Designation: D6756 – 17

Standard Test Method for Determination of the Red Dye Concentration and Estimation of the ASTM Color of Diesel Fuel and Heating Oil Using a Portable Visible Spectrophotometer[1]

This standard is issued under the fixed designation D6756; 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 the red dye concentration of diesel fuel and heating oil and the estimation of the ASTM color of undyed and red-dyed diesel fuel and heating oil. The test method is appropriate for use with diesel fuel and heating oil of Grades 1 and 2 described in Specifications D396, D975, D2880, and D3699. Red dye concentrations are determined at levels equivalent to 0.1 mg⁄L to 20 mg⁄L of Solvent Red 26 in samples with ASTM colors ranging from 0.5 to 5. The ASTM color of the base fuel of red-dyed samples with concentration levels equivalent to 0.1 mg⁄L to 20 mg⁄L of Solvent Red 26 is estimated for the ASTM color range from 0.5 to 5. The ASTM color of undyed samples is estimated over the ASTM color range of 0.5 to 5.

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

1.3 *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.*

1.4 *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
D1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)
D2880 Specification for Gas Turbine Fuel Oils
D3699 Specification for Kerosine
D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D6045 Test Method for Color of Petroleum Products by the Automatic Tristimulus Method
D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
E203 Test Method for Water Using Volumetric Karl Fischer Titration
E1655 Practices for Infrared Multivariate Quantitative Analysis
E2056 Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures

3. Terminology

3.1 *Definitions:*

3.1.1 *ASTM color, n*—the name of an empirical scale of expressing the color of a petroleum liquid darker than Saybolt

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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.

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

color based on a scale of 0.5 (lightest) to 8 Dil (darkest) and determined by Test Method D1500.

3.1.2 *surrogate calibration, n*—a multivariate calibration that is developed using a calibration set which consists of mixtures with pre-specified and reproducible compositions that contain substantially fewer chemical components than the samples which will ultimately be analyzed. **E2056**

3.1.3 *surrogate method, n*—a standard test method that is based on a surrogate calibration. **E2056**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *red dye, n*—substance that, when added to fuel, absorbs green light and imparts a red color to the product. For this test method, red dyes are:

3.2.1.1 *product dyes, n*—alkyl derivatives of azobenzene-4-azo-2-naphthol (methyl derivatives of Color Index No. 26105) which are more soluble in diesel fuel.

3.2.1.2 *solvent red 26, n*—an azobenzene-4-azo-2-naphthol dye of a specific chemical structure that is used to gage the amount of red dye present in a given sample.

4. Summary of Test Method

4.1 A sample is introduced into the liquid specimen cell. The cell is placed into the light path of the apparatus. A beam of visible light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the spectrum, which correlate highly with the red dye concentration and the ASTM color, are selected for analysis using selective bandpass filters. A multivariate mathematical model converts the absorption values from the filters to the red dye concentration and the estimated ASTM color.

5. Significance and Use

5.1 In the United States, high sulfur content (defined by the United States Environmental Protection Agency (USEPA)) middle distillate products and diesel fuel used for off-road purposes, other than aviation turbine fuel, are required by government agencies to contain red dye. The dye concentration required to be present in high-sulfur and off-road diesel products is regulated by the United States Environmental Protection Agency and the United States Internal Revenue Service, respectively.

5.2 Some fuels that are readily exchanged in the market have a color specification. The color of the base fuel is masked by the presence of the red dye. This test method provides a means of estimating the base color of Number 1 and Number 2 diesel fuel and heating oil in the presence of red dye.

5.3 The test method provides a means to indicate conformance to contractual and legal requirements.

6. Interferences

6.1 The presence of colorants other than the hydrocarbons typical of Number 1 and 2 diesel fuel and heating oils, or the presence of red dye other than the specified types, can interfere with the accurate determination of the red dye concentration reported as Solvent Red 26 equivalent or the base fuel ASTM color.

7. Apparatus

7.1 *Filter Spectrophotometer,* is equipped with specimen chamber, visible wavelength source, four 10 nm ± 2 nm (full width at half transmission maximum) bandpass wavelength discriminating filters having center wavelengths at 450 nm ± 2 nm, 520 nm ± 2 nm, 650 nm ± 2 nm, and 700 nm ± 2 nm. The bandpass filters are used in conjunction with the visible wavelength source to produce light in the blue, green, red, and far-red regions of the electromagnetic spectrum. A detector converts the transmitted light to an electronic signal that is processed by an A-D converter and a microprocessor.[3,4]

7.2 *Specimen Cell,* constructed of polymethacrylate or clear optical glass having a path length of approximately 1 cm. If more than one cell is used for calibration, qualification, and sample measurement, the path length of the cells must be matched to ±0.001 cm.

