



Designation: D 1016 – 99

An American National Standard

Standard Test Method for Purity of Hydrocarbons from Freezing Points¹

This standard is issued under the fixed designation D 1016; 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 sampling and determination of purity of essentially pure compounds for which the freezing points for zero impurity and cryoscopic constants are given.² The compounds to which the test method is applicable are: (**Warning:** Extremely flammable liquids and liquefied gases.)

<i>n</i> -butane	1,3-butadiene
isobutane	isoprene(2-methyl-1,3-butadiene)
<i>n</i> -pentane	benzene
isopentane	toluene (methylbenzene)
<i>n</i> -hexane	ethylbenzene
<i>n</i> -heptane	<i>o</i> -xylene (1,2-dimethylbenzene)
<i>n</i> -octane	<i>m</i> -xylene (1,3-dimethylbenzene)
2,2,4-trimethylpentane	<i>p</i> -xylene (1,4-dimethylbenzene)
methylcyclohexane	styrene (ethenylbenzene)
isobutene	

1.2 The values stated in SI units are to be regarded as the standard. The values in parentheses are for information only.

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.* For specific hazard statements, see Sections 1, 6, 8, and 10-26.

NOTE 1—This test method covers systems in which the impurities form with the major component a substantially ideal or sufficiently dilute solution, and also systems which deviate from the ideal laws, provided that, in the latter case, the lowering of the freezing point as a function of the concentration is known for each most probable impurity in the given substance.

2. Referenced Documents

2.1 ASTM Standards:

D 1015 Test Method for Freezing Points of High-Purity Hydrocarbons³

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0D on Physical Methods.

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² Numerical constants in this test method were taken from the most recently published data appearing in “Tables of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,” or *ASTM DS 4A, Physical Constants of Hydrocarbons C₁ to C₁₀*, or both, prepared by the American Petroleum Institute, Research Project 44.

³ *Annual Book of ASTM Standards*, Vol 05.01.

3. Summary of Test Method

3.1 After measurement of the freezing point of the actual sample, purity can be calculated from the value of the determined freezing point and the values given for the freezing point for zero impurity and for the applicable cryoscopic constant or constants.⁴

3.2 For the equilibrium between an infinitesimal amount of the crystalline phase of the major component and a liquid phase of the major component and one or more other components, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase is expressed by the equation:⁵

$$- \ln N_1 = - \ln (1 - N_2) = A(t_f - t_p)[1 + B(t_f - t_p) + \dots] \quad (1)$$

where:

- N_1 = mole fraction of the major component,
- N_2 = $(1 - N_1)$ = sum of the mole fractions of all the other components,
- t_f = freezing point, in degrees Celsius, of the given substance (in which the mole fraction of the major component is N_1), defined as the temperature at which an infinitesimal amount of crystals of the major component is in thermodynamic equilibrium with the liquid phase (see Note 3 of Test Method D 1015),
- t_{f0} = freezing point for zero impurity, in degrees Celsius, for the major component when pure, that is, when $N_1 = 1$ or $N_2 = 0$,
- A = first or main cryoscopic constant, in mole fraction per degree, and
- B = secondary cryoscopic constant, in mole fraction per degree.

Neglecting the higher terms not written in the brackets, Eq 1 can be transformed to the equation:

$$\log_{10} P = 2.00000 - (A / 2.3026)(t_{f0} - t_p)[1 + B(t_{f0} - t_p)] \quad (2)$$

⁴ For a more complete discussion of this test method, see Glasgow, Jr., A. R., Streiff, A. J., and Rossini, F. D., “Determination of the Purity of Hydrocarbons by Measurement of Freezing Points,” *Journal of Research*, JRNBA, National Institute of Standards and Technology, Vol 35, No. 6, 1945, p. 355.

⁵ For details, see Taylor, W. J., and Rossini, F. D., “Theoretical Analysis of Time-Temperature Freezing and Melting Curves as Applied to Hydrocarbons,” *Journal of Research*, JRNBA, Nat. Bureau Standards, Vol 32, No. 5, 1944, p. 197; also Lewis, G. N., and Randall, M., “Thermodynamics and the Free Energy of Chemical Substances,” 1923, pp. 237, 238, McGraw-Hill Book Co., New York, NY.

where:

P = purity of the given substance in terms of mole percent of the major component.

