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

This standard is issued under the fixed designation D3524; 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 ($\varepsilon$) 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 diesel fuel in used engine lubricating oil. This test is limited to SAE 30 oil. The diesel fuel diluent is analyzed at concentrations up to 12 mass %.

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 This test method is limited to gas chromatographs equipped with flame ionization detectors and temperature programmable ovens.

NOTE 2—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 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.

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

1.5 *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 requirements prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4626 Practice for Calculation of Gas Chromatographic Response Factors

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 dilution*, n—the amount, expressed as a percentage, of diesel fuel 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, is the unburned fuel components that enter the engine crankcase causing dilution of the oil.

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

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.

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

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

## 4. Summary of Test Method

4.1 Gas chromatographic techniques are used for analyzing the samples, by adding a known percentage of *n*-decane as an internal standard, in order to determine the mass percent of diesel fuel in the lubricating oil. A calibration curve is previously constructed which plots the diesel fuel to *n*-decane response ratio versus the mass percent of diesel fuel in lubricating oil mixtures containing a constant amount of internal standard. The mass percent of diesel fuel in the samples is determined by interpolation from the calibration curve.

## 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 and to take appropriate action.

## 6. Apparatus

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

6.1.1 *Detector*—A flame ionization detector is 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 data acquisition device under the conditions prescribed in this method. Follow the directions given in 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). Although thermal conductivity detectors have been used for this test, their use is not recommended.

NOTE 3—It is not desirable to operate a thermal conductivity detector at a temperature 5 to 10°C higher than the maximum column temperature employed. Operation at higher temperature generally contributes to higher noise levels and greater drift, and can also shorten the useful life of the detector.

6.1.2 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed 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 before reaching the upper end of the temperature program. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.1 min (6 s) for each component in the calibration mixture described in 7.8.

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, or provide an on-column inlet with some means of programming the inlet, including the point of sample introduction, up to the maximum temperature required. Connection of the column to the sample inlet system must be such that no temperature zones below the column temperature (cold spots) exist.

6.2 *Data Acquisition System*:

6.2.1 *Integrator*—Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of an electronic integrator or computer based chromatography data system. The integrator/computer system must have chromatographic software for 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 4—Best precision and automatic operation can be achieved with an electronic integration system using a computer for data acquisition and control of the gas chromatograph.

NOTE 5—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. Moreover, the column must meet the performance requirements described in 8.2.1. The column resolution, *R*, shall be at least 3 and not more than 8. Since a stable baseline is an essential requirement of this method, compensation is required 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 $\pm 1$ % 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 *Vial*, 15-mL, screw cap.

## 7. Reagents and Materials

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

**TABLE 1 Typical Operating Conditions**

| | Packed Columns | Open Tubular Capillary Columns |
|---|---|---|
| Column length, m (ft) | 0.610 (2) | 5 – 10 |
| Column outside diameter, mm (in.) | 3.2 (1/8) | — |
| Column inside diameter, mm (in.) | 2.36 (0.093) | 0.53 |
| Liquid phase | methylsilicone gum or liquid | cross-linked bonded polydimethylsiloxane |
| Percent liquid phase | 10 | — |
| Support material | crushed fire brick or diatomaceous earth | — |
| Treatment | acid washed, silanized | — |
| Support mesh size | 80/100 | — |
| Stationary phase thickness, microns | — | 0.88 – 2.65 |
| Column temperature, initial, °C | 70 | 70 |
| Column temperature, final, °C | 325 | 325 |
| Programming rate, °C/min | 16 | 16 |
| 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 | 350 | 350 |
| Injection port temperature, °C | 300 | 300 |
| Sample size, µL | 1 | 0.1 – 0.2 (from 1/10 dilution in $CS_2$) |

such specifications are available.[3] 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*—Methylsilicone gums and liquids provide the proper chromatographic hydrocarbon elution characteristics for this test method.

7.3 *Solid Support*—Usually crushed fire brick or diatomaceous earth is used for the packed columns. Sieve size and support loading should be such as will give optimum resolution and analysis time. In general, particle size 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), with a purity of 99.99 mole% or better. 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*—(**Warning**—Hydrogen is an extremely flammable gas under high pressure) of high purity (99.99 mole% or better) 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), of high purity (99.99 mole% or better) is used as the oxidant for the flame ionization detector (FID).

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

7.8 *Calibration Mixtures*—A minimum of three mixtures of diesel fuel and lubricating oil (**Warning**—Combustible liquid) of a similar type to that being analyzed are prepared to cover the range up to 12 mass % diesel fuel. If open tubular columns

are used, this calibration mixture shall be diluted 1/10 with carbon disulfide ($CS_2$).

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

7.9 *n-Decane*, 99 % minimum purity. (**Warning**—Combustible liquid; vapor harmful.)

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

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

7.12 To test column resolution, prepare a mixture of 1 volume % each of $C_{16}$ and $C_{18}$ 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.

