



Standard Test Method for Refractive Index of Viscous Materials¹

This standard is issued under the fixed designation D1747; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the measurement of refractive indexes, accurate to two units in the fourth decimal place, of transparent and light-colored viscous hydrocarbon liquids and melted solids that have refractive indexes in the range between 1.33 and 1.60, and at temperatures from 80 to 100°C. Temperatures lower than 80°C can be used provided that the melting point of the sample is at least 10°C below the test temperature.

1.2 This test method is not applicable, within the accuracy stated, to liquids having colors darker than ASTM Color No. 4, ASTM color as determined by Test Method D1500, to liquids which smoke or vaporize readily at the test temperature, or to solids melting within 10°C of the test temperature.

NOTE 1—The instrument can be successfully used for refractive indices above 1.60; but since certified liquid standards for ranges above 1.60 are not yet available, the accuracy of measurement under these conditions has not been evaluated.

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 **Warning**—Mercury has been designated by EPA and many state agencies as a hazardous material that can cause central nervous system, kidney, and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury-containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website (<http://www.epa.gov/mercury/faq.htm>) for additional information. Users should be aware that selling mercury or mercury-containing products, or both, in your state may be prohibited by state law.

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 appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 *ASTM Standards:*²

D362 Specification for Industrial Grade Toluene (Withdrawn 1989)³

D841 Specification for Nitration Grade Toluene

D1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

E1 Specification for ASTM Liquid-in-Glass Thermometers

E77 Test Method for Inspection and Verification of Thermometers

3. Terminology

3.1 *Definitions:*

3.1.1 *refractive index*—the ratio of the velocity of light (of specified wavelength) in air, to its velocity in the substance under examination. The relative index of refraction is defined as the sine of the angle of incidence divided by the sine of the angle of refraction, as light passes from air into the substance. If absolute refractive index (that is, referred to vacuum) is desired, this value should be multiplied by the factor 1.00027, the absolute refractive index of air. The numerical value of refractive index of liquids varies inversely with both wavelength and temperature.

4. Summary of Test Method

4.1 The refractive index normally is measured by the critical angle method using monochromatic light from a sodium lamp. The instrument is previously adjusted by means of calibration obtained with certified liquid standards.

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 D02.04.0D on Physical and Chemical Methods.

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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.

³ The last approved version of this historical standard is referenced on www.astm.org.

TABLE 1 Primary Liquid Standards

Certified Standard	Approximate Refractive Index,	
	n_D	
<i>n</i> -Hexadecane	1.41	
<i>trans</i> -Decahydronaphthalene	1.44	
1-Methylnaphthalene	1.59	

5. Significance and Use

5.1 Refractive index is a fundamental physical property that can be used in conjunction with other properties to characterize pure hydrocarbons and their mixtures.

5.2 The use of refractive index in correlative methods for the determination of the gross composition of viscous oils and waxes often requires its measurement at elevated temperatures.

6. Apparatus

6.1 *Refractometer*, precision Abbé-type,⁴ having a range in refractive index from 1.30 to 1.63. Other instruments reading to at least four decimal places may be used.

NOTE 2—When other instruments are used, follow the manufacturer's instructions for operation, maintenance, calibration, and analysis. For accepting the instrumentation for use, analysis of an NIST traceable certified material to ensure accuracy should be performed.

6.2 *Thermostat and Circulating Pump*, capable of maintaining the indicated prism temperature constant within 0.02°C. The circulating fluid consists of ethylene glycol or a mixture of 30 to 40 volume % of glycerin in water flowing through the prisms at a fixed rate of at least 2.5 L/min. For work at 100°C, properly controlled wet steam is also suitable.

NOTE 3—The constancy of the prism temperature can be seriously affected by variations in ambient conditions, such as air drafts or changes in room temperature. Reasonable precautions should be taken to minimize these factors. Insulation placed on the thermostat, circulating fluid lines, and refractometer also may prove to be helpful.

6.3 *Thermometers, or Equivalent Temperature Measuring Devices*, conforming to Thermometer 21C for determinations at 80°C or Thermometer 22C for determinations at 100°C as given in Specification E1 are recommended. See Test Method E77 for guidance on inspection and verification of mercury in glass thermometers. Equivalent temperature measuring devices should have the same accuracy and resolution as Thermometers 21C and 22C.

