



Designation: D6550 – 20

Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography¹

This standard is issued under the fixed designation D6550; 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 determination of the total amount of olefins in blended motor gasolines and gasoline blending stocks by supercritical-fluid chromatography (SFC). Results are expressed in terms of mass percent olefins. The method working range is from expected concentration of 1 % by mass to expected concentration of 25 % by mass total olefins.

1.2 This test method can be used for analysis of commercial gasolines, including those containing varying levels of oxygenates, such as methyl *tert*/butyl ether (MTBE), diisopropyl ether (DIPE), methyl *tert*/amyl ether (TAME), and ethanol, without interference.

NOTE 1—This test method has not been designed for the determination of the total amounts of saturates, aromatics, and oxygenates.

1.3 This test method includes a relative bias section based on Practice D6708 accuracy assessment between Test Method D6550 mass percent and Test Method D1319 volume percent for total olefins in spark-ignition engine fuels as a possible Test Method D6550 alternative to Test Method D1319 for U.S. EPA regulations reporting. The Practice D6708 derived correlation equation is only applicable for test result range from 0.53 % to 26.88 % by mass as reported by Test Method D6550.

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.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

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 D02.04.0C on Liquid Chromatography.

Current edition approved July 1, 2020. Published July 2020. Originally approved in 2000. Last previous edition approved in 2015 as D6550 – 15. DOI: 10.1520/D6550-20.

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
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D5186 Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography
- D6296 Test Method for Total Olefins in Spark-ignition Engine Fuels by Multidimensional Gas Chromatography
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
- D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
- D6839 Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

- 3.1.1 *critical pressure, n*—the pressure needed to condense a gas to a liquid at the critical temperature.
- 3.1.2 *critical temperature, n*—the highest temperature at which a gaseous fluid can be condensed to a liquid by means of compression.
- 3.1.3 *supercritical fluid, n*—a fluid maintained above its critical temperature and critical pressure.

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

3.1.4 *supercritical-fluid chromatography (SFC), n*—a type of chromatography that employs a supercritical fluid as the mobile phase.

4. Summary of Test Method

4.1 A small aliquot of the fuel sample is injected onto a set of two chromatographic columns connected in series and transported using supercritical carbon dioxide (CO₂) as the mobile phase. The first column is packed with high-surface-area silica particles. The second column contains either high-surface-area silica particles loaded with silver ions or strong-cation-exchange material loaded with silver ions.

4.2 Two switching valves are used to direct the different classes of components through the chromatographic system to the detector. In a forward-flow mode, saturates (normal and branched alkanes, cyclic alkanes) pass through both columns to the detector, while the olefins are trapped on the silver-loaded column and the aromatics and oxygenates are retained on the silica column. Aromatic compounds and oxygenates are subsequently eluted from the silica column to the detector in a back-flush mode. Finally, the olefins are back-flushed from the silver-loaded column to the detector.

4.3 A flame-ionization detector (FID) is used for quantitation. Calibration is based on the area of the chromatographic signal for olefins, relative to standard reference materials, which contain a known mass % of total olefins as corrected for density.

5. Significance and Use

5.1 Gasoline-range olefinic hydrocarbons have been demonstrated to contribute to photochemical reactions in the atmosphere, which result in the formation of photochemical smog in susceptible urban areas.

5.2 The California Air Resources Board (CARB) has specified a maximum allowable limit of total olefins in motor gasoline. This necessitates an appropriate analytical test method for determination of total olefins to be used both by regulators and producers.

5.3 This test method compares favorably with Test Method **D1319** (FIA) for the determination of total olefins in motor gasolines. It does not require any sample preparation, has a comparatively short analysis time of about 10 min, and is readily automated. Alternative methods for determination of olefins in gasoline include Test Methods **D6839** and **D6296**.

6. Apparatus

6.1 *Supercritical-fluid Chromatograph (SFC)*—Any SFC instrumentation can be used that has the following characteristics and meets the performance requirements specified in Section 8.

NOTE 2—The SFC instruments suitable for Test Method **D5186** are suitable for this test method, if equipped with two switching valves, as described under 6.1.7.

6.1.1 *Pump*—The SFC pump shall be able to operate at the required pressures (typically up to about 30 MPa) and deliver a sufficiently stable flow to meet the requirements of retention-time precision (better than 0.3 %) and detection background (see Section 8). The characteristics of the pump will largely determine the optimum column diameter. The use of 4.6 mm internal diameter (i.d.) columns requires a pump capacity of at least 1 mL/min of liquid CO₂. Columns with an inside diameter of 2 mm and 1 mm require minimum pump capacities of 200 µL/min and 50 µL/min, respectively.

6.1.2 *Detectors*—A FID is required for quantitation. A flow restrictor shall be installed immediately before the FID. This restrictor serves to maintain the required pressure in the column, while allowing the pump and detector to perform as specified. A (diode-array or variable wavelength) UV detector for establishing optimum switching times (see Sections 8 and 9) is optional. Such a detector can be incorporated in two different manners.

6.1.2.1 A UV detector with a very small dead volume can be inserted between the column and the FID and operated in series.

6.1.2.2 A post-column splitting device, consisting of a T-junction with an appropriate flow restrictor to the FID, can be inserted between the column and the UV detector. Using the T-junction, the two detectors can be operated in parallel. The combination of restrictors (before the FID and after the UV detector) shall allow the pump and detector to perform as specified.

