Designation: D7827 – 12

Standard Test Method for Measuring n-Heptane Induced Phase Separation of Asphaltene from Heavy Fuel Oils as Separability Number by an Optical Device[1]

This standard is issued under the fixed designation D7827; 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 quantitative measurement, either in the laboratory or in the field, of how easily asphaltene-containing heavy fuel oils diluted in toluene phase separate upon addition of heptane. The result is a separability number (%). See also Test Method D7061.

1.2 The test method is limited to asphaltene-containing heavy fuel oils. ASTM specification fuels that generally fall within the scope of this test method are Specification D396, Grade Nos. 4, 5, and 6, Specification D975, Grade No. 4-D, and Specification D2880, Grade Nos. 3-GT and 4-GT. Refinery fractions from which such blended fuels are made also fall within the scope of this test method.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D396 Specification for Fuel Oils

D975 Specification for Diesel Fuel Oils

D2880 Specification for Gas Turbine Fuel Oils

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D7061 Test Method for Measuring n-Heptane Induced Phase Separation of Asphaltene-Containing Heavy Fuel Oils as Separability Number by an Optical Scanning Device

3. Terminology

3.1 *Definitions:*

3.1.1 *asphaltenes* (rarely used in the singular), *n—in petroleum technology*, represent an oil fraction that is soluble in a specified aromatic solvent but separates upon addition of an excess of a specified paraffinic solvent.

3.1.1.1 *Discussion*—In this test method, the aromatic solvent is toluene and the paraffinic solvent is heptane.

3.1.2 *compatibility, n—of crude oils or of heavy fuel oils*, the ability of two or more crude oils or fuel oils to blend together within certain concentration ranges without evidence of separation, such as the formation of multiple phases.

3.1.2.1 *Discussion*—Incompatible heavy fuel oils or crude oils, when mixed or blended, result in the flocculation or precipitation of asphaltenes. Some oils may be compatible within certain concentration ranges in specific mixtures, but incompatible outside those ranges.

3.1.3 *flocculation, n—of asphaltenes from crude oils or heavy fuel oils*, the aggregation of colloidally dispersed asphaltenes into visibly larger masses that may or may not settle.

3.1.4 *peptization, n—of asphaltenes in crude oils or heavy fuel oils*, the dispersion of asphaltenes to produce a colloidal dispersion.

3.1.5 *stability reserve, n—in petroleum technology*, the property of an oil to maintain asphaltenes in a peptized state and prevent flocculation of the asphaltenes.

3.1.5.1 *Discussion*—An oil with a low stability reserve is likely to undergo flocculation of asphaltenes when stressed (for example, extended heated storage) or blended with a range of other oils. Two oils each with a high stability reserve are likely to maintain asphaltenes in a peptized state and not lead to flocculation when blended together.

3.1.6 *transmittance, n—of light*, the fraction of the incident light of a given wavelength that is not reflected or absorbed, but passes through a substance.

3.2 *Definitions of Terms Specific to This Standard:*

[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 D02.14 on Stability and Cleanliness of Liquid Fuels.

Current edition approved Nov. 1, 2012. Published March 2013. DOI: 10.1520/D7827-12.

[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.

3.2.1 *SEPView 6.1, n*—the name of a proprietary computer program designed to allow automatic control of test and calculations of the results in Test Method D7827.

3.2.2 *separability number, n—in petroleum technology*, the standard deviation of the average transmittance, determined in this test method, expressed as a percentage figure.

3.2.2.1 *Discussion*—The separability number estimates the stability reserve of the oil, where a high separability number indicates that the oil has a low stability reserve and a low separability number that the oil has a high stability reserve.

3.2.3 *SEPCalc, n*—the name of a proprietary computer program modul of SEPView, designed to allow automatic calculation of the results in Test Method D7827.

3.2.4 *STEP-Technology, n*—parallel light (I_0) illuminates the entire sample cell and the transmitted light I is detected by multiple sensors with a µm-scale resolution arranged linearly from top to bottom. Transmission is recorded time- and space-resolved and may be converted into extinction by lg I/I_0.

4. Summary of Test Method

4.1 Dilution of oil with toluene followed by addition of heptane causes asphaltenes to flocculate, and the oil to phase separate. The rate of the phase separation is determined by measuring the increase in transmittance in the sample from the bottom of a test tube to the top (or a portion thereof) over time. The standard deviation of the average transmittance from a number of consecutive automatic measurements gives a separability number (%).

