



Designation: D7593 – 22

Standard Test Method for Determination of Fuel Dilution for In-Service Engine Oils by Gas Chromatography¹

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

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.

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.

*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 = $n\text{-C}_{20}$.

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 $\pm 1\%$ 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.