4. Significance and Use

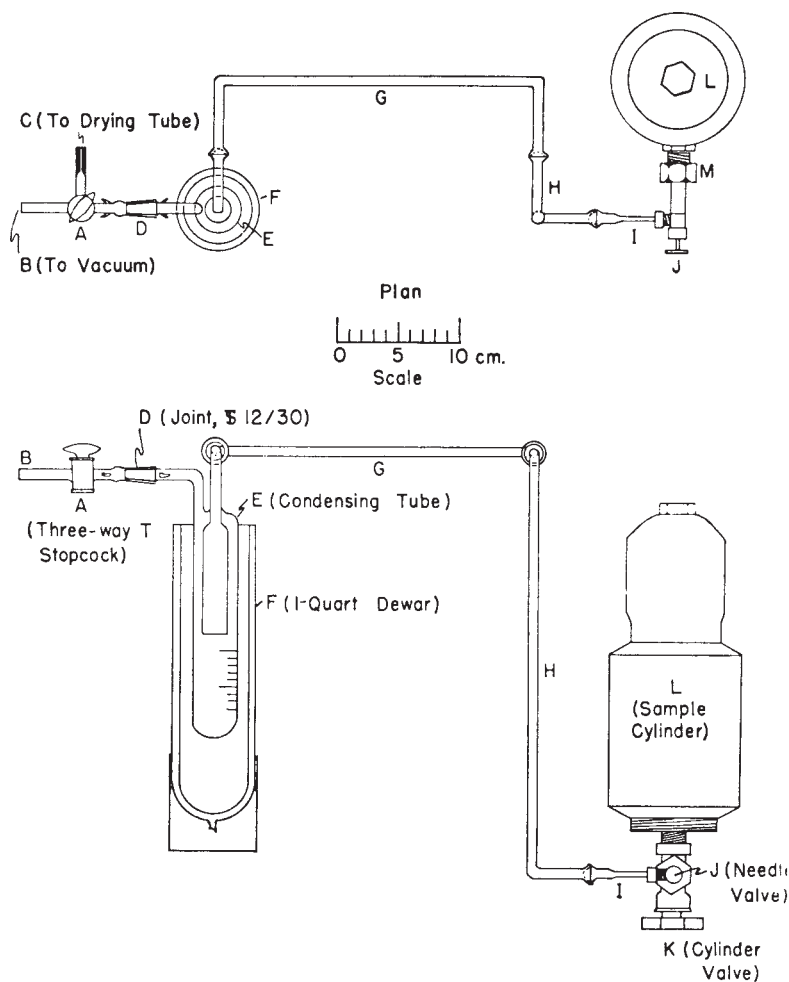
4.1 The experimental procedures and physical constants provided by this test method, when used in conjunction with Test Method D 1015, allow the determination of the purity of the material under test. A knowledge of the purity of these hydrocarbons is often needed to help control their manufacture and to determine their suitability for use as reagent chemicals or for conversion to other chemical intermediates or finished products.

5. Apparatus

5.1 *Sampling Apparatus*, as shown in Fig. 1, for withdrawing liquefied gases (for example, 1,3-butadiene) from pressure storage cylinders.

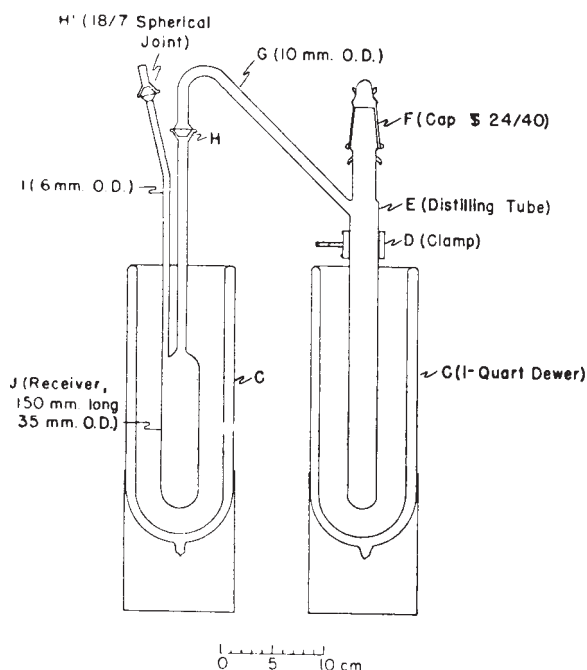
5.2 *Distilling Apparatus*, as shown in Fig. 2, for removing small amounts of polymer from low-boiling compounds (for example, 1,3-butadiene) by simple distillation at atmospheric pressure.

