Designation: D7593 – 22

Standard Test Method for Determination of Fuel Dilution for In-Service Engine Oils by Gas Chromatography[1]

This standard is issued under the fixed designation D7593; 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 fuel dilution for in-service engine oil by gas chromatography.

1.2 Analysis can be performed directly by this test method without pretreatment or dilution of the sample.

1.3 There is no limitation for the determination of the dilution range, provided the amount of sample is within the linear range of the gas chromatograph detector. However, sample dilution can add potential error to the result and may affect the precision obtained as compared to the values presented in Section 14, which were obtained with no dilution.

1.4 This test method covers a quantitation range up to 10 % (m/m) for diesel and biodiesel, and up to 5 % (m/m) for gasoline.

1.5 The values stated in SI units are to be regarded as standard. Where non-SI units are provided, they are shown in parentheses.

1.6 *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.*

1.7 *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]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D3524 Test Method for Diesel Fuel Diluent in Used Diesel Engine Oils by Gas Chromatography

D3525 Test Method for Gasoline Fuel Dilution in Used Gasoline Engine Oils by Wide-Bore Capillary Gas Chromatography

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.1.2 This test method makes reference to common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355 and E594.

3.1.3 *fuel diluent, n—in service oil analysis*, is the unburned fuel components that enter the engine crankcase causing dilution of the oil.

3.1.4 *fuel dilution, n*—the amount, expressed as a percentage, of engine fuel found in the in-service lubricating oil.

3.1.5 *in-service oil, n*—lubricating oil that is present in a machine that has been at operating temperature for at least one hour.

3.1.6 *Marker Peak (MP), n*—a marker peak is a chromatographic peak used to differentiate sections of a chromatogram by retention time.

3.1.6.1 *Discussion*—For example, components that elute before this marker peak may be considered "fuel," while components that elute after this marker peak would be considered "oil." This marker peak retention time could also serve as the timing for physical changes in the chromatographic system, such as the time to initiate a valve change or a back-flush.

[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 D02.96.02 on Chemistry for the Evaluation of In-Service Lubricants.

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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

3.2 *Abbreviations:*

3.2.1 A common abbreviation of carbon compounds is to designate the number of carbon atoms in the compound. A prefix is used to designate the carbon chain form, while a subscripted suffix denotes the number of carbon atoms. For example, normal eicosane = n-C_{20}.

4. Summary of Test Method

4.1 A representative aliquot of in-service engine oil is introduced into a gas chromatograph through a programmable split injector. Carrier gas transports the vaporized aliquot through the dimethyl polysiloxane bonded phase capillary column where the hydrocarbons are separated by the chromatographic process. Once the hydrocarbons of interest are sensed by the flame ionization detector, the carrier gas pressure/flow at the head of the column is lowered and an auxiliary gas supply located at the end of the column is increased. The change in pressure forces the direction of the carrier gas to reverse direction and flow back through the injector. The residual hydrocarbons on the column are back-flushed out of the injector through a charcoal trap and out the split vent. The detector signal is processed by an electronic data acquisition system and the fuel profile is grouped into gasoline, diesel, and biodiesel. The components are identified by comparing their retention times to ones identified by analyzing standards under identical conditions. The concentrations of all components are determined by percent area by normalization of the peak areas.

5. Significance and Use

5.1 Some fuel dilution of in-service engine oil is normal under typical operating conditions. However, excessive fuel dilution can lead to decreased performance, premature wear, or sudden engine failure. This test method provides a means of quantifying the level of fuel dilution, allowing the user to take necessary action. This test method does not purport to accurately quantify the specific fuel present in the in-service lubricant samples due to limitations associated with the aging and degradation of the fuel in the crankcase. Rather, quantification of diesel fuel is normalized using a simulated aged fuel.

6. Interferences

6.1 There may be some overlap of the boiling ranges of gasoline, diesel, and biodiesel fuels and some new oils could have light hydrocarbons or formulated additives present from manufacturing. As a result, small deviations in quantitative analysis could accrue when testing unknown or mixed brands of in-service engine oil.

