Designation: ~~D3525 – 04 (Reapproved 2016)~~ D3525 – 20

Standard Test Method for
Gasoline ~~Diluent~~ 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~~ Scope*

1.1 This test method ~~covers the use of gas chromatography to determine~~ 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 There is no limitation for the determination of the dilution range, provided that the amount of sample plus internal standard is within the linear range of the gas chromatograph detector.~~

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.

~~NOTE 1—The use of other detectors and instrumentation has been reported. However, the precision statement applies only when the instrumentation specified is employed.~~

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 ~~The applicability of this method to gelled used engine oils has not been adequately investigated in order to ensure compliance with the indicated repeatability and reproducibility. Gelled oils are defined as oils that develop structure on standing, but that return to their original fluidity with light agitation.~~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~~ safety, health, and ~~health~~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]

~~E260 Practice for Packed Column Gas Chromatography~~
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.

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[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**

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 ~~cause~~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 decane~~	~~n-C_{10}~~
normal hexadecane	n-C_{16}
iso-tetradecane	i-C_{14}

4. Summary of Test Method

4.1 A gas chromatographic technique is ~~used~~described for analyzing ~~the samples,~~ used engine oils by adding a known ~~percentage~~amount of *n*~~-tetradecane~~ -hexadecane (n-C_{16}) as an internal ~~standard,~~ standard (ISTD), in order to determine the weight

TABLE 1 Typical Operating Conditions

	~~Packed Columns~~
~~Column length, m (ft)~~	~~0.610 (2)~~
~~Column outside diameter, mm (in.)~~	~~3.2 (1/8)~~
~~Column inner diameter, mm (in.)~~	~~2.36 (0.093)~~
~~Liquid phase~~	~~methylsilicone gum or liquids~~
~~Percent liquid phase~~	~~10~~
~~Support material~~	~~crushed fire brick or diatomaceous earth~~
~~Treatment~~	~~acid wash~~
~~Support mesh size~~	~~80/100~~
~~Stationary phase thickness, microns~~	~~—~~
~~Column temperature, initial °C~~	~~30~~
~~Column temperature, final °C~~	~~255~~
~~Programming rate, °C/min~~	~~6~~
~~Carrier gas~~	~~helium or nitrogen~~
~~Carrier gas flow rate, mL/min~~	~~30~~
~~Detector~~	~~flame ionization detector~~
~~Detector temperature, °C~~	~~300~~
~~Injection port temperature, °C~~	~~255~~
~~Sample size, μL~~	~~0.7~~

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

percent of gasoline fuel in the lubricating oil. ~~A calibration curve is previously constructed which plots the gasoline fuel to~~Samples are chromatographed under the conditions described in this method, which separate and detect the gasoline diluent, internal ~~n~~standard, ~~-tetradecane response ratio versus the weight percent of gasoline fuel in lubricating oil mixtures containing a constant amount of internal standard. Mass percent of gasoline fuel~~ 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} ~~in the samples is determined by interpolation from the calibration curve.~~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 ~~a flame ionization detector~~ 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 ~~1.0 %~~the ~~n~~entire~~-tetradecane with a peak height of at least 40 % of full scale on the data acquisition devise~~ range of gasoline concentrations of interest under the conditions prescribed in this method. ~~For further guidance on testing flame ionization detectors, refer to Practice E594. When operating at this sensitivity level, detector stability must be such that a baseline drift of not more than 1 % full scale per hour is obtained.~~ The detector must be capable of operating continuously at a temperature equivalent to or greater than the maximum column temperature employed. ~~Connection of the column to the detector must be such that~~For further guidance on testing flame ionization detectors, refer to Practice E594~~no temperature zones exist below the column temperature (cold spots).~~.

~~6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of temperature program operation of the oven over a range sufficient to establish a retention time of 0.25 min (15 s) for the initial peak and to elute the internal standard totally. A retention time repeatability of 0.3 min (18 s) must be achieved.~~

~~6.1.3 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. An on-column inlet with some means of programming the inlet temperature, including the point of sample introduction, up to the maximum temperature required can also be used. Connection of the column to the sample inlet system must be such that no temperature zones exist below the column temperature (cold spots).~~

6.2 *Data Acquisition System*—Means must be provided for ~~measuring the accumulated area under the chromatogram. This can be done~~capturing, storing, integrating, and processing the signal generated by the FID and represented in the resulting chromatograms. This is typically accomplished by means of ~~an electronic integrator or computer based chromatography data system.~~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.

~~6.2.1 *Integrator/Computer System*—The integrator/computer system must have chromatographic software capable of measuring the retention times and areas of eluting peaks (peak detection mode). The electronic range of the integrator/computer (for example, 1 V, 10 V) must be within the linear range of the detector/electrometer system used. It is desirable that the system be capable of subtracting each area slice of a blank run from the corresponding area slice of a sample run.~~

~~NOTE 2—Best precision and automatic operation can be achieved with electronic integration.~~

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 ~~points~~point and the column performance requirements described in 8.2.1 are met. The column resolution, *R*, shall be at least ~~3 and not more than~~ 8 (see ~~8.2.1.1~~8.2.1). ~~Since a stable baseline is an essential requirement of this method, electronic single~~ When there is evidence of a rising baseline that may be interfering with the integration of the gasoline profile, electronic column compensation is ~~required~~recommended to compensate for column ~~bleed, septum bleed, detector temperature control, constancy of carrier gas flow and instrument drift.~~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. ~~The~~An inlet pressure of ~~the carrier gas supplied to the gas chromatograph must be sufficiently high to compensate for the~~approximately 10 kPa to 20 kPa (2 psig to 3 psig) is appropriate for wide-bore capillary columns as described in Table 1~~increase in column back-pressure as the column temperature is raised. An inlet pressure of 550 kPa (80 psig) has been found to be satisfactory with the columns described in~~. 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 ~~Table 1.~~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, ~~usually~~ typically 1 µL to 10 µL, is used for sample ~~introduction.~~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,* ~~1 dram (3.7 mL),~~ 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.~~determination