## 8. Preparation of Apparatus

8.1 *Column Preparation*:

8.1.1 *Packed Columns*—Any satisfactory method used in the practice of gas chromatography (for example, 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 a minimum.

NOTE 6—Difficulty in achieving the stable baseline requirement may indicate injection port or column 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.

8.1.1.1 The packed column can be conditioned very rapidly and effectively using the following procedure:

*(1)* Connect the column to the inlet, but leave the detector end free.

*(2)* Purge the column thoroughly at ambient temperature with carrier gas.

*(3)* Turn off the carrier gas and allow the column to depressurize completely.

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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.

*(4)* Seal off the detector free end of the column with an appropriate fitting.

*(5)* 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.

*(6)* Cool the column to ambient temperature. Then remove the cap from the detector end of the column and turn the carrier gas back on.

*(7)* Program the column temperature up to the maximum several times with normal carrier gas flow.

*(8)* Connect the free end of the column to the detector and obtain the chromatogram by the procedure described in Section 11.

NOTE 7—An alternative method of packed 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, while detached from the detector.

8.1.2 *Open Tubular Columns*—Open tubular columns with cross-linked and bonded stationary phases containing polydimethylsiloxane 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. 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 in the gas chromatograph 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. Follow the recommendation as stated in Practice E1510.

8.1.2.2 Increase the oven temperature about 5 to 10°C per minute to the final operating temperature and hold for about 30 min.

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

8.2 *System Performance Specification*:

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 2 following the analysis of a column resolution test mixture (see 7.12) of $C_{16}$ and $C_{18}$ *n*-paraffin peaks as illustrated in Fig. 1. Resolution, *R*, is calculated 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:

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

where:
$R$ = resolution,
$d_1$ = retention time distance for the *n*-$C_{16}$ peak maximum,
$d_2$ = retention time distance for the *n*-$C_{18}$ peak maximum,
$Y_1$ = width of peak *n*-$C_{16}$ at the baseline, and
$Y_2$ = width of peak *n*-$C_{18}$ at the baseline.

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

8.2.2 *Detector Response Verification*—This test method assumes that the detector response to petroleum hydrocarbons is proportional to the mass of individual components. This must be verified when the system is put into service, and whenever any changes are made to the system or operational parameters. Analyze the calibration mixture using the identical procedure to be used for the analysis of samples (see Section 10). Calculate the relative response factor for each *n*-paraffin (relative to *n*-decane) in accordance with Practice D4626 and Eq 3:

$$F_n = (M_n/A_n) / (M_{10}/A_{10}) \qquad (3)$$

where:
$F_n$ = relative response factor,
$M_n$ = mass of the *n*-paraffin, in the mixture,
$A_n$ = peak area of the *n*-paraffin in the mixture,
$M_{10}$ = mass of the *n*-decane in the mixture, and
$A_{10}$ = peak area of the *n*-decane in the mixture.

The relative response factor ($F_n$) of each *n*-paraffin must not deviate from unity (1) by more than ± 10 %.

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

8.3.1 If a flame ionization detector is used, regularly remove the deposits formed in the detector from combustion of the silicone rubber or liquid phase decomposition products. 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 analysis must be performed after a new septum is installed, to insure that no extraneous detector response is 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 septa at the end of a series of analyses rather than at the beginning of the analysis.

## 9. Preparation of Sample

9.1 Weigh 1.0 ± 0.01 g of *n*-decane (**Warning**—Combustible liquid; vapor harmful) 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**—Combustible liquid). Cap and mix well. If open tubular columns are used, this sample solution shall be diluted 1/10 with carbon disulfide ($CS_2$).
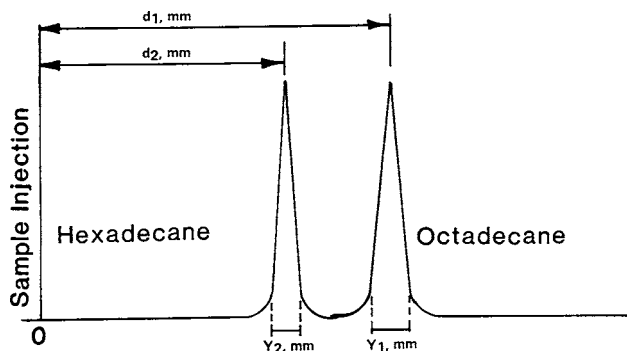


**FIG. 1 Column Resolution**

## 10. Calibration

10.1 Analyze each of the calibration mixtures prepared in 7.8 by the procedures described in Sections 9 and 11. Inject approximately the same volume as chosen for the sample (1 μL of sample solution for packed columns; 0.1 to 0.2 μL of 1/10 dilution of the sample solution for open tubular columns). Record the total areas due to *n*-decane and to the fuel portion in each mixture.

10.1.1 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 when minimum overlap occurs. 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.

