



# Standard Test Method for Oxygenates and Paraffin, Olefin, Naphthene, Aromatic (O-PONA) Hydrocarbon Types in Low-Olefin Spark Ignition Engine Fuels by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 6293; 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.

<sup>ε1</sup> NOTE—Warning notes were editorially moved into the standard text in August 2003.

## 1. Scope

1.1 This test method provides for the quantitative determination of oxygenates, paraffins, olefins, naphthenes, and aromatics in low-olefin 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 through C<sub>10</sub>, except for olefins, which can only be reported through C<sub>9</sub>. Higher boiling hydrocarbons cannot be reported by type and are reported as a composite group. The lower limit of detection for a single hydrocarbon component or carbon number type is 0.05 mass %.

NOTE 1—There can be an overlap between the C<sub>9</sub> and C<sub>10</sub> aromatics; however, the total is accurate. Isopropyl benzene is resolved from the C<sub>8</sub> aromatics and is included with the other C<sub>9</sub> aromatics. Naphthalene is determined with the C<sub>11+</sub> components.

1.2 This test method is applicable for total olefins in the range from 0.05 to 13 mass %. The test method can quantitatively determine olefins in samples where the olefin concentration does not exceed 0.6 % C<sub>4</sub> or 4.0 % C<sub>5</sub> or 4.5 % of the combined C<sub>4</sub> and C<sub>5</sub>. Although the precision for benzene was determined in the range from 0.3 to 1.0 mass %, this test method can be used to determine benzene concentrations up to 5.0 mass %.

1.3 This test method is not intended to determine individual hydrocarbon components except for those hydrocarbon types for which there is only one component within a carbon number. Individually determined hydrocarbons are benzene, toluene, cyclopentane, propane, propylene, and cyclopentene.

1.4 Precision data has only been obtained on samples containing MTBE. Application of this test method to determine other oxygenates shall be verified in the user's laboratory. Methanol cannot be determined and shall be quantitated by an appropriate oxygenate method such as Test Method D 4815 or

D 5599. Methanol is fully resolved and does not interfere with the determination of other components or groups.

1.5 Although specifically written for spark-ignition engine fuels containing oxygenates, this test method can also be applied to other hydrocarbon streams having similar boiling ranges, such as naphthas and reformates.

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

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 4307 Practice for Preparation of Liquid Blends for Use As Analytical Standards<sup>2</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>2</sup>

D 5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection<sup>3</sup>

## 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

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<sup>2</sup> Annual Book of ASTM Standards, Vol 05.02.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.03.

into hydrogen saturated compounds of the same carbon number and structure. Monoolefins and diolefins convert to paraffins while cycloolefins and cyclodienes 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.

## 4. Summary of Test Method

4.1 A representative sample is introduced into a computer controlled gas chromatographic system<sup>4</sup> 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 method such as Test Method D 4815 or D 5599. 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 and E85 fuels, which contain 85 % methanol and ethanol, respectively.

## 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 not been found to interfere with this test method.

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

6.4 Dissolved water in spark-ignition engine fuels has not been found 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 below and in Section 8. Fig. 1 illustrates a typical instrument configuration (see Note 5). Other configurations, components, or conditions may be utilized provided they are capable of achieving the required component separations and produce a precision that is equivalent, or better, than that shown in the precision tables.

7.2 *Gas Chromatograph*, capable of isothermal operation at specified temperatures, equipped with a heated flash vaporization inlet that can be packed (packed column inlet), a flame ionization detector, necessary flow controllers, and computer control.

7.3 *Sample Introduction System*, automatic liquid sampler, capable of injecting a 0.1 to 0.5- $\mu$ L injection volume of liquid. The total injected sample shall be introduced to the chromatographic system thus excluding the use of split injections or carrier gas purging of the inlet septum. An auto injector is recommended but optional.

7.4 *Gas Flow and Pressure Controllers*, with adequate precision to provide reproducible flow and pressure of helium 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).