7. Apparatus

7.1 *Gas Chromatograph*—The following gas chromatographic system performance characteristics are required:

7.2 *Detector*—This test method requires a flame ionization detector (FID). The detector shall have sufficient sensitivity to detect 0.5 % by mass fuel dilution by area on the data acquisition device under the conditions recommended in this test method. The detector shall meet or exceed the specifications as detailed in Practice E594. The detector shall be capable of operating continuously at 350 °C and connected to the column such that no temperature zones below the column temperature (cold spots) exist.

7.3 *Injector*—The preferred injector is a programmable pneumatically controlled split capillary injector capable of operating continuously at 350 °C and maintaining a split ratio of 100/1. Connection of the column to the injector shall be such that no temperature zones below the column temperature (cold spots) exist. It is recommended the injector contain an injector liner packed with silanized glass wool or equivalent liner and that the split vent flows through a trap packed with activated charcoal before releasing the carrier gas to the atmosphere. The programmable injector is preferred for its rapid cooling during injector maintenance but an isothermal split injector can be used with slower cooling.

7.4 *Back-Flush Device*—Sufficient injector carrier gas pressure/flow should be maintained until the marker peak elutes, marking the point of back-flush. Under the recommended conditions within this test method the dodecane marker peak (for gasoline fuel dilution) should elute within 0.6 min and 0.9 min. The eicosane marker peak (for diesel fuel dilution) should elute within 1.5 min and 2.1 min. The heneicosane marker peak (for biodiesel fuel dilution) should elute within 1.8 min and 2.4 min. Once the marker peaks elute, reduce injector carrier gas pressure/flow and increase the back-flush carrier gas pressure/flow to allow back-flush of oil matrix off the column. Consult instrument vendor for specific hardware and operational conditions.

7.5 *Pneumatic Controllers*—The gas chromatograph shall be capable of maintaining carrier gas pressure constant to ±1 % for both the injector and the detector. Most modern gas chromatographs can control carrier gas in either pressure control mode or flow control mode. The back-flush procedure can be accomplished with either differential pressure or differential flow. The basic function is to inject with a high injector carrier and a low auxiliary carrier at the back-flush device so that a forward flow of carrier is established for chromatography. At the desired time, decrease the injector carrier and increase the auxiliary carrier to cause the back-flush. The difference in carrier between the injector and the back-flush device will determine the direction of carrier flow. The reverse flow shall be higher than the forward flow to cause the back-flush. Nominal dimensions of all tubing and restrictors will affect pressures and flows as well as temperatures in multiple heated zones such as injector, oven and detector. This analysis utilizes an isothermal oven temperature therefore constant flow control will not improve chromatographic throughput or efficiency. At isothermal oven temperatures, both pressure and flow will remain constant.

7.6 *Column Conditions*—This test method utilizes a fused silica open tubular column with dimethyl polysiloxane cross bond phase internal coating operating isothermally at 225 °C.

7.6.1 Open tubular column with a cross bond 100 % dimethyl polysiloxane phase internal coating, 15 m by 0.25 mm ID with a 0.25 µm film thickness.

7.7 *Sample Introduction Devices:*

7.7.1 *Microsyringe*—A microsyringe is used for sample introduction capable of precise 0.1 µL injections.

7.7.2 *Autosampler*—Automatic sampling device that reproducibly injects 0.1 µL volume is required. The sample introduction device should operate in a synchronous manner with the gas chromatograph.

7.8 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantification of these analyses shall meet or exceed these minimum requirements:

7.8.1 Normalized percent calculations based on peak area or peak height.

7.8.2 Ability to construct a first order linear regression calibration curve for up to as many as 10 levels of calibration.

7.8.3 Identification of individual components based on retention time, named groups, or timed groups.

7.8.4 Baseline corrections for positive or negative sloping baseline.

7.8.5 Non-resolved peaks separated by perpendicular drop line.

7.8.6 Ability to turn on and off integration.

7.8.7 Ability to adjust integration stop and start of each component.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is pure enough to be used without lessening the accuracy of the determination.

8.1.1 *Base Oil*—75 mm^2/s (cSt) @ 40 °C mineral oil. Used as a base oil to make the calibration standards and can be used as the preferred solvent to rinse the syringe. Other base stocks may be used, however alternate materials such as new additized engine oils may yield a bias in the results.

8.1.2 *Carbon Disulfide (CS_2), 99+ %* pure. (**Warning—** Extremely flammable and toxic liquid.) One of the solvents that can be used as a solvent to rinse the syringe.

