Designation: D6258 − 17

Standard Test Method for Determination of Solvent Red 164 Dye Concentration in Diesel Fuels[1]

This standard is issued under the fixed designation D6258; 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 procedure for determining the concentration of dye Solvent Red 164 in commercially available diesel and burner fuels using visible spectroscopy.

NOTE 1—This test method is suitable for all No. 1 and No. 2 grades in Specifications D396 and D975 and for grades DMA and DMB in Specification D2069.

1.2 The concentration ranges specified for the calibration standards are established in response to the Internal Revenue Service dyeing requirements which state that tax-exempt diesel fuel satisfies the dyeing requirement only if it contains the dye Solvent Red 164 (and no other dye) at a concentration spectrally equivalent to 3.9 lb of the solid dye standard Solvent Red 26 per thousand bbl (11.1 mg/L) of diesel fuel.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D396 Specification for Fuel Oils
D975 Specification for Diesel Fuel Oils
D2069 Specification for Marine Fuels (Withdrawn 2003)[3]
D3699 Specification for Kerosine
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
E131 Terminology Relating to Molecular Spectroscopy
E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
E288 Specification for Laboratory Glass Volumetric Flasks
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E969 Specification for Glass Volumetric (Transfer) Pipets

2.2 *Federal Regulation:*

26 CFR 48.4082-1(b) Federal Excise Tax Regulation

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology E131.

4. Summary of Test Method

4.1 The absorbance of each sample is recorded over a specified wavelength range, and the scan is analyzed using derivative analysis software to determine the dye concentration.

4.2 Derivative analysis methodology is employed to minimize interferences caused by variations in the color and composition of the fuel samples regularly tested using this test method.

4.2.1 Naturally occurring diesel test fuels range in color from water white to nearly black, and many of the samples tested using this test method have also had used oils and other products blended with them. These variations in color and composition have a significant effect upon absorbance characteristics of the samples in the region of the visible spectrum where azo dyes absorb. Standard operating procedures to correct for these background variations would involve running

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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 D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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

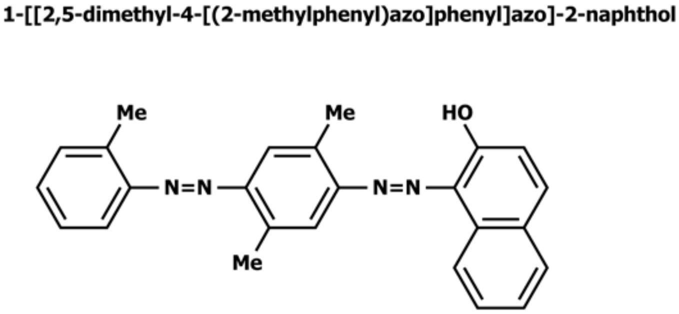

FIG. 1 Structure of Solvent Red 26

a neat (undyed) sample and subtracting out the background absorbance. In most situations involved with the application of this test method, however, neat material is not available, so no background corrections can be made.

4.2.2 The second derivative of the absorbance of these dyes in the visible region is a function of the fine structure of the dye's absorbance peak (versus its height or area) and is relatively unaffected by changes in background absorbance. Further, the specific sections (maxima and minima) of the second derivative spectra employed for this analysis are a function of the fine structure of the top of the absorbance curve which has been found to be unique to the azo dyes.

5. Significance and Use

5.1 This test method was developed to provide for the enforcement of 26 CFR 48.4082-1(b), which mandates that all tax-exempt diesel fuels be dyed with an amount of Solvent Red 164 at a concentration that is spectrally equivalent to 3.9 lb/10^3 bbl (11.1 mg/L) of Solvent Red 26. It is employed to verify that the correct amount of Solvent Red 164 is being added to tax-exempt product at terminals or refineries prior to sale, and to detect the presence of Solvent Red 164 in taxed product intended for on-road use.

5.1.1 Solvent Red 26 is the azo dye shown in Fig. 1. It is the standard against which the concentration of Solvent Red 164 is measured because it is available in a certified pure form. Solvent Red 164 is identical in structure to Solvent Red 26 except that it has hydrocarbon (alkyl) chains incorporated to increase its solubility in diesel and burner fuels. The exact composition of Solvent Red 164 will vary from manufacturer to manufacturer and lot to lot depending upon the extent of alkylation that occurs during production; however, its visible spectrum is virtually identical to the spectrum of Solvent Red 26. Solvent Red 164 is employed in the field (instead of Solvent Red 26) to dye tax-exempt diesel and burner fuels because of its higher solubility and relatively low cost.

