Designation: D 6293 – 98 (Reapproved 2003)ε1

An American National Standard

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

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 (ε) indicates an editorial change since the last revision or reapproval.

ε[1] 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_{10}, except for olefins, which can only be reported through C_9. 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_9 and C_{10} aromatics; however, the total is accurate. Isopropyl benzene is resolved from the C_8 aromatics and is included with the other C_9 aromatics. Naphthalene is determined with the C_{11}+ 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_4 or 4.0 % C_5 or 4.5 % of the combined C_4 and C_5. 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[2]

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[2]

D 5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection[3]

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

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.02.

[3] *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[4] 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-µL 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).

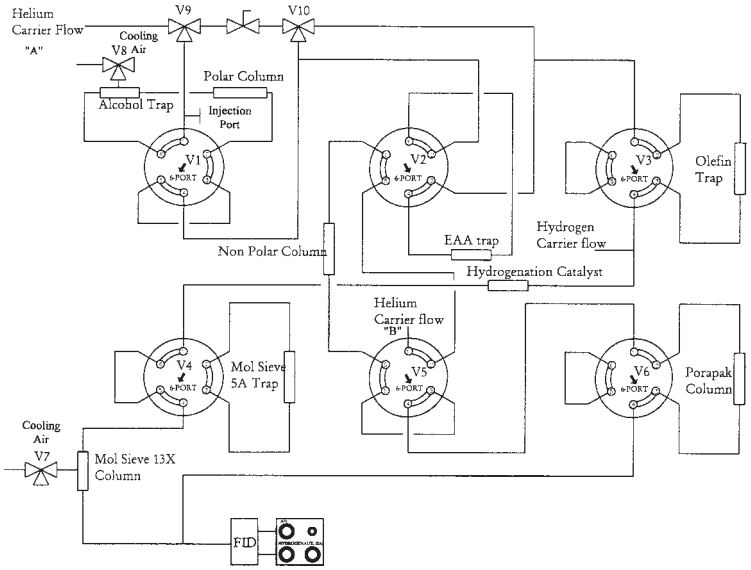
7.5.5 Peak width detection for narrow and broad peaks.

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

[4] 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,[1] 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 ±20°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[5] and Vespel[5] 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_2O. (**Warning**—Compressed gas under high pressure that supports combustion.)

8.2 *Helium*, 99.999 % pure, <0.1 mg/kg H_2O. (**Warning**—Compressed gas under high pressure.)

8.3 *Hydrogen*, 99.999 % pure, <0.1 mg/kg H_2O. (**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

[5] PFA and Vespel are trademarks of E. I. DuPont de Nemours and Co.

valve V4 that are not required for the O-PONA analysis. They are included in Fig. 1 because they were present in the instrumentation used to generate the precision data. They can be used for more detailed analyses outside the scope of this test method, where an iso-normal paraffin, iso-normal olefin determination is desired. There is no statistical data included in this test method relating to their use.

8.4.1 *Alcohol Trap*—Within a temperature range from 140 to 160°C, this trap must elute benzene, toluene, all paraffins, olefins, naphthenes, and ethers within the first 2 min after sample injection while retaining C_8+ aromatics, all alcohols, and any other sample components.

8.4.1.1 At a temperature of 280°C, all retained components from 8.4.1 shall elute within 2 min of when the trap is backflushed.

8.4.2 *Polar Column*—At a temperature of 130°C, this column must retain all aromatic components in the sample longer than the time required to elute all non-aromatic components boiling below 185°C, within the first 5 min after sample injection.

8.4.2.1 The column shall elute benzene and toluene within 10 min of the introduction of these compounds into the column.

8.4.2.2 This column shall elute all retained aromatic components from 8.4.2 within 10 min of when this column is backflushed.

8.4.3 *Non-Polar Column*—At a temperature of 130°C, this column shall elute and separate aromatics by carbon number boiling below 200°C. Higher boiling paraffins, naphthenes, and aromatics are backflushed.