6.3.1 In case of dispute, the test method shall be carried out using the specified mercury in glass thermometer.

6.3.2 The temperature measuring device, suitably calibrated, shall be positioned to measure the temperature of the prism (see Note 4) within an appropriate holder. The holder shall provide for adequate immersion of the temperature measuring device and for free flow of the circulating fluid. The temperature measuring device holder assembly shall be insulated with a suitable material, such as cork.

NOTE 4—In the precision Abbé type refractometer, the thermostating

⁴ The Abbé-type precision refractometer is no longer available but may be obtainable from instrument exchanges or used equipment suppliers. Other precision refractometers may be suitable, but they have not as yet been tested cooperatively.

liquid should pass the thermometer on leaving, not on entering, the prism assembly.

6.4 *Thermocouple*,⁵ copper-constantan foil type, 0.013-mm thickness, and precision potentiometer. The thermocouple is calibrated by immersing to a depth of 25 mm in a circulating liquid thermostat and comparing with a thermometer of known accuracy.

6.5 *Light Source, Sodium Arc Lamp*—The light source shall be a sodium arc lamp, which shall be used only after the removal of Amici compensating prisms, if there are any present in the instrument.

NOTE 5—If the field division as observed in 12.2 shifts when the Amici prism is rotated, the prism should be removed to avoid incorrect readings.

7. Solvents

7.1 *Cleaning Solvent*, any suitable solvent capable of cleaning the apparatus as described in Section 10. *1,1,1*, Trichloroethane has been found suitable to use. (**Warning**—Harmful if inhaled. High concentration can cause unconsciousness or death. Contact can cause skin irritation and dermatitis.)

7.2 *Toluene*, conforming to Specification D362 or Specification D841. (**Warning**—Flammable. Vapor harmful.)

8. Reference Standards

8.1 *Primary Liquid Standards*—Organic liquids listed in Table 1, with the values of their refractive indexes for the sodium *D* line certified at 20, 25, 30, 80, and 100°C.⁶ (**Warning**—Primary standards are combustible.)

8.2 *Working Standards*—For working standard hydrocarbons, reasonably well purified samples of *n*-hexadecane, *trans* -decahydronaphthalene, and 1-methylnaphthalene may be used. Their exact values are determined by comparison with standard samples of the same hydrocarbons having certified values of refractive index. (**Warning**—Working standards are combustible.)

9. Sample

9.1 A sample of at least 0.5 mL is required. The sample shall be free of suspended solids, water, or other materials that tend to scatter light. Water can be removed from hydrocarbons by treatment with calcium chloride followed by filtering or centrifuging to remove the desiccant. The possibility of changing the composition of a sample by action of the drying agent, by selective adsorption on the filter, or by fractional evaporation, shall be considered.

10. Preparation of Apparatus

10.1 The refractometer shall be kept scrupulously clean at all times. Dust and oil, if allowed to accumulate on any part of the instrument, will find its way into the moving parts, causing

⁵ The sole source of supply of the apparatus known to the committee at this time is RdF Corp., 23 Elm Avenue, Hudson, NH 03051. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹, which you may attend.

⁶ Available from API Standard Reference Office, Carnegie-Mellon University, Pittsburgh, PA 15213.

wear and eventual misalignment. If permitted to collect on the prism, dust will dull the polish, resulting in hazy lines.

10.2 Thoroughly clean the prism faces with fresh clean lens tissue or surgical grade absorbent cotton saturated with a suitable solvent. Pass the swab very lightly over the surface until it shows no tendency to streak. Repeat the procedure with a fresh swab and solvent until both the glass and adjacent polished metal surfaces are clean. Do not dry the prism faces by rubbing with dry cotton.

10.3 Adjust the thermostat so that the temperature as indicated by the thermocouple inserted between the prism faces and wet with oil is within 0.2°C of the desired test temperature. This temperature is to be held constant to within 0.02°C during the test. Observe and record the thermometer reading corresponding to the test temperature. Turn on the sodium arc lamp and allow it to warm up for 30 min.

11. Standardization with Reference Liquids

11.1 Introduce a sample of the API Standard *trans*-decahydronaphthalene to the prism which is adjusted to the chosen test temperature of 80 or 100°C, turn the telescope adjustment screw until a refractive index scale reading corresponding to the certified refractive index for *trans*-decahydronaphthalene is observed, and adjust the instrument according to the instructions given by the manufacturer until the sharp boundary between the light and dark portions of the field passes through the intersection of the cross hairs of the telescope.