6. Apparatus

6.1 *Spectrophotometer,* equipped with automated scanning, background correction, and electronic data storage capabilities, and the ability to automatically record absorbance or transmittance of solutions in the spectral region from 400 nanometers (nm) to 800 nm with a spectral slit width of 1.0 nm or less (Note 2). Wavelength measurements shall be repeatable and known to be accurate to within ±0.2 nm or less at deuterium peak 656.1 nm. In the absorbance range from 0.01 to 1.0, absorbance measurements shall have a photometric accuracy of ±0.005 or less and a photometric repeatability of ±0.002 or less.

NOTE 2—Instruments having different specifications, for example, minimum slit width 2 nm to 4 nm, no data storage, diode array spectrophotometers, and so forth, may be used if they provide demonstrably equivalent results. Equivalence can be demonstrated by successful (within reproducibility limits) participation in inter- or intra-laboratory studies using this test method.

6.1.1 For applicable general techniques and methods of testing spectrophotometers to be used in this test method, refer to Practices E169 and E275.

6.2 *Sample Cells (Cuvettes),* one or more fused silica or glass cells having sample path length of 1.0 cm.

6.3 *Analytical Balance,* 0.1 mg sensitivity, ±0.05 mg precision.

6.4 *Volumetric Pipettes,* 1, 2, 3, 4, and 5 mL, Class A, according to Specification E969.

6.5 *Volumetric Flasks,* 100 mL and 250 mL, Class A, borosilicate glass, according to Specification E288.

7. Reagents

7.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] 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 *Solvent Red 26 (Dye Standard)*—Dye, Color Index Solvent Red 26, 1-[[2,5-dimethyl-4-[(2-methylphenyl) azo]phenyl]azo]-2-naphthol, Chemical Abstract Services Registry No. 4477-79-6, dry powder with certified purity, and maximum absorbance at 512 nm ± 20 nm.

7.3 *Kerosine*—1-K, water-white, conforming to Specification D3699, and having a maximum absorbance against air of 0.08 absorbance units over the wavelength range 450 nm to 750 nm (1.0 cm cell, 120 nm/min scan rate, slit width 1.0 nm). (**Warning**—Flammable; harmful if swallowed, inhaled, or brought into contact with skin or eyes.)

7.4 *Xylene*—(**Warning**—Extremely flammable; harmful if swallowed, inhaled, or brought into contact with skin or eyes.)

8. Sampling

8.1 Use the principles of Practice D4057 in acquisition of test sample(s).

8.2 Precautions must be taken to shield the samples from sunlight prior to analysis.

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[4] *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.

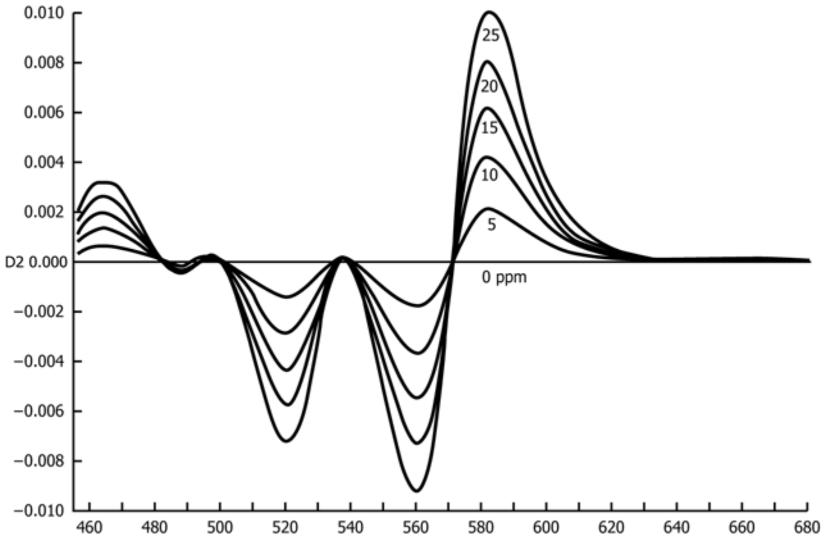

FIG. 2 Second Derivative Scans of Solvent Red 26 Dye in Kerosine

NOTE 3—Studies have shown that exposure to direct sunlight will show a decrease in dye concentration over time.