8.4.4 *Olefin Trap*—Within a temperature range from 120 to 170°C, this trap shall retain (trap) all olefins in the sample for at least 10 min and elute all non-olefinic components in less than 10 min after the sample is injected.

8.4.4.1 At a temperature of 280°C, this trap shall quantitatively elute all retained olefins.

8.4.5 *Molsieve 13X Column*—This column shall separate paraffin and naphthene hydrocarbons by carbon number when temperature programmed from 90 to 430°C at approximately 10°/min.

8.4.6 *Porapak Column*—At a temperature from 130 to 140°C, this column shall separate individual oxygenates, benzene, and toluene.

8.4.7 *Ether-Alcohol-Aromatic (EAA) Trap*—Within a temperature range from 130 to 140°C, this trap shall retain all of the ethers in the sample and elute all non-ethers boiling above 174°C within the first 6 min after sample injection.

8.4.7.1 At a temperature of 280°C, this trap shall elute all retained components.

8.4.8 *Hydrogenation Catalyst*, platinum. At a temperature of 180°C and an auxiliary hydrogen flow of 14 ± 2 mL/min, this catalyst shall quantitatively hydrogenate all olefins to paraffinic compounds of the same structure without cracking.

8.5 *Test Mixtures*—Three quantitative synthetic mixtures of pure hydrocarbons and oxygenates are required to verify that all instrument components, temperatures, and cut times are satisfactory to produce accurate analyses and to aid in making operating adjustments as columns and traps age. The mixtures may be purchased or prepared according to Practice D 4307. Each component used in the test mixture preparations shall have a minimum purity of 99 %. The actual concentration levels are not critical but shall be accurately known.

8.5.1 *System Validation Test Mixture*, used to monitor and make adjustments to the total operation of the system. The composition and approximate component concentrations are shown in Table 2.

8.5.2 *Olefin Test Mixture*, used to adjust the olefin and EAA trap temperatures so that C_5 through C_9 olefins are quantitatively determined. The composition and approximate component concentrations are shown in Table 3.

8.5.3 *Paraffin Test Mixture*, used to adjust the olefin and EAA trap temperatures. The composition and approximate component concentrations are shown in Table 4. (**Warning—** Extremely flammable. Harmful if inhaled.)

8.6 *Quality Control Sample*, used to routinely monitor the operation of the chromatographic system and verify that reported concentrations are within the precision of the test method. Any sample that is similar in composition to samples typically analyzed may be designated as the quality control (QC) sample. When samples to be analyzed contain olefins of carbon number C_4, C_5, or both, the QC sample shall contain these to monitor olefin traps capacity. The QC sample shall be of sufficient volume to provide an ample supply for the intended period of use and it shall be homogeneous and stable under the anticipated storage conditions.

9. Preparation of Apparatus

9.1 Assemble the analyzer system (gas chromatograph with independent temperature controlled components) as shown in Fig. 1 or with an equivalent flow system. If using a commercial system, install and place the system in service in accordance with the manufacturer's instructions.

9.2 Impurities in the helium carrier gas, hydrogen, or air will have a detrimental effect on the performance of the columns and traps. Therefore, it is important to install efficient gas purifiers in the gas lines as close to the system as possible and to use good quality gases. The helium and hydrogen gas connection lines shall be made of metal. Check that all gas connections, both exterior and interior to the system, are leak tight.

9.3 The gas flow rates on commercial instruments are normally set prior to shipment and normally require little adjustment. Optimize flow rates on other systems to achieve the required separations. Typical flow rates for the commercial instrument used in the precision study are given in Table 5; however, the flows can differ somewhat from system to system.

9.3.1 Set air flow rates for column/trap cooling and for operation of air actuated valves, if required.

9.4 *System Conditioning*—When gas connections have been disconnected or the flow turned off, as on initial start up, condition the system by permitting carrier gas to flow through the system for at least 30 min while the system is at ambient temperature. After the system has been conditioned, analyze the system validation test mixture, as described in Section 11, discarding the results.

