



Designation: ~~D2008–12 (Reapproved 2018)~~ D2008 – 23

## Standard Test Method for Ultraviolet Absorbance and Absorptivity of Petroleum Products<sup>1</sup>

This standard is issued under the fixed designation D2008; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. ~~Scope~~ Scope\*

1.1 This test method covers the measurement of the ultraviolet absorption of a variety of petroleum products. It covers the absorbance of liquids or the absorptivity of liquids and solids, or both, at wavelengths in the region from 220 nm to 400 nm of the spectrum.

1.2 The use of this test method implies that the conditions of measurement—wavelength, solvent (if any), sample path length, and sample concentration—are specified by reference to one of the examples of the application of this test method in the annexes or by a statement of other conditions of measurement.

1.3 Examples of the application of this test method are the absorptivity of refined petroleum wax, and the absorptivity of USP petrolatum.

1.4 The values stated in SI units are to be regarded as the standard. The values stated in Fahrenheit, feet, and inches, indicated in parentheses, are for information only.

~~1.5 **Warning**—Mercury has been designated by many regulatory agencies as a hazardous substance that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Use Caution when handling mercury and mercury-containing products. See the applicable product Safety Data Sheet (SDS) for additional information. The potential exists that selling mercury or mercury-containing products, or both, is prohibited by local or national law. Users must determine legality of sales in their location.~~

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific warning statements, see 7.3.1, 7.3.3, and 13.4.*

1.6 *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:*<sup>2</sup>

<sup>1</sup> 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 D02.04.0F on Absorption Spectroscopic Methods.

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<sup>2</sup> 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

D1193 Specification for Reagent Water

E131 Terminology Relating to Molecular Spectroscopy

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

### 3. Terminology

3.1 Definitions of terms and symbols relating to absorption spectroscopy in this test method shall conform to Terminology E131. Terms of particular significance are the following:

3.2 *Definitions:*

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

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

3.2.3 *transmittance, T, n*—the molecular property of a substance that determines its transportability of radiant power, expressed by:

$$T = \frac{P}{P_o} \quad (1)$$

where:

$P$  = the radiant power passing through the sample and

$P_o$  = the radiant power incident upon the sample.

3.2.1 *absorbance, A, n*—the molecular property of a substance that determines its ability to take up radiant power, expressed by:

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

where T is the transmittance as defined in 3.2.33.2.6.

3.2.1.1 *Discussion*—

Absorbance expresses the excess absorption over that of a specified reference or standard. It is implied that compensation has been affected for reflectance losses, solvent absorption losses, and refractive effects, if present, and that attenuation by scattering is small compared with attenuation by absorption.

3.2.2 *absorptivity, a, n*—the specific property of a substance to absorb radiant power per unit sample concentration and path length, expressed by:

$$a = A/fbc \quad (2)$$

where:

$A$  = the absorbance defined in 3.2.1,

$f$  = the dilution factor defined in 3.2.3,

$b$  = sample cell path length, and

$c$  = the quantity of absorbing substance contained in a volume of solvent.

3.2.3 *dilution factor, f, n*—the proportion of solvent increase made to reduce the concentration and thus the absorbance of a solute, expressed by the ratio of the volume of the diluted solution to the volume of original solution containing the same quantity of solute as the diluted solution.

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

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

3.2.6 *absorptivity, a, transmittance, T, n*—the specific molecular property of a substance to absorb radiant power per unit sample concentration and path length, that determines its transportability of radiant power, expressed by:

$$a = A/fbc \quad (3)$$

$$T = \frac{P}{P_o} \quad (3)$$

where:

- $A$  = the absorbance defined in 3.2.4,
- $f$  = the dilution factor defined in 3.2.5,
- $b$  = sample cell path length, and
- $e$  = the quantity of absorbing substance contained in a volume of solvent.

