Standard Test Method for Determination of the Red Dye Concentration and Estimation of Saybolt Color of Aviation Turbine Fuels and Kerosine Using a Portable Visible Spectrophotometer[1]

1. Scope

1.1 This test method covers the determination of the red dye concentration of aviation turbine fuel and kerosine and the estimation of the Saybolt color of undyed and red dyed (<0.750 mg⁄L of Solvent Red 26 equivalent) aviation turbine fuel and kerosine. The test method is appropriate for use with aviation turbine fuel and kerosine described in Specifications D1655 and D3699. Red dye concentrations are determined at levels equivalent to 0.026 to 0.750 mg/L of Solvent Red 26 in samples with Saybolt colors ranging from +30 to –16. The Saybolt color of the base fuel for samples dyed red with concentration levels equivalent to 0.026 to 0.750 mg/L of Solvent Red 26 is estimated in the Saybolt Color range +30 to –16. The Saybolt Color for undyed samples is estimated in the Saybolt color range from +30 to –16.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D156 Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)
D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
D1655 Specification for Aviation Turbine Fuels
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
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 *Saybolt color, n*—an empirical definition of the color of a clear petroleum liquid based on a scale of –16 to +30 and determined by Test Method D156.

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.

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

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.2 *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 dye is:

3.2.2.1 *Solvent Red 26*—an azobenzene-4-azo-2-naphthol dye of a specific chemical structure that is used to gauge the amount of red dye present in a given sample.

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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.

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 with the estimation of Saybolt color, are selected for analysis using selective bandpass filters. A multivariate mathematical analysis converts the detector response for the selected wavelengths to the red dye concentration and the estimated Saybolt color.

5. Significance and Use

5.1 In the United States, high sulfur content distillate products and diesel fuel used for off-road purposes, other than aviation turbine fuel, are required to contain red dye. A similar dye requirement exists for tax-free distillates. Contamination of aviation turbine fuel by small quantities of red dye has occurred. Such contamination presents major problems because airframe and engine manufacturers have severely limited operation on aviation turbine fuel containing red dye.

5.2 An alternate methodology for the determination of the presence of red dye in aviation turbine fuel is the observation of the color of the fuel when placed in a white bucket. The presence of the dye can be masked in aviation turbine fuels having dark Saybolt color. This test method provides an objective means of quickly measuring red dye concentration, but to avoid confusion with trace levels of other materials which will be indicated by the instrument, the method requires that instrument readings below 0.026 mg/L be reported as No Dye Present.

5.3 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 aviation turbine fuel and kerosine in the presence of red dye.

6. Interferences

6.1 The presence of colorants resulting from the refining process or crude oil or the presence of red dye other than the quantified types (alkyl derivatives of azobenzene-4-azo-2-naphthol) can interfere with the accurate determination of the red dye concentration reported as Solvent Red 26 equivalent, or the accurate estimation of the base fuel color. If there is controversy over whether the indicated dye concentration is from the alkyl derivatives of azobenzene-4-azo-2-naphthol, the procedure described in Annex A5 shall be used to confirm the presence of a red dye.

7. Apparatus

7.1 *Filter Spectrophotometer,* is equipped with specimen chamber, visible wavelength source, three 10 ± 2 nm bandpass wavelength discriminating filters having center wavelengths at approximately 420 ± 5 nm, 520 ± 5 nm, and 650 ± 5 nm. The bandpass filters are used in conjunction with the visible wavelength source to produce light in the blue, green, and 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 *Sample Cell,* constructed of polymethacrylate or clear optical glass having a path length of approximately 12 cm. If more than one cell is used for calibration, validation, and sample measurement, the path length of the cells must be matched to ±0.005 cm.

8. Sampling

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

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

9. Calibration and Standardization of the Apparatus

9.1 Calibrate the instrument according to the procedure described in Annex A2.

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

9.2 Qualify the instrument according to the procedure described in Annex A3.

NOTE 2—The instruments[3] 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 Checks

10.1 To confirm the performance of the instrument periodically, measure the red dye concentration and the estimated Saybolt color of three control samples using the procedure outlined in Section 11. The quality control check standards shall 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.

11. Procedure

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

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

11.3 Fill a clean, dry, sample cell. The external optical surfaces must be clean. If not, wipe clean, and dry with a piece of lint free paper (for example, lens paper).

