



Designation: D3525 – 04

Standard Test Method for Gasoline Diluent in Used Gasoline Engine Oils by Gas Chromatography¹

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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 the 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

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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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.

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

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

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

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

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 $n\text{-C}_{10}$
iso-tetradecane $i\text{-C}_{14}$

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.

*A Summary of Changes section appears at the end of this standard.

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 device 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 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 Table 1.

6.5 *Sample Introduction Devices*:

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