- $\frac{P}{P_o}$  = the radiant power passing through the sample and
- $\frac{P_o}{P_o}$  = the radiant power incident upon the sample.

### 3.3 Definitions of Terms Specific to This Standard:

3.3.1 concentration,  $c$ ,  $n$ —the quantity of absorbing substance in grams per litre.

3.3.2 sample cell pathlength,  $b$ ,  $n$ —the distance in centimetres, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

#### 3.3.2.1 Discussion—

This distance does not include the thickness of the cell in which the specimen is contained.

~~3.3.2 concentration,  $c$ ,  $n$~~ —the quantity of absorbing substance in grams per litre.

## 4. Summary of Test Method

4.1 The ultraviolet absorbance of a liquid is determined by measuring the absorption spectrum of the undiluted liquid in a cell of known path length under specified conditions.

4.2 The ultraviolet absorptivity of a solid or a liquid is determined by measuring the absorbance, at specified wavelengths, of a solution of the liquid or solid at known concentration in a cell of known path length.

## 5. Significance and Use

[ASTM D2008-23](https://standards.iteh.ai/catalog/standards/sist/5342ada4-4b03-4b4b-9bae-aa7ba833230b/astm-d2008-23)

<https://standards.iteh.ai/catalog/standards/sist/5342ada4-4b03-4b4b-9bae-aa7ba833230b/astm-d2008-23>

5.1 The absorbance of liquids and the absorptivity of liquid and solids at specified wavelengths in the ultraviolet are useful in characterizing petroleum products.

## 6. Apparatus

6.1 *Spectrophotometer*, equipped to handle liquid samples in cells having sample path lengths up to 10 cm and capable of measuring absorbance in the spectral region from 220 nm to 400 nm with a spectral slit width of 2 nm or less. Wavelength measurement shall be repeatable and known to be accurate within  $\pm 0.2$  nm or less as measured by the ~~mercury emission line at 313.16 nm or the~~ absorption spectrum of either holmium oxide glass at 287.5 nm or holmium oxide solution at 287.1 nm. At the 0.4 absorbance level in the spectral region between 220 nm and 400 nm, absorbance measurements shall be repeatable within  $\pm 1.0$  %.

6.2 For recommended methods of testing spectrophotometers to be used in this test method, refer to Practice E275.

6.3 An instrument is considered suitable when it can be operated in a manner to give test results equivalent to those described in 6.1.

6.4 Measurements requiring the use of cells having sample path lengths less than 10 cm can be made on instruments equipped to handle only these cells. It is desirable, but not essential, that the instrument be automatic recording when an extended range of the spectrum must be examined. Manually operated spectrometers are suitable for obtaining absorbance readings at specified analytical wavelengths. If measurements are to be made at temperatures higher than room temperature, the spectrophotometer must be provided with a means for maintaining cells at the selected test temperature.

6.5 One or more pairs of fused silica cells having sample path lengths in the range from 0.1000 cm to 10.00 cm are required. Sample path lengths must be known to within  $\pm 0.5\%$  of nominal sample path length or better. Unless otherwise specified, 1 cm sample path length cells are recommended. Suitable procedures for testing and cleaning cells are described in Practice E275.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>3</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type III.

7.3 *Solvents*:

7.3.1 *Isooctane*—(**Warning**—Extremely flammable, harmful if inhaled.), for use as the preferred spectroscopic solvent.

7.3.2 Technical *isooctane* is a satisfactory base stock for the preparation of spectroscopic solvent. Allow about 4 L or 5 L of this material to percolate through a column of activated silica gel 50 mm to 75 mm (2 in. to 3 in.) in diameter and 0.6 m to 0.9 m (2 ft to 3 ft) in depth. Collect only the portion of the solvent that has an absorbance less than 0.05 over the entire spectral range from 240 nm to 300 nm in a 1 cm cell when compared to water in a 1 cm cell.