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

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

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[3] JT100S instruments, manufactured by PAC, LP, 300 Bammel Westfield Road, Houston, TX 77090, were used in the development of this test method. This is not an endorsement or certification by ASTM International.

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

12. Report

12.1 Report the dye concentration below 0.026 mg/L as No Dye Present.

12.2 Report the red dye concentration at or above 0.026 mg⁄L to the nearest 0.001 mg⁄L as Solvent Red 26 equivalent dye.

12.3 Report the color value as units of estimated Saybolt color.

13. Precision and Bias

13.1 Interlaboratory tests of the procedure were carried out using 18 samples covering the red dye concentration range equivalent from 0.000 to 0.374 mg/L of Solvent Red 26 equivalents and covering the range of Saybolt color from –13 to +30. Seven laboratories participated in the interlaboratory tests. The precision of this procedure, as determined by the statistical examination of the interlaboratory test results,[5] is as follows:

13.1.1 *Repeatability*—The difference between successive 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:

13.1.1.1 for Solvent Red 26 equivalent dye concentrations between 0 to 0.750 mg/L:

$$r = 0.006\ \text{mg/L}$$

13.1.1.2 for samples in the Saybolt color range of –16 to +30:

$$r = 1.1\ \text{Saybolt color units}$$

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:

13.1.2.1 for Solvent Red 26 dye concentrations between 0 to 0.750 mg/L:

$$R = 0.026\ \text{mg/L}$$

13.1.2.2 for samples in the Saybolt color range of –16 to +30:

$$R = 4.6\ \text{Saybolt color units}$$

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)*—Among certain samples, some bias[5] proportional to the dye concentration was observed when the dye concentration results were compared to the expected concentrations. The observed bias does not appear to be of a systematic nature and is not known to be related to the accuracy of this test method, since the activity levels of the dye in sample preparation have not been determined, only estimated.

13.4 *Relative Bias (Saybolt Color)*—Some bias[5] was observed when the color results were compared to the Test Method D156 results, however, this bias was observed only for samples that had high concentration of the dye (>0.180 mg/L). The bias for the base fuels was within the standard error of Test Method D156.

13.5 The precision statements in 13.1 were derived from the 1997 interlaboratory test program. Participants analyzed seven sets of undyed base fuels and 13 sets of dyed base fuel/color combinations in duplicate in the Saybolt color range of –16 to +30 and dye concentration from 0 to 0.374 mg/L, seven laboratories participated with the automatic apparatus and five laboratories participated with the manual Test Method D156 apparatus.[5]

14. Keywords

14.1 aviation turbine fuel; kerosine; red dye concentration; Saybolt color; visible spectrometry

ANNEXES

(Mandatory Information)

A1. PROCEDURE FOR PREPARATION OF RED DYE/SAYBOLT 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 to 780 nm with an effective spectral slit width of 10 ± 2 nm or 5 ± 1 nm. Wavelength measurements shall be repeatable and known to be

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

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[5] Supporting data, results of the 1997 Interlaboratory Cooperative Test Program, have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1521.

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 *Sample Cells,* constructed of optical glass or quartz having a path length of 1 ± 0.001 cm for use with the spectrophotometer described in A1.2.1.

A1.2.3 *Filter Spectrophotometer,* see 7.1.

A1.2.4 *Sample Cell,* see 7.2. For use with the spectrophotometer described in A1.2.3.

A1.2.5 *Balance,* with a readability of 0.1 mg, or better.

A1.2.6 *Pipettes,* 0.5 mL, 1 mL, and 2 mL capacity, Class A.

A1.2.7 *Volumetric Flasks,* 100 mL, 200 mL, and 250 mL capacity, Class A.

A1.2.8 *Beaker,* 50 mL capacity.

A1.3 Reagents

A1.3.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless other wise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used, provided it is first asserted that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

A1.3.2 *Dyes:*

A1.3.2.1 *3-Methyl-1-(phenyl azo)-pyrazol-5-ol* (Yellow 5GS-EX), with CAS Registry No. 4314-14-1.

A1.3.2.2 *1-(phenyl azo)-2-naphthalenol* (Orange EX), with CAS Registry No. 842-07-9.

A1.3.2.3 *1,4 bis (butylamino)-9,10-anthracenedione* (Blue SB), with CAS Registry No. 17354-14-2.

A1.3.2.4 *1-[[2,5-dimethyl-4[(2-methylphenyl)azo]phenyl] azo]-2-naphthol* (Solvent Red 26), with CAS Registry no. 4477-79-6.

