



Designation: D8071 – 21

Standard Test Method for Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)¹

This standard is issued under the fixed designation D8071; 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 is a standard procedure for the determination in percent mass or percent volume of hydrocarbon group types (paraffins, isoparaffins, olefins, naphthenes, aromatics), methanol, ethanol, benzene, toluene, ethylbenzene, xylenes, naphthalene, and methylnaphthalenes in automotive spark-ignition engine fuels using gas chromatography and vacuum ultraviolet detection (GC-VUV).

1.1.1 The concentration ranges for which precision has been determined are as follows:

Property	Units	Applicable Range
Paraffins	% Volume	3.572 to 23.105
Isoparaffins	% Volume	22.697 to 71.993
Olefins	% Volume	0.011 to 44.002
Olefins	% Mass	0.027 to 41.954
Naphthenes	% Volume	0.606 to 18.416
Aromatics	% Volume	14.743 to 58.124
Methanol	% Volume	0.063 to 3.426
Ethanol	% Mass	0.042 to 15.991
Benzene	% Volume	0.09 to 1.091
Toluene	% Volume	0.698 to 31.377
Ethylbenzene	% Volume	0.5 to 3.175
Xylenes	% Volume	3.037 to 18.955
Naphthalene	% Volume	0.019 to 0.779
Methylnaphthalenes	% Volume	0.21 to 1.484

1.1.2 This test method may be applicable to other concentration ranges, to other properties, or to other hydrocarbon streams, however precision has not been determined.

1.2 Individual hydrocarbon components are typically not baseline-separated by the procedure described in this test method, that is, some components will coelute. The coelutions are resolved at the detector using VUV absorbance spectra and deconvolution algorithms.

1.3 While this test method reports percent mass and percent volume for several specific components that may be present in

automotive spark-ignition engine fuel, it does not attempt to speciate all possible components that may occur in automotive spark-ignition engine fuel. In particular, this test method is not intended as a type of detailed hydrocarbon analysis (DHA).

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. See specific hazard statements in subsection 8.4 and Section 9.*

1.6 *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.*

2. Referenced Documents

2.1 ASTM Standards:²

- D1319** Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- D3606** Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography
- D4057** Practice for Manual Sampling of Petroleum and Petroleum Products
- D4307** Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D5599** Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

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 D02.04.01 on Gas Chromatography Methods.

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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.

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

- D5769** Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry
- D5842** Practice for Sampling and Handling of Fuels for Volatility Measurement
- D6300** Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
- D6550** Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
- D6708** Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
- D6730** Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *integration filter, n*—a mathematical operation performed on an absorbance spectrum for the purpose of converting the spectrum to a single-valued response suitable for representation in a two-dimensional chromatogram plot.

3.1.2 *library reference spectrum, n*—an absorbance spectrum representation of a molecular species stored in a library database and used for identification of a compound/compound class or deconvolution of multiple coeluting compounds.

3.1.3 *response area, n*—generally refers to a response summed over a given time interval and has units of absorbance units (AU).

3.1.3.1 *Discussion*—A time factor necessary to convert a response area to a true mathematical area cancels out of all critical calculations and is omitted.

3.2 Abbreviations:

- 3.2.1 AU—absorbance units
- 3.2.2 DHA—detailed hydrocarbon analysis
- 3.2.3 GC-VUV—gas chromatography with vacuum ultraviolet spectroscopy detection
- 3.2.4 RI—retention index
- 3.2.5 RRF—relative response factor

4. Summary of Test Method

4.1 An automotive spark-ignition fuel sample is introduced to a gas chromatographic (GC) system. After volatilization, the effluent is introduced onto a GC column for separation, and then detected by a vacuum ultraviolet absorption spectroscopy detector.³ The separation is accomplished using a 30 m, non-polar phase capillary column and a moderately fast temperature ramp (typical operating parameters of this test method are

given in Table 1). Coelutions are resolved by the detector using vacuum ultraviolet absorbance spectra and deconvolution.

4.2 The result of the measurement is the determination of the total response areas of the five hydrocarbon classes of paraffins, isoparaffins, olefins, naphthenes, and aromatics, in addition to several individual species components. The percent mass concentrations are calculated from the response areas using class-based or compound-specific relative response factors, as appropriate. The percent volume concentrations are calculated from the mass concentrations.

5. Significance and Use

5.1 The determination of class group composition of automotive spark-ignition fuels as well as quantification of various individual species such as oxygenates and aromatics in automotive fuels is useful for evaluating quality and expected performance, as well as compliance with various governmental regulations.

6. Interferences

6.1 Interferences with this test method, if any, have not been determined.

7. Apparatus

7.1 *Gas chromatograph*, equipped with automated oven temperature control and split/splitless inlet.

7.1.1 *Flow Controllers*—The gas chromatograph must be equipped with mass flow controllers capable of maintaining carrier gas flow constant to $\pm 1\%$ over the full operating temperature range of the column. The inlet pressure of the carrier gas supplied to the gas chromatograph must be at least 485 kPa. This will ensure that the minimum pressure needed to compensate for the increase in column back-pressure as the column temperature is maintained.

TABLE 1 Typical Instrument Settings for GC-VUV Automotive Spark-Ignition Fuel Measurement

Column dimensions	Capillary, 30 m $\times$ 0.25 mm ID $\times$ 0.25 μ m film thickness
Column phase ^A	Nonpolar (for example, 100 % dimethyl polysiloxane)
Inlet temperature	250 °C
Injection volume ^B	1.0 μ L
Split ratio ^B	300:1
Column flow ^C	1.0 mL/min
Oven initial temperature	35 °C
Initial hold time	10 min
Oven ramp	7 °C/min
Final oven temperature	200 °C
Final hold time	0 min
Detector makeup gas pressure (gauge)	2.1 kPa
Detector scan rate	4.5 Hz
Detector flow cell temperature	275 °C
Transfer tube temperature	275 °C

^A Columns with low bleed phases such as MS grade have been successfully used for this application (see 11.6)

^B Other injection volumes (see 7.1.2) and split ratios may be used to achieve the required benzene response (see 13.2)

^C Gas chromatograph manufacturer's column flow systems must be set to maintain constant flow or gas velocity throughout the temperature ramp. Do not use constant pressure.

³ The sole source of supply of the apparatus known to the committee at this time is VUV-Analytics, Cedar Park, Texas. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.