Designation: D 3524 – 90 (Reapproved 1999)

An American National Standard

Standard Test Method for Diesel Fuel Diluent in Used Diesel Engine Oils by Gas Chromatography[1]

This standard is issued under the fixed designation D 3524; 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 determination of diesel fuel as a contaminant in used lubricating oil. The method is limited to SAE 30 oil.

NOTE 1—This test method may be applicable to higher viscosity grade oils. However, such oils were not included in the program used to develop the precision statement.

1.2 There is some overlap of the boiling ranges of diesel fuel and SAE 30 engine oils. Moreover, the boiling range of SAE 30 oils from various sources can vary appreciably. As a result, the calibration can be altered by as much as 2 %, in terms of fuel dilution. When testing unknown or mixed brands of used engine oil, it should be realized that the precision of the method may be poorer than the precision obtained when calibrating with a new oil representative of the used oil being tested.

1.3 The values stated in SI units are to be regarded as the standard. The values stated in inch-pound units are for information only.

1.4 *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.

For example: normal decane $n–C_{10}$
iso-tetradecane $i–C_{14}$

3. Summary of Test Method

3.1 A mixture of *n*-decane and used lubricating oil is introduced into a gas chromatographic column which separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate and the resulting chromatogram is interpreted for diesel fuel dilution.

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 can be used that has the following performance characteristics:

5.1.1 *Detector*—Either a thermal conductivity or flame ionization detector can be used. The detector must have sufficient sensitivity to detect 1.0 % decane with a peak height of at least 10 % of full scale on the recorder under the conditions prescribed in this method, and without loss of resolution as defined in 7.1.3. The detector also 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. Under the conditions described for the method, the drift should not be more than 1 % of full scale per hour.

5.1.2 *Column Temperature Programmer*— The chromatograph must be capable of program temperature operation over a range sufficient to establish a retention time of at least 1 min for the initial peak(s) and to elute the entire sample. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.1 min for each component in the calibration mixture (6.4).

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, or provide on-column injection with some means of programming the entire column, including point of sample introduction up to the

[1] This test method is under the jurisdiction of ASTM Committe D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0H on Chromatographic Methods.

Current edition approved Oct. 26, 1990. Published December 1990. Originally published as D 3524 – 76. Last previous edition D 3524 – 86.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States.

maximum temperature required. The sample inlet system must be connected to the chromatographic column so as to avoid any cold spots.

5.2 *Recorder*—A recording potentiometer with a full-scale response time of 2 s or less must be used. If a manual method of area measurement, such as a planimeter, is employed, the chart speed must be at least 152 cm/h (60 in./h) to minimize errors in peak area measurements. This requirement is waived if a ball-and-disc integrator or an electronic integrator is employed.

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 5 (7.1.3). Since a stable baseline is an essential requirement of this method, matching dual columns are required to compensate for column bleed, which cannot be eliminated completely by conditioning alone.

5.4 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done manually by means of a polar planimeter. Mechanical means, such as the disc integrator, may be used also. However, best precision and automatic operation can be achieved with electronic integration.

5.5 *Flow Controllers*—Chromatographs using thermal conductivity detectors also must be equipped with constant-flow controllers capable of holding carrier gas flow constant to ±1 % over the full operating temperature range.

5.6 *Sample Device*:

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

5.6.2 Automatic sampling devices or other sampling means, such as indium encapsulation, may be used, provided the system can be operated at a temperature sufficiently high to vaporize completely hydrocarbons with an atmospheric boiling point of 538°C (1000°F), and the sampling system is connected to the chromatographic column so as to avoid any cold spots.

5.7 *Vial*, 15-mL, screw cap.

6. Reagent and Material

6.1 *Liquid Phase for Columns*—See Note 2.

NOTE 2—The following materials have been used successfully as liquid phases:

Silicone Gum Rubber UC-W98[2]
Silicone Gum Rubber GE-SE-30[3]
Silicone Gum Rubber OV-1[4]
Silicone Gum Rubber OV-101[4]

6.2 *Solid Support*—Usually crushed fire brick or diatomaceous earth. Sieve size and support loading should be such as will give optimum resolution and analysis time. In general, support loadings of 3 to 10 % have been found most satisfactory.

