Designation: D6550 – 10

StandardTest Method for
Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography [1]

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 % olefins. The application range is from 1 to 25 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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:*[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 and Aviation Turbine 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

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.

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 (CO_2) 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.

---

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0C on Liquid Chromatography.

Current edition approved Oct. 1, 2010. Published November 2010. Originally approved in 2000. Last previous edition approved in 2005 as D6550–05. DOI: 10.1520/D6550-10.

[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**

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

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 CO_2. Columns with an inside diameter of 2 and 1 mm require minimum pump capacities of 200 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 valve[3] 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 and 50 nL for columns with inside diameters of 2 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 m^2/g.

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 claimed[4] to yield more stable columns. Typically, one 50 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 *Computor 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.

---

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

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

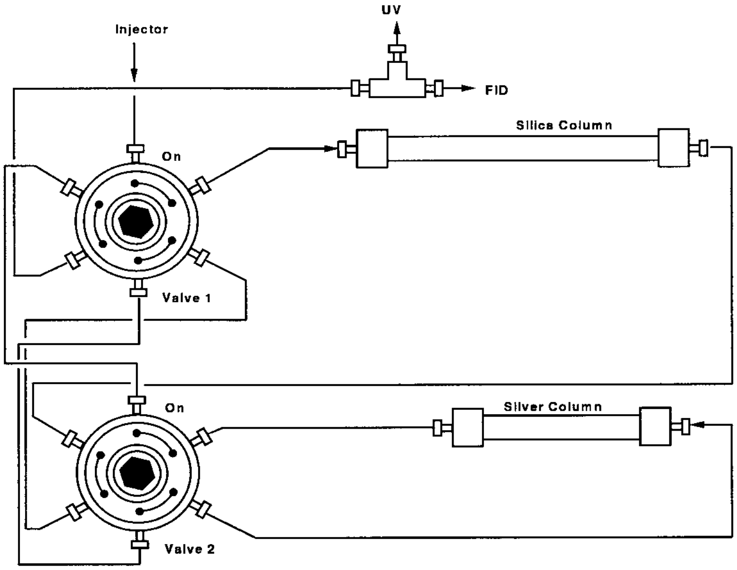

FIG. 1 Configuration of Switching Valves (Shown in Position A)

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.

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 of hydrocarbons with a known mass % of olefins of the type and concentration found in typical gasolines. This olefin mixture can be diluted by weight with olefin-free components, such as alkylate, toluene, xylenes, and oxygenates, such as MTBE, as appropriate to approximate the composition of the fuels being tested.

7.4 *Carbon Dioxide (CO_2)* —Supercritical-fluid-chromatographic grade, 99.99 % minimum purity, supplied pressurized in a cylinder with a dip tube for removal of liquid CO_2. (**Warning**—Liquid at high pressure. Release of pressure results in production of extremely cold, solid CO_2 and gas, which can dilute available atmospheric oxygen.)

7.5 *Hydrogen*—Hydrogen of high quality (hydrocarbon-free) is used as the fuel for the FID. (**Warning**—Hydrogen is usually supplied under high pressure and is extremely flammable.)

7.6 *Loading-time Mixture*—A mixture of a typical alkane and an olefin, which can be used to determine the loading time (see 8.2.2.3 (*1*) and 8.2.2.3 (*2*)) while protecting the silver-loaded column from exposure to aromatic compounds.

7.7 *Performance Mixture*—A mixture of a typical alkane, a mono-aromatic (usually toluene), and a typical mono-olefin can be used to fine-tune this test method and to check its performance. A mixture of *n*-heptane, toluene, and 3-methyl-2-pentene has been successfully used for this purpose.

7.8 *Quality Control Sample*—A motor gasoline containing olefins to be used to establish and monitor the precision of the analytical measurement system.

8. Preparation of Apparatus

8.1 Install the SFC instrumentation in accordance with the manufacturer's instructions. System operating conditions will

---

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.

depend on the column used and optimization of performance. The conditions listed in Table 1 have been used successfully. If the performance characteristics in terms of retention and resolution, specified in 8.2, are not achieved, the temperature, pressure, or mobile-phase flow rate can be modified to achieve compliance. A silica column of low activity can be reactivated by solvent rinsing, using accepted liquid-chromatographic activation strategies.

8.2 *System Performance:*

8.2.1 *System Optimization*—The operation of the SFC system shall be optimized in order to achieve the required separation on the silica column. This process is different if an optional UV detector is available.