8.2 *Gas*—The following compressed gases are utilized for the operation of the gas chromatograph.

8.2.1 *Helium,* 99.999 %. (**Warning—**Compressed gas under high pressure.) This gas can be used as carrier gas. Ensure sufficient pressure for a constant carrier gas flow rate. Precision in this method is based on helium as the carrier gas; however, nitrogen, hydrogen and argon have been successfully used as the carrier gas.

8.2.2 *Nitrogen,* 99.999 %. (**Warning—**Compressed gas under high pressure.) May be used as an alternative carrier gas.

8.2.3 *Argon,* 99.999 %. (**Warning—**Compressed gas under high pressure.) May be used as an alternative carrier gas.

8.2.4 *Hydrogen,* 99.999 %. (**Warning—**Extremely flammable compressed gas under high pressure.) This gas is used to supply fuel to the flame ionization detector (FID).

8.2.5 *Air,* (**Warning—**Compressed gas under high pressure.) This gas is used to supply oxidant to the flame ionization detector (FID).

8.3 *Aged Fuel*—Aged diesel fuel is prepared by distilling the fuel in accordance with Test Method D86 and stopping the distillation process after 10 % of the fuel has been distilled over. The 90 % fuel remaining in the distillation flask is the aged diesel fuel.

8.4 Quantification of unknown samples may be affected by the specific sources of fuel used in the calibration. In addition, fuel may age and degrade at different rates and by varying mechanisms once present in the engine's lubricant. Biodiesel blends and many ultra-low sulfur diesel fuels contain varying concentrations of fatty acid methyl esters and the specific concentration of biodiesel in any given vehicle's fuel tank may not be known with certainty. It is beyond the scope of this test method to require that calibration standards closely match the fuel found in the samples. The aging of the fuel standards provides an approximation of the actual fuel degradation in the engine oil and it should be noted that this test method is for the determination of fuel dilution and not for specific quantification of fuel blends or types.

8.5 *Marker Peak Definitions:*

8.5.1 *n-Dodecane* 99 % minimum purity ($n\text{-}C_{12}$) Used to signify the end boiling range of gasoline.

8.5.2 *n-Eicosane* 99 % minimum purity ($n\text{-}C_{20}$). Used to signify the end boiling range of diesel.

8.5.3 *n-Heneicosane* 99 % minimum purity ($n\text{-}C_{21}$). Used to signify the end boiling range of biodiesel.

9. Preparation of Apparatus

9.1 *Gas Chromatograph Setup:*

9.1.1 Install the gas chromatograph and place into operation in accordance with the manufacturer's instructions. Example conditions are listed in Appendix X1.

9.1.2 The injector liner and septum should be periodically inspected and replaced if necessary to remove extraneous deposits and improve injection precision.

9.1.3 It is recommended to periodically inspect the split gas flow through the charcoal trap and replace the trap if necessary to remove extraneous deposits and improve injection precision. Liquid oil will tend to build up in the charcoal trap after thousands of injections.

9.1.4 The rinse solvent to clean the syringe should be periodically inspected and replaced if necessary to remove extraneous deposits and improve injection precision.

9.2 *Column Conditioning*—Open tubular columns with cross-linked and bonded stationary phases containing dimethyl polysiloxane are available from many manufacturers and are usually pre- conditioned. Column conditioning is still recommended. The column can be conditioned very rapidly and effectively using the guidelines outlined in Practice E1510.

9.3 *System Performance Specification:*

9.3.1 *Column Resolution*—Resolution between hydrocarbons is not required in this test method as the method is designed to quantify a composite peak in the fuel range.

[3] *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.

10. Calibration

10.1 Analyze each of the calibration mixtures prepared in 10.3. Inject the same volume as chosen for the sample. Record the area due to the fuel portion in each mixture.

10.2 Prepare a linear regression calibration curve by plotting the area of the specific fuel group versus the percent of fuel. The correlation coefficient for each component should meet or exceed $r^2 = 0.998$.

$$rsp_i = (m_i)(amt_i) + b_i$$

where:

rsp_i = response for fuel (y-axis),
m_i = slope of linear equation,
amt_i = amount for fuel in mass (x-axis), and
b_i = y-axis intercept.

