Designation: D6550 – 20

Standard Test 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 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 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.

---

*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 (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.

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 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 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 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 m^2/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 claimed[4] 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 *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.

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 to (*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 (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 % *iso*octane and 25 % toluene combined with the mixture of olefins found in Table 2 is appropriate to approximate the composition of the fuels being tested.

---

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

[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.
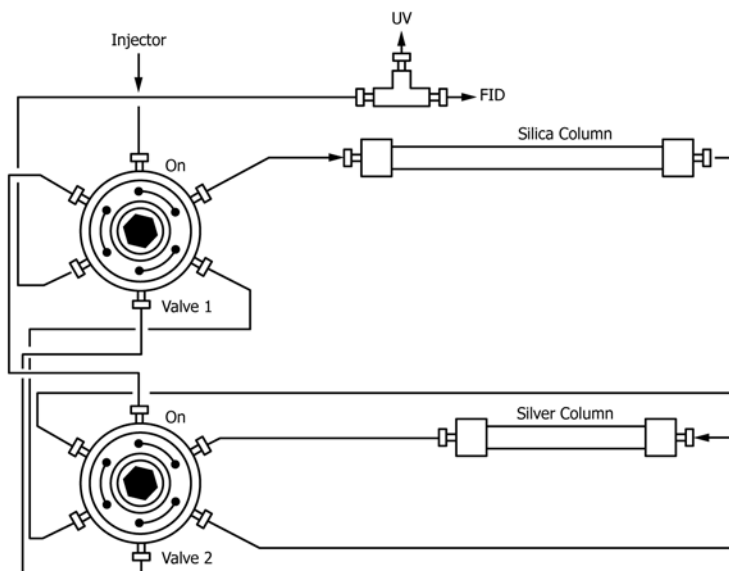

FIG. 1 Configuration of Switching Valves (Shown in Position A)

TABLE 2 Type and Concentration of Olefins used in the Calibration Solutions

Olefin Mixture	Concentration (%)
1-Hexene	9.30 %
Cyclohexene	14.00 %
2-Methyl-1-hexene	3.90 %
2-Methyl-1-heptene	3.90 %
3-Methyl-2-pentene	27.90 %
1-Heptene	24.70 %
1-Octene	12.40 %
1-Nonene	3.90 %

TABLE 3 Typical Densities of Calibration Standards Using the Olefins Listed in Table 2 in 75/25 *Iso*octane/Tolune

Olefin Concentration (Wt%)	Density (60 °F) (g/cm³)
0.25	0.73144
1.06	0.73142
5.16	0.72888
12.92	0.72722
17.74	0.72889
24.55	0.72592
AVE Density	0.7290

7.4 *Carbon Dioxide (CO₂)*—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 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,

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

Note 6—It may be necessary to change the operating conditions in order to meet the requirement of Eq 5. Increasing the mobile-phase density or the column temperature may facilitate the elution of the olefins. However, the best precision can be achieved if the conditions are kept constant.

8.2.3 *Retention-time Precision:*

8.2.3.1 *Repeatability*—The repeatability of the retention times has a direct influence on the precision of the total olefin content determined because column switching is performed on a time basis (see Section 9). Retention times obtained for performance mixtures and standard gasolines on a given instrument and column set shall be repeatable within 0.5 % (relative) over a period of several days.

Note 7—It has been observed that the first analysis after an idle period often results in somewhat different retention times than those previously determined for the test method.

8.2.3.2 *Reproducibility*—The reproducibility of the retention times from column to column and from instrument to instrument is not critical, provided that the column performance requirements (see 8.2) are met.

8.2.4 *Calibration Curve:*

8.2.4.1 A calibration curve shall be generated by blending at least four different calibration solutions of known olefin content. The type of olefins and the concentration of each that shall be used is shown in Table 2. A mixture of 75 % *iso*octane and 25 % toluene shall be used to dilute the known olefin mixture to prepare the calibration solutions. These calibration solutions shall be of known density (see 9.1).

8.2.4.2 These calibration standards shall be blended to cover the entire range of olefin content for which the test method will be used. The calibration curve is a plot of the observed peak area for the entire olefin signal against the known mass percentage of olefins in the calibration standards. Analysis of a blank shall also be used to confirm no olefin contamination in the hydrocarbon mixture used to prepare the standards.

8.2.4.3 Analyze the calibration standards and establish the standard linear regression curve by plotting the peak area of the olefin group versus the corresponding known concentrations of each standard.

(1) The value of the absolute term intercept/slope (b/m) shall be equal to or less than 0.25 where b is the y-intercept and m is the slope of the linear fit line. The calculated b/m value is based on plotting Y=area and X=concentration. For example, using the equation in Fig. 4 for the given slope and y-intercept the calculated value is 0.20.

