



Designation: D 6748 – 02a

An American National Standard

Standard Test Method for Determination of Potential Instability of Middle Distillate Fuels Caused by the Presence of Phenalenes and Phenalenones (Rapid Method by Portable Spectrophotometer)^{1,2}

This standard is issued under the fixed designation D 6748; 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 This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.14 on Stability and Cleanliness of Liquid Fuels.

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² This test method is being jointly developed with the Institute of Petroleum where it is designated IP 463.

1. Scope

1.1 This test method covers a procedure³ for the rapid determination of phenalenes and phenalenones in middle distillate fuels, including marine, automotive, heating, and gas turbine fuel such as those specified in Specifications D 396, D 975, D 2069, and D 2880. Phenalenes and phenalenones affect the potential instability of fuels, leading to fuel degradation products during storage, which may cause performance problems.

1.2 This test method is applicable to both dyed and undyed fuels at all points in the distribution chain from refinery to end-user. It is not applicable to fuels containing residual oil. The portable apparatus allows the whole test to be conducted on site or in a laboratory and does not require the test sample to be heated.

1.3 This test method is suitable for testing samples with a relative absorbance of up to 5.00 absorbance units (AU).

NOTE 1—The precision of the test method has been established on relative absorbance up to 1.00 AU. For relative absorbance above 1.00 AU the precision may not apply.

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:

D 396 Specification for Fuel Oils⁴

D 975 Specification for Diesel Fuel Oil⁴

D 2069 Specification for Marine Fuels⁴

D 2880 Specification for Gas Turbine Fuel Oils⁵

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁵

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁵

D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination⁵

D 4625 Test Method for Distillate Fuel Storage Stability at 43°C (110°F)⁵

D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products⁶

D 6468 Test Method for High Temperature Stability of Distillate Fuels⁷

E 131 Terminology Relating to Molecular Spectroscopy⁸

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible and Near-Infrared Spectrophotometers⁸

2.2 Other Standards:⁹

Def Stan 05-50 Methods for Testing Fuels and Lubricants and Associated Products, Part 40 — Storage Stability of Diesel Fuels

Def Stan 91-4 Fuel, Naval, Distillate NATO Code: F76 Joint Service, Designation DIESO F76

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms relating to absorption spectroscopy see Terminology E 131. Terms of particular significance are the following:

3.1.2 *radiant energy, n*—energy transmitted as electromagnetic waves.

3.1.3 *radiant power P, n*—the rate at which energy is transported in a beam of radiant energy.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *absorbance, A, n*—the logarithm to the base 10 of the reciprocal of the transmittance, *T*. In symbols:

$$A = \log_{10}(1/T) = -\log_{10}T \quad (1)$$

where:

T = transmittance as defined in 3.2.5.

3.2.2 *absorbance units (AU), n*—units of relative absorbance reported by the portable spectrophotometer.

3.2.3 *pathlength of test portion b, n*—the distance in mm, measured in the direction of propagation of the beam of radiant energy, between the surfaces of the portion on which the radiant energy is incident and the surface of the test portion from which it emerges.

³ This process is covered by US Patent 5,378,632. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patented item to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

⁴ Annual Book of ASTM Standards, Vol 05.01.

⁵ Annual Book of ASTM Standards, Vol 05.02.

⁶ Annual Book of ASTM Standards, Vol 05.03.

⁷ Annual Book of ASTM Standards, Vol 05.04.

⁸ Annual Book of ASTM Standards, Vol 03.06.

⁹ Available from United Kingdom Defence Standardization, Room 1138, Kentigern House, 65 Brown Street, Glasgow, G2 8EX. United Kingdom.

3.2.4 *relative absorbance, n*—the difference between the absorbance (near infrared-visible band results) measured at the two wavelengths, and reported in AU.

3.2.5 *transmittance, T, n*—the ratio of the radiant power transmitted by the test portion in the test cuvette to the radiant power transmitted by the Reagent 1 control in the cuvette. Expressed in the following equation.

$$T = P_T/P_{R1} \quad (2)$$

where:

P_T = radiant power transmitted by the test portion, and

P_{R1} = the radiant power transmitted by the Reagent 1 control.

4. Summary of Test Method

4.1 A 5 mL volume of middle distillate fuel is mixed with an equal volume of an immiscible reagent solution. A second reagent is then added, the new blend mixed and allowed to settle for 30 min. for two phases to separate. The top reagent layer (darker) is then placed in the portable spectrophotometer and the relative absorbance of near infrared and visible light, at fixed single wavelengths, is measured instantaneously and automatically, and reported in AU.