8. Sampling

8.1 Samples shall be taken in accordance with Practice D4057 or D4177.

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

9. Calibration and Standardization of the Apparatus

9.1 The instrument is calibrated according to the procedure described in Annex A2.

NOTE 1—The DT100C[3] instruments are calibrated at the factory by the vendor.

9.2 The instrument is qualified according to the procedure described in Annex A3.

NOTE 2—The DT100C instruments are qualified at the factory by the vendor.

9.2.1 If the qualification procedure is performed by the vendor, then the user shall perform a quality control check according to the procedure described in Section 10.

10. Quality Control Check

10.1 To confirm the performance of the instrument, periodically measure the red dye concentration and the ASTM color of three control samples using the procedure outlined in Section 11. The quality control check standards should be analyzed at least once a week or before the sample analysis if the instrument is used less frequently than weekly or if the instrument is moved to a different laboratory or field location.

NOTE 3—Quality control samples are available from DT100C.[3]

10.1.1 A standard of known dye concentration and ASTM color is made according to the information in A1.4. The set of quality control samples shall have a low, medium, and high red

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[3] DT100C instruments used to develop this precision statement are available from PetroSpec, Inc., 530 Main St., Acton, MA 01720.

[4] The sole source of supply of the apparatus known to the committee at this time is PetroSpec, Inc. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

dye concentration (0 mg ⁄L to 14 mg ⁄L ± 2 mg ⁄L) and a low, medium, and high ASTM color (0 to 5 ASTM color units).

10.1.2 The standards are stable for at least one year when stored in the dark in tightly sealed bottles.

10.2 If the red dye concentration determined for one of the quality control samples differs from the known value by more than 1.0 mg ⁄L or if the estimated ASTM color for one of the quality control samples differs from the known value by more than 0.5 units, then the measurement system is out-of-control and cannot be used to determine the red dye concentration or used to estimate the ASTM color until the cause of the out-of-control behavior is corrected.

10.3 If correction of out-of-control behavior requires repair to the instrument or recalibration of the instrument, the qualification of instrument performance described in Annex A3 shall be performed before the system is used to measure red dye concentration or used to estimate ASTM color.

11. Procedure

11.1 Prepare the filter spectrophotometer for operation in accordance with the manufacturer's instructions.

11.2 Equilibrate the sample to between 20 °C and 25 °C.

11.3 Without filtering the sample (see 13.6), fill a clean, dry specimen cell. The external optical surfaces shall be clean. If not, wipe clean and dry with a piece of lint-free paper (for example, lens paper).

11.4 Insert the specimen cell into the cell chamber of the instrument.

11.5 Record the Solvent Red 26 equivalent concentration and the estimated ASTM color.

12. Report

12.1 Report the red dye concentration to the nearest 0.1 mg ⁄L as Solvent Red 26 equivalent dye.

NOTE 4—The number of milligrams per litre of Solvent Red 26 equivalents measured by the DT100C instrument is labeled as *ppm* on the display. The ppm unit reported by the DT100C instrument is equivalent to mg/L.

12.2 Report the estimated ASTM color value as: *estimated ASTM color using ASTM D6756*. Report the result to the nearest 0.1 color value.

12.2.1 The reported estimated ASTM color value can be converted to a value that mimics the reporting convention of Test Method D1500. For estimated ASTM color values that are x.0 or x.5, the estimated value is reported unchanged. For estimated color values between x.1 and x.4, round up the value to the nearest x.5 and place an *L* before the result. For estimated color values between x.6 and x.9, round up the value to the nearest whole number and place an *L* before the result. If the estimated color value is greater than 8.0, report the estimated result as >8.