10. Standardization

10.1 The elution of components from the columns and traps depends on the applied temperatures. The switching valves

TABLE 2 System Validation Test Mixture

Component	Approximate Concentration, mass %	**Warning**
Cyclopentane	1.5	Extremely flammable. Harmful if inhaled
Pentane	1.5	Extremely flammable. Harmful if inhaled
Cyclohexane	2.0	Extremely flammable. Harmful if inhaled
2,3-Dimethylbutane	2.0	Extremely flammable. Harmful if inhaled
Hexane	2.0	Extremely flammable. Harmful if inhaled
1-Hexene	1.5	Extremely flammable. Harmful if inhaled
Methylcyclohexane	3.5	Extremely flammable. Harmful if inhaled
4-Methyl-1-hexene	1.5	Extremely flammable. Harmful if inhaled
Heptane	3.0	Flammable. Harmful if inhaled
1-*cis*-2-Dimethylcyclohexane	4.5	Extremely flammable. Harmful if inhaled
2,2,4-Trimethylpentane	4.0	Flammable. Harmful if inhaled
Octane	4.0	Flammable. Harmful if inhaled
1-*cis*-2-*cis*-4-Trimethylcyclohexane	3.5	Flammable. Harmful if inhaled
Nonane	3.0	Flammable. Harmful if inhaled
Decane	3.5	Flammable. Harmful if inhaled
Undecane	2.0	Flammable. Harmful if inhaled
Dodecane	2.0	Flammable. Harmful if inhaled
Benzene	2.5	Flammable. Harmful if inhaled
Methylbenzene (Toluene)	2.5	Flammable. Harmful if inhaled
trans-Decahydronaphthalene (Decalin)	3.5	Flammable. Harmful if inhaled
Tetradecane	2.0	Flammable. Harmful if inhaled
Ethylbenzene	3.5	Extremely flammable. Harmful if inhaled
1,2-Dimethylbenzene (*o*-Xylene)	3.0	Extremely flammable. Harmful if inhaled
Propylbenzene	3.5	Extremely flammable. Harmful if inhaled
1,2,4-Trimethylbenzene	3.0	Extremely flammable. Harmful if inhaled
1,2,3-Trimethylbenzene	2.0	Extremely flammable. Harmful if inhaled
1,2,4,5-Tetramethylbenzene	2.0	Flammable. Harmful if inhaled
Pentamethylbenzene	2.5	Harmful if inhaled
Ethanol	5.0	Extremely flammable. Harmful if inhaled
tert-Butanol	4.0	Extremely flammable. Harmful if inhaled
MTBE	8.0	Extremely flammable. Harmful if inhaled
ETBE	3.0	Extremely flammable. Harmful if inhaled
TAME	5.0	Extremely flammable. Harmful if inhaled
Group Totals		
Paraffins 29.0 Olefins 3.0 Naphthenes 15.0 Aromatics 24.5 Polynaphthenes 3.5 Oxygenates 25.0		
TOTAL 100		

TABLE 3 Olefin Test Mixture

Component	Approximate Concentration, mass %	**Warning**
1-Pentene	5.00	Extremely flammable. Harmful if inhaled
1-Hexene	2.00	Extremely flammable. Harmful if inhaled
1-Heptene	2.00	Extremely flammable. Harmful if inhaled
1-Octene	2.00	Flammable. Harmful if inhaled
1-Nonene	3.00	Flammable. Harmful if inhaled
Hexane/Heptane 50:50	Balance	Extremely flammable. Harmful if inhaled

TABLE 4 Paraffin Test Mixture

Component	Approximate Concentration, mass %	**Warning**
Nonane	3.00	Flammable. Harmful if inhaled
Decane	3.00	Flammable. Harmful if inhaled
Hexane/Heptane 50:50	Balance	Extremely flammable. Harmful if inhaled

