



# Standard Test Method for Gasoline Diluent in Used Gasoline Engine Oils by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 3525; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Warning notes were editorially moved into the standard text in March 2003.

## 1. Scope

1.1 This test method utilizes gas chromatography to determine the amount of dilution in used gasoline fuel engine oils.

1.2 This test method is limited to gas chromatographs equipped with flame ionization detector and programmable oven.

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 The applicability of this method to gelled used engine oils has not been adequately investigated 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.

1.4 The values stated in SI units are to be regarded as the standard. Inch-pound units are provided for information only.

1.5 *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 limitations prior to use.*

## 2. Terminology

### 2.1 Definitions of Terms Specific to This Standard:

2.1.1 *fuel dilution*—the amount, expressed as a percentage, of engine fuel found in engine lubricating oil. This may be the result of engine wear or improper performance.

### 2.2 Abbreviations:

2.2.1 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  $i\text{-C}_{14}$

## 3. Summary of Test Method

3.1 Gas chromatographic techniques are used with the sample, containing a known percentage of  $n$ -tetradecane as an internal standard, to determine the weight percent of the sample boiling below the boiling point of the internal standard.

## 4. Significance and Use

4.1 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.

## 5. Apparatus

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

5.1.1 *Detector*—Only a flame 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 recorder under the conditions prescribed in this method, and without loss of resolution. The detector must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed, and it must be connected to the column so as to avoid any cold spots. When operating at this sensitivity level, detector stability must be such that the baseline drift of not more than 1 % per hour is obtained.

5.1.2 *Column Temperature Programmer*—The chromatograph must be capable of temperature program operation 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. For determination of fuel dilution the reproducibility of the programming rate is not significant, although a retention time repeatability of 0.3 min (18 s) should be available.

5.1.3 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. The

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0H on Chromatographic Distribution Methods.

Current edition approved Dec. 10, 2002. Published March 2003. Originally approved in 1976. Last previous edition approved in 1997 as D 3525 – 93 (1997).

sample inlet system must be connected to the chromatograph column so as to avoid any cold spot.

5.2 *Recorder*—A recording potentiometer with a full-scale response time of 1 s or less can be used.

5.3 *Column*—Any column and conditions may be used, provided, under the conditions of the test, separations are in order of boiling points and the column resolution,  $R$ , is at least 3 and not more than 8. Since a stable baseline is an essential requirement of this method, electronic single column compensation is required to compensate for column bleed, which cannot be eliminated completely by conditioning alone.

5.4 Means must be provided for measuring the accumulated area under the chromatogram. This can be done by a computer or electronic integrator. The computer or integrator must have the capability of subtracting an area profile obtained in a blank run from the corresponding area profile obtained during a sample run.

NOTE 2—Some commercially available gas chromatographs permit the storing of data as a baseline profile of a blank run (without sample injection). With such instruments, sample run data can be corrected for baseline drift through subtraction of the internally stored baseline profile data from the sample run profile data. With this feature, further baseline correction need not be required.

5.5 *Flow Controllers*—Control of baseline drift to not more than 1 % of full scale per hour as covered in 5.1.1 will require that the gas chromatograph be equipped with constant-flow controllers.

5.6 *Sample Introduction Apparatus*—The sample is introduced by use of a micro syringe, automatic sampling devices, or indium encapsulation; provided that the temperature is sufficiently high to vaporize completely hydrocarbons with an atmospheric boiling point of 315°C, and that the sampling system is connected to the chromatograph column so as to avoid any cold spots.

5.7 *Syringes*, 1-mL, graduated in 0.01 mL; 25- $\mu$ L and 1- $\mu$ L.

5.8 *Vials*, 1-dram (3.7-mL), septum-capped.

## 6. Reagents and Materials

6.1 *Liquid Phase for Columns*—Any nonpolar liquid phase suitable for column operation above 300°C may be used.

6.2 *Solid Support*—Usually crushed fire brick or diatomaceous earth, 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, support loading of 3 to 10 % has been found most satisfactory.

6.3 *Carrier Gas*—Helium, nitrogen, or argon shall be used with the flame ionization detector. (**Warning**—Hydrogen, which is used with the flame ionization detector, is an extremely flammable gas under pressure.) (**Warning**—Helium, nitrogen, and argon are compressed gases under pressure.)

6.4 *n-Tetradecane* of 95 % minimum purity. (**Warning**—Combustible, vapor harmful.)

6.5 *n-Hexadecane* of 95 % minimum purity. (**Warning**—Combustible, vapor harmful.)