13. Precision and Bias[5]

13.1 Interlaboratory tests of the procedure were carried out using sixteen samples covering the red dye concentration range equivalent to 0 mg ⁄L to 16 mg ⁄L of Solvent Red 26 equivalents and covering the range of ASTM color from 0.5 to 3.0. Seven laboratories participated in the interlaboratory tests. The precision of this procedure as determined by the statistical examination of the interlaboratory test results is as follows:[5]

13.1.1 *Repeatability*—The difference between successive test results obtained with the same apparatus under constant operating conditions on identical samples would in the long run, in normal and correct operation of the test method, exceed the following value in only one case in twenty:

$$r = 0.22 \text{ mg/L}$$

for Solvent Red 26 equivalent dye concentrations between 0.1 mg ⁄L and 20.0 mg ⁄L, and

$$r = 0.085 \text{ ASTM color units}$$

for samples in the ASTM color range of 0 to 5.

13.1.2 *Reproducibility*—The difference between two single and independent results obtained from different instruments on identical samples, would in the long run, in normal and correct operation of the test method, exceed the following value in only one case in twenty:

$$R = 0.86 \text{ mg/L}$$

for Solvent Red 26 equivalent dye concentrations between 0.1 mg ⁄L and 20.0 mg ⁄L, and

$$R = 0.20 \text{ ASTM color units}$$

for samples in the ASTM color range of 0 to 5.

13.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias has not been determined.

13.3 *Relative Bias (Dye Concentration)*—Some relative bias,[5] among certain samples, was observed when the Solvent Red 26 concentration results were compared to the expected Solvent Red 26 concentrations. The bias between the theoretical and measured Solvent Red 26 concentration is observed with the test samples that were made using Solvent Red 164, the chemical used to commercially dye diesel fuel. The observed bias does appear to be of a systematic nature and is not known to be related to the accuracy of this test method, since the Solvent Red 26 equivalency of the Solvent Red 164 used in sample preparation has not been determined, only estimated.

13.4 *Relative Bias (ASTM Color)*—Relative bias,[5] for one sample, was observed when the color results were compared to the Test Method D1500 results; however, this bias is near the

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1521. Contact ASTM Customer Service at service@astm.org.

reproducibility of the test methods and is inconclusive. The overall relative bias to Test Method D1500 is not significant.

NOTE 5—The average bias of the estimated ASTM color relative to Test Method D1500 was −0.17. The largest average biases, −0.4 to −0.5, were observed for four samples that had an ASTM color of 0.5 and red dye concentrations that ranged from 10 mg⁄L to 20 mg⁄L.

13.5 *Relative Bias (Unfiltered versus Filtered Samples)*—A single laboratory analyzed a total of 99 separate split samples (unfiltered versus filtered) to determine the impact that filtering samples can have on reported red dye concentration results.[5] Based on a Practice D6708 analysis of the results, where the Y-method was unfiltered samples and the X-method was filtered samples, a bias correction formula of Y = X – 0.107 was determined. In short, filtering the samples led to a statistically significant bias being determined. As such, to ensure testing consistency between laboratories, samples are not to be filtered as indicated in 11.3. Inclusion of the Test Method D1500 analysis formula is for information only and not intended to be used by laboratories as an official offset to apply to their data if samples were filtered.

13.6 The precision statements in 13.1 were derived from the 1997 interlaboratory test program. Participants analyzed four sets of undyed base fuels and twelve sets of dyed base fuel/color combinations in duplicate in the ASTM color range of 0.5 to 3.0 and Solvent Red 26 equivalent dye concentration from 0 mg⁄L to 16 mg⁄L. Seven laboratories participated with the automatic filter apparatus and six laboratories participated with the manual Test Method D1500 apparatus. Information on the types of samples and their dye concentrations and colors are in the research report available at ASTM International Headquarters. Request ASTM RR: RR:D02-1521.

14. Keywords

14.1 ASTM color; diesel fuel, heating oil; red dye concentration; visible spectrophotometry

ANNEXES

(Mandatory Information)

A1. PROCEDURE FOR PREPARATION OF RED DYE/ASTM COLOR STANDARDS, QUALIFICATION SAMPLES, AND QUALITY CONTROL SAMPLES

A1.1 Scope

A1.1.1 This annex is a description of the preparation of dye concentration and color standard samples used for calibration and qualification. It also describes the preparation of possible standard samples that can be used for periodic checks.

A1.2 Apparatus

A1.2.1 *Spectrophotometer,* equipped to measure the absorbance of solutions in the spectral region from 380 nm to 780 nm with an effective spectral slit width of 10 nm ± 2 nm or 5 nm ± 1 nm. Wavelength measurements shall be repeatable and known to be accurate to 0.1 nm. The photometric linearity is to be ±0.5 % of full scale and a photometric reproducibility of ±0.2 %.