6.1.3 *Sample-inlet System*—A liquid-sample injection valve³ is required, capable of introducing (sub-)microlitre volume with a precision better than 0.5 %. A 1 µL injection volume was found to be adequate in combination with 4.6 mm inside diameter columns. Corresponding injection volumes are 200 nL and 50 nL for columns with inside diameters of 2 mm and 1 mm, respectively. The sample inlet system shall be installed and operated in a manner such that the chromatographic separation is not negatively affected.

6.1.4 *Columns*—Two columns of equal inside diameter are required:

6.1.4.1 A high-surface-area-silica column, capable of separating alkanes and olefins from aromatics as specified in Section 8. Typically, one or several 250 mm long columns are used. These columns are packed with particles having an average diameter of 5 µm or less, 600 nm (60 Å) pores, and a surface area of ≥350 m²/g.

³ Sample valves with loop volumes down to 50 nL are commercially available from Valco (Houston, TX).

TABLE 1 Typical Columns

Silica Column		Silver-loaded Column	
Vendor	Merck	Vendor	Hypersil, Phenomenex, Selerity
Packing material	Lichrospher SI 60	Packing material	Hypersil SCX, Selectosil SCX, Ag+ form
Particle size, µm	5	Particle size, µm	5
Length, mm	250	Length, mm	100 or 50
Internal diameter, mm	4.6	Internal diameter, mm	4.6

NOTE 3—Columns suitable for Test Method D5186 are also suitable for the present method. A typical example is shown in Table 1.

6.1.4.2 A silver-loaded-silica column or a cation-exchange column in the silver form. Cation-exchange columns are claimed⁴ to yield more stable columns. Typically, one 50 mm or 100 mm long column packed with particles with an average diameter of 5 μm is used for the analysis.

NOTE 4—Some columns that have been used successfully are shown in Table 1.

6.1.5 *Column-temperature Control*—The chromatograph shall be capable of column temperature control to within 0.5 °C or less.

6.1.6 *Computer or Electronic Integrator*—Means shall be provided for the determination of accumulated peak areas. This can be done by means of a computer or electronic integrator. The computer or integrator shall have the capability of correcting for baseline shifts during the run.

6.1.7 *Switching Valves*—Two six-way switching valves are configured in accordance with the scheme shown in Fig. 1. This configuration allows four different valve positions, defined as follows:

6.1.7.1 *Position A*—Silica column (forward-flush mode) and silver-loaded column (forward-flush mode) connected in series. This position is used (1) to inject the sample on the two columns, (2) to elute the saturates, (3) to trap the olefins on the silver-loaded column, and (4) to retain the aromatics and oxygenates on the silica column.

6.1.7.2 *Position B*—Silica column (backflush mode) connected in-line; silver-loaded column not in flow path. This position is used to elute the aromatics and polar compounds.

6.1.7.3 *Position C*—Silica column not in flow path; silver-loaded column (backflush mode) connected in-line. This position is used to elute the olefins.

6.1.7.4 *Position D*—Silica column (forward-flush mode) connected in-line; silver-loaded column not in flow path. This position is used to optimize the separation. Also, this position allows Test Method D5186 to be performed without changing the system.

6.1.8 *Sample Filter*—A microfilter of a porosity of 0.20 μm , which is chemically-inert to hydrocarbon solvents, may be used for the removal of microscopic particulate matter from the sample solution that potentially may harm the injection valve and affect system performance.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Air*—Zero-grade (hydrocarbon-free) air is used as the FID oxidant. (**Warning**—Air is usually supplied as a compressed gas under high pressure, and it supports combustion.)

7.3 *Calibration Solution*—A mixture or standard of hydrocarbons with a known mass percent of olefins of the type and concentration found in typical gasolines. A mixture of 75 % isooctane and 25 % toluene combined with the mixture of olefins found in Table 2 is appropriate to approximate the composition of the fuels being tested.

⁵ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁴ Anderson, P. E., Demirbueker, M., and Blomberg, L. G., *Journal of Chromatography*, 596, 1991, pp. 301-311.

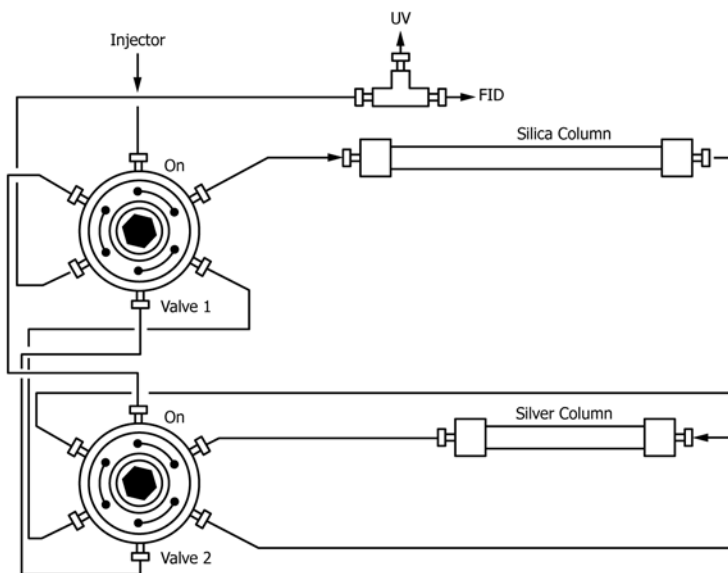


FIG. 1 Configuration of Switching Valves (Shown in Position A)