7.2 ~~*Liquid Phase for Columns*—~~*Column Stationary Phase*—Any ~~nonpolar liquid phase suitable for column operation above 300 °C~~ suitable nonpolar stationary phase may be used. ~~Methylsilicone gums and liquids have~~ 100 % dimethyl polysiloxane has been found to provide the proper chromatographic hydrocarbon elution characteristics for this test method.

~~7.3 *Solid Support*—Usually crushed fire brick or diatomaceous earth is used in the case of packed columns. Where solid support is used, sieve size and support loading should be such as will give optimum resolution and analysis time. In general, particle sizes ranging from 60 to 100 sieve mesh, and support loadings of 3 % to 10 %, have been found most satisfactory.~~

7.3 *Carrier Gas*—Helium ~~or nitrogen~~ (**Warning—**Helium ~~and nitrogen are~~ 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, is~~ 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*—~~*n-Tetradecane* (C_{14})—**Warning—**(Combustible liquid; vapor harmful), 95 % minimum purity.

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

7.8 ~~*n-Octane*—~~*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 *Packed Columns*—Any satisfactory method used in the practice of gas chromatography (see Practice E260) that will produce a column meeting the requirements of 6.3 may be used. The column must be conditioned at the maximum operating temperature until baseline drift due to column bleeding has been reduced to less than 1 % per hour.~~

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[3] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Annual*~~*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.

~~8.1.1.1 The packed column can be conditioned very rapidly and effectively using the following procedure: Connect the column to the inlet but leave the detector end free. Purge the column thoroughly at ambient temperature with carrier gas. Turn off the carrier gas and allow the column to depressurize completely. Seal off the open end (detector end) of the column with an appropriate fitting. Raise the column temperature to the maximum operating temperature and hold at this temperature for at least 1 h with no flow through the column. Cool the column to ambient temperature. Then remove the cap from the detector end of the column and turn the carrier gas back on. Program the column temperature up to the maximum several times with normal carrier gas flow. Connect the free end of the column to the detector.~~

~~NOTE 4—Difficulty in achieving the baseline drift requirement may indicate column bleed due to insufficient conditioning.~~

~~NOTE 5—An alternative method of column conditioning, which has been found effective for packed columns with an initial loading of 10 % liquid phase, consists of purging the column with carrier gas at the normal flow rate while holding the column at maximum operating temperature for 12 h to 16 h, while detached from the detector.~~

8.1.1 ~~*Open Tubular Columns*—~~*Wide-Bore Capillary Columns (0.53 mm)—*~~Open tubular~~Wide-bore capillary columns with cross-linked and bonded non-polar stationary phases are available from many manufacturers and are usually ~~pre-conditioned. These columns have much lower column bleed than packed columns. Column conditioning is still necessary (see~~ pre-conditioned (although column conditioning may still be necessary, see Practice E1510). ~~The column can be conditioned very rapidly and effectively using the following procedure.~~

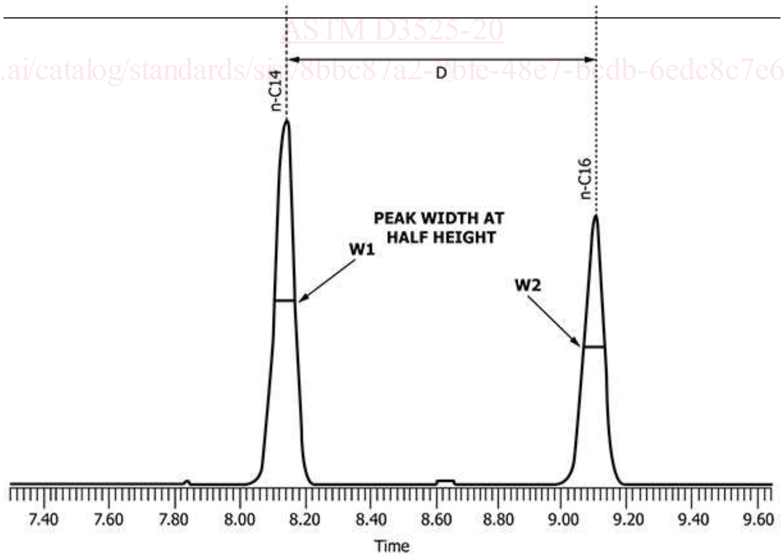
~~8.1.2.1 Once the open tubular column has been properly installed into the gas chromatograph inlet and tested to be leak free, set the column and detector gas flows. Before heating the column, allow the system to purge with carrier gas at ambient temperature for at least 30 min.~~

~~8.1.2.2 Increase the oven temperature about 5 °C to 10 °C per minute to the final operating temperature and hold for about 30 min or until a stable baseline is observed.~~

~~8.1.2.3 Cycle the gas chromatograph several times through its temperature program until a stable baseline is obtained.~~

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 ~~a~~the column resolution ~~test~~ mixture ~~prepared~~ of C_{14} and C_{16} n-paraffin peaks (see 7.10~~as follows.~~). 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):



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

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.