4.2 When mixed with the oil sample containing phenalenes, the oxidizing Reagent 2 oxidizes the phenalenes to phenalenones which are subsequently converted to coloured indolylphenalene salts by the acidic Reagent 1. The spectrophotometer measures the absorbance of light caused by the colored salts while eliminating the effect of the initial color of the fuel. The absorbance of light is a measure of the concentration of the colored salts that are formed.

5. Significance and Use

5.1 Storage stability depends on complex interactions. It varies with feedstock type and source, and the processing used. The rate of degradation may not change uniformly with temperature. Chemical reactions may lead to a change in color followed by the formation of soluble gums and insoluble sediments. Insoluble sediments may overload filters, and plug nozzles and injectors.

5.2 This test method, which does not require the test sample to be heated, uses a portable apparatus and allows tests to be carried out on site or in the laboratory to give a result within 35 mins.

5.3 The potential beneficial effects of stability additives in fuels may not be recognized by this test method. Therefore, the actual storage stability of middle distillate fuels with stability additives may not be correctly indicated by these test results.

5.4 The unstable reactive compounds (phenalenes and phenalenones) detected by this test method may be present in fuels containing catalytically cracked or straight run materials and can affect the potential instability of the fuel.

5.5 If this test method is used by any party for a rapid assessment of stability, it is the responsibility of parties concerned to decide whether or not this procedure yields meaningful results.

5.6 Interpretation of results and correlation with other test methods is given in Appendix X1.

6. Apparatus ¹⁰

6.1 *Spectrophotometer*, double beam, capable of measuring absorbance at one visible wavelength in the range 600-800 nm and one near infra-red wavelength in the range 800-850 nm with a spectral bandwidth of 10 nm ± 2 nm and an accuracy of ± 3 nm (see Fig. 1). The display shall have a resolution of 0.01 of AU, and a repeatability of measurement of ± 0.02 AU for ranges up to 1.00 AU. See Practice E 275.

¹⁰ The equipment, as listed in RR: D02-1522 was used to develop the precision statement. The apparatus described in Section 6 and the reagents listed in Section 7 are both supplied by Stanhope-Seta, Chertsey, Surrey KT16 8AP, United Kingdom. To date, no other equipment has demonstrated through ASTM interlaboratory testing the ability to meet the precision of this test. This is not an endorsement or certification by ASTM International.

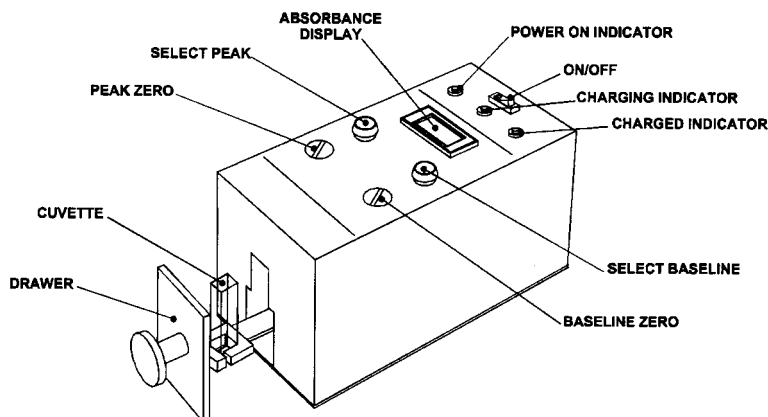


FIG. 1 Spectrophotometer

NOTE 2—The two wavelengths used are proprietary and are not adjustable.

6.1.1 *Zero Adjustment*, a facility shall be incorporated to allow the absorbance measured at the two individual wavelengths to be set to zero when using Reagent 1 as a control.

6.1.2 *Absorbance Display*, the relative absorbance, in AU, shall be the instantaneous difference between the absorbance measured at the two wavelengths. The peak wavelength represents the absorption due to the colored indolylphenalene salts which are formed, and the baseline wavelength is for normalizing the result.

6.2 *Timer*, capable of measuring 35 mins to an accuracy of ± 0.2 mins.

6.3 *Dispenser*, for Reagent 1 made of polyethylene, polypropylene, or glass and capable of dispensing 5 mL of reagent with an accuracy of ± 0.5 mL.

6.4 *Syringe 1*, for test portion, 5 mL, polyethylene, polypropylene, or glass, with an accuracy of ± 0.25 mL.

6.5 *Syringe 2*, for Reagent 2, pre-set at 35 μL , glass, with an accuracy of ± 0.35 μL .

6.6 *Test Tube with Stopper*, nominally 15 mL, polyethylene, polypropylene, or glass.

6.7 *Pipette*, 5 mL, polyethylene, polypropylene, or glass.

