Designation: D3525 – 20

Standard Test Method for Gasoline Fuel Dilution in Used Gasoline Engine Oils by Wide-Bore Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D3525; 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 describes a gas chromatographic technique for determining the amount of gasoline fuel dilution in used lubricating oils arising from their use in gasoline engines.

1.2 This test method is limited to gas chromatographs accommodating wide-bore (0.53 mm) capillary columns and that are equipped with flame ionization detectors (FIDs) and temperature programmable ovens.

1.3 There is no limitation regarding the fuel dilution concentration range that can be determined by this method, however the precision statements apply only to the concentration range of 0.5 % to 20.3 % gasoline. A reporting limit of 0.5 % gasoline fuel dilution has also been included in the method.

1.4 Lubricating fluids recovered from engine crankcases have undergone changes due to heating, volatilization, sheering, oxidation and other reactions, and, as a result, the chromatographic profiles of the gasoline diluents and engine oils often differ significantly from their original patterns. Caution is accordingly advised when comparing quantitative determinations made using new verses used or in-service materials.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 requirements 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]

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 definition of gas chromatography terms, refer to Practice E355.

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.1.1 *Discussion*—In this method, the fuel diluent components being determined originate from gasoline.

3.2.2 *fuel dilution, n*—the amount, expressed as a percentage, of gasoline found in engine lubricating oil.

3.2.2.1 *Discussion*—Fuel dilution may be the result of engine wear or improper performance.

3.3 *Abbreviations:*

3.3.1 A common abbreviation of hydrocarbon compounds is to designate the number of carbon atoms in the compound. A prefix is used to indicate the carbon chain form, while a subscripted suffix denotes the number of carbon atoms.

Example:

normal hexadecane $n\text{-}C_{16}$
iso-tetradecane $i\text{-}C_{14}$

4. Summary of Test Method

4.1 A gas chromatographic technique is described for analyzing used engine oils by adding a known amount of

[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.B0 on Automotive 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

TABLE 1 Typical Instrument Operating Conditions

	Wide-Bore Capillary Column
Column length	5 m – 30 m (16 ft – 90 ft)
Column inner diameter, mm (in.)	0.53 mm (0.021 in.)
Liquid phase / Stationary phase	100 % Dimethylpolysiloxane, cross-linked, bonded
Stationary phase thickness, microns	0.50 µm – 3.00 µm
Column temperature, initial °C	30 °C
Column temperature, initial hold time (min.)	1 min
Column temperature, initial ramp rate (°C/min.)	10 °C/min
Column temperature, first plateau,	50 °C
Column temperature, second hold time (min.)	0 min
Column temperature, 2nd ramp rate(°C/min.)	25 °C/min
Column temperature, final °C	300 °C
Column temperature, final hold time (min.)	7 min. – 15 min.
Carrier gas	Helium (He)
Carrier gas flow rate, mL/min	8 mL/min – 22 mL/min
Detector	flame ionization detector (FID)
Detector temperature, °C	300 °C – 350 °C
Injection port temperature, °C	275 °C – 300 °C
Injection Volume	0.1 µL – 0.2 µL

n-hexadecane (n-C_{16}) as an internal standard (ISTD), in order to determine the weight percent of gasoline fuel in the lubricating oil. Samples are chromatographed under the conditions described in this method, which separate and detect the gasoline diluent, internal standard, and engine oil peaks, and displays them in the resulting chromatogram. Quantitation is accomplished by comparing the area under the gasoline profile to the C_{16} internal standard peak area, and relating this ratio to the mass of the C_{16} internal standard and that of the sample.

5. Significance and Use

5.1 Some fuel dilution of the engine oil may take place during normal operation. However, excessive fuel dilution is of concern in terms of possible performance problems. This method provides a means to determine the magnitude of the fuel dilution, providing the user with the ability to predict performance problems and to take appropriate action.

6. Apparatus

6.1 *Gas Chromatograph*—Any gas chromatograph may be used that has the following performance characteristics:

6.1.1 *Sample Inlet System*—The sample inlet system shall be capable of operation at temperatures required to completely volatilize and transfer the sample to the column. Non-splitting, split/splitless, and on-column inlets configured for use with wide-bore capillary columns are appropriate.

6.1.2 *Column Temperature Programmer*—The gas chromatograph must be capable of linear oven temperature programmed operation over a range sufficient to elute the entire sample before reaching the end of the temperature program. The temperature programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.1 min (6 s) for the internal standard peak.

6.1.3 *Detector*—Only flame ionization detectors (FID) configured for use with wide-bore capillary columns can be used in this method. The detector must have sufficient sensitivity to reliably detect the entire range of gasoline concentrations of interest under the conditions prescribed in this method. The detector must be capable of operating continuously at a temperature equivalent to or greater than the maximum column temperature employed. For further guidance on testing flame ionization detectors, refer to Practice E594.

