Designation: D3525 – 04 (Reapproved 2016)

Standard Test Method for Gasoline Diluent in Used Gasoline Engine Oils by 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 covers the use of gas chromatography to determine the amount of gasoline 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.

1.3 This test method is limited to gas chromatographs equipped with flame ionization detectors and 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.

1.4 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.

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 and health practices and determine the applicability of regulatory requirements prior to use.*

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.

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 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}
iso-tetradecane	i-C_{14}

4. Summary of Test Method

4.1 A gas chromatographic technique is used for analyzing the samples, by adding a known percentage of *n*-tetradecane as an internal standard, in order to determine the weight percent of gasoline fuel in the lubricating oil. A calibration curve is previously constructed which plots the gasoline fuel to *n*-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 in the samples is determined by interpolation from the calibration curve.

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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.

TABLE 1 Typical Operating Conditions

	Packed Columns	Open Tubular Columns
Column length, m (ft)	0.610 (2)	5 – 10
Column outside diameter, mm (in.)	3.2 (1/8)	—
Column inner diameter, mm (in.)	2.36 (0.093)	0.53
Liquid phase	methylsilicone gum or liquids	cross-linked, bonded polydimethylsiloxane
Percent liquid phase	10	—
Support material	crushed fire brick or diatomaceous earth	—
Treatment	acid wash	—
Support mesh size	80/100	—
Stationary phase thickness, microns	—	0.88 – 2.65
Column temperature, initial °C	30	30
Column temperature, final °C	255	255
Programming rate, °C/min	6	6
Carrier gas	helium or nitrogen	helium or nitrogen
Carrier gas flow rate, mL/min	30	30
Detector	flame ionization detector	flame ionization detector
Detector temperature, °C	300	300
Injection port temperature, °C	255	255
Sample size, µL	0.7	0.1 – 0.2 (from 1/10 dilution in CS_2)

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 *Detector*—Only a flame ionization detector can be used in this method. The detector must have sufficient sensitivity to detect 1.0 % *n*-tetradecane with a peak height of at least 40 % of full scale on the data acquisition devise 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 the maximum column temperature employed. Connection of the column to the detector must be such that 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 by means of an electronic integrator or computer based chromatography data system.

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 3—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 *Column*—Any column and conditions may be used, provided that, under the conditions of the test, the separations occur in order of increasing boiling points 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). Since a stable baseline is an essential requirement of this method, electronic single column compensation is required to compensate for column bleed, septum bleed, detector temperature control, constancy of carrier gas flow and instrument drift.

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 inlet pressure of the carrier gas supplied to the gas chromatograph must be sufficiently high to compensate for the increase in column backpressure 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 Table 1.

6.5 *Sample Introduction Devices:*

6.5.1 *Micro Syringe*—A micro syringe, usually 10 µL, is used for sample introduction.

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), 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 *Liquid Phase for Columns*—Any nonpolar liquid phase suitable for column operation above 300 °C may be used. Methylsilicone gums and liquids have 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.

7.4 *Carrier Gas*—Helium or nitrogen (**Warning—**Helium and nitrogen are 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).

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

7.6 *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).

7.7 *n-Tetradecane*—**Warning—**(Combustible liquid; vapor harmful), 95 % minimum purity.

7.8 *n-Hexadecane*—**Warning—**(Combustible liquid; vapor harmful), 95 % minimum purity.

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

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

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.

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.

8.1.2 *Open Tubular Columns*—Open tubular columns with cross-linked and bonded non-polar stationary phases are available from many manufacturers and are usually preconditioned. These columns have much lower column bleed than packed columns. Column conditioning is still 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 column resolution test mixture prepared as follows.

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[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.

8.2.1.1 To test column resolution, prepare a mixture of 1 % by volume 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). If open tubular columns are used, this mixture shall be diluted 1/10 with carbon disulfide (CS_2). Inject the same volume of this mixture as to be used in sample analysis and obtain the chromatogram by the procedure described in Section 10. Calculate the resolution, *R*, from the distance between the C_{14} and C_{16} normal paraffin peaks at the peak maximum, *d*, and the width of the peaks at the baseline, Y_1 and Y_2, as follows:

$$R = [2\ (d_1 - d_2)]/Y_1 + Y_2 \tag{1}$$

where:

R = resolution,
d_1 = retention time distance for the n-C_{14} peak maximum,
d_2 = retention time distance for the n-C_{16} peak maximum,
Y_1 = width of peak n-C_{14} at the baseline, and
Y_2 = width of peak n-C_{16} at the baseline.