6.8 *Test Cuvette*, 4.5 mL volume, optical methacrylate, disposable, with two opposite ribbed sides. Dimensions shall be 45 mm high, 12.5 mm by 12.5 mm in width with a test portion pathlength 10 mm ± 0.25 mm.

7. Reagents and Materials

7.1 *Reagent 1*, proprietary, methanol solvent containing a Lowry-Bronsted acid¹⁰ (**Warning**—Acidic, flammable, toxic, irritant-).

7.2 *Reagent 2*, proprietary solution containing potassium permanganate¹⁰ an oxidizing agent (**Warning**—Oxidizing agent, toxic, irritant-).

7.3 *Water*, distilled or deionized, for flushing Syringe 2 used for Reagent 2.

8. Sampling

8.1 *Field Sampling*—Take field samples in accordance with Practices D 4057, D 4177, or other comparable sampling practices. Record the sampling date. Sample bulk fuel above its cloud point and thoroughly mix prior to aliquot sampling. For shipping field samples, use only epoxy-lined steel cans that have been cleaned according to Practice D 4306.

8.2 Store samples at normal room temperature (20 to 25°C) or colder.

8.3 Filter samples which contain free water or a water haze through a qualitative filter paper or a loose plug of cotton to remove such water.

8.4 *Laboratory Subsampling*—Sample fuel above its cloud point and thoroughly mix prior to aliquot sampling. At least 5 mL of sample is required for each test. Follow Practices D 4057 and D 5854. Use clean amber or clean borosilicate glass containers for laboratory handling. Shield fuel in clear bottles from sunlight to prevent photochemical reactions. Other laboratory containers may be used provided they are shown not to affect the results of the test.

8.5 Allow the test sample to reach the local ambient temperature (10 to 30°C) before commencing the test.

9. Preparation and Calibration of Apparatus

9.1 For portable use ensure that the battery has been charged.

9.2 *Zeroing the Spectrophotometer*— Turn on the portable spectrophotometer for at least 2 mins. Fill a test cuvette with Reagent 1, to within 5 mm of its top. Place the filled test cuvette into the spectrophotometer drawer. Zero both wavelengths individually by separately pressing each select button and turning the corresponding zero button until 0.00 AU is displayed.

9.2.1 Dispose of the cuvette and the aliquot of Reagent 1. Do not reuse the cuvette.

NOTE 3—The spectrophotometer is correctly calibrated if the two wavelength readings are 0.00 ± 0.01 AU.

9.3 *Verification*—A verification fluid is under development.

10. Procedure

10.1 Pour 5 mL of Reagent 1 into a test tube and add a 5 mL aliquot of the test sample using Syringe 1. Stopper the test tube and vigorously shake the test tube for $10 \text{ s} \pm 2 \text{ s}$.

10.2 Remove the stopper and add 35 μL of Reagent 2 using Syringe 2. Stopper the test tube and vigorously shake the test tube for $10 \text{ s} \pm 2 \text{ s}$. Allow to settle for 30 to 35 mins.

10.3 Switch on the spectrophotometer at least 2 mins before the end of the 30 min period.

10.4 At the end of the 30 min period, use a pipette to draw the darker reagent layer (at the top) from the test tube and to transfer that liquid to the test cuvette. Fill the cuvette to within 5 mm of its top. (**Warning**—Hold the cuvette using the two ribbed sides to avoid affecting the optical path.)

10.5 Place the cuvette (with the ribbed side towards the drawer handle) in the spectrophotometer and close the drawer.

10.6 Record the results from the digital display every $60 \text{ s} \pm 5 \text{ s}$ until two readings agree within 0.02 AU and report the second of these reading as the measured relative absorbance. Record a negative result as zero.

11. Report

11.1 Report the source, type, and identification of the material tested, plus the dates sampled and tested.

11.2 Refer to this test method and report any deviation, by agreement or otherwise, from the procedure specified.

11.3 Report the result of the test in absorbance units to the nearest 0.01 AU.

12. Precision and Bias ¹¹

12.1 The precision of this test method, as determined by statistical analyses of interlaboratory results, is as follows:

12.2 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions, on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following only in one case in twenty.

$$r = 0.0876 (x + 0.2) AU \quad (3)$$

where:

x = average of results being compared.

12.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal correct operation of the test method, exceed the following only in one case in twenty.

$$R = 0.1799 (x + 0.2) AU \quad (4)$$

where:

x = average of results being compared.

12.4 *Bias*—Since there is no accepted reference material suitable for determining the bias of the procedures in Test Method D 6748, bias cannot be determined.