4.2 The oil is diluted with toluene in ratios that depend on the oil type. Mix 2 mL of the oil/toluene solution with 23 mL of heptane. Transfer 3.5 mL of the oil/toluene/heptane mixture into a disposable optical cell that is inserted into an optical scanning device.

4.3 The change in light transmittance through the cell is recorded by proprietary STEP-Technology instantaneously over the entire sample height without scanning. Measurements are taken periodically every 10 s for 15 min. An average of the transmittance is calculated from each reading of each of the 91 transmission profiles at each 0.007 mm distance along the optical cell, starting from the bottom of the cell and continuing up to 44 mm. The separability number from multiple measurements is calculated and reported.

5. Significance and Use

5.1 This procedure describes a rapid and sensitive method for estimating the stability reserve of an oil. The stability reserve is estimated in terms of a separability number, where a low value of the separability number indicates that there is a stability reserve within the oil. When the separability number is between 0 to 5, the oil can be considered to have a high stability reserve and asphaltenes are not likely to flocculate. If the separability number is between 5 to 10, the stability reserve in the oil will be much lower. However, asphaltenes are, in this case, not likely to flocculate as long as the oil is not exposed to any worse conditions, such as storing, aging, and heating. If the separability number is above 10, the stability reserve of the oil is very low and asphaltenes will easily flocculate, or have already started to flocculate.

5.2 This test method can be used by refiners and users of heavy oils, for which this test method is applicable, to estimate the stability reserves of their oils. Hence, this test method can be used by refineries to control and optimize their refinery processes. Consumers of oils can use this test method to estimate the stability reserve of their oils before, during, and after storage.

5.3 This test method is not intended for predicting whether oils are compatible before mixing, but can be used for determining the separability number of already blended oils. However, experience shows that oils exhibiting a low separability number are more likely to be compatible with other oils than are oils with high separability numbers.

6. Apparatus

6.1 *Computer executing software SEPView*[3], from a portable storage media or directly from the computer. SEPView controls the apparatus, acquires the data and accumulates it in a database on the portable storage media, the hard disk in the computer or at a server.

6.2 *Optical Device*—The apparatus[3] consists of an illumination system, composed of a pulsed infrared light source that uses a wavelength of 870 nm (± 10 nm) and means to parallelize and expand the light to illuminate the entire specimen height. A high-resolution line detector is situated opposite from the light source and reads the transmittance through the vertical midline of the optical cell (6.3) containing the specimen. The transmittance is automatically and instantaneously recorded at every pixel with a position resolution of 0.007 mm (STEP-Technology (trademarked)[3]). Time interval between each recording shall be 10 s. Total measurement time shall be 15 min. The measuring principle is schematically shown in Fig. 1. Each measured transmittance profile along the optical cell is automatically stored on the hard disk in the computer or at a server and can be further processed as described in Section 10 and Annex A2.

6.3 *Rectangular Transparent Disposable Optical Polyamid cells (PA-cells) with PP-stopper,* 5 mL capacity, cross-section 8 mm × 10 mm (optical path), wall thickness 1 mm and 80 mm high, shall be used as a sample container.

6.4 *Pipette, Graduated or Automatic,* 5 and 10 mL.

6.5 *Graduated Cylinder,* 25 mL.

6.6 *Clear Glass Bottle with Cap,* 250 mL.

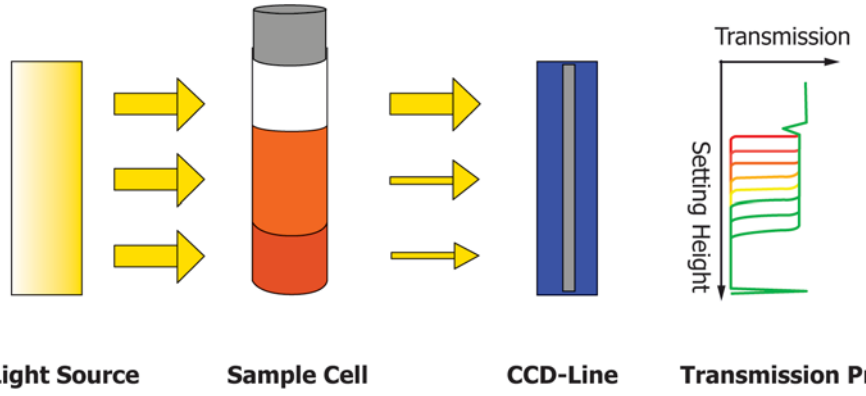
6.7 *Clear Glass Bottle with Cap,* 50 mL.