A1.2.2 *Filter Spectrophotometer,* see 7.1.

A1.2.3 *Sample Cells,* see 7.2.

A1.2.4 *Balance,* with a readability of 0.1 mg or better.

A1.2.5 *Pipettes,* 0.5 mL, 1 mL, and 2 mL capacity, Class A.

A1.2.6 *Volumetric Flasks,* 100 mL, 200 mL, and 250 mL capacity, Class A.

A1.2.7 *Beaker,* 50 mL capacity.

A1.3 Reagents

A1.3.1 *Dyes:*

A1.3.1.1 *3-Methyl-1-(phenyl azo)-pyrazol-5-ol,* (Yellow 5GS-EX), CAS registry number 4314-14-1.

A1.3.1.2 *1-(phenyl azo)-2-naphthalenol,* (Orange EX), CAS registry number 842-07-9.

A1.3.1.3 *1,4 bis (butylamino)-9,10-anthracenedione,* (Blue SB), CAS registry number 17354-14-2.

A1.3.1.4 *1-[[(4-[dimethylphenyl)azo]dimethylphenyl]azo]-2-naphthalenol,* (Red 5B-SP), CAS registry 1320-06-5.

A1.3.1.5 *1,5 (or 1,8)-bis[(4-methylphenyl)amino]-9,10-anthracenedione,* (Violet 3R), CAS registry number 8005-40-1.

A1.3.1.6 *1-hydroxy-4-[(4-methylphenyl)amino]-9,10-anthracenedione,* (Violet B-2R), CAS registry number 81-48-1.

A1.3.1.7 *1,4-bis[(4-butylphenyl)amino]-5,8-dihydroxy-9,10-anthracenedione,* (Green SG), CAS registry number 28198-05-2.

A1.3.1.8 *1-[[2,5-dimethyl-4[(2-methylphenyl)azo]phenyl]azo]-2-naphthol,* (Solvent Red 26), CAS registry number 4477-79-6.

A1.3.2 *1,1-bis(3,4-dimethylphenyl)ethane,* 90 % minimum purity, CAS registry number 1742-14-9.

A1.3.3 *Dodecane,* anhydrous, 99 % minimum purity, CAS registry number 112-40-3.

A1.3.4 *Xylenes-* isomers plus ethylbenzene, A.C.S. reagent grade, CAS registry number 1330-20-7.

A1.4 Preparation Procedure for the ASTM Standard Samples

A1.4.1 Measure 0.2500 g ± 0.0005 g of Yellow 5GS-EX into a 50 mL beaker and dissolve the dye in 20 mL of 1,1-bis(3,4-dimethylphenyl)ethane. Quantitatively transfer the Yellow 5GS-EX solution to a 250 mL volumetric flask, dilute to the mark with 1,1-bis(3,4-dimethylphenyl)ethane and mix well. This solution is called the Yellow 5GS-EX dye solution.

A1.4.2 Repeat the above procedure for the Orange EX, Blue SB, Red 5B-SP, Violet 3R, Violet B-2R, and Green SG. These solutions are called Orange EX dye solution, the Blue SB dye solution, the Red 5B-SP dye solution, the Violet 3R dye solution, the Violet B-2R dye solution, and the Green SG dye solution, respectively.

A1.4.3 Pipette 2 mL of the Yellow 5GS-EX solution into a 200 mL volumetric flask, dilute to the mark with dodecane, and mix well. Using separate flasks, repeat this procedure with the Orange EX dye solution, the Blue SB dye solution, the Red 5B-SP dye solution, the Violet 3R dye solution, the Violet B-2R dye solution, and the Green SG dye solution.

A1.4.4 At the wavelengths indicated in Table A1.1, measure the absorbance of these solutions using cells with 1 cm path lengths and dodecane as the reference material. If the measured absorbances are not within the indicated ranges, adjust the solution by either adding more of the solid dye, if the measured absorbances are less than the indicated absorbance range, or by adding more 1,1-bis(3,4-dimethylphenyl)ethane if the measured absorbances exceed the indicated absorbance range.

A1.4.5 Prepare the Solvent Red 26 solution by weighing 0.0750 g of Solvent Red 26 into a 250 mL volumetric flask, diluting to the mark with xylenes and mixing well. Calculate the concentration of the solution as follows:

$$C_i = \left(\frac{W}{0.250}\right) \tag{A1.1}$$

where:

C_i = concentration Solvent Red 26 solution, mg/L, and
W = mass of the solid Solvent Red 26, mg.