A1.3.3 *1,1-bis(3,4-dimethylphenyl)ethane,* (90 % min purity).

A1.3.4 *Dodecane,* anhydrous (99 % min purity).

A1.3.5 *Xylenes,* A.C.S. reagent grade.

A1.4 Preparation Procedure for the Saybolt Standard Samples

A1.4.1 Measure 0.2500 ± 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 and Blue SB dyes. These solutions are called Orange EX dye solution and Blue SB dye solution, respectively.

A1.4.3 Pipet 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 and the Blue SB dye solution.

A1.4.4 At the wavelengths indicated in Table A1.1, measure the absorbance of these solutions using the spectrophotometer and cells described in A1.2.1 and A1.2.2, respectively. Use dodecane as the reference material. If the measured absorbances are not within the indicated ranges, adjust the solution either by 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 If the dye solutions meet the criteria of Table A1.1, then weigh 30.000 ± 0.010 g of the Yellow 5GS-EX dye solution, 10.000 ± 0.005 g of Orange EX dye solution and 1.000 ± 0.001 g of Blue SB dye solution into a 100 mL amber glass bottle. Weigh 45.000 ± 0.001 g of dodecane into the same bottle and mix well. This solution is called the Saybolt color mixed dye solution.

TABLE A1.2 Indicated Dye Mixture Masses (g) for Synthesis of Calibration Standards

Samples	Saybolt Number	Amount of the Saybolt Color Mixed Dye Solution (g)	Amount of the Solvent Red 26 Solution
1	30	0.200 ± 0.001	0.000
2	25	0.472 ± 0.002	0.000
3	19	1.087 ± 0.002	0.000
4	15	1.724 ± 0.003	0.000
5	12	2.083 ± 0.004	0.000
6	0	4.545 ± 0.005	0.000
7	-15	8.772 ± 0.010	0.000
8	30	0.200 ± 0.001	0.050
9	25	0.472 ± 0.002	0.050
10	19	1.087 ± 0.002	0.050
11	15	1.724 ± 0.003	0.050
12	12	2.083 ± 0.004	0.050
13	0	4.545 ± 0.005	0.050
14	-15	8.772 ± 0.010	0.050
15	30	0.200 ± 0.001	0.100
16	25	0.472 ± 0.002	0.100
17	19	1.087 ± 0.002	0.100
18	15	1.724 ± 0.003	0.100
19	12	2.083 ± 0.004	0.100
20	0	4.545 ± 0.005	0.100
21	-15	8.772 ± 0.010	0.100
22	30	0.200 ± 0.001	0.200
23	25	0.472 ± 0.002	0.200
24	19	1.087 ± 0.002	0.200
25	15	1.724 ± 0.003	0.200
26	12	2.083 ± 0.004	0.200
27	0	4.545 ± 0.005	0.200
28	-15	8.772 ± 0.010	0.200
29	30	0.200 ± 0.001	0.500
30	25	0.472 ± 0.002	0.500
31	19	1.087 ± 0.002	0.500
32	15	1.724 ± 0.003	0.500
33	12	2.083 ± 0.004	0.500
34	0	4.545 ± 0.005	0.500
35	-15	8.772 ± 0.010	0.500

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[6] *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.

A1.4.6 Prepare the Solvent Red 26 solution by weighing 0.0750 ± 0.0005 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:

$$C_i = (W/0.250) \tag{A1.1}$$

where:

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

A1.4.7 To generate the color standard samples, weigh the amount of the Saybolt color mixed dye solution and the Solvent Red 26 solution specified in Table A1.2 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:

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

where:

C = concentration Solvent Red 26 in the color standard sample, mg/L,
C_i = concentration of Solvent Red 26 solution from A1.4.6,
W = weight mass of the Solvent Red 26 solution from A1.4.6, g, and
d = density at 15.6°C of the xylenes mixture using Test Method D4052.

A1.4.8 The Saybolt color values assigned to the calibration samples listed in Table A1.2 can be confirmed using the device described in either Test Method D156 or D6045, or the tristimulus method described in Annex X2.2 of Test Method D6045. Use the samples (1–6) detailed in Table A1.2 that do not contain Solvent Red 26 for the Saybolt color determination.

A2. PROCEDURE FOR 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 Saybolt color.

A2.2 Terminology

A2.2.1 *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.