TABLE 5 Typical Gas Flow Rates

Gas	Flow Rate, ± 2 mL/min
He (Flow A)	22
He (Flow B)	12
H_2(hydrogenator)	14
H_2(FID)	30
Air (FID)	450

also need to be actuated at exact times to make separations of compounds into groups, for example, to retain specific compounds in a column or trap while permitting other compounds to elute. Therefore, the separation temperatures of the columns/traps and the valve timing are critical for correct operation of the system. These parameters need to be verified on the start up of a new system (see Note 6) for correctness. They also require evaluation and adjustment as necessary on a regular basis to correct for changes to columns and traps as a result of aging. To do this, the analyst shall analyze several test mixtures and make changes, as required, based on an evaluation of the resulting chromatograms and test reports.

10.2 Using the procedure outlined in Section 11, analyze the system validation test mixture. Carefully examine the chromatogram obtained to verify that all the individual components

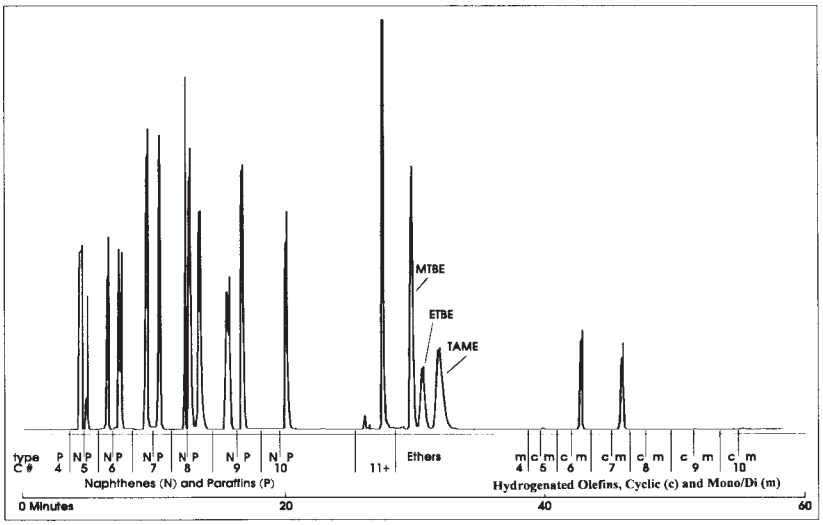


FIG. 2 Typical Chromatogram of the System Validation Test Mixture—First Half

of the test mixture are correctly identified as compared to the reference chromatogram (Figs. 2 and 3). Test results for group totals shall agree with the known composition (see Table 2) within ±0.5 mass %. If these specifications are met, proceed to the analysis of the olefin test mixture (see 10.3).

10.2.1 If the specifications in 10.2 are not met, adjust the temperature of specific columns and traps or valve timing according to the manufacturer's guidelines and reanalyze the system validation test mixture until they are met.

10.3 Analyze the olefin test mixture and compare the results obtained to the actual values, Table 3. If the results do not agree within ±0.3 mass % for the individual C_5 through C_8 olefins and ±0.5 mass % for 1-nonene, adjust the temperatures of the olefin and EAA traps to ensure that the five olefins are retained on the olefin trap and not on the EAA trap. Reanalyze the olefin test mixture until specifications are met.

10.4 Analyze the paraffin test mixture and compare the results obtained to the actual values, Table 4. Ensure that <0.05 mass % of the nonane is retained by the olefin trap. Some or all of the decane may be retained by the olefin trap. If necessary, adjust the temperatures of the olefin and EAA traps. Reanalyze the paraffin test mixture until the specification for nonane is met.

10.5 Analyze the quality control sample, see 8.6. Verify that results are consistent with those previously obtained and that there is no breakthrough of olefins into the saturates region of the chromatogram. Breakthrough is indicated by a rising baseline under the C_5 - C_6 saturates region. If breakthrough is observed, optimize the olefin trap temperature or, if necessary, replace the trap. Loadability limits are as shown in 1.2. These limits depend on the condition of the olefin trap, and an aged trap may not have this capacity. Use the quality control sample, see 8.6, to verify olefin capacity.