9. Calibration and Standardization

9.1 *Preparation of Stock Standard:*

9.1.1 *Solvent Red 26*—Weigh approximately 0.0750 g of the dye standard to the nearest 0.1 mg on an analytical balance, quantitatively transfer the dye to a 250 mL volumetric flask, and dilute to mark with xylene. Mix the prepared solution thoroughly.

9.1.2 Determine the exact concentration of dye in the stock standard using the following equation:

$$C = \frac{(M)\,(P)\,(1000)}{0.250} \tag{1}$$

where:

C = concentration of active dye ingredient in the stock standard, mg/L,
M = mass of certified dye standard used in preparing the stock standard, g, and
P = purity of certified dye standard used in preparing the stock standard, purity %/100, for example, for a 99.0 % Solvent Red 26 material, $P = 0.99$.

9.1.3 Store the stock standard in tightly capped/sealed brown glass bottles and store in a dark place when not in use to prevent deterioration.

9.2 *Preparation of Working Calibration Standards:*

9.2.1 Pipet the volumes of the stock standard specified below into separate 100 mL volumetric flasks and dilute to volume with kerosine.

Volume of Stock Standard/100 mL	Approximate Concentration of Working Standards
0.0 mL	0 mg/L
1.0 mL	3 mg/L
2.0 mL	6 mg/L
3.0 mL	9 mg/L
4.0 mL	12 mg/L
5.0 mL	15 mg/L

9.2.2 Determine the exact concentration of dye in each working standard using the following equation:

$$Cs = \frac{(V)(Cm)}{100} \tag{2}$$

where:

Cs = concentration of each working standard, mg/L,
V = volume of stock standard, mL, and
Cm = concentration of active dye in stock standard, mg/L.

9.2.3 Store the working calibration standards in tightly capped/sealed brown glass bottles and store in a dark place when not in use to prevent deterioration.

9.3 Using a clean 1.0 cm sample cell, scan each of the working standards against air (empty reference sample compartment) from 450 nm to 750 nm, recording the absorbance for each using a scan rate of 120 nm/min, maximum data recording interval of 0.11 nm, and a maximum slit width of 1.0 nm.

NOTE 4—Other instrument conditions may be used if they can be demonstrated to give equivalent results to this test method (see Note 2).

9.4 Using derivative analysis software, calculate and plot the second derivative spectra for each standard over this wavelength range using an instrument noise level dampening setting of sufficient level to provide a smooth second derivative curve.

9.5 Measure the amplitude difference for the maximum and minimum listed below:

Solvent Red 26:	538 nm ± 20 nm (peak max, Fig. 2)
	561 nm ± 20 nm (peak min, Fig. 2)

NOTE 5—Specific amplitude units employed will vary, depending on instrumentation or software used, or both.

10. Procedure

10.1 Using a clean 1.0 cm sample cell, scan the sample against air (empty reference sample compartment) from 450 nm to 750 nm using the same instrument settings employed for the working standards and record the absorbance.

10.2 Using derivative analysis software and the same noise level dampening settings used in 9.4, calculate and plot the second derivative spectrum of the sample.

10.3 Measure the amplitude difference between the derivative maximum and minimum specified in 9.5 (see Note 5).

10.3.1 The wavelengths of the derivative minima and maxima for the dye in actual diesel fuel samples normally vary from those observed for the working standards due to variations in the composition of the Solvent Red 164 dye used and sample matrix effects. On instruments that automatically record amplitudes at preset wavelengths, adjustments must be made to compensate for this shift to ensure that actual minimum and maximum amplitudes are used in determining amplitude differences.

11. Calculation

11.1 Prepare a calibration curve, plotting the amplitude difference for each working calibration standard on the y axis versus the dye concentration on the x axis.

11.2 Determine the concentration of dye in the sample by comparing the amplitude difference measured in 10.3 for the sample against the calibration curve.

11.2.1 Computer systems/software having appropriate multipoint calibration program capabilities may be used instead of a manual interpolation from calibration curves.