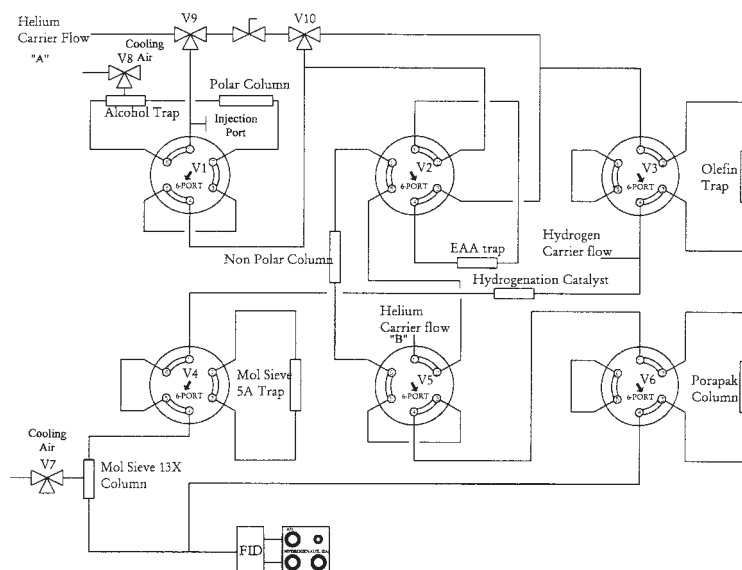
7.5.5 Peak width detection for narrow and broad peaks.

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

<sup>4</sup> The sole source of supply of the apparatus known to the committee at this time, the AC Reformulyzer, is AC Analytical Controls, Inc., 3494 Progress Dr., Bensalem, PA 19020. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.



NOTE—Valve V4 and the Mol Sieve 5A Trap are not required but were present in the instrumentation used to generate the precision data.

FIG. 1 Typical Instrument Configuration

TABLE 1 Temperature Control Ranges of System Components

Component	Typical Operating Temperature Range, °C	Maximum Heating Time, min	Maximum Cooling Time, min
Alcohol trap	60 to 280	2	5
Polar column	130	isothermal	
Non-polar column	130	isothermal	
Olefin trap	120 to 280	1	5
Molsieve 13X column	90 to 430	temperature programmed, ~10°/min	
Porapak column	130 to 140	isothermal	
Ether-alcohol-aromatic (EAA) trap	70 to 280	1	5
Hydrogenation catalyst	180	isothermal	
Column switching valves	130	isothermal	
Sample lines	130	isothermal	

the system components and operating temperatures (see Note 3). 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 capability of operating at temperatures  $\pm 20^\circ\text{C}$  of those indicated to accommodate specific systems. Temperature control may be by any means that will meet the requirements listed in Table 1.

NOTE 3—The system components and temperatures listed in Table 1 and Section 8 are specific to the analyzer used to obtain the precision data shown in Section 14. Other columns and traps that can adequately perform the required separations are also satisfactory but may require different temperatures.

7.7 Valves, Column and Trap Switching—Automated, rotary valves are recommended. The valves shall be intended for gas chromatographic usage and meet the following requirements:

7.7.1 The valves must be capable of continuous operation at operating temperatures that will prevent sample condensation.

7.7.2 The valves shall be constructed of materials that are non-reactive with the sample under analysis conditions. Stainless steel, PFA<sup>5</sup> and Vespel<sup>5</sup> are satisfactory.

7.7.3 The valves shall have a small internal volume but offer little restriction to carrier gas flow under analysis conditions.

7.8 Valves, air, to control pressurized air for column and trap cooling. Automated valves are recommended.

NOTE 4—New valves, tubing, catalyst, columns, traps, and other materials that contact the sample or gases may require conditioning prior to operation in accordance with the manufacturer's recommendations.

7.9 Gas Purifiers, to remove moisture and oxygen from helium, moisture and hydrocarbons from hydrogen; and moisture and hydrocarbons from air.

## 8. Reagents and Materials

8.1 Air, compressed, <10 mg/kg each of total hydrocarbons and H<sub>2</sub>O. (**Warning**—Compressed gas under high pressure that supports combustion.)

8.2 Helium, 99.999 % pure, <0.1 mg/kg H<sub>2</sub>O. (**Warning**—Compressed gas under high pressure.)

8.3 Hydrogen, 99.999 % pure, <0.1 mg/kg H<sub>2</sub>O. (**Warning**—Extremely flammable gas under high pressure.)

8.4 Columns, Traps, and Hydrogenation Catalyst (System Components)—This test method requires the use of four columns, two traps, and a hydrogenation catalyst (see Note 3). Each system component is independently temperature controlled as described in 7.6 and Table 1. Refer to Fig. 1 for the location of the components in the system (see Note 5). The following list of components contains guidelines that are to be used to judge suitability.

NOTE 5—Fig. 1 shows an additional trap, Molsieve 5A, and rotary

<sup>5</sup> PFA and Vespel are trademarks of E. I. DuPont de Nemours and Co.