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

$$R = A/B \qquad (4)$$

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

10.3 Prepare a calibration curve by plotting the ratio *R* versus the mass % of diesel fuel as calculated in 7.8.

## 11. Procedure

11.1 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 analysis schedule, inject a carefully measured volume of sample (1 μL if packed columns; 0.1 to 0.2 μL of 1/10 dilution if open tubular columns). Start programming the column temperature upward at a rate that will produce the desired separations as specified in 6.3. The data acquisition system must be synchronized with the injection of the sample.

## 12. Calculation

12.1 Record the total areas due to the fuel portion of the sample and the area due to decane as described in 10.1 and determine the ratio, *R*, as described in 10.2.
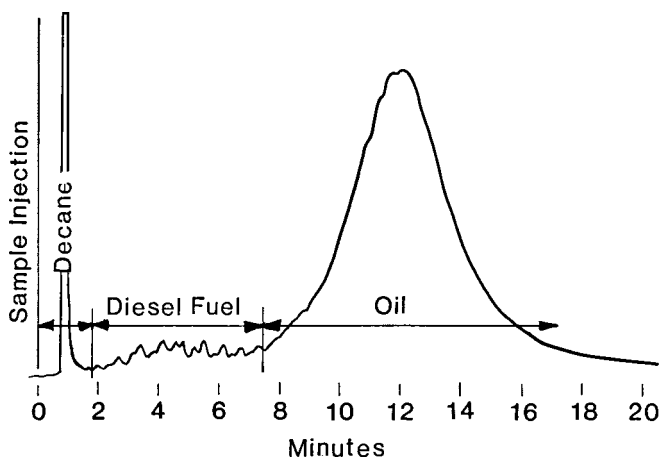


**FIG. 2 Typical Chromatogram**

12.2 Determine the mass percent of diesel fuel in the samples by relating the *R* values obtained to the previously determined calibration curve as follows:

$$C_S = C_1 + \frac{(C_2 - C_1)\,(R_S - R_1)}{(R_2 - R_1)} \qquad (5)$$

or

$$C_S = (R_S) \times \frac{(C_2 - C_1)}{(R_2 - R_1)} \qquad (6)$$

where:
$C_S$ = % mass of diesel fuel in the sample,
$C_1$ = % mass of unused diesel fuel in unused lubricating oil corresponding to $R_1$, calculated from Eq 1,
$C_2$ = % mass of unused diesel fuel in unused lubricating oil corresponding to $R_2$, calculated from Eq 1,
$R_S$ = ratio of sample to *n*-decane in the sample mixture,
$R_1$ = ratio of the calibration mixture lower than the ratio of the sample fuel portion to *n*-decane portion, and
$R_2$ = ratio of the calibration mixture higher than the ratio of the sample fuel portion to *n*-decane portion.

## 13. Report

13.1 Report the results to the nearest 0.1 % mass percent of diesel fuel in the sample as follows:

Diesel fuel, ASTM D3524: xx.x % mass

## 14. Precision and Bias

14.1 The following criteria should be used for judging the acceptability of results with 95 % confidence limit (see Notes 8 and 9):

14.1.1 *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 mass %

14.1.2 *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 mass %

NOTE 8—The above precision is based on the use of packed columns and electronic integrators to measure areas, and may not be indicative when using other types of columns.

NOTE 9—This precision statement applies only to SAE 30 oils.

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

## 15. Keywords

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

## SUMMARY OF CHANGES

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D3524–90(1999)) that may impact the use of this standard.

Note—Although the following encompasses the major changes involved, the user is advised to review the entire standard, since this revision represents a major rewrite of Test Method D3524.

(*1*) Reworded section 1.1. Added a statement on applicable dilution range, and section 1.2 and Note 2.

(*2*) Added Referenced Documents as Section 2.

(*3*) Introduced definitions and discussions in Section 3.

(*4*) Reworded Summary of Test Method (see Section 4).

(*5*) Revised Detector description (6.1.1) and added new Note 3.

(*6*) Revised Integrator description as 6.2.1 and added Notes 4 and 5.

(*7*) Revised description of Flow Controllers (see 6.4).

(*8*) Added new 7.1 on Purity of Reagents.

(*9*) Revised Liquid Phase for Columns subsection to remove trademarked phases.

(*10*) Revised Carrier Gas subsection (see 7.4) and added subsections on hydrogen, air, and carbon disulfide.

(*11*) Revised Calibration Mixtures (see 7.8).

(*12*) Divided Column Preparation subsection into packed versus open tubular columns (see 8.1).

(*13*) Added System Performance Specification as 8.2.

(*14*) Modified Column Resolution subsection (see 8.2.1).

(*15*) Added Detector Response Calibration as 8.2.2.

(*16*) Defined variables in Eq 2 and 3. Added Eq 5 in Section 12 for Calculation.

(*17*) Modified previous subsections 7.2.2, 8.1, 9.1, 10.1, 10.2, 12.1, and Note 7.

(*18*) Added a Report section as Section 13.

(*19*) Modified Table 1 to remove trademarked items and references thereto, and indicate that operating conditions are for packed columns.

(*20*) Corrected packed column length in Table 1 from "0.610 m" to "0.91."