10.6 Reanalyze the system validation test mixture whenever the quality control sample does not conform to expected results, see 10.5, and make adjustments as necessary, see 10.2.

11. Procedure

11.1 Load the necessary system set-point conditions, which include initial component temperatures, times at which column and trap temperature are changed, the initial positions of switching valves, and times when valve switches occur (see Note 6).

NOTE 6—Commercial systems will have all parameters predetermined and accessible through the software. Other constructed systems will require experimentation and optimization of parameters to achieve the required component separation and precision.

11.2 When all component temperatures have stabilized at the analysis conditions, inject a representative 0.1 to 0.3-µL aliquot of sample (or test mixture) and start the analysis.

NOTE 7—A 0.1-µL volume was used by cooperators for the precision study.

11.2.1 Starting the analysis should begin the data acquisition and should begin the timing function that controls all of the various programmed temperature changes and valve switching.

11.2.2 Upon completion of its programmed cycle, the system should automatically stop, generate a chromatogram, and print a report of concentrations.

12. Calculation

12.1 Calculations produce results that are reported in mass % and liquid volume %. Examine the report carefully to ensure that all peaks have been properly identified and integrated.

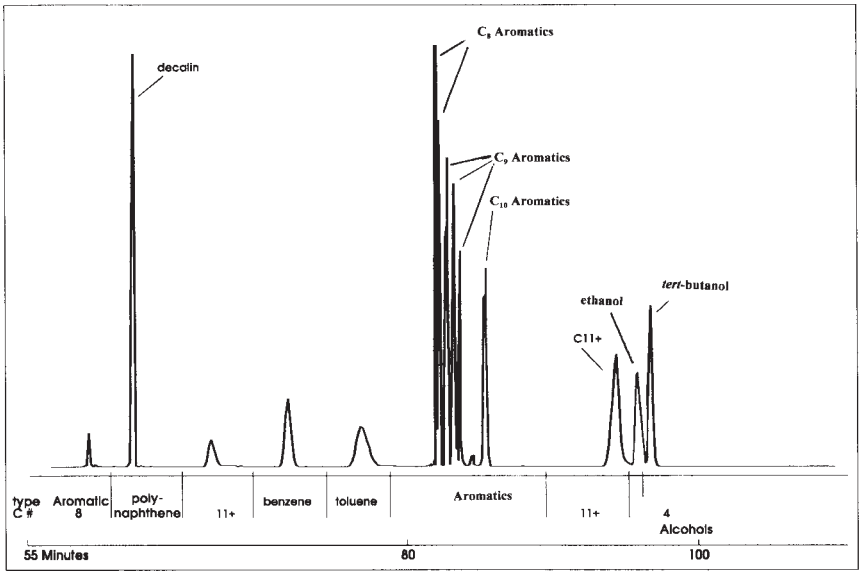


FIG. 3 Typical Chromatogram of the System Validation Test Mixture—Second Half

12.1.1 Calculate the mass % of each identified hydrocarbon group of a particular carbon number and individual oxygenate using Eq 1.

$$M = \frac{A \times F \times 100}{\sum A \times F} \quad (1)$$

where:

M = mass % of an identified hydrocarbon group of a particular carbon number or individual oxygenate,
A = integrated area of the hydrocarbon group of a particular carbon number or individual oxygenate,
F = relative response factor for the hydrocarbon group, RRf, calculated using Eq 2 or from Table 6. For oxygenates, use the response factors from Table 7, or factors determined on the specific system (see 12.1.1.2), and
100 = factor to normalize corrected area % to 100 %.