A1.4.6 Prepare the ASTM mixed dye solutions by weighing into separate amber glass bottles the dye solutions prepared in A1.4.1 and A1.4.2 using the masses specified in Table A1.2. The ASTM color mixed dye solutions are called M1, M3, M5, and M7.

A1.4.7 To generate the color standard samples, weigh the amount of the ASTM color mixed dye solution and the Solvent Red 26 solution specified in Table A1.3 into a 250 mL volumetric flask, dilute to the mark with dodecane, and mix well. Calculate the concentration of the Solvent Red 26 in the color standard samples as follows:

$$C = C_i \times \frac{W}{(d \times 250)} \tag{A1.2}$$

where:

C = concentration Solvent Red 26 in the color standard sample, mg/L,
C_i = concentration of Solvent Red 26 solution from A1.4.5,
W = mass of the Solvent Red 26 solution from A1.4.5, g, and
d = density at 15.6 °C of the xylenes mixture using Test Method D4052.

A1.4.8 The ASTM color values assigned to the calibration samples listed in Table A1.3 can be confirmed using the device described in either Test Method D1500 or D6045, or the tristimulus method described in Annex X2.2 of Test Method D6045. Use the samples (1 to 4) detailed in Table A1.3 that do not contain Solvent Red 26 for the ASTM color determination. For samples 5 through 28, assign an ASTM color of 0 if no mixed dye solution is present. If the sample contains mixed dye solution M1, M3, or M5, assign it the same ASTM color as the sample 1, 2, or 3, respectively.

TABLE A1.1 Dye Solution Absorption Range

Dye Solution	Wavelength (nm)	Absorption
Yellow 5GS-EX	395	0.881 to 0.935
Orange EX	465	0.519 to 0.541
Blue SB	600	0.412 to 0.438
	645	0.465 to 0.494
Red 5 B-SP	515	0.673 to 0.715
Violet 3R	545	0.332 to 0.353
Violet B-2R	585	0.332 to 0.353
	635	0.400 to 0.424
Green SG	680	0.467 to 0.498

TABLE A1.2 Dye Solution Masses (g) for Synthesis of ASTM Color Mixed Dye Solutions

Dye Solution	M1	M3	M5	M7
Yellow 5GS-EX	42.000 ± 0.01	40.000 ± 0.01	40.000 ± 0.01	36.600 ± 0.01
Orange EX	5.200 ± 0.005	5.800 ± 0.005	11.600 ± 0.005	10.600 ± 0.005
Blue SB	0.400 ± 0.001	0.400 ± 0.001	. . .	0.200 ± 0.001
Red 5B-SP	. . .	1.400 ± 0.001	2.000 ± 0.001	2.600 ± 0.001
Violet 3R	2.600 ± 0.001	1.200 ± 0.001	3.200 ± 0.001	2.200 ± 0.001
Violet B-2R	. . .	0.800 ± 0.001	1.600 ± 0.001	3.200 ± 0.001
Green SG	0.600 ± 0.001	0.800 ± 0.001	1.600 ± 0.001	0.600 ± 0.001