(2) Check the correlation r^2 value for the calibration curve obtained. The r^2 value shall be at least 0.99 or better. See Fig. 4 for an example.

8.2.4.4 *Verification of Calibration*—Immediately after the performance of the calibration, analyze a calibration verification check standard, certified standard and/or a sample from a proficiency testing (e.g. PTP) of known olefin value mass. The difference between the value calculated by this test method shall be less than or equal to 0.75R where R is the reproducibility at the concentration of the standard. Analysis of more than one standard is recommended, one preferable at the upper and one at the lower range of samples to be analyzed

9. Procedure

9.1 *Determination of Density of Samples and Standards*—Determine density of samples at 60 °F and standards using Test Method D4052 or equivalent.
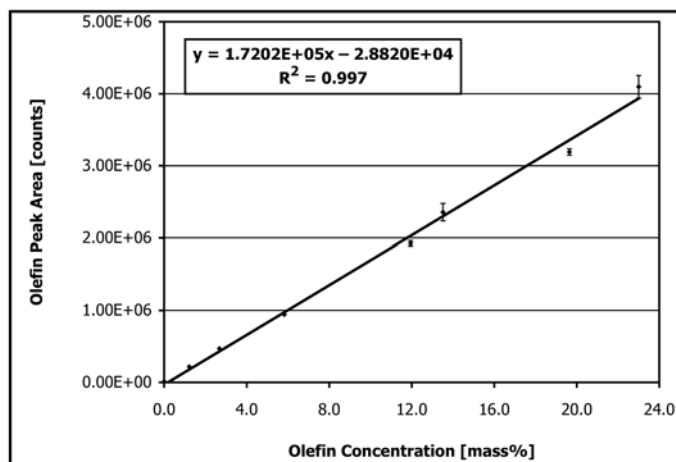
9.2 *Switching Times:*

FIG. 4 Typical Calibration Curve

9.2.1 Establish the loading time period, t_L, between injection ($t = 0$) and the onset of the aromatic peak, as described in 8.2.2.1.

9.2.1.1 Only the silica column need be in the flow path to the detector (forward-flush mode; see 6.1.7.4) for this step. This will protect the silver-loaded column from aromatics (see 8.2.2.2) when using a quality control sample to determine the loading time period.

9.2.1.2 If both columns are positioned in the flow path, use the loading-time mixture (see 7.5) to protect the silver-loaded column.

9.2.2 Determine the time period, t_{AR}, required to back-flush all aromatic and polar compounds from the silica column after the loading-time period, t_L, using a quality control sample. Columns are initially connected in series (see 6.1.7.1). Valves are switched at the end of time period, t_L, such that only the silica column is in the flow path (back-flush mode; see 6.1.7.2). Measurement of t_{AR} can then be made while protecting the silver-loaded column from aromatics.

9.2.3 Determine the time period, t_C, required to clean all saturated and cyclic compounds from the silver-loaded column in the forward-flush mode, using a quality control sample. Columns are initially connected in series (see 6.1.7.1). Valves are switched at time, t_L, such that only the silica column is in the flow path (see 6.1.7.2). Valves are then switched at the end of time period, t_{AR}, (total time = $t_L + t_{AR}$). The silica and silver-loaded columns are connected in series (see 6.1.7.1), allowing the elution of the saturated and cyclic compounds. *The time period, t_C, shall be short enough to avoid the onset of the elution of olefins from the silver-loaded column.*

9.2.4 Determine the time period, t_{BF}, required to elute all olefins from the silver-loaded column in the backflush mode. Columns are initially connected in series (see 6.1.7.1). Valves are switched at the end of time period, t_L, such that only the silica column is in the flow path (see 6.1.7.2). Valves are then switched at the end of time period, t_{AR}, such that the two columns are again connected in series (see 6.1.7.1). Valves are switched at the end of time period, t_C, (total time $t_L + t_{AR} + t_C$) such that only silver-loaded column is in the flow path in the backflush mode (see 6.1.7.3), allowing the elution of the olefins. The resulting switching table, with typical values corresponding to the conditions listed in Table 4, is shown as Table 5.

9.3 *Application of this Test Method:*

9.3.1 *Calibration Curve*—Record the calibration curve, as described in 8.2.4.

9.3.2 *Analyzing Samples*—Inject undiluted aliquots of all gasoline samples. An example chromatogram is shown as Fig. 2 (see Fig. 3 for the details of Fig. 2). It is recommended to filter the sample prior to analysis to remove any micro-particles that may affect the performance of the instrument.

10. Calculation

10.1 Determine the total area of the olefins peak. Determine the total concentration of olefins directly from the calibration curve. An example of a calibration curve is shown in Fig. 4.

