.2.1.1 *Discussion*—Hydrogenation is accomplished when olefins in the sample contact platinum at a temperature of 180 °C in the presence of hydrogen. The olefins are converted into hydrogen saturated compounds of the same carbon number and structure. Monoolefins and diolefins convert to paraffins while cycloolefins and cycloienes convert to cycloparaffins.

3.2.2 *trap, n*—a device utilized to selectively retain specific portions (individual or groups of hydrocarbons or oxygenates) of the test sample and to release the retained components by changing the trap temperature.

3.3 Acronyms:

3.3.1 *ETBE*—ethyl-*tert*-butylether

3.3.2 *MTBE*—methyl-*tert*-butylether

3.3.3 *TAME*—*tert*-amyl-methylether

3.3.4 *DIPE*—*di*-isopropylether

4. Summary of Test Method

4.1 A representative sample is introduced into a computer controlled gas chromatographic system consisting of switching

valves, columns, and an olefin hydrogenation catalyst, all operating at various temperatures. The valves are actuated at predetermined times to direct portions of the sample to appropriate columns and traps. As the analysis proceeds, the columns separate these sample portions sequentially into groups of different hydrocarbon types that elute to a flame ionization detector.

4.2 The mass concentration of each detected compound or hydrocarbon group is determined by the application of response factors to the areas of the detected peaks followed by normalization to 100 %. For samples containing methanol or other oxygenates that cannot be determined by this test method, the hydrocarbon results are normalized to 100 % minus the value of the oxygenates as determined by another test method such as Test Method **D4815** or **D5599**.

4.3 The liquid volume concentration of each detected compound or hydrocarbon group is determined by application of density factors to the calculated mass concentration of the detected peaks followed by normalization to 100 %.

5. Significance and Use

5.1 A knowledge of spark-ignition engine fuel composition is useful for regulatory compliance, process control, and quality assurance.

5.2 The quantitative determination of olefins and other hydrocarbon types in spark-ignition engine fuels is required to comply with government regulations.

5.3 This test method is not applicable to M85 fuels, which contain 85 % methanol.

6. Interferences

6.1 Some types of sulfur-containing compounds are irreversibly adsorbed in the olefin trap reducing its capacity to retain olefins. Sulfur containing compounds are also adsorbed in the alcohol and ether-alcohol-aromatic (EAA) traps. However, a variety of spark-ignition engine fuels have been analyzed without significant performance deterioration of these traps.

6.2 Commercial dyes used to distinguish between grades and types of spark-ignition engine fuels have been found not to interfere with this test method.

6.3 Commercial detergent additives utilized in spark-ignition engine fuels have been found not to interfere with this test method.

6.4 Dissolved water in spark-ignition engine fuels has been found not to interfere with this test method.

7. Apparatus

7.1 The complete system that was used to obtain the precision data shown in Section 14 is comprised of a computer controlled gas chromatograph, automated sample injector, and specific hardware modifications. These modifications include columns, traps, a hydrogenator, and valves, which are described in 7.7 and in Section 8. Fig. 1 illustrates a typical instrument configuration (see Note 4). Other configurations, components, or conditions may be utilized provided they are

² 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.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