11.2 Check the accuracy of this setting by loading a fresh sample of *trans*-decahydronaphthalene and measure its refractive index at the test temperature following the procedure described in Section 12. If the value for the refractive index differs from the certified value by 0.0001 or more units, then repeat the procedure given in 11.1 until a satisfactory check is obtained.

11.3 Measure the refractive index of API Standard *n*-hexadecane and 1-methylnaphthalene at the test temperature following the procedure described in Section 12.

11.4 Construct a calibration curve for use at the chosen test temperature. Plot the difference between the observed refractive index for *n*-hexadecane and its certified value along the ordinate against the refractive index level along the abscissa. Also plot the difference between the observed and certified refractive indices for 1-methylnaphthalene in the same manner. Draw a straight line from the point representing the deviation found for *n*-hexadecane to zero at the certified refractive index of *trans*-decahydronaphthalene. Likewise, draw a straight line from this same zero point to the deviation found for 1-methylnaphthalene.

11.5 If it is desired to measure the refractive index of samples at a temperature other than 80 or 100°C, obtain calibration data by repeating 11.1 – 11.4 at this desired temperature. Determine the refractive indices for the API Standard compounds, *n*-hexadecane, *trans*-decahydronaphthalene, and 1-methylnaphthalene at the desired temperature by plotting the certified refractive indices at 20,

25, 30, 80, and 100°C against temperature and drawing a smooth curve between the points.

11.6 *Precautions*—In using pure liquids for calibration or checking of calibration of an Abbé-type refractometer, the following precautions should be observed:

11.6.1 Before inserting the hydrocarbon calibrating liquids, the prisms should be flushed with solvents and cleaned as described in 8.2. It is advisable to preheat the solvent before use to minimize thermal shock to the prism. This should be followed by several such flushings with the test liquid and wiping with lens paper. After such cleaning, a reading with the test liquid should be taken as described in Section 11. This should be followed by another flushing with the test liquid before taking another reading of the test liquid in the prescribed manner. The prisms cannot be considered free from contaminating substances until two such determinations on the test liquid agree within the limits given in 11.6.2.

11.6.2 In setting the edge of the field on the cross hairs, readings should be taken in pairs, approaching the alidade setting from one direction only as recommended by the manufacturer. Several such sets will probably be necessary before satisfactory agreement is obtained. Satisfactory agreement is 0.00005 to 0.0001.

11.6.3 For results of highest accuracy, the calibration with hydrocarbons of known properties should be made immediately before the determination on the sample.

11.6.4 Fluctuations in ambient temperatures should be minimized as much as possible during the test.

12. Procedure

12.1 Thoroughly clean the prism faces as described in 10.2. Adjust the thermostat so that the temperature indicated by the thermocouple placed between the faces of the closed prism (loaded with oil) is within 0.2°C of the desired value. The thermocouple is used for establishing the correct temperature level and may be removed during measurements of refractive index. The observed reading of the thermometer at this temperature must be held constant to 0.02°C in the measurements to follow.

12.2 Close the prism box and let it stand for 3 to 5 min to ensure temperature equilibrium between the prisms and the circulating bath liquid. Melt samples which are normally solid in a small container and charge as a liquid to the prism. Charge the sample from a small pipet or medicine dropper through the refractometer opening or onto the prisms open just enough to admit the sample. About 0.2 to 0.5 mL of the sample should be allowed to flush through before completely closing the prisms. Samples of low volatility or high viscosity may be placed directly onto the prism surface by means of a stirring rod, *being careful not to touch the prism surface with the rod*. If not enough sample has been used to fill the space between the prisms completely, or evaporation causes the field division in the telescope to become uneven, clean the prisms thoroughly before employing a new portion of the sample.

12.3 Set the light source to pass rays into the illuminating prism. Move the telescope by means of the adjustment screw until the field division is visible in the telescope.

12.4 Adjust the angle of incidence until the field consists of a light and a dark portion separated by a sharp boundary, which may be brought into focus by sliding the telescope eyepiece. In the case of colloidal or suspended matter in the sample, the boundary line may appear diffused or hazy, even though the telescope is perfectly focused. Filtration of the sample will sometimes correct this condition. Water in the sample may also give this hazy effect.