6.3 *Carrier Gas*—Helium (**Warning**—See Note 3.) or hydrogen (**Warning**—See Note 4) for use with thermal conductivity detectors; or nitrogen, (**Warning**—See Note 3.) helium, or argon for use with flame ionization detectors.

6.4 *Calibration Mixtures*—A minimum of three mixtures of diesel fuel and lubricating oil (**Warning**—See Note 5.) of a similar type to that being analyzed are prepared to cover the range from 0 to 12 weight% (mass%) diesel fuel, calculated as follows:

$$\text{Diesel fuel, wt\% (mass \%)} = \frac{\text{weight (mass) of fuel}}{\text{weight (mass) of fuel and oil}} \times 100 \quad (1)$$

NOTE 3—**Warning:** Argon, helium, and nitrogen are compressed gases under pressure.

NOTE 4—**Warning:** Hydrogen is an extremely flammable gas under pressure.

NOTE 5—**Warning:** Combustible liquid.

6.5 *n-Decane*, 99 % pure. (**Warning**—See Note 6.)

NOTE 6—**Warning:** Combustible, vapor harmful.

7. Preparation of Apparatus

7.1 *Column Preparation*—Any satisfactory method used in the practice of the gas chromatography that will produce a column meeting the requirements of 5.3 may be used. The column must be conditioned at the maximum operating temperature until baseline shift due to column bleeding has been reduced to a minimum.

7.1.1 The column can be conditioned very rapidly and effectively by the following procedure:

7.1.1.1 Disconnect the column from the detector.

7.1.1.2 Purge the column thoroughly at ambient temperature with carrier gas.

7.1.1.3 Turn off the carrier gas and allow the column to depressurize completely.

7.1.1.4 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.

7.1.1.5 Cool the column to at least 100°C before turning on carrier gas again.

7.1.1.6 Program the column temperature up to the maximum several times with normal carrier gas flow. The column then should be ready for use.

7.1.2 An alternative method of column conditioning, which has been found effective for 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 to 16 h.

7.1.3 *Column Resolution*—To test column resolution use Fig. 1 and calculate the resolution, *R*, from the distance between the C_{16} and C_{18} *n*-paraffin peaks at the peak maxima, *d*, and the width of the peaks at the baseline, Y_1 and Y_2, as follows:

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

Resolution, *R*, using the above equation, must be at least 3 and not more than 5.

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

7.2.1 If a flame ionization detector is used, the deposits formed in the detector from combustion of the silicone rubber

[2] Registered trademark of Union Carbide Corp.
[3] Registered trademark of General Electric Co.
[4] Registered trademark of Ohio Valley Specialty Chemicals Co.

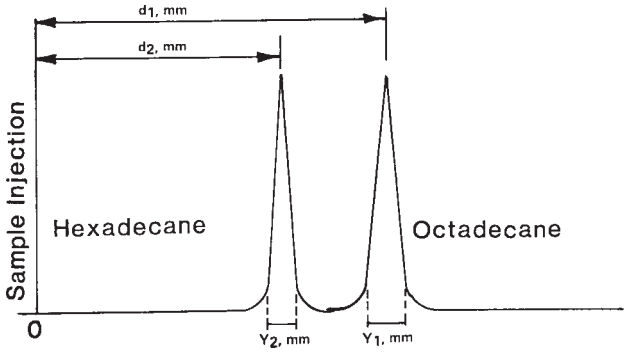

FIG. 1 Column Resolution

TABLE 1 Typical Operating Conditions

Column length, m (ft)	0.610 (3)
Column outside diameter, mm (in.)	3.2 (1/8)
Liquid phase	Silicone gum rubber OV-101[A]
Support material	Chromosorb W[B]
Treatment	acid washed, silanized
Mesh size	80/100
Column temperature, initial, °C	70
Column temperature, final, °C	325
Programming rate, °C/min	16
Detector	FID[C]
Detector temperature, °C	350
Injection port temperature, °C	300
Sample size, µL	1
Flow rate, cm^3/min	30

[A]Registered trademark of Ohio Valley Specialty Chemical Co.
[B]Registered trademark of Johns-Manville Products Corp.
[C]Flame ionization detector.

decomposition products 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 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. Recommended practice is to change septums at the end of the day's operation rather than at the beginning.