7.3.3 *Decahydronaphthalene (Decalin)*—(**Warning**—Combustible, vapors harmful.), for use as the first alternative spectroscopic solvent.

7.3.4 The silica gel percolation described in 7.3.2 is also recommended for the preparation of decahydronaphthalene as a spectroscopic solvent.

7.3.5 Some common, commercially available solvents of “spectroscopic purity” are listed in Practices E169. One of them can be selected for use in absorptivity measurements but only when indicated in Section 13.

7.4 *Holmium Oxide Glass or Holmium Oxide Solution*—Used to verify the wavelength accuracy of the spectrophotometer.

## 8. Sampling

8.1 Precautions must be taken to ensure that a representative sample is obtained since ultraviolet absorption is very sensitive to small amounts of extraneous material contaminating the sample through careless handling. If possible, samples should be obtained from packaged products that have been protected from accidental contamination.

8.2 If the petroleum product to be tested is available as a bulk sample weighing more than 1 kg, a representative sample of approximately 1 kg shall be taken and made homogeneous.

8.3 If the petroleum product to be tested is available as a bulk sample weighing less than 1 kg but more than 100 g, the entire sample shall be taken and made homogeneous.

8.4 In no case shall a sample of a petroleum product be considered representative if it weighs less than 100 g. However, measurements may be made on samples weighing less than 100 g if the origin, sampling procedure, and basis of selection of the sample are recorded and reported as part of the results of this test method.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications, ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Analytical 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.

## ABSORBANCE OF UNDILUTED LIQUIDS

### 9. Procedure

9.1 Fill a 1.0 cm reference cell with water. Make sure the cell windows are clean. Position the cells in the cell compartment of the spectrophotometer and obtain absorbance at the wavelengths of interest within the range from 220 nm to 400 nm. This data gives a cell correction for the 1.0 cm cell. It can be ignored at all wavelengths where the absorbance is between  $-0.01$  and  $+0.01$ . After the cell correction data has been determined, the cells shall be designated reference and sample cells and shall be maintained as such.

9.2 Fill a 1.0 cm sample cell with undiluted liquid sample (after complete removal of water) and obtain the absorbance as described in 9.1.

9.3 The absorbance-wavelength curve can be conveniently obtained starting at the long wavelength end of the spectrum. Take readings at successively shorter wavelengths until an absorbance greater than 1.0 is obtained. When using automatic recording instruments (recommended) make the cell correction scan and the sample scan on the same chart. In the longer wavelength region of the spectrum, it may be desirable to use longer path length cells than those recommended to obtain readable absorbances. See the applicable paragraph of Practices E169. In the shorter wavelength region of the spectrum, absorbances can become too high for accurate measurement in the 0.1 cm cell. Record these values only as greater than 1.0. If numerical values are required it is recommended that absorptivity be measured rather than absorbance.

9.4 Repeat 9.1 and 9.2 using a 0.1 cm cell, or a 0.5 cm cell when appropriate, in place of the 1.0 cm cell (9.3). Record all measurements.

### 10. Calculation

10.1 Calculate the absorbance of an undiluted liquid sample at each analytical wavelength as follows:

$$A = A_L - A_C \quad (4)$$

where:

$A$  = absorbance of undiluted liquid sample,

$A_L$  = chart or absorbance reading of sample-filled sample cell, and

$A_C$  = chart or absorbance reading of water-filled sample cell.

10.2 Calculate the absorbance per centimetre path length that is equal to  $A/b$ , where  $b$  is the sample cell path length in centimetres.

### 11. Report

11.1 If the numerical value of the absorbance of an undiluted liquid sample is reported, accompany it with a statement of the wavelength of measurement and the sample path length expressed in centimetres.

11.2 If the numerical value of the absorbance per centimetre of an undiluted liquid sample is reported, it must accompany it with a statement of the wavelength of measurement.