6.2 *Data Acquisition System*—Means must be provided for capturing, storing, integrating, and processing the signal generated by the FID and represented in the resulting chromatograms. This is typically accomplished by means of a computer-based chromatographic data system capable of measuring the retention times and areas of eluting peaks (peak detection mode). Systems be capable of subtracting an instrument blank chromatogram from subsequent sample chromatograms (for example, a column compensation) are also appropriate.

NOTE 1—Some gas chromatographs have an algorithm built into their operating software that allows a mathematical model of the baseline profile to be stored in memory. This profile is automatically subtracted from the detector signal on subsequent sample analyses to compensate for any baseline offset. Some integration systems also store and automatically subtract a blank analysis from subsequent analytical determinations.

6.3 *Analytical Column*—Any megabore capillary column and conditions may be used, provided that, under the conditions of the test, the separations occur in order of increasing boiling point and the column performance requirements described in 8.2.1 are met. The column resolution, *R*, shall be at least 8 (see 8.2.1). When there is evidence of a rising baseline that may be interfering with the integration of the gasoline profile, electronic column compensation is recommended to compensate for column bleed.

6.4 *Flow Controllers*—The gas chromatograph must be equipped with mass flow controllers capable of maintaining carrier gas flow constant to ±1 % over the full operating temperature range of the column. An inlet pressure of approximately 10 kPa to 20 kPa (2 psig to 3 psig) is appropriate for wide-bore capillary columns as described in Table 1. Gas chromatographs equipped with electronic pressure control (EPC) devices are able maintain constant column flow rates throughout the temperature program (since the viscosity of gases increases with temperature, a constant column flow rate can be maintained by increasing the column head pressure as temperature increases). The use of EPC is preferable to setting the column head pressure higher than optimal to compensate for this effect.

6.5 *Sample Introduction Devices:*

6.5.1 *Micro Syringe*—A micro syringe, typically 1 µL to 10 µL, is used for sample introduction to capillary columns.

6.5.2 Automatic sampling devices that reproducibly inject the same volume are highly recommended. The sample introduction devices should operate in a synchronous manner with the gas chromatograph.

6.6 *Vials,* 2 mL, septum-capped, or those recommended by the manufacturer of the automatic sampling device.

7. Reagents and Materials[3]

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. 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 *Column Stationary Phase*—Any suitable nonpolar stationary phase may be used. 100 % dimethyl polysiloxane has been found to provide the proper chromatographic hydrocarbon elution characteristics for this test method.

7.3 *Carrier Gas*—Helium (**Warning—**Helium is a compressed gases under high pressure), 99.99 mole % or greater, shall be used with the flame ionization detector. Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure must be sufficient to ensure a constant carrier gas flow rate (see 6.4).

7.4 *Hydrogen*—Hydrogen (**Warning—**Hydrogen is an extremely flammable gas under high pressure), 99.99 mole % purity or greater used as the fuel for the flame ionization detector (FID).

7.5 *Air*—Compressed air (**Warning—**Compressed air is a gas under high pressure and supports combustion), 99.99 mole % purity or greater, is used as the oxidant for the flame ionization detector (FID).

7.6 *n-Tetradecane (C_{14})*—**Warning—**(Combustible liquid; vapor harmful), 95 % minimum purity.

7.7 *n-Hexadecane (C_{16})*—**Warning—**(Combustible liquid; vapor harmful), 95 % minimum purity.

7.8 *n-Octane (C_8)*—(**Warning—**Flammable liquid; harmful if inhaled), 95 % minimum purity.

7.9 *Carbon Disulfide* (CS_2)—(**Warning—**Carbon disulfide is extremely volatile, flammable, and toxic.)

7.10 *Column Resolution Mixture*—To test column resolution, prepare a mixture of 0.1 % (v/v) each of C_{14} and C_{16} normal paraffins (**Warning—**Combustible liquids; vapor harmful) in a suitable solvent such as n-octane (**Warning—**Flammable liquid; harmful if inhaled).