6.8 *Magnetic Bar,* PTFE-coated.

6.9 *Magnetic Stirrer.*

6.10 *Balance,* precision ±0.01 g.

[3] The sole source of supply of the optical device (LUMiReader 413-1 (one channel) or LUMiReader 413-3 (three channel)), and corresponding software (SEPView 6), known to the committee at this time is available from LUM GmbH, Justus-von-Liebig-Str.3, 12489 Berlin, Germany.



NOTE 1—First measured profile after 1 s in red. Last profile after 15 min in green.

FIG. 1 Representation of a Typical Measurement Scheme Using an Optical Device Based on STEP-Technology.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagents of technical grade (95 % purity) and higher are adequate for this test.

7.2 *Heptane.* (**Warning—**Flammable. Vapor harmful. Vapor may cause flash fire.)

7.3 *Toluene.* (**Warning—**Flammable. Vapor harmful. Vapor may cause flash fire.)

8. Sampling and Test Specimens

8.1 The oil sample collected for the purpose of this test method shall be representative of the batch of oil. Obtain the sample in accordance with the procedures of Practice D4057 or D4177, if possible.

8.2 When working with the oil sample in the laboratory, the oil shall be stirred either manually or mechanically until the mixture is homogenous and representative for the whole sample before withdrawing an aliquot for testing.

8.3 When working with solid or highly viscous oils, the oil may be heated (for example, on a heating plate, in an oven, or, if a drum is heated, by an electrical heating belt or steam shed) to obtain a lower viscosity prior to weighing and mixing. It is then important that the whole sample is fluid to ensure a homogenous mixture and that the sample withdrawn is representative of the whole sample.

8.3.1 Heating has to be performed in closed containers. Avoid heating above 60°C and more than 60 min.

9. Procedure

9.1 With the aim to increase and achieve a comparable transmittance for all types of oils, weigh 15 g of the oil sample and dilute with toluene, in a weight ratio in accordance with Annex A1, in a bottle with cap (6.6), and shake the bottle well. Add a magnetic bar to the oil-toluene solution. Put the bottle on a magnetic stirrer and stir the mixture for a minimum of 1 h but not more than 3 h.

9.2 Prepare the instrument for measuring by turning it on and make preparations so that consecutive measurements can be run automatically every 10 s for 15 min. For more detailed instructions, see Annex A2.

9.3 Using a graduated cylinder, transfer 23 mL of n-heptane into a glass bottle (6.7). Use a pipette to add 2 mL of the oil/toluene mixture prepared in 9.1 to the heptane and shake the mixture briskly for exactly 6 s.

9.4 Use a pipette to transfer 3.5 mL of the oil-toluene-heptane mixture immediately into the optical cell and close with the stopper (6.3).

9.5 Immediately place the cell, with stopper, in the instrument (6.2) at ambient temperature (for example, 25°C), close the lid. Measurements start automatically.

NOTE 1—The transmittance through the rectangular optical cell is now recorded every 10 s for 15 min and stored by the software on the hard disk of the computer or the server.

9.6 When the measurements are finished, remove the disposable optical cell from the optical device, and dispose of it in an environmentally safe way.

10. Calculation and Interpretation of Results

10.1 *Calculation of Results:*

10.1.1 The following calculations may be run automatically, using the modul SEPCalc of the software SEPView (described in Annex A2) or the data may be exported to another piece of software for manual analysis.

10.1.2 Analyze the transmittance between 0 to 44 mm, that is, calculate the average transmittance (X_i) recorded in this region for each transmission profile.

10.1.3 Calculate the total average transmittance (X_T) of each of the 91 measurements.

10.1.4 Calculate the separability number using Eq 1.

$$\text{Separability number} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - X_T)^2}{n-1}} \quad (1)$$

where in the case of 91 profiles:

X_i = average transmittance for each of the transmission profiles,

X_T = average of $X_i (X_T = (X_1 + X_2 \ldots + X_{91}) / 91)$ and

n = the number of replicated profiles (91 in the test method).