8.2.1.1 When the optional UV detector is installed, the separation between the three different classes of compounds can be monitored directly. Saturates show no UV absorption. Olefins show significant absorption at wavelengths up to about 220 nm but no absorption at 250 nm or higher. Aromatics show considerable absorption at low wavelengths, extended to a wavelength of 250 nm and higher. The onset of the elution of the olefin fraction (following the saturates fraction) can be monitored at 220 nm. The elution of the aromatic fraction can be monitored at 250 nm. In this case, the performance mixture (see 7.6) can be used to optimize the separation of the olefins and aromatics.

8.2.1.2 Without a UV detector being installed, individual pure components and the performance mixture (see 7.6) can be used to optimize the system.

8.2.2 *Column Requirements:*

8.2.2.1 *Silica Column*—The critical requirement for the silica column is its ability to achieve a quantitative separation between the olefins and aromatics. The performance of this column can be verified independently of that of the silver-loaded column by switching the valves to the appropriate position (see 6.1.7.4).

(1) When using a UV detector, the requirement is baseline resolution between the olefin and aromatic signals. The resulting switching time (see Section 9) shall be chosen to occur just before the onset of the aromatics signal.

(2) When using only an FID, the resolution (R_{AO}) between the olefinic compound and the aromatic compound in the performance mixture shall be at least three when measured as follows:

$$R_{AO} = \frac{2 \times (t_A - t_O)}{1.699 \times (y_A + y_O)} \tag{1}$$

where:

t_A = retention time for the aromatic reference compound, s,
t_O = retention time for the olefinic reference compound, s,
y_A = peak width at half height for the aromatic reference compound, s, and
y_O = peak width at half height for the olefinic reference compound, s.

8.2.2.2 All aromatic compounds, as well as oxygenates and other polar molecules, are eluted from the silica column in the backflush mode during a time, t_{AR}, which shall be less than five times the loading time, t_L. The elution of the aromatics and polars can be observed using an FID. Complete elution is thought to have occurred if the detector value (S_{End}) has returned to the baseline value observed before the elution of any peaks ($S_{Baseline}$) to within 0.1 % of the height of the aromatics peak ($h_{Aromatics}$), that is,

$$S_{End} \leq S_{Baseline} + h_{Aromatics}/1000 \tag{2}$$

8.2.2.3 *Silver-loaded Column*—This column is operated exclusively as an olefin trap. Its stability and chromatographic efficiency are not critical as long as the following two requirements are met. The column shall allow a quantitative separation between the saturates and the olefins and the quantitative release of all olefins under appropriate conditions. The performance of the silver-loaded column can be verified independently of that of the silica column by switching the valves to the appropriate position (see 6.1.7.3).

NOTE 5—It is recommended that aromatic solutes should not be introduced on the silver-loaded column. This can be achieved by using a loading-time mixture, which does not contain aromatics, or by using the silica column to trap the latter.

(1) When using a quality control sample for optimization, as will typically be the case when a UV detector is installed, no olefins shall elute from the silver-loaded column in the forward-flush mode in a time, t_L, defined as:

$$t_L = t_{SAT} + 3 \times y_{SAT} \tag{3}$$

where:

t_{SAT} = time for the saturated-peak apex, s, and
y_{SAT} = peak width at half height of the saturates peak, s.

(2) When using a performance mixture for optimization, as will typically be the case when using only an FID detector, no olefins shall elute from the silver-loaded column in the forward-flush mode in a time, t_L, defined as:

$$t_L = t_S + 5 \times y_S \tag{4}$$

where:

t_S = retention time for the saturates reference compound, s, and
y_S = peak width at half height for the saturates reference compound, s.

(3) All olefins shall be released from the silver-loaded column in the backflush mode within a time, t_{BF}, that is less than five times the total time during which the olefins are loaded onto the column in the forward-flush mode (t_{FF}), that is,

$$t_{BF} \leq 5 \times t_{FF} \tag{5}$$

The total time t_{FF} is the sum of the loading time (t_L) and a cleaning time (t_C):

$$t_{FF} = t_L + t_C \tag{6}$$

During the time t_C, any non-olefinic (saturates or cyclic) compounds that have remained in the olefin trap are eluted in the forward-flush mode. The absence of an FID signal at the end of the time t_C confirms proper separation between saturated (including cyclic) and olefinic compounds. The elution of the olefins can be observed using either a UV-absorbance detector set at 220 nm or an FID. Complete elution is thought to have occurred if the detector value (S_{End}) has returned to the baseline value observed before the elution of the saturates or olefins ($S_{Baseline}$), or both, to within 0.1 % of the height of the olefins peak ($h_{Olefins}$), that is,

$$S_{End} \leq S_{Baseline} + h_{Olefins}/1000 \tag{7}$$