TABLE A1.3 Indicated Dye Mixture Masses (g) for Synthesis of Calibration

Sample	ASTM Color	M1	M3	M5	M7	Solvent Red 26
1	1	2.467 ± 0.001	. . .	. . .	. . .	. . .
2	3	. . .	12.987 ± 0.006	. . .	. . .	. . .
3	5	. . .	. . .	23.956 ± 0.010	. . .	. . .
4	7	. . .	. . .	. . .	41.822 ± 0.020	. . .
5	1	2.467 ± 0.001	. . .	. . .	. . .	0.500 ± 0.005
6	3	. . .	12.987 ± 0.006	. . .	. . .	0.500 ± 0.005
7	5	. . .	. . .	23.956 ± 0.010	. . .	0.500 ± 0.005
8	0	. . .	. . .	. . .	. . .	0.500 ± 0.005
9	1	2.467 ± 0.001	. . .	. . .	. . .	1.000 ± 0.005
10	3	. . .	12.987 ± 0.006	. . .	. . .	1.000 ± 0.005
11	5	. . .	. . .	23.956 ± 0.010	. . .	1.000 ± 0.005
12	0	. . .	. . .	. . .	. . .	1.000 ± 0.005
13	1	2.467 ± 0.001	. . .	. . .	. . .	3.500 ± 0.005
14	3	. . .	12.987 ± 0.006	. . .	. . .	3.500 ± 0.005
15	5	. . .	. . .	23.956 ± 0.010	. . .	3.500 ± 0.005
16	0	. . .	. . .	. . .	. . .	3.500 ± 0.005
17	1	2.467 ± 0.001	. . .	. . .	. . .	7.000 ± 0.005
18	3	. . .	12.987 ± 0.006	. . .	. . .	7.000 ± 0.005
19	5	. . .	. . .	23.956 ± 0.010	. . .	7.000 ± 0.005
20	0	. . .	. . .	. . .	. . .	7.000 ± 0.005
21	1	2.467 ± 0.001	. . .	. . .	. . .	14.000 ± 0.01
22	3	. . .	12.987 ± 0.006	. . .	. . .	14.000 ± 0.01
23	5	. . .	. . .	23.956 ± 0.010	. . .	14.000 ± 0.01
24	0	. . .	. . .	. . .	. . .	14.000 ± 0.01
25	1	2.467 ± 0.001	. . .	. . .	. . .	28.000 ± 0.01
26	3	. . .	12.987 ± 0.006	. . .	. . .	28.000 ± 0.01
27	5	. . .	. . .	23.956 ± 0.010	. . .	28.000 ± 0.01
28	0	. . .	. . .	. . .	. . .	28.000 ± 0.01

A2. PROCEDURE FOR THE CALIBRATION OF THE APPARATUS

A2.1 Scope

A2.1.1 This annex describes the procedure for calculating the model for determining the Solvent Red 26 equivalents and the model for estimating ASTM color.

A2.2 Terminology

A2.2.1 *calibration transfer*—a process for transferring the calibration model from one master instrument to one or more subject instruments using multivariate regression techniques.

A2.2.2 *multivariate calibration*—a process for creating a calibration model in which multivariate mathematics is applied to correlate the absorbances measured for a set of calibration samples to reference component concentrations or property values for the set of samples.

A2.2.2.1 *Discussion*—The multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the component concentration or property value for the unknown sample.

A2.2.2.2 *Discussion*—The multivariate calibration algorithm used in this test method to calculate the model is multilinear regression (MLR).

A2.3 Calibration of the Apparatus

A2.3.1 *Calibration Matrix*—Prepare calibration standards in accordance with the information in A1.4.

A2.3.2 *Calibration*—Using the filter spectrophotometer described in 7.1, acquire the absorption values for each of the calibration solutions listed in Table A1.3.

A2.3.2.1 Use MLR to develop a calibration model based on the correlation of the set of calibration sample absorbances at the four wavelengths listed in 7.1 to the known Solvent Red 26 dye concentration by fitting to the following set of simultaneous equations:

$$C_i = a_1x_1 + ... + a_nx_n + e \tag{A2.1}$$

where:

C_i = the calculated red dye concentration, mg/L, of the i^{th} calibration sample from A1.4.7 and Table A1.3,
a_n = the regression coefficient for the absorbance at the n^{th} optical filter,
x_n = the absorbance at the n^{th} optical filter, and
e = the intercept.

NOTE A2.1—Consult Practices E1655 and the references therein for an explanation of MLR calculation.

A2.3.2.2 Use MLR to develop a calibration model based on the correlation of the set of calibration sample absorbances at the four wavelengths listed in 7.1 to the known ASTM color by fitting to the following set of simultaneous equations:

$$ASTM_i = b_1x_1 + ... + b_nx_n + e \tag{A2.2}$$

where:

$ASTM_i$ = the ASTM color of the i^{th} calibration sample from Table A1.3,
b_n = the regression coefficient for the absorbance at the n^{th} optical filter,
x_n = the sample absorbance at the n^{th} optical filter, and
e = the intercept.

NOTE A2.2—Consult Practices E1655 and the references therein for an explanation of MLR calculation.

A2.4 Calibration Transfer

A2.4.1 Follow the procedure described in A1.4.1 and A1.4.3 to synthesize a series of six transfer solutions by using 0.300 g, 0.200 g, 0.100 g, 0.050 g, and 0.025 g of Yellow 5GS-EX dye.

A2.4.2 Repeat the procedure from A2.4.1 using Blue SB and Red 5B-SP dyes.