10.2 *Interpretation of Results:*

10.2.1 The separability number is a rate-related factor that gives a measure of how easily asphaltenes destabilize upon addition of heptane. Phase separation is due to asphaltene flocculation and sedimentation. As asphaltenes fall out of solution, the transmittance through the sample increases. There will be a rapid change in transmittance if this process is quick, resulting in a high separability number. A high number shows that the stability reserve of the oil is poor, while a low number shows that there is a stability reserve in the oil. The separability number is presented in percent transmittance.

11. Report

11.1 Report the following information:

11.1.1 The toluene dilution ratio (in accordance with Annex A1).

11.1.2 The separability number of the oil sample as the change in percent transmittance to the nearest 0.1 %.

12. Precision and Bias

12.1 *Interim Precision*—The repeatability standard deviation obtained by the same operator with the same apparatus under constant operating conditions is presented below:

Sample	Mean of Separability Number (%)	Number of Samples	Standard Deviation (%)	95% Confidence interval (1.96 σ)
a)	0.16	8	0.04	0.08
b)	1.84	6	0.33	0.65
c)	1.68	6	0.15	0.29
d)	5.41	4	0.64	1.25
e)	9.92	15	0.40	0.78
f)	13.64	3	0.35*	0.69

Legend:
crude oil*
a) East Africa
b) Alaska
c) GOM
d) North Sea
e) Baker
f) CLOF C

12.1.1 The data displayed above were obtained for heavy fuel oils and one crude oil*. The number of measurements made for each sample is indicated in column 2. The toluene dilution ratio was 1:9.

12.2 *Reproducibility*—A round robin test is being developed and the reproducibility of this test method will be determined and available within five years.

12.3 *Bias*—Today there is no accepted reference material suitable for testing the stability reserve of oils (in this test method estimated as a separability number) and bias has so far been impossible to determine.

13. Keywords

13.1 asphaltene; asphaltene separation; compatibility; heavy fuels oils; phase separation; separability number; stability reserve; transmittance

ANNEXES

(Mandatory Information)

A1. OIL: TOLUENE DILUTION RATIOS

TABLE A1.1 Dilution Ratios (in Mass Ratio) of Oil with Toluene

Standard Specification for Fuel Oils	Oil: Toluene Ratio (Weight)
D396	
Grade No. 4[A]	1:3
Grade No. 5	1:6
Grade No. 6	1:9
D975	
Grade No. 4D	1:9
D2880	
Grade No. 3-GT[A]	1:6
Grade No. 4-GT[A]	1:9
Refinery Fractions	
Straight run fuels	1:6
Residue from visbreaker	1:9
Unknown Oil Grade, Refinery Fraction or Blended Oil Samples	1:9

[A] In the presence of asphaltenes in the fuel.

A2. CALCULATION OF SEPARABILITY NUMBER WHEN USING THE SOFTWARE SEPView

A2.1 To prepare the measurement (9.2), lock into the software SEPView 6.1 or higher.

A2.1.1 Choose under "SEPView Explorer" folder "SOP."

A2.1.2 Click on "Separability Number Determination, 91 Profiles." The predefined SOP will be displayed.

A2.1.3 Click on "Next" and enter the sample name(s) and compulsatory any commentary(ies). Start measurement.

A2.1.4 Prepare the sample (according to 9.3 and 9.4).

A2.1.5 After the optical cell(s) has(ve) been inserted in the instrument (9.5), close the lid and measurement starts automatically without delay.

A2.1.6 After 15 min, data and all settings are automatically stored into the database and measurements stops.

A2.2 The separability number will be calculated automatically by the modul SEPCalc of SEPView.

A2.2.1 Choose "SEPView Explorer."

A2.2.2 Choose up to 24 "Sample data records" of interest. After clicking corresponding transmission profiles are displayed.

A2.2.3 Click on "Advanced Analysis" at the Ribbon line and thereafter on "SEPCalc."

A2.2.4 A table of Separability Numbers according to 10.1 is displayed together with an estimate of the stability reserve of the oil (low, medium, or high) and all measurement and statistical details.

A2.2.5 Print the report or save the analysis report under an assigned name.

NOTE A2.1—Raw data (transmission values for each position within the sample and the measurement time) for manual evaluation may be transferred to any program importing CSV-formatted files.