11.3 Report the dye concentration results for the sample in mg/L to one decimal place, for example, 11.1 mg/L.

12. Precision and Bias[5]

12.1 *Precision*—The precision of the test method, as obtained by statistical examination of inter- and intra-laboratory test results obtained in accordance with the requirements of Practice E691, is as follows:

12.1.1 *Repeatability*—Within-laboratory precision, a quantitative expression of the random error associated with a single operator in a given laboratory obtaining repetitive results with the same apparatus under constant operating conditions on identical test material. It is defined as the difference between two such results at the 95 % confidence level. The repeatability expression is valid for the concentration range covered by the interlaboratory study samples (1.20 mg⁄L to 18.2 mg/L).[5]

$$\text{Repeatability } (r) = 0.1847\ (x)^{0.5} \tag{3}$$

where:

x = mean dye concentration (mg/L) of two results from the same laboratory.

12.1.2 *Reproducibility*—Between-laboratory precision, a quantitative expression of the random error associated with different operators using different test apparatus in different laboratories and obtaining test results when applying the same method. It is defined as the 95 % confidence limit for the difference between two such single and independent results. The reproducibility expression is valid for the concentration range covered by the interlaboratory study samples (1.20 mg⁄L to 18.2 mg/L).[5]

$$\text{Reproducibility } (R) = 0.7652\ (x)^{0.5} \tag{4}$$

where:

x = mean dye concentration (mg/L) of two results from different laboratories.

12.2 *Bias*—Bias cannot be determined because there was no acceptable reference material suitable for determining bias for this test method.

13. Keywords

13.1 dyed diesel fuel; second derivative spectroscopy; Solvent Red 26 Dye; Solvent Red 164 Dye; tax-exempt diesel fuels; visible spectroscopy

APPENDIX

(Nonmandatory Information)

X1. POTENTIAL FALSE "POSITIVE" RED DYE RESULTS

X1.1 Natural Color Bodies

X1.1.1 Diesel with an orange-colored hue that can yield false positive red dye values by this test method have been observed when diesel fuel is being severely hydrotreated, when the catalyst is at the end of life, or when certain types of crude oils are processed, or a combination thereof. GC-MS testing has shown that higher levels of carbazoles and other nitrogen-containing polyaromatic hydrocarbons are present in these diesel fuels. These compounds yield wavelength peaks in the spectral regions similar to that of the red dye compounds, thus giving values for red dye when none is present. False positive values from 0.8 mg⁄L to 3.5 mg/L red dye were observed in some cases.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1425. Contact ASTM Customer Service at service@astm.org.

X1.2 Suggestions for Confirming the Presence or Absence of Red Dye

X1.2.1 In the event that a "positive" red dye value is obtained when no dye is anticipated, the following may assist in determining if the red dye is actually present:

X1.2.2 *Standard Addition of Red Dye*—In some cases, standard additions of red dye can be used to distinguish red dye additive from natural color bodies. The effectiveness of this approach depends on which natural color bodies are present. Certain species will continue to be interpreted as red dye. The addition of a standard amount of red dye to the diesel in question will give a red dye value that equals the amount of red dye added plus the amount previously observed in the sample, if red dye is present in the diesel sample initially or if the sample contains those species of color bodies that respond similarly to the red dye. If red dye is not actually present and other, less responsive natural color bodies are interfering with the test results, then the addition of a standard amount of red dye to the diesel in question will yield a red dye value similar to the standard amount added.

X1.2.3 *Extraction of Color Bodies*—Another technique that has been successful in determining whether red dye or natural color bodies are responsible for the red dye value determined, is to use silica gel cartridges to conduct solid phase extraction (SPE) of 100 mL of the diesel in question. Backflushing the silica gel with n-pentane to remove residual diesel, and then extracting the colored materials with a polar solvent like dichloromethane, concentrating the materials, and conducting GC-MS testing will show whether the red dye compounds or carbazoles and other polyaromatic compounds are present. This works best when a diesel with a known amount of red dye is extracted in the same manner and used as a "control" sample.

X1.2.4 *Other Techniques*—There may be other techniques or methods to verify the presence or absence of red dye that have not been discussed in this appendix that are also acceptable.

SUMMARY OF CHANGES

Subcommittee D02.05 has identified the location of selected changes to this standard since the last issue (D6258 – 09 (2014)) that may impact the use of this standard. (Approved May 1, 2017.)

(1) Revised subsection X1.2.2.