A2.4.3 Acquire the absorbance values for each solution generated in A2.4.1 and A2.4.2 using the master instrument and the subject instrument.

A2.4.4 Use MLR to calculate a model for each filter that transforms the subject instrument absorbance into the master instrument absorbance.

A2.4.5 The red dye concentration model and the ASTM color estimation model calculated for the master instrument are used with the transformed subject instrument absorbance values to perform the analyses using the subject instrument.

A3. PROCEDURE FOR THE QUALIFICATION OF THE APPARATUS

A3.1 Introduction

A3.1.1 Once a calibration has been established, the calibrated instrument must be qualified to ensure that the instrument accurately and precisely measures red dye concentration and estimates the ASTM color.

A3.2 Scope

A3.2.1 This annex describes the qualification procedure for the apparatus.

A3.3 Qualification of Instrument Performance

A3.3.1 Prepare at least twelve qualification samples according to the procedures described in A1.4. These qualification samples shall be similar to, but not the same as, the mixtures established for the calibration samples. Prepare the qualification samples such that the red dye concentration and the ASTM color spans at least 95 % of the calibration range.

NOTE A3.1—The qualification procedure was developed before Practice E2056 was written and this procedure does not completely conform to the requirements of Practice E2056.

A3.3.2 Use the procedure described in Section 11 to determine the Solvent Red 26 equivalent dye concentration and the estimated ASTM color for each of the qualification samples.

A3.3.3 For each of the surrogate qualification samples, calculate the difference, d_i, between the measured red dye concentration, *y-hat*, and the red dye concentration calculated from the prepartion of the sample, *y*. Calculate the average, *d-bar*, of the difference values, d_i.

A3.3.4 The standard error of qualification, $SEQ_{surrogate}$, is calculated as follows:

$$SEQ_{surrogate} = \sqrt{\frac{\sum_{i=1}^{q} (\hat{y}_i - y_i)^2}{q}} \tag{A3.1}$$

where:

q = number of qualification samples used for the red dye concentration measurement.

A3.3.5 Calculate the Student's *t* value using Eq A3.2.

$$t = \left| \frac{\bar{d}\sqrt{q-1}}{SEQ_{surrogate}} \right| \tag{A3.2}$$

A3.3.6 Repeat the calculations described in A3.3.3 – A3.3.5 using the estimated ASTM color results.

A3.3.7 Compare both *t* values to the critical *t* value for *n*−1 degrees of freedom. If either of the *t* values is greater than the critical *t* value, then there is a 95 % probability that the results are biased, and the instrument is not qualified to perform the test. Have maintenance performed on the instrument and repeat the calibration and qualification procedures as required.

A3.3.8 Compare the standard error of qualification to the pooled error of qualification calculated for the instruments used in the method round robin.

A3.3.8.1 For the red dye concentration, calculate an *F* value by dividing $SEQ_{surrogate}$ by 0.213. Compare the result to the critical *F* value for *q* degrees of freedom in the numerator and 77 degrees of freedom in the denominator. If the calculated *F* value is greater than the critical *F* value (Table A3.2), the instrument is not qualified to estimate the red dye concentration. Perform maintenance on the instrument and repeat the calibration and qualification procedures as required. If the calculated *F* value for the red dye is less than the critical *F* value, the instrument is qualified to determine the red dye concentration.

A3.3.8.2 For the ASTM color, calculate an *F* value by dividing $SEQ_{surrogate}$ by 0.205. Compare the result to the critical *F* value for *q* degrees of freedom in the numerator and 84 degrees of freedom in the denominator. If the calculated *F* value is greater than the critical *F* value, the instrument is not qualified to estimate the ASTM color. Perform maintenance on the instrument and repeat the calibration and qualification procedures as required. If the calculated *F* value is less than the critical *F* value, the instrument is qualified to estimate the ASTM color.