## ABSORPTIVITY OF SOLIDS AND LIQUIDS

### 12. Summary of Test Methods

12.1 The range of absorptivities for petroleum products can be very wide. Probably most absorptivities of interest would fall in the range from  $10^{-4}$  L/g-cm to 10 L/g-cm.

12.2 In determining absorptivities it is necessary to measure absorbances in the range from 0.1 to 1.0 for optimum results. This is done by preparing solutions and selecting cells of sample path length to give absorbances in the 0.1 to 1.0 range. For an individual petroleum product the absorptivity may change so rapidly with wavelength that it is necessary to prepare several

solutions in order to cover the required wavelength interval. Consideration must be given to the selection of solvent, the selection of concentration levels, and the selection of sample paths lengths to obtain optimum results.

### 13. Selection of Solvent

13.1 Refer to the applicable section of Practices E169 for a brief discussion of solvents for ultraviolet use. The choice of solvent is dictated by the solubility of the petroleum product and the transparency of the solvent in the region of interest.

13.2 Use *isooctane* unless restricted by solubility requirements.

13.3 Use decahydronaphthalene as the first alternative solvent to be used if the sample is not sufficiently soluble in *isooctane*.

13.4 If neither *isooctane* nor decahydronaphthalene will dissolve a sufficient quantity of sample to prepare the required solution, then one of the solvents listed in the table in Practices E169 may be used. As indicated in the table in Practices E169, not all of these solvents are usable over the entire spectral range covered by this test method. For the purposes of this test method a solvent shall be considered to have sufficient “spectroscopic purity” when its absorbance in a 1 cm cell, using reagent water in a 1 cm cell as a reference, is less than 0.05 at all wavelengths where a sample absorbance is to be measured in a 1 cm cell. Cyclohexane (**Warning**—Extremely flammable. Harmful if inhaled.), carbon tetrachloride, chloroform (**Warning**—Carbon tetrachloride and chloroform can be fatal if swallowed. Harmful if inhaled. Can produce toxic vapors if burned.), and the alcohols listed in the table in Practices E169 are useful alternative spectroscopic solvents.

### 14. Selection of Solution Concentration

14.1 Select an initial concentration of the sample high enough to provide measurable absorbance (0.1 to 1.0) at the wavelength of weakest absorption to be measured but not over 40 g/L and necessarily within the solubility limitations of the solvent.

14.2 The lowest concentration that can be prepared conveniently in the initial solution is about 1 g/L. If the sample is not sufficiently soluble at room temperature to prepare such a solution, then proceed at elevated temperature in accordance with Section 16.

14.3 Table 1 lists four recommended concentration levels for the initial solution and the required sample weights and solution volumes. Column 4 gives the range of absorptivities that will give absorbance readings between 0.1 and 1.0 when the solution is measured in a 1 cm cell.

14.4 Select from Table 1 the concentration required to measure the lowest absorptivity of interest in the sample. Note the recommended sample weights and solution volumes. These shall be used in preparing the initial solution of the sample.

14.5 If concentration levels lower than 1 g/L are required because absorptivities at the wavelengths of interest exceed 1, prepare an initial solution at the 4 g/L level (Table 1) and dilute as follows: pipet 1 mL to 10 mL of the initial solution into a 25 mL to 100 mL volumetric flask to obtain a dilution factor in the range from 2.5 to 100. Select dilution factors to obtain an absorbance reading in the range from 0.1 to 1.0 at the wavelength of measurement.

NOTE 1—For example, 1 mL of the initial solution (4 g/L) pipetted into a 25 mL volumetric flask, which is then filled to the mark with solvent and shaken, will give a dilution factor of 25 and a concentration level of 0.160 g/L in the first dilution. Repeating this procedure on the first dilution would produce

**TABLE 1 Recommended Sample Weights and Solution Volumes for Initial Solution of Sample**

Concentration, g/L	Sample Weight, mg <sup>A</sup>	Volumetric Flask, mL	Range of Absorptivities Measurable in 1 cm Cell <sup>B</sup>
40	1000	25	0.0025 to 0.0250
10	250	25	0.010 to 0.100
4	100	25	0.025 to 0.250
1	100	100	0.100 to 1.000

<sup>A</sup> The sample should be weighed to the nearest 0.1 mg and be within ±5 % of the nominal weight listed.