A2.2.1.1 *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.

A2.2.1.2 *Discussion*—The multivariate calibration algorithm used in this test method to calculate the model is Multilinear Regression (MLR).

A2.2.2 *calibration transfer*—a process for transferring the calibration model from one master instrument to one or more subject instruments using multivariate regression techniques.

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 A1.2.

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

$$C_i = a_1 \cdot x_{1,i} + \ldots.. + a_n \cdot x_{n,i} + e \tag{A2.1}$$

where:

C_i = the calculated red dye concentration, mg/L, of the *i*th calibration sample from A1.4.7 and Table A1.2,
a_n = the regression coefficient for the absorbance at the *n*th optical filter,
$x_{n,i}$ = the absorbance at the *n*th optical filter for the *i*th calibration sample, 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 three wavelengths listed in 7.1 to the known Saybolt color by fitting to the following set of simultaneous equations:

$$\text{Saybolt}_i = b_1 \cdot x_{1,i} + \ldots.. + b_n \cdot x_{n,i} + e \tag{A2.2}$$

where:

Saybolt_i = the Saybolt color of the *i*th calibration sample from Table A1.2,
b_n = the regression coefficient for the absorbance at the *n*th optical filter,
$x_{n,i}$ = the sample absorbance at the *n*th optical filter for the *i*th calibration sample, 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, 0.200, 0.100, 0.050, 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 Saybolt 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

INTRODUCTION

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

A3.1 Scope

A3.1.1 This annex describes the qualification procedure for the apparatus.

A3.2 Qualification of Instrument Performance

A3.2.1 Prepare at least 12 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 Saybolt color spans at least 95 % of the calibration range.

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

A3.2.2 Use the procedure described in Section 12 to determine the Solvent Red 26 equivalent dye concentration and the estimated Saybolt color for each of the qualification samples.

A3.2.3 For each of the surrogate qualification samples, calculate the difference, d_i, between the measured red dye concentration, $\hat{y}$, and the red dye concentration calculated from the preparation of the sample, y. Calculate the average, $\bar{d}$, of the difference values, d_i.

A3.2.4 The Standard Error of Qualification, $SEQ_{surrogate}$, is calculated as:

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

A3.2.4.1 The variable q is the number of qualification samples used for the red dye concentration measurement.

A3.2.5 Calculate the Student's t value using Eq A3.2.

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

A3.2.6 Repeat the calculations described in A3.2.3, A3.2.4, and A3.2.5 using the estimated Saybolt color results.

A3.2.7 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.

A3.2.8 Compare the standard error of qualification to the pooled error of qualification calculated for the instruments used in the test method's round robin.

A3.2.8.1 For the red dye concentration, calculate an F value by dividing $(SEQ_{surrogate})^2$ by 0.005. Compare the result to the critical F value for q degrees of freedom in the numerator and 67 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. Have maintenance performed 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.

A3.2.8.2 For the Saybolt color, calculate an F value by dividing $(SEQ_{surrogate})^2$ by 0.88. Compare the result to the critical F value for q degrees of freedom in the numerator and 67 degrees of freedom in the denominator. If the calculated F

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 Numerator	Denominator 67
10	1.975
11	1.935
12	1.900
13	1.869
14	1.842
15	1.818
16	1.797
17	1.777
18	1.760
19	1.744
20	1.729
21	1.716
22	1.703
23	1.692
24	1.681
25	1.671

value is greater than the critical *F* value, the instrument is not qualified to estimate the Saybolt color. Have maintenance performed 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 Saybolt color.

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

INTRODUCTION

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.

A4.1 Scope

A4.1.1 This annex describes the determination of the purity of the Solvent Red 26 dye standard.

A4.2 Apparatus

A4.2.1 *Vacuum Filtration Apparatus.*

A4.2.2 *Balance,* capable of reading to 1.0 mg, or better, and able to weigh up to a 500 g capacity.

A4.2.3 *Balance,* capable of reading to 0.1 mg, or better.

A4.2.4 *400 mL Beaker.*

A4.2.5 *Stirrer/Hot Plate.*

A4.2.6 *Stirring Bar.*

A4.2.7 *Whatman No. 1 Filter Paper.*

A4.2.8 *Oven,* capable of controlling temperature at 100°C to at most ±5°C.

A4.2.9 *Desiccator.*

A4.2.10 *Thermometer or Thermocouple,* capable of controlling temperature at 70°C to at most ±5°C.