12.1.1.1 Calculate the flame ionization detector response factor relative to methane, which is considered to have a response factor of unity (*1*), for each hydrocarbon group type of a particular carbon number using Eq 2. Olefin response is calculated on a hydrogenated basis.

$$RRf = \frac{[(C_{aw} \times C_n) + (H_{aw} \times H_n)] \times 0.7487}{(C_{aw} \times C_n)} \quad (2)$$

where:

RRf = relative response factor for a hydrocarbon type group of a particular carbon number,
C_{aw} = atomic mass of carbon, 12.011,
C_n = number of carbon atoms in the hydrocarbon type group, of a particular carbon number,
H_{aw} = atomic mass of hydrogen, 1.008,
H_n = number of hydrogen atoms in the hydrocarbon type group of a particular carbon number, and
0.7487 = factor to normalize the result to a methane response of unity, (1).

TABLE 6 Calculated Response Factors for Hydrocarbons[A]

NOTE—Use a factor of 0.883 for polynaphthenes and 0.840 for the C_{11}+ fractions.

No. of Carbon Atoms	Naphthenes	Paraffins	Cyclo-olefins[B]	Monoolefins and Dioolefins[B]	Aromatics
3		0.916		0.916	
4		0.906		0.906	
5	0.874	0.899	0.874	0.899	
6	0.874	0.895	0.874	0.895	0.811
7	0.874	0.892	0.874	0.892	0.820
8	0.874	0.890	0.874	0.890	0.827
9	0.874	0.888	0.874	0.888	0.832
10	0.874	0.887			0.837

[A] Based on percentage by mass of carbon, normalized to methane = 1.
[B] Corrected for hydrogenation of olefins.

TABLE 7 Experimentally Determined Response Factors for Oxygenates

Compound	Response Factor
Ethanol	1.910
tert-Butanol	1.229
MTBE	1.334
ETBE	1.313
TAME	1.242

12.1.1.2 Oxygenate flame ionization detector response factors used in the precision study were determined experimentally and are listed in Table 7.

12.1.2 Calculate the liquid volume % of each identified hydrocarbon group and oxygenate using Eq 3.

$$V = \frac{\frac{M}{D}}{\sum \frac{M}{D}} \quad (3)$$

where:

V = liquid volume % of an identified hydrocarbon group of a particular carbon number or individual oxygenate,
M = previously defined, Eq 1, and
D = average relative density, kg/L at 20°C, (see Note 8) for the hydrocarbon group of a particular carbon number or individual oxygenate. For hydrocarbons, use Table 8 and for oxygenates, use Table 9.

NOTE 8—Relative density of 15.5°C can also be used but Tables 8 and 9 will not apply.

13. Report

13.1 Report the mass % and liquid volume % for each oxygenate and hydrocarbon group type to the nearest 0.1 % as listed in Table 10 and report the mass % and liquid volume % for individual carbon number components to the nearest 0.01 %.

14. Precision and Bias [6]

14.1 *Precision*—The precision of any individual measurement resulting from the application of this test method depends on several factors related to the individual or group of components including the volatility, concentration, and degree to which the component or group of components is resolved from closely eluting components or groups of components. As it is not practical to determine the precision of measurement for every component or group of components at different levels of concentration separated by this test method, Tables 11 and 12 present the repeatability and reproducibility values for selected, representative components, and groups of components.

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the repeatability values shown in Tables 11 and 12 only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials would, in the long run, in the correct operation of the test method, exceed the values shown in Tables 11 and 12 only in one case in twenty.

NOTE 9—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 concentration up to 5.0 mass %.

14.2 *Bias*—No information can be presented on the bias of the procedure in Test Method D 6293 for measuring hydrocarbon types because no material having an accepted reference value is available.

15. Keywords

15.1 aromatics; gas chromatography; gasoline, hydrocarbon type; multi-dimensional gas chromatography; naphthenes; olefins; oxygenates; paraffins; spark-ignition engine fuels

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1432.