TABLE A3.1 Values of *t* for Various Degrees of Freedom (df) at the 95th Percentile

df	t_{95}	df	t_{95}	df	t_{95}	df	t_{95}	df	t_{95}	df	t_{95}
1	12.706	6	2.447	11	2.201	16	2.120	21	2.080	26	2.056
2	4.303	7	2.365	12	2.179	17	2.110	22	2.074	27	2.052
3	3.182	8	2.306	13	2.160	18	2.101	23	2.069	28	2.048
4	2.776	9	2.262	14	2.145	19	2.093	24	2.064	29	2.045
5	2.571	10	2.228	15	2.131	20	2.086	25	2.060	30	2.042

TABLE A3.2 Values for *F* at the 95th Percentile

Degrees of Freedom	Denominator	
Numerator	77	84
10	1.956	1.945
11	1.915	1.905
12	1.880	1.869
13	1.849	1.838
14	1.822	1.811
15	1.798	1.787
16	1.777	1.765
17	1.757	1.746
18	1.739	1.728
19	1.723	1.712
20	1.708	1.697
21	1.695	1.683
22	1.682	1.670
23	1.670	1.659
24	1.660	1.648
25	1.649	1.637

A4. DETERMINATION OF THE PURITY OF THE SOLVENT RED 26 RED DYE STANDARD

A4.1 Introduction

A4.1.1 This annex is an explanation about determining the active component concentration of the Solvent Red 26 red dye standard that is used to prepare the calibration and qualification solutions.

A4.2 Scope

A4.2.1 This annex describes the determination of the purity of the Solvent Red 26 dye standard.

A4.3 Apparatus

A4.3.1 *Vacuum Filtration Apparatus.*

A4.3.2 *Balance,* capable of reading to 1 mg or better and able to weigh up to a 500 g capacity.

A4.3.3 *Balance,* capable of reading to 0.1 mg or better.

A4.3.4 *400 mL Beaker.*

A4.3.5 *Stirrer/Hot Plate.*

A4.3.6 *Stirring Bar.*

A4.3.7 *Whatman No. 1 Filter Paper.*

A4.3.8 *Oven.*

A4.3.9 *Desiccator.*

A4.3.10 *Thermometer.*

A4.3.11 *Weighing Dish.*

A4.3.12 *Watch Glass.*

A4.4 Reagents

A4.4.1 *Xylenes,* A.C.S. reagent grade.

A4.5 Procedure

A4.5.1 The procedure is used to determine the amount of insoluble material in the Solvent Red 26.

A4.5.1.1 Into a clean 400 mL beaker, weigh 2.0 g of the solid dye and record the mass to the nearest 0.0001 g. To the same beaker add 100 g ± 2.5 g of xylenes.

A4.5.1.2 Place the stirring bar into the dye solution and cover the beaker with the watch glass.

A4.5.1.3 Stir and heat the solution to 70 °C ± 1 °C for approximately 15 min. Monitor the temperature using a thermometer.

A4.5.1.4 Dry two Whatman No. 1 filter papers in a 100 °C ± 1 °C oven for approximately 15 min. Remove both filter papers from the oven and place them in the desiccator to cool.

A4.5.1.5 After cooling for at least 10 min, weigh the filter papers to the nearest 0.0001 g.

A4.5.1.6 Place the weighed filter papers on the filter apparatus and transfer the contents of the beaker to the filter paper.

A4.5.1.7 Wash the beaker with xylenes to transfer any remaining particulate matter.

A4.5.1.8 Wash the filter papers with xylenes until there is an absence of color in the solution passing through the filters.

A4.5.1.9 Place the filter papers in the 100 °C ± 1 °C oven. After approximately 15 min, remove the filter papers from the oven and place in a desiccator to cool.

A4.5.1.10 After cooling for at least 10 min, weigh the filter papers and record the mass to the nearest 0.0001 g.

A4.5.2 Use Test Method E203 to determine the moisture content of the Solvent Red 26 dye using Karl Fischer titration. The solid dye Solvent Red 26 is dissolved in xylenes to perform the titration.

A4.6 Calculations

A4.6.1 The mass % of the insoluble is calculated as follows:

$$I = \frac{(W_3 - W_2)}{W_1 \times 100} \tag{A4.1}$$

where:

I = mass % of the sample insoluble in xylenes,
W_1 = mass of the Solvent Red 26 sample,
W_2 = mass of the filter papers, and
W_3 = mass of the filter papers and residue.

A4.6.2 The mass % of the active dye is calculated as follows:

$$D = 100 - I - M \tag{A4.2}$$

where:

D = the mass % of the sample that is active Solvent Red 26,
I = mass % of the sample insoluble in xylenes, and
M = mass % moisture from the Karl Fischer water titration.

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.

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 (D6756 – 10 (2015)) that may impact the use of this standard. (Approved May 1, 2017.)

(1) Revised subsection X1.2.2.