10.2 A density correction shall be applied. Obtain the density of the sample and the density of the calibration standards as per 9.1. Use the average density value of the standards for ρ_{std} in Eq 8. See Table 3 for an example of the densities for calibration standards analyzed by Test Method D4052. The density correction can be accomplished using the following calculation:

$$M_{cor} = M_{cal}\left[(\rho_{std})/(\rho_{sam})\right] \qquad (8)$$

where:

TABLE 4 Typical SFC Conditions

Parameter	Value
Temperature, °C	75
Column-outlet pressure, MPa	22.3[A]
CO_2 flow rate, mL/min	2.5[B]
Injection volume, μL	1
FID temperature, °C	350
Air, mL/min	300
Hydrogen, mL/min	50
Air make-up, mL/min	15
Analysis time, min	5-20

[A] As regulated at the column-outlet.
[B] Liquid CO_2 under pump conditions.

TABLE 5 Switching Table with Typical Time Values

NOTE 1—Other times can be used if they produce equivalent or better results.

Time Period	Valve Position	Typical Time, min	Action
t_L	A	initial–1.4	loading sample onto columns; eluting saturates
t_{AR}	B	1.4–4	eluting aromatics
t_C	A	4–4.5	eluting remaining saturates from olefin trap
t_{BF}	C	4.5–10	eluting olefins

M_{cor} = corrected mass % olefin,
M_{cal} = mass % olefins as interpolated from calibration curve,
ρ_{std} = average density at 60 °F of all the calibration standard solutions (for example, see Table 3) used to make the calibration curve, and
ρ_{sam} = density at 60 °F of gasoline sample.

NOTE 8—The calculation in 10.2 is not to convert this test method's mass percent calculated result to volume percent, but to correct for the different amount of mass of sample and calibration standards introduced into the SFC column using a fixed volume valve injection.

11. Quality Control

11.1 Prior to the analysis of any samples in a given 24 h period, the laboratory shall analyze at least one quality control sample, using the procedure defined in 9.2. Results from the analysis of the quality control sample shall be in statistical control in accordance with Practice D6299, or other equivalent practice. Otherwise, if agreement with the expected value is not attained, corrective action shall be taken, verified by successful analysis of the quality control sample.

12. Report

12.1 Report the total olefin concentration to the nearest 0.1 mass % for values exceeding 1 mass %.

13. Precision and Bias[6]

13.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows.

13.1.1 *Repeatability*—The difference between two independent results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would exceed the values in Table 6 with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method:

$$\text{Repeatability} = 0.11\, X^{0.75}$$

where: X is the average of two results; each result is to be within the range 0.53 % to 30.25 % by mass total olefins inclusive (see Table 7).

13.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would exceed the values in Table 6 with an approximate probability of 5 % (one case in 20 in the long run) in the normal and correct operation of the test method:

$$\text{Reproducibility} = 0.47\, X^{0.75}$$

where: X is the average of two results; each result is to be within the range 0.53 % to 30.25 % total olefins by mass inclusive (see Table 7).

13.2 *Bias*—No information can be presented on the bias of this test method because no material having an accepted reference value is available.

13.3 *Relative Bias*—A relative bias assessment of Test Method D6550 versus Test Method D1319 for the determination of total olefins in spark-ignition engine fuel (gasolines) was conducted using data from the ASTM D02 Interlaboratory Crosscheck Program. The assessment was performed in accordance with the requirements of Practice D6708 with a successful outcome. It was based on measurements of total olefins in spark-ignition engine fuels supplied to the ASTM Proficiency Test Program by participating laboratories between February 2007 and October 2014 and is documented in Research Report RR:D02-1817.[7]

NOTE 9—In the United States, the EPA requires the measurement of total olefins in spark-ignition engine fuels by Test Method D1319. Effective Jan. 1, 2016, there is an allowance in the Performance Based Measurement System (PBMS) regulation to use other test methods if they are formally correlated with the specified test method by a consensus organization, for example, ASTM. This relative bias statement is intended to satisfy the requirement and allow use of Test Method D6550 bias-corrected results in the stated concentration ranges in place of Test Method D1319 for total olefins content. Regulations and specified test methods may change, the user should consult current regulations on use of this test and related methods.

13.3.1 The degree of agreement between results from Test Method D6550 mass percent and Test Method D1319 volume percent can be further improved by applying correlation equation (Eq 9) (Research Report RR:D02-1817),[7] and this correlation equation shall be utilized when reporting compliance with EPA fuels program. Sample-specific bias, as defined in Practice D6708, was observed for some samples which appear random after applying the bias-correction for the material types and property range listed below.