A4.2.11 *Weighing Dish.*

A4.2.12 *Watch Glass.*

A4.3 Reagents

A4.3.1 *Xylenes,* A.C.S. reagent grade.

A4.4 Procedure

A4.4.1 The procedure is used to determine the amount of insoluble material in the Solvent Red 26.

A4.4.1.1 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 ± 2.5 g of xylenes.

A4.4.1.2 Place the stirring bar into the dye solution and cover with the watch glass.

A4.4.1.3 Stir and heat the solution to 70 ± 5°C for approximately 15 min. Monitor the temperature using a thermometer or thermocouple.

A4.4.1.4 Dry two Whatman No. 1 filter papers in a 100 ± 5°C oven for approximately 15 min. Remove both filter papers from the oven and place them in the desiccator to cool.

A4.4.1.5 After cooling for at least 10 min, weigh the filter papers to the nearest 0.0001 g.

A4.4.1.6 Place the weighed filter papers on the filter apparatus and transfer the contents of the beaker to the filter paper.

A4.4.1.7 Wash the beaker with xylenes to transfer any remaining particulate matter.

A4.4.1.8 Wash the filter papers with xylenes until there is an absence of color in the solution passing through the filters.

A4.4.1.9 Place the filter papers in the 100 ± 5°C oven. After approximately 15 min, remove the filter papers from the oven and place in a desiccator to cool.

A4.4.1.10 After cooling for at least 10 min, weigh the filter papers and record the mass to the nearest 0.0001 g.

A4.4.2 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.

A4.5 Calculations

A4.5.1 The mass % of the insoluble is calculated as follows:

$$I = (W_3 - W_2)/W_1 \cdot 100 \quad (A4.1)$$

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.

A4.5.2 The mass % of the active dye is calculated as follows:

$$D = 100 - I - M \quad (A4.2)$$

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.

A5. QUALITATIVE CONFIRMATION OF RED DYE

INTRODUCTION

This annex is an explanation about extracting and concentrating very low levels of red dye (see 3.2.1) in the aviation turbine fuel to confirm the result obtained using this test method, results from red dye and not color bodies arising from the crude oil or the refining process.

A5.1 Scope

A5.1.1 This annex describes the concentration of the red dye in the aviation turbine fuel. The presence of the dye is confirmed qualitatively by comparing the spectrum of the concentrated red dye with the spectrum reproduced in Fig. A5.1.