12.5 Turn the adjustment screw so that the field division passes through the intersection of the crossed lines in the telescope. With the exception of extremely volatile samples, an interval of 2 to 3 min should be allowed before taking readings to permit the sample to come to the same temperature as the refractometer. In setting the edge of the field on the cross hairs, at least two determinations should be obtained that agree within 0.00005 to 0.0001 for precision work. The final reading is best obtained by approaching this setting successively from both light and dark sides of the field. Read the scale through the microscope provided. Focus by sliding the eyepiece in or out. Measure and record the refractive index using at least two separate loadings of sample.

NOTE 6—For more reliable results with a sample that shows a diffused or hazy boundary line even after filtration, there are two possible remedies: (1) back window reflection if the refractometer is so equipped, or (2) dilution with a suitable solvent.

(1) Back window reflection also permits measurements of samples too dark for normal operation. The sample is charged in the normal manner. Remove the cover plate on the back of the prism housing and position the light source so that it shines directly into the opening. Bring the boundary line into view. The fields will be reversed and considerably reduced in contrast. Read the refractive index as described above. Care should be exercised during the measurement since the sharp boundary line is faint and difficult to distinguish.

(2) The dilution procedure is generally unsatisfactory and should only be used if it is impossible to obtain consistent readings in any other way. The sample is diluted with an equal volume of high boiling solvent whose density and refractive index are known and an appropriate correction

applied to the results. Highly aromatic or olefinic samples in the gas oil range can be measured by this procedure. The possibility of volume change on mixing should be considered. A check on the density of the mixture will show if this occurs.

13. Calculation and Reporting

13.1 Correct the observed refractive index by the amount shown in the calibration curve. Report the value of refractive index as:

$$n_D^t = \dots$$

14. Precision and Bias

14.1 The precision of the test method as obtained by statistical examination of interlaboratory test results is as follows:

14.1.1 *Repeatability*—The difference between successive 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 0.00007 units of refractive index only in one case in twenty.

14.1.2 *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 and correct operation of the test method, exceed 0.0006 units of refractive index only in one case in twenty.

NOTE 7—The precision for this test method was not obtained in accordance with RR:D02-1007.

14.2 The bias for this test method has not been determined. Subcommittee D02.04.0D plans to cooperatively test modern refractometers and determine the bias.

15. Keywords

15.1 oils; purity; refractive index; refractometer; wax

APPENDIXES

(Nonmandatory Information)

X1. FACTORS THAT AFFECT PRECISION AND ACCURACY

X1.1 Temperature

X1.1.1 Refractive index varies inversely and non-linearly with temperature. The relative change in refractive index with temperature (temperature coefficient) is different for each liquid under test. Hydrocarbon liquids have a higher temperature coefficient than water and aqueous solutions. For example, at 20°C, the temperature coefficient for water is -9×10^{-5} units of refractive index per °C. For hydrocarbon liquids, the coefficient will typically be in the range -3×10^{-4} to -5×10^{-4} .

X1.2 Wavelength (Light Source)

X1.2.1 Refractive index also varies inversely and non-linearly with the wavelength of light. Refractive index should, therefore, be measured using light of a single wavelength

(monochromatic light). Most measurements traditionally have been made at the sodium *D* line (589.3 nm) because of the purity and availability of a sodium source such as an arc lamp. Other light sources include mercury, cadmium, helium, and hydrogen where filters are used with the refractometer to eliminate unwanted emission lines.

X1.2.2 The effect of wavelength on refractive index is called dispersion. Different substances have varying degrees of refractive dispersion (sometimes called dispersive power).

X1.2.3 Optical-mechanical refractometers (often called Abbé refractometers or critical angle refractometers) can be used with a variety of spectral light sources. Some instruments can utilize a white light source, but often these instruments are limited in accuracy because of the light source. High accuracy

Abbé refractometers require a pure spectral light source such as a sodium arc lamp (see 6.5).

X1.2.4 Modern electronic digital refractometers function at a single wavelength, invariably that of sodium light (589 nm). The refractive index at this wavelength is denoted as n_D .

X1.2.5 One of two types of light source tends to be used in digital refractometers: (1) filtered white light source such as that obtained using a tungsten-halogen lamp, or (2) light emitting diode (LED).

X1.2.6 With both types of light source, the wavelength is not a single value but is a narrow band spanning typically

10 nm or more about the nominal value (589 nm). The degree of impurity (band width) will cause a dispersion of the detected light from the sample. Instrument software can be used to compensate for and thus minimize this error source, but it will nevertheless be a factor in determining the limiting accuracy of the instrument. The dispersion error will, however, differ according to the substance measured. This is why instrument manufacturers may specify the instrument accuracy as *typically* or *better than* in order to cover a broad application scope.