10.3 *Calibration Mixtures*—Prepare a minimum of three mixtures of fuel and 75 mm^2/s (cSt) base oil covering the range of up to 10 % (m/m) diesel and biodiesel fuel, and up to 5 % (m/m) gasoline fuel. A blank 75 mm^2/s (cSt) base oil should be used as a zero concentration in the calibration curve. Calibration standards are to be prepared on a mass to mass basis. Calibration standards may be prepared on a volume to volume basis but this approach is not addressed in this Test Method. Diesel fuel standards should be prepared using aged fuel as described in 8.3 whereas biodiesel and gasoline may be used as is. As described in 5.1, this standardized procedure for calibration mixture preparation allows for uniform reporting .The concentrations of calibration standards used should reflect that which is anticipated in the samples or threshold values, or both, for triggering action to be taken on the in-service engine oil. This test method has been shown to be linear from 0.5 % (m⁄m) to 40 % (m/m) for diesel fuel; see Fig. 1. If a sample result is above the calibration range, it is recommended to increase the calibration dynamic range to cover the concentration range desired or dilute the sample in the 75 mm^2/s (cSt) base oil but in no case may sample results be reported beyond the calibration range.

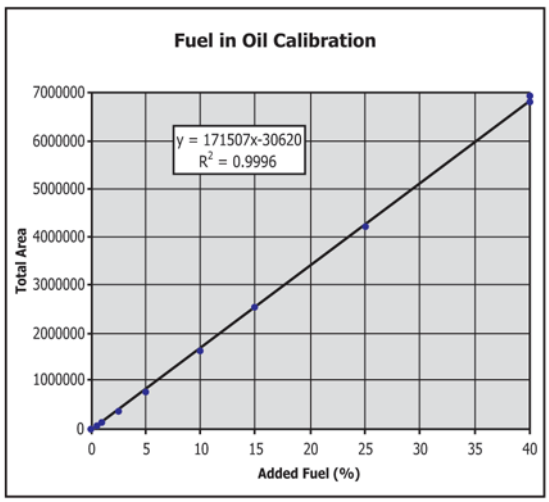

FIG. 1 Diesel Fuel in Oil Calibration Curve

11. Procedure

11.1 *Analysis Sequence Protocol*—Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule will include setting the heated zones to the analysis temperature, establishing set carrier pressure/flow, establishing set auxiliary pressure/flow, establishing split ratio, injection of samples into the gas chromatograph, syringe rinse, chromatography software collection and processing of data.

11.2 The time at which back-flush begins is predetermined by injection of a n-C_{12} standard for gasoline, n-C_{20} standard for diesel, and n-C_{21} standard for biodiesel in 75 mm^2/s (cSt) base oil. By examination of the chromatograph of these standards, the time at which back-flush is to begin is established by the elution of the marker peak. The back-flush time should be set once the majority of the marker peak is back to the baseline. As shown in Fig. 2 (C_{20} chromatogram) the tail of the marker peak is not incorporated into the peak area; therefore, if the marker peak tails, this area will be omitted from the area of the marker peak because it is advantageous that the back-flush time be as soon as possible. This will allow the majority of the undesired higher boiling components of the oil to be back-flushed.

11.3 Once the back-flush time of the marker peak is known, the chromatographic analytical method can be established. It is recommended that the analytical method be programmed with conditions provided in Appendix X1. The inlet pressure/flow is maintained high until the marker peak has eluted through the detector. Once the marker peak has eluted, the inlet pressure/flow is dropped and the auxiliary pressure/flow is increased to initiate back-flush. The auxiliary pressure/flow should remain high for at least the retention time of the marker peak. (example marker peak = 1.5 min, the back-flush should remain on for at least 1.5 min. Total analysis time 3 min.)

11.4 *Baseline Blank*—Perform a baseline blank with the 75 mm^2/s (cSt) oil. This blank should also be used as a zero concentration calibration standard.

11.5 *Sample Preparation*—A representative aliquot of in-service engine oil is transferred into the appropriate gas chromatograph vial. The vial should be sealed with the appropriate vial cap specified by the vender of the instrumentation.

11.6 *Quality Control Check*—A quality control sample representative of the type and range of fuel dilutions expected should be run on a daily basis to check instrument conditions.

11.7 *Sample Analysis*—Using the analysis sequence protocol; inject 0.1 µL of in-service oil into the gas chromatograph. Collect the entire analysis and let the chromatographic software process the data with the calibrated analytical method. Typical in-service oil chromatograms are presented in Fig. 2.