Resolution, *R*, using the above equation, must be at least 3 and not more than 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.

8.3.1 After prolonged use of a flame ionization detector, the deposit build up resulting from combustion of the silicone rubber or liquid phase decomposition products should be periodically removed. These deposits will change the response characteristics of the detector.

8.3.2 If the sample inlet system is heated above 300 °C (572 °F), a blank run analysis must be made after a new septum is installed, to check for extraneous peaks produced by septum bleed. At the sensitivity levels commonly employed in this method, conditioning of the septum at the operating temperature of the sample inlet system for several hours will minimize this problem. A recommended practice is to change the septum at the end of the day's operation rather than at the beginning of a series of analyses.

9. Preparation of Sample

9.1 Using a 1 mL syringe, inject 0.5 mL of sample into a tared 1 dram vial, weigh, and record. Into this vial add 10 µL of *n*-tetradecane (C_{14}), weigh, and record. If the sample is too viscous for injection into the gas chromatograph at room temperature, add 0.5 mL of a suitable solvent to the vial. Use of *n*-hexadecane has been found to be acceptable as a solvent. Stopper the vial with a septum cap and shake for at least 2 min. If open tubular columns are used, this sample solution shall be diluted 1/10 with carbon disulfide (CS_2).

10. Procedure

10.1 Prepare the apparatus as per Table 1.

10.2 Inject the desired volume of sample.

10.2.1 Care must be taken that the sample size chosen does not allow some peaks to exceed the linear range of the detector. With hydrogen flame ionization detectors, the usual sample size ranges from 0.2 µL to 1.0 µL. If open tubular columns are used, inject 0.1 µL to 0.2 µL of 1/10 dilution of the sample solution.

10.2.2 The syringe needle must remain in the injection port manifold for 5 s to 10 s after injection to avoid any sample fractionation in the needle.

10.3 Immediately start programming the column temperature upward at the rate in Table 1, or at a rate that will produce the separation specified in 6.3. Begin data acquisition/recording upon, or immediately after, injection of the sample. Set the attenuation to allow maximum peak height of the area prior to and including the *n*-tetradecane reference peak without overloading the method of measurement.

10.4 Area accumulation and recording may be discontinued after elution of the *n*-tetradecane. This method is not intended to define the nature of the lubricating oil peak.

10.5 Removal of non-eluted oil from the system prior to subsequent operation may be achieved by techniques such as back flush or increased system temperature.

11. Calculation

11.1 Record the cumulative area under the chromatogram from time zero to the start of the *n*-tetradecane peak. Record the area under the *n*-tetradecane peak.

11.2 Calculate the mass percent of fuel dilution in the sample as follows:

$$F = A_1 \times W_1 \times 100/X_1 \times A_2 \tag{2}$$

where:

F = fuel dilution, mass %,
A_1 = area counts under the chromatogram before the *n*-tetradecane peak,
A_2 = area counts under the *n*-tetradecane peak on the chromatogram,
W_1 = mass of *n*-tetradecane used in 9.1, and
X_1 = mass of sample used in 9.1.

NOTE 6—The conditions specified have not shown evidence of the appearance of additive or base oil decomposition. Appearance of abnormal peaks in the chromatogram may indicate such decomposition. If this occurs, it would be desirable to obtain a chromatogram of the unused oil, if available. Subsequently, make a correction to the indicated fuel dilution.

12. Report

12.1 Report the results to the nearest 0.01 % mass percent of gasoline fuel in the sample as follows:

Gasoline fuel, ASTM D3525: xx.xx % mass

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results (95 % probability):

13.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty:

0.28 mass %

13.1.2 *Reproducibility*—The difference between two, single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty:

1.64 mass %

13.2 *Bias*—No estimate of the bias of this test method is possible because of the empirical nature of this test method.

14. Keywords

14.1 fuel dilution; gas chromatography; gasoline; lubricating oil

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