<sup>B</sup> If a 10 cm cell were used, the range of absorptivities measurable would be lowered by a factor of 10.

a second dilution containing 0.0064 g/L. The dilution factor for the second dilution would be 625.

## 15. Selection of Sample Path Length

15.1 Unless otherwise specified in a particular application of this test method, use a sample path length of 1.0 cm, and the alternative sample path length of 10.0 cm.

15.2 The procedures given in Sections 16 and 17 were written assuming the use of the recommended sample path length, 1 cm, and the use of the alternative sample path length, 10.0 cm. If in a particular application of this test method different sample path lengths are specified, the smaller shall become the recommended sample path length and shall be used where a 1.0 cm cell is specified. The larger shall become the alternative sample path length and shall be used where a 10.0 cm cell is specified.

## 16. Procedure at Room Temperature

16.1 Weigh by difference the recommended sample weight into the volumetric flask (see Table 1). Add solvent to partially fill the flask and shake to dissolve the sample. Fill to the mark with solvent. Mix well.

16.2 If sample does not go into solution rapidly, warm the solution by heating the flask under warm tap water. When the sample has dissolved, dilute to volume and shake to make homogeneous. Cool to room temperature. Add solvent to the mark.

16.3 Fill a 1.0 cm sample cell with the initial solution or dilution to be measured. Fill a 1.0 cm reference cell with solvent. Make sure the windows are clean. Position the cell in the cell compartment of spectrophotometer and measure the absorbance of the sample at wavelengths of interest within the range from 220 nm to 400 nm.

16.4 If the absorbance reading in the 1.0 cm cell is less than 0.1 at one or more of the wavelengths of interest, repeat 16.3 using a pair of 10 cm cells to obtain an absorbance reading in the 0.1 to 1.0 range.

16.5 If the absorbance reading in the 1.0 cm cell is greater than 1.0 at one or more of the wavelengths of interest, dilute to obtain absorbances in the readable range (0.1 to 1.0). Dilution factors of 2.5 to 100 can be obtained by pipetting volumes of 1 mL to 10 mL of the initial solution into 25 mL to 100 mL volumetric flasks and filling to the mark with solvent.

16.6 Determine the cell correction by measuring the absorbance of the solvent-filled sample cell compared to the solvent-filled reference cell.

## 17. Procedure at Elevated Temperature

17.1 If it is not possible to obtain a homogeneous solution of the sample at room temperature in the recommended solvents (16.2), it will be permissible to determine the absorbance at a test temperature high enough to ensure solubility. However, do not exceed 66°C (150°F)-the boiling point of the solvent used for sample preparation or 66°C, whichever is the lower temperature.

17.2 Weigh by difference the recommended sample weight into a clean, calibrated volumetric flask and record the weight to the nearest 0.1 mg (see Table 1).

17.3 Partially fill the flask with solvent, and place the flask in a water bath at the test temperature. When the sample is completely dissolved, dilute to volume using solvent at the test temperature. Shake to make homogeneous and bring to the test temperature in a water bath.

17.4 Prepare spectrophotometer cell holders capable of maintaining the sample cell and reference cell at the desired test temperature.

17.5 Take proper precautions to ensure that the temperature of the solution at the time of absorbance measurement is within  $\pm 1.1$  °C (2 °F) of the test temperature at which the solution was diluted to volume.

17.6 Transfer a sample of the solution (hypodermic syringe heated to the test temperature is convenient) into a 1.0 cm sample cell previously heated to the test temperature. Fill a 1.0 cm reference cell with solvent at the test temperature in a similar manner.