NOTE 1—The chromatogram in Fig. 2 was obtained from a soy-based biodiesel sample. Biodiesels derived from other source materials may affect the chromatography.

12. Interpretation of Results

12.1 Determine the mass percent of fuel in the samples by relating the area from the fuel components obtained to the previously determined calibration curves.

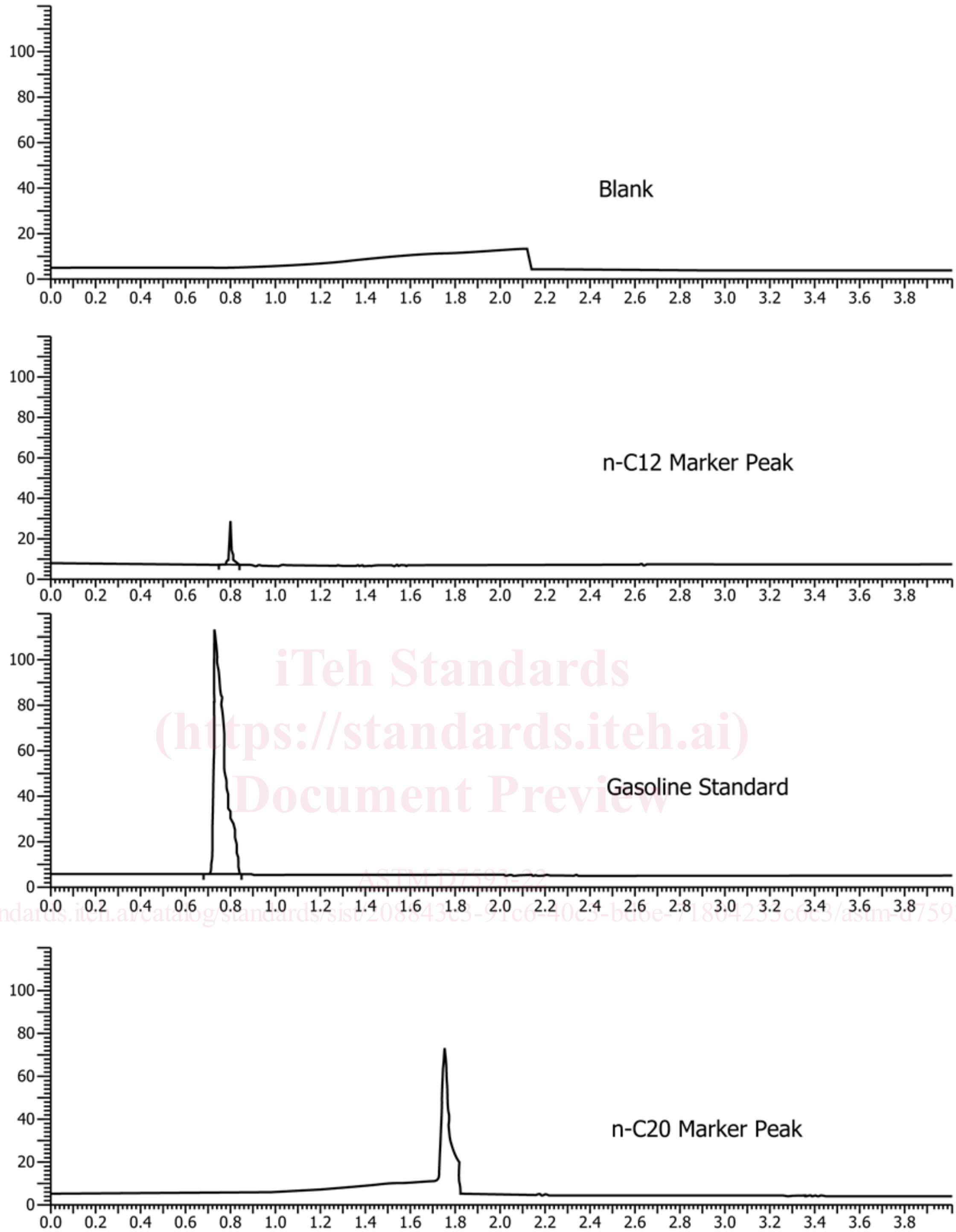

FIG. 2 Example Chromatograms