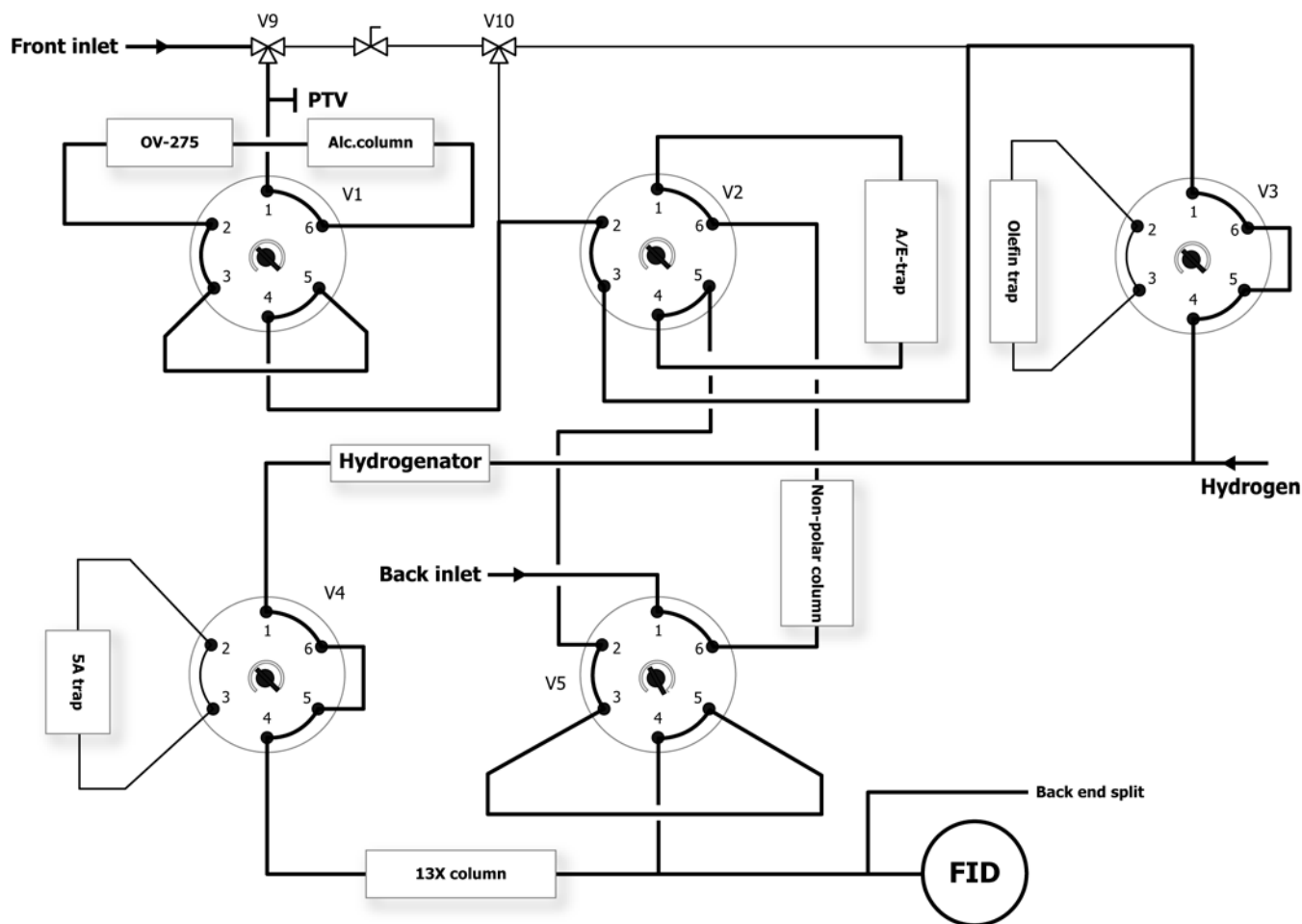


FIG. 1 Typical Instrument Configuration

capable of achieving the required component separations and produce a precision that is equivalent to, or better than, that shown in the precision tables.

7.2 *Gas Chromatograph*, capable of temperature programmed operation at specified temperatures, equipped with a heated flash vaporization inlet, a flame ionization detector, necessary flow controllers, and computer control.

7.3 *Sample Introduction System*, using an automatic liquid injector, the injection volume shall be chosen in a way such that the capacity of the column is not exceeded and that the linearity of the detector is valid.

7.3.1 An injection volume of 0.1 μL has been found satisfactory.

7.4 *Gas Flow and Pressure Controllers*, with adequate precision to provide reproducible flow and pressure of the carrier gas to the chromatographic system, hydrogen for the hydrogenator, and hydrogen and air for the flame ionization detector. Control of air flow for cooling specific system components and for automated valve operation is also required.

7.5 *Electronic Data Acquisition System*, shall meet or exceed the following specifications (see Note 2):

7.5.1 Capacity for 150 peaks for each analysis.

7.5.2 Normalized area percent calculation with response factors.

7.5.2.1 Area summation of peaks that are split or of groups of components that elute at specific retention times.

7.5.3 Noise and spike rejection capability.

7.5.4 Sampling rate for fast (<0.5 s) peaks (>20 Hz to give 10 points across peak).

7.5.5 Peak width detection for narrow and broad peaks.

7.5.6 Perpendicular drop and tangent skimming, as required.

NOTE 2—Standard supplied software is typically satisfactory.

7.6 *Temperature Controllers of System Components*—The independent temperature control of numerous columns and traps, the hydrogenation catalyst, column switching valves, and sample lines is required. All of the system components that contact the sample shall be heated to a temperature that will prevent condensation of any sample component. Table 1 lists the system components and operating temperatures (see 7.6.1). Some of the components require isothermal operation, some require rapid heating and cooling, while one requires reproducible temperature programming. The indicated temperatures are typical; however, the control systems utilized shall have the