8. Preparation of Apparatus

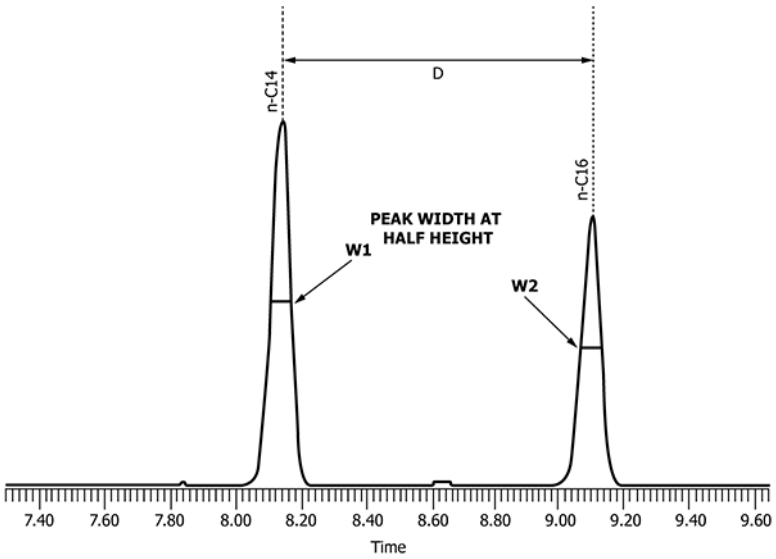
8.1 *Column Preparation:*

8.1.1 *Wide-Bore Capillary Columns (0.53 mm)*—Wide-bore capillary columns with cross-linked and bonded non-polar stationary phases are available from many manufacturers and are usually pre-conditioned (although column conditioning may still be necessary, see Practice E1510).

8.2 *System Performance Specifications:*

8.2.1 *Column Resolution*—Resolution is specified to maintain equivalence between different systems or laboratories employing this test method. Resolution is determined using Eq 1 following the analysis of the column resolution mixture of C_{14} and C_{16} n-paraffin peaks (see 7.10). Inject the same volume of this mixture as to be used for sample analysis and obtain the chromatogram by the procedure described in Section 10. Resolution, R, is calculated from the distance between the C_{14} and C_{16} n-paraffin peaks at the peak maxima, D, and the width of the peaks at half height, W_1 and W_2, as follows (this calculation can be performed using either time in seconds or distance in mm):

[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.



$$R = \frac{2D}{1.699(W_1 + W_2)}$$

where:

R = resolution,
D = distance between the n-C_{14} and the n-C_{16} peak maxima,
W_1 = width of peak n-C_{14} at half height, and
W_2 = width of peak n-C_{16} at half height.

Resolution, R, using the above equation, must be at least 8 ($R \geq 8$).

8.3 *Chromatograph and Related Equipment*—Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1 (the conditions given in Table 1 should be considered as guidance only and not as mandatory requirements for implementing this test method).

8.3.1 Although column bleed and its resulting deposits are significantly reduced with the use of capillary columns with bonded phases, deposits may still build up in the detector after prolonged use. These should be periodically removed since they can change the response characteristics of the detector.

9. Preparation of Sample

9.1 *Sample Preparation*—Place approximately 0.040 g (~50 µL) of C_{16} internal standard in a tared 4 mL to 10 mL vial and record the weight to the nearest 0.1 mg. Re-tare the vial and transfer approximately 2.0 g of sample to the vial and record the weight to the nearest 0.1 mg. Vortex to ensure thorough mixing. Transfer approximately 0.2 g of the spiked sample to a 2 mL GC autosampler vial, add 1 mL to 2 mL of CS_2, cap, and vortex to ensure sufficient mixing. The sample is now ready for GC analysis.

9.2 Other sample preparation schemes are allowed provided the masses of the sample and C_{16} internal standard are recorded, and the sample loading does not exceed the capacity of the column and the peaks of interest remain within the linear operating range of the detector.

10. Procedure

10.1 Prepare the gas chromatograph and equipment as per Table 1.

10.2 Inject the desired volume of sample.

10.2.1 The typical injection volumes range from 0.1 µL to 0.2 µL. Larger injection volumes can be used with sample splitting (for example, 1 µL with a 1:10 split ratio, etc.), which can be increased with increasing sample splitting ratios.

10.2.2 Ensure that the column loading does not exceed the capacity of the column or the linear range of the detector (column loading is a function of the sample preparation scheme, injection volume, and the inlet split ratio). Column overloading often results in asymmetrical peak shape (for example, leading, tailing, shark-fin peaks, etc.), while detector saturation is revealed by flat peak tops (that is, increasing sample amount with no signal increase).

10.3 Simultaneously initiate the oven temperature program used to facilitate effective chromatographing of the sample through the column (see Table 1). When using a computer-based data system it is convenient to set the display parameters of the real-time detector signal such that the gasoline and hexadecane peaks are easily visible but do not go off scale.

10.4 Area integration, accumulation, and recording may be discontinued after elution of the n-hexadecane internal standard peak, since this method is not intended to define the nature of the lubricating oil peak nor is it need for quantitation of the gasoline diluent. Removal of non-eluted oil from the system prior to subsequent operation may be achieved by increased column temperature (that is, column "baking") or column back flushing.

10.5 Integrate the area of the gasoline profile by establishing a horizontal baseline under the chromatographic trace once a stable baseline is achieved after injection but before the first gasoline peak, and continuing it horizontally to the leading