8. Preparation of Sample

8.1 Weigh 1.0 ± 0.01 g of decane (**Warning**—see Note 6) into a 15-mL vial. Shake the sample in the delivered bottle and add 10.00 ± 0.01 g of sample to the vial (**Warning**—see Note 5). Cap and mix well.

9. Calibration

9.1 Run each of the calibration mixtures (6.4) by the procedure described in Sections 8 and 10, injecting approximately the same volume as chosen for the sample. Record the total areas due to decane and to the fuel portion in each mixture.

9.1.1 There can be an overlap between the diesel fuel and lube oil peaks. Using a chromatogram of one of the calibration mixtures, select the retention time of the minimum overlap. Use this retention time as the end of the area due to the diesel fuel for all subsequent analyses. See Fig. 2 for a typical chromatogram.

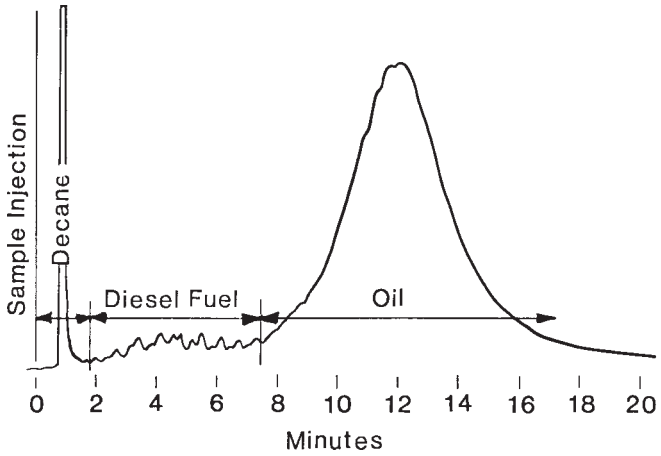

FIG. 2 Typical Chromatogram

9.2 Determine the ratio, *R*, for each standard as follows:

$$R = A/B \quad (3)$$

where:
A = total area due to diesel fuel peaks, and
B = area due to n-decane.

9.3 Plot a calibration curve relating *R* to the weight percent of diesel fuel.

10. Procedure

10.1 Program the column temperature upward to a temperature sufficiently high to elute all the components from the column. Following a rigorously standardized procedure, cool the column down to the starting temperature and, at the exact time set by the schedule, inject a carefully measured volume of sample (1 µL). Start programming the column temperature upward at a rate that will produce the desired separations as specified in 5.3. Turn on the recorder chart drive and integrator immediately after injecting the sample. Record the peaks at a sensitivity setting that allows the maximum peak height compatible with the method of measurement being used.

10.2 Since complete resolution of sample peaks is not expected, the sensitivity setting should not be changed during the test. If a ball-and-disc integrator or manual means are used for measuring peak areas, the sensitivity setting must be such that the maximum peak of the fuel portion of the chromatograph remains on the scale of the recorder.

11. Calculation

11.1 Record the total areas due to the fuel portion of the sample and the area due to decane as described in 9.1 and determine the ratio, *R*, as described in 9.2.

11.2 Determine the weight percent (mass percent) of diesel fuel of the samples by relating the *R* values obtained to the previously determined calibration curve. Report the results to nearest 0.1 %.

12. Precision and Bias

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

12.1.1 *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:

0.3 weight (mass %)

12.1.2 *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 one case in twenty:

1.6 weight (mass %)

NOTE 7—The above precision is based on the use of electronic integrators to measure areas and may not be indicative when other means of measurement are used.

NOTE 8—This precision statement applies only to SAE 30 oils.

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

13. Keywords

13.1 diesel fuel; fuel dilution; gas chromatography; lubricating oil

The American Society for Testing and Materials 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 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, 100 Barr Harbor Drive, West Conshohocken, PA 19428.