NOTE X1.1—Sodium actually emits a doublet of lines at 589.1 and 589.6 nm. However, for practical purposes, because of the proximity of the lines, it is regarded as a single wavelength source and the average value of 589.3 nm is often cited.

X2. INSTRUMENT CALIBRATION

X2.1 A refractometer must be calibrated using one or more reliable calibration standards. The optical system in a refractometer is subject to microscopic movement as materials expand and contract with fluctuating ambient thermal conditions. This effect leads to calibration drift, which must be periodically corrected to ensure measurement reliability.

X2.2 Calibration materials are available as two types: solids (test plates) and liquids. Solid plates are often preferred for their stability (shelf life), but have the disadvantage of limited accuracy in use because of the errors associated with the placing of the plate on the refractometer prism. Typically, a plate may not allow an accuracy better than ± 0.0001 units of refractive index. Test plates are particularly difficult to apply to sapphire prisms of the type typically used in digital electronic refractometers. This is because the micro-roughness of sapphire is greater than that of softer (optically flatter) glasses used in optical (Abbé) refractometers. Invariably, liquid reference standards will be preferred and will be recommended by instrument manufacturers for this reason.

X2.3 An optical-mechanical instrument may require calibration at only one point on the scale. Automatic digital refractometers may require a single (zero), two-point, or multi-point calibration. For each calibration a suitable calibration standard should be used.

X2.4 The frequency of calibration will depend upon a number of factors. When an electronic instrument is first

switched on and the liquid bath circulation is started, a period of thermal adjustment is required to allow the internal environment, and particularly the optical system, to adjust to the new condition. Calibration should not take place until the instrument is in a steady-state. Experience will demonstrate that this may be typically up to an hour. Similarly, if the circulating liquid temperature is changed, a new calibration sequence will be required. In circumstances where the instrument is used continuously and in a constant thermal condition, the need for recalibration should be minimal.

X2.5 For each calibration point, a calibration standard is required. Any calibration fluid could be used. However, it is best practice to select fluids with a refractive index close to the intended measuring range or, where a pair or group of standards is needed, select liquids that adequately span the working range.

X2.6 Whether an electronic digital instrument or an optical-mechanical instrument is being used, the laboratory needs to adopt a strict protocol for calibration frequency and procedure. This will entail regular checks on measurement accuracy (verification) using reliable standards. The calibration should only be reset when measured values are outside of the stated tolerance. The protocol should also include procedures that govern the control of calibration materials: storage (shelf-life), contamination-prevention and staff competence (approved users).

X3. REFLECTED VERSUS TRANSMITTED LIGHT

X3.1 Critical angle refractometers can function by using light transmission through the sample (usually a thin film sandwiched between two prisms) or by light reflection. A light reflection mechanism has the advantage that effects of absorption (highly colored samples) are minimized. A disadvantage of reflectance is the difficulty of observing the borderline in

optical-mechanical (Abbé) instruments because of the low light intensity and poor contrast.

X3.2 Digital electronic refractometers usually work with a reflected light mechanism.

X4. GUIDELINES FOR QUALITY CONTROL

X4.1 The performance of the instrument or the test procedure should be confirmed by analyzing a quality control (QC) sample.

X4.2 It is recommended that the QC sample be representative of the material routinely analyzed. However, pure materials may be used, if so desired. An ample supply of QC sample material should be available for the intended period of use, and should be homogeneous and stable under the anticipated storage conditions.

X4.3 Prior to monitoring the measurement process, the average value and control limits of the QC sample need to be established (see Practice **D6299** and ASTM MNL⁷). When a new QC sample material is required, control limits for the new material should be established before the old QC sample is exhausted.

X4.4 The QC results should be recorded, and analyzed by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice **D6299** and ASTM MNL⁷). Any out of control data should trigger an investigation of root cause(s). The results of such investigation may, but not necessarily, result in instrument recalibration.

X4.5 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, the length of time required to do the test, and customer requirements. The QC testing frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the test method is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM method precision to ensure quality of results.

X4.6 Consult Practice **D6299** and ASTM MNL⁷ for further guidance on QC and control charting techniques.

⁷ ASTM MNL7, *Manual on Presentation of Data Control Chart Analysis*, 6th Edition, ASTM International.

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