13. Keywords

13.1 absorbance units; burner fuel; diesel fuel; infra-red; infrared spectrophotometer; marine fuel; middle distillate fuel; potential instability; spectrometer; spectrophotometer; storage stability; turbine fuel; visible spectrophotometer

¹¹ Supporting data have been filed at ASTM International Headquarters. ~~R~~ and may be obtained by requesting Research Report RR: D02-1522.

APPENDIX

(Nonmandatory Information)

X1. INTERPRETATION OF RESULTS AND CORRELATION WITH OTHER TEST METHODS

X1.1 *Interpretation of Results:*

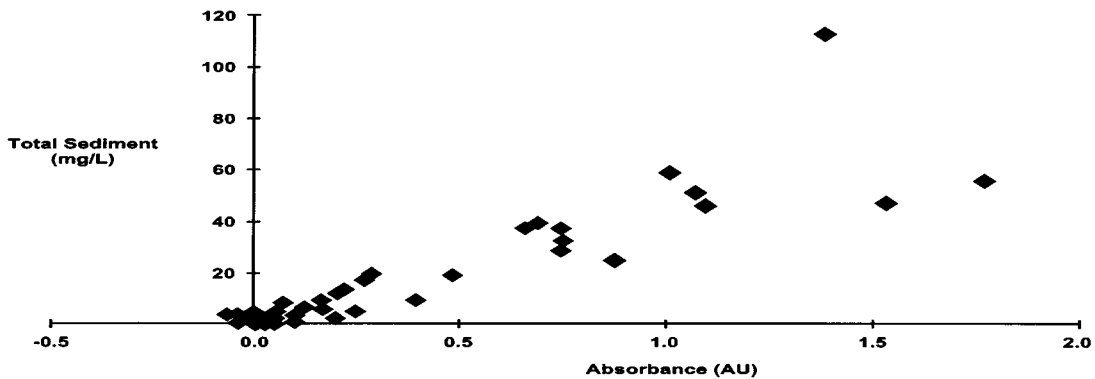
X1.1.1 The United Kingdom defense standard for NATO F-76 diesel fuel, Def Stan 91-4, allows the requirement to test the fuel by Def Stan 05-50 Part 40 (long test) (similar to Test Method D 4625) to be waived, if the result by this PI test, gives a relative absorbance of less than 0.20 AU. This level of absorbance has been deemed to be equivalent to 10 mg/L total sediment.

X1.1.2 The significance of results from this test method can be further estimated by comparing results with other test methods.

X1.2 *Correlation with Other Test Methods*—Further details of these correlations are available in the research report which is being prepared.

X1.2.1 *Results From a 1993 Test Program* —See Fig. X1.1.

X1.2.2 *Results From the 1999 Interlaboratory Test Program*—Fig. X1.2 compares the results determined by this test method (PI test) with results originally measured by Test Method D 4625 (three laboratories) during the Test Method D 6468 interlaboratory test program.



NOTE 1—These test results are reproduced by permission of the Defence Evaluation and Research Agency, United Kingdom.

FIG. X1.1 Correlation Between Test Method D 4625 and the Absorbance of 46 Fuels

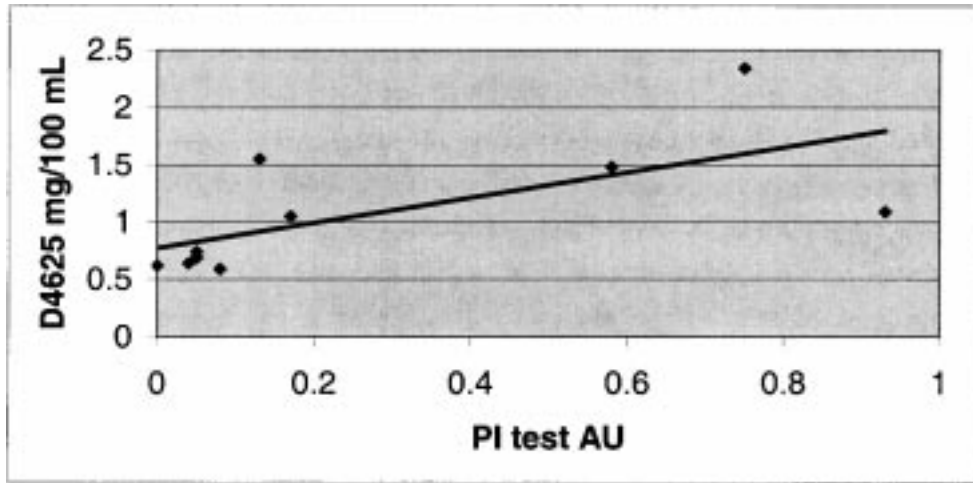


FIG. X1.2 Correlation Between Results Obtained by the PI Test and Test Method D 4625

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