TABLE 8 Average Relative Density, kg/L at 20°C, of Hydrocarbon Type Groups[A]

NOTE—Use an average relative density of 0.8832 for the polynaphthenes and 0.8400 for the C_{11}+ fractions.

No. of Carbon Atoms	Naphthenes	Paraffins	Cyclo-olefins	Monoolefins and Dioolefins	Aromatics
3		0.5005		0.5139	
4		0.5788		0.6037	
5	0.7454	0.6262	0.7720	0.6474	
6	0.7636	0.6594	0.7803	0.6794	0.8789
7	0.7649	0.6837	0.7854	0.7023	0.8670
8	0.7747	0.7025	0.8000	0.7229	0.8681
9	0.7853	0.7176	0.8073	0.7327	0.8707
10	0.8103	0.7300			0.8724

[A] ASTM publication DS 4A, *Physical Constants of Hydrocarbons*. C_{11}+ groups utilize an average of data available from the *Handbook of Chemistry and Physics*, 69th Ed, 1988-1989. Available from ASTM Headquarters.

TABLE 9 Relative Density, kg/L at 20°C, of Oxygenates[A]

Oxygenate	Relative Density
Ethanol	0.7967
tert-Butanol	0.7910
MTBE	0.7459
ETBE	0.7440
TAME	0.7710

[A] ASTM publication DS 4B, *Physical Constants of Hydrocarbons*, available from ASTM Headquarters.

TABLE 10 Reporting of Components

Hydrocarbon Group Type and Oxygenates	Report, Mass % and LV %
Paraffins	by carbon number through C_{10}
Olefins, iso and normal	by carbon number through C_9
Olefins, cyclic	by carbon number through C_9
Naphthenes	by carbon number through C_{10}
Aromatics	by carbon number through C_{10}
Higher boiling, >200°C	C_{11}+ composite (includes C_{10} olefins)
Polynaphthenes	total
Oxygenates	by component

TABLE 11 Repeatability and Reproducibility for Selected Oxygenate and Hydrocarbon Type Components and Groups of Components

NOTE—X is the average of two results in mass % (or liquid volume %).

Category	Repeatability	Reproducibility	Range of Concentration Low	Range of Concentration High
Aromatics	0.0247•(4.3353+X)	0.1249•(4.3353+X)	12	44
Olefins	$0.046•X^{0.7444}$	$0.255•X^{0.7444}$	0.2	13
Paraffins	0.97	3.90	34	60
Naphthenes	0.028•X	0.1659•X	2	15
MTBE	0.0155•(1.858+X)	0.0641•(1.858+X)	0	12
Benzene	0.02	0.14	0.3	1
Toluene	0.019•X	0.0545•X	2	11
C_8 Aromatics	0.0255•(1.5172+X)	0.0708•(1.5172+X)	3.5	15

TABLE 12 Calculated Repeatability and Reproducibility at Various Concentration Levels

NOTE—*X* is the average of two results in mass % (or liquid volume %).

Category	X	Repeatability	Reproducibility
Aromatics	12	0.4	2.0
	15	0.4	2.4
	20	0.6	3.0
	25	0.7	3.6
	30	0.8	4.3
	35	0.9	4.9
	40	1.1	5.5
Olefins	0.2	0.1	0.1
	1	0.1	0.3
	3	0.1	0.5
	5	0.1	0.8
	10	0.2	1.4
	13	0.3	1.7
Paraffins	35-60	1.0	3.9
Naphthenes	2	0.1	0.3
	5	0.2	0.8
	10	0.3	1.6
	15	0.4	2.5
MTBE	2	0.1	0.2
	5	0.1	0.4
	8	0.1	0.6
	12	0.2	0.9
Benzene	0.3-1	0.02	0.14
Toluene	2	0.04	0.11
	5	0.10	0.27
	8	0.15	0.44
	11	0.21	0.60
C_8 Aromatics	4	0.14	0.39
	8	0.24	0.67
	12	0.34	0.96
	15	0.42	1.17