6.6 *n-Octane* of 95 % minimum purity. (**Warning**—Flammable, harmful if inhaled.)

## 7. Preparation of Apparatus

7.1 *Column Preparation*—Any satisfactory method used in the practice of gas chromatography that will produce a column meeting the requirements of 4.3 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.

NOTE 3—Difficulty in achieving the baseline drift requirement may indicate injection port or column overloading from contamination. Remove and clean the injection port. Reassemble and increase the temperature of the injection port, column oven, and detector to the maximum limits of the gas chromatographic column employed.

7.1.1 To test column resolution prepare a mixture of 1 volume % each of  $C_{14}$  and  $C_{16}$  normal paraffins in a suitable solvent such as octane (**Warning**— $C_{14}$  and  $C_{16}$  *n*-paraffins. Helium, nitrogen, and argon are compressed gases under pressure.) (**Warning**—*n*-octane. Combustible, vapor harmful.) Inject the same volume of this mixture as to be used in analysis of samples and obtain the chromatogram by the procedure described below. Calculate the resolution,  $R$ , from the distance between  $C_{14}$  and  $C_{16}$  normal paraffin peaks at the peak maxima,  $d$ , and the width of the peaks at the baseline,  $Y_1$  and  $Y_2$ , as follows:

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

Resolution,  $R$ , using the above equation, must be at least 3 and not more than 8.

7.2 *Chromatograph and Related Equipment*—Place in service in accordance with manufacturer's instructions. Typical operating conditions are shown in Table 1.

7.2.1 The deposits formed in the flame ionization detector from combustion must be removed regularly, since they change the response characteristics of the detector.

7.2.2 If the sample inlet system is heated above 300°C, a blank run must be made after new septums are installed, to check for extraneous peaks produced by septum bleed. At the sensitivity levels employed in this method, conditioning of the septum at the operating temperature of the sample inlet system for several hours will minimize this problem. Recommended practice is to change septums at the end of the day's operation rather than at the beginning.

**TABLE 1 Typical Operating Conditions**

Column ID, in. (mm)	0.093 (2.36)
column length, ft (m)	2 (0.610)
Liquid phase	Dexsil 300 <sup>A</sup>
Percent liquid phase	10
Support material	Chromosorb WAW <sup>B</sup>
Support mesh size	80/100
Initial column temperature, °C	30
Final column temperature, °C	255
Programming rate, °C/min	6
Carrier gas	helium
Carrier gas flow rate, mL/min	30
Detector	FID <sup>C</sup>
Detector temperature (manifold), °C	260
Injection port temperature, °C	255
Sample size, $\mu$ L	0.7
Column resolution	4.85

<sup>A</sup> Registered trademark of Olin Corp.

<sup>B</sup> Registered trademark of Johns-Manville Products Corp.

<sup>C</sup> Flame ionization detector.

## 8. Preparation of Sample

8.1 Using a 1-mL syringe, inject 0.5 mL of sample in a tared 1-dram vial, weigh, and record. Into this vial add 10 µL of *n*-tetradecane (C<sub>14</sub>), 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.

## 9. Procedure

9.1 Prepare the apparatus as per Table 1.

9.2 Inject the desired volume of sample.

9.2.1 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 to 1.0 µL.

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

9.3 Immediately start programming the column temperature upward at the rate in Table 1, or at a rate that will produce the separation specified in 5.3. Turn on the recorder chart drive and integrator 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.

9.4 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.

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

## 10. Calculation

10.1 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.

10.2 Calculate the weight percent (mass percent) of fuel dilution in the sample as follows:

$$F = \frac{A_1 \times W_1 \times 100}{X_1 \times A_2} \quad (2)$$

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 8.1, and

$X_1$  = mass of sample used in 8.1.

NOTE 4—The conditions specified have not shown evidence of additive or base oil decomposition. Appearance of abnormal peaks on the chromatograph may indicate such decomposition. In this event it would be desirable to obtain a chromatogram on the unused oil if available and to make a correction to the indicated fuel dilution.

## 11. Precision and Bias

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

11.1.1 *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 values only in one case in twenty:

0.28 mass %

11.1.2 *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 values only in one case out of twenty:

1.64 mass %

NOTE 5—This precision was developed using single-flame ionization detectors and column temperature programming. The stated precision does not apply to other chromatographic systems.

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

## 12. Keywords

12.1 fuel dilution; gas chromatography; gasoline; lubricating oil

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).*