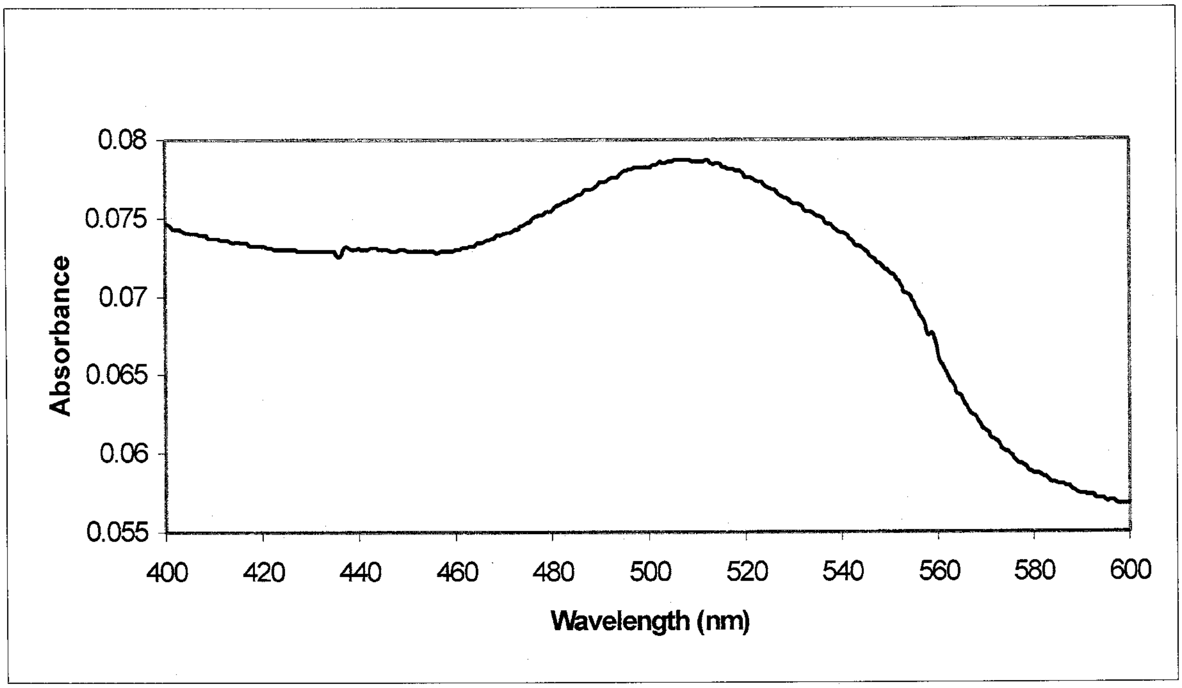

FIG. A5.1 Spectrum of Red Dye (0.12 ppm) in MTBE Acquired Using a 10 cm Cell

A5.2 Apparatus

A5.2.1 *Standard Chromatographic Tube,* Corning No. 38450.

A5.2.2 *Spectrophotometer,* equipped to measure the absorbance of solutions in the spectral region from 380 to 780 nm with an effective spectral slit width of 10 ± 2 nm or 5 ± 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 %.

A5.2.3 *Sample Cells,* constructed of optical glass or quartz having a path length of 1 ± 0.001 cm.

A5.2.4 *Beakers,* 50 mL and 250 mL.

A5.2.5 *Graduated Cylinder,* 100 mL.

A5.2.6 *Oven,* capable of controlling temperature at 160°C to at most ±5°C.

A5.2.7 *Stirring Rod.*

A5.2.8 *Hot Plate.*

A5.2.9 *Desiccator.*

A5.3 Reagents and Materials

A5.3.1 *Silica Gel,* manufactured to conform to the specifications described in Test Method D1319.

A5.3.2 *Hexane.*

A5.3.3 *Methyl Tert-butyl Ether,* MTBE.

A5.4 Procedure

A5.4.1 Activate the silica gel by transferring 50 g to a clean, dry, 250 mL beaker. Place the beaker containing the silica gel into an oven set at 160 ± 5°C. After 1 h remove the silica gel from the oven, and let it cool to room temperature in a desiccator.

A5.4.2 Pour the cooled silica gel into the clean, dry chromatographic tube. Rinse the column with hexane while tapping to ensure the column is well packed. If the aviation turbine fuel has a Saybolt color less than +22, add an additional 100 mL of hexane.

A5.4.3 Measure 100 ± 1 mL of the aviation turbine fuel sample using a graduated cylinder and add sample to the top of the column. Rinse the graduated cylinder with a small portion of hexane and add the washing to the column. Gently stir to mix the aviation turbine fuel with the hexane previously added to the column. Rinse the stirring rod with hexane into the column with no more than 10 mL of fresh hexane.

A5.4.4 Pass the aviation turbine fuel sample and hexane mixture over the silica gel at a rate not exceeding 8 mL/min. Collect the effluent in a beaker. If visible color is observed to elute from the column, immediately stop the elution, and replace the collection beaker with a clean, dry beaker. Proceed with the elution. Rinse the sides and walls of the column. Discard the colorless effluent.

A5.4.5 Elute the dye using at least 20 mL of MTBE. Use a 50 mL beaker to collect the eluent.

A5.4.6 If colored hexane is collected from A5.4.4, treat the colored hexane eluent collected in A5.4.4 by repeating A5.4.1, A5.4.2, A5.4.4, and A5.4.5. Combine the portions obtained from A5.4.5.

A5.4.7 Evaporate the MTBE solution to less than 10 mL. Heat (<50°C) may be used to assist the evaporation.

A5.4.8 Transfer the MTBE solution to a spectrophotometer sample cell having a 10 cm path length. Wash the beaker with additional portions of MTBE then completely fill the spectrophotometer cell with MTBE. Gently agitate the contents of the cell to ensure complete mixing.

A5.4.9 Record the absorption spectrum in the 400 to 600 nm spectral region using a 10 cm cell. Measure the absorption spectrum compared to MTBE. Compare the spectrum of the sample to the spectrum of red dye reproduced in Fig. A5.1. A spectral profile in the 520 nm wavelength region of the sample spectrum similar to the spectral profile in the 520 nm wavelength region of the red dye spectrum in Fig. A5.1 qualitatively confirms the presence of red dye.