5.3 *Distilling Apparatus*, as shown in Fig. 3, for removing small amounts of polymer from compounds with boiling points near room temperature (for example, isoprene) by distillation at atmospheric pressure.



- A—Three-way T stopcock, borosilicate glass (similar to Corning Pyrex No. 7420).
- B—Connection to vacuum for purging and for evacuating system CDEGHI.
- C—Capillary tube for venting, to which drying tube is also connected.
- D—Joint, standard taper, 12/30, borosilicate glass.
- E—Condensing tube, borosilicate glass.
- F—Dewar flask, 1-qt size, borosilicate glass (similar to American Thermos Bottle Co. No. 8645).
- G—Tubing, borosilicate glass, 10 mm in outside diameter, with spherical ground-glass joints, 18/7.
- H—Tubing, silicate glass, 10 mm in outside diameter, with spherical ground-glass joints, 18/7.
- I—Metal connection, brass spherical male joint at one end fitting to connection to needle valve at other end.
- J—Needle valve, brass.
- K—Valve on cylinder containing hydrocarbon material.
- L—Standard cylinder containing hydrocarbon material.
- M—Fitting to connect needle valve J to valve K on cylinder.

FIG. 1 Apparatus for Obtaining Sample



- C—Dewar vessel, 1-qt capacity, borosilicate glass.
D—Clamp.
E—Distilling tube, borosilicate glass, 25 mm in outside diameter.
F—Standard-taper ground-glass joint, 24/40 borosilicate glass.
G—Tubing, 10 mm in outside diameter, borosilicate glass.
H, H'—Spherical ground-glass joints, 18/7, borosilicate glass.
I—Tubing, 6 mm in outside diameter, borosilicate glass.
J—Receiver, 35 mm in outside diameter, 150 mm in length, borosilicate glass.

FIG. 2 Simple Distilling Apparatus for Normally Gaseous Substances

5.4 *Vacuum Distilling Apparatus and Transfer Trap*, as shown in Fig. 4, for removing dissolved air and large amounts of polymer from a compound (for example, 1,3-butadiene or styrene), by repeated freezing and evacuation, followed by distillation of the compound in vacuum in a closed system.

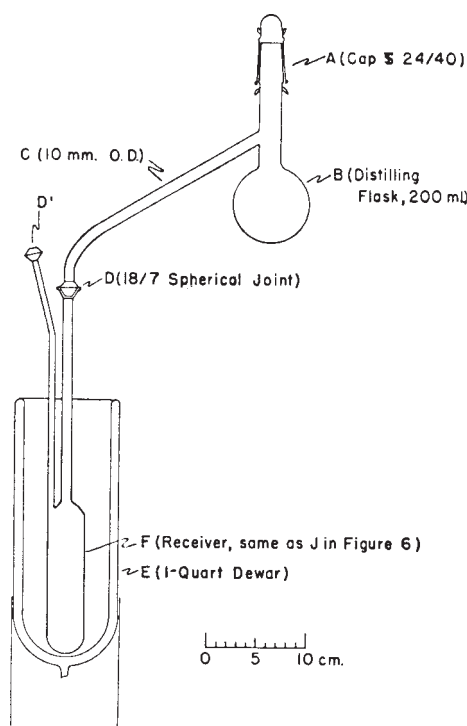
6. Materials

6.1 *Carbon Dioxide Refrigerant*—Solid carbon dioxide in a suitable liquid. Acetone is recommended.

NOTE 2—*Solid Carbon Dioxide*—**Warning:** Extremely cold (-78.5°C). Liberates heavy gas which can cause suffocation. Contact with skin causes burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys. **Acetone:** **Warning:** Extremely flammable. Harmful if inhaled. High concentrations can cause unconsciousness or death. Contact can cause skin irritation and dermatitis. Use refrigerant bath only with adequate ventilation!

6.2 *Liquid Nitrogen or Liquid Air*—(**Warning:** Extremely cold. Liberates gas which can cause suffocation. Contact with skin burns or freezing, or both. Vapors can react violently with hot magnesium or aluminum alloys.) For use as a refrigerant. If obtainable, liquid nitrogen is preferable because of its safety.

6.2.1 Use liquid nitrogen refrigerant only with adequate ventilation. If liquid air is used as a refrigerant, it is imperative that any glass vessel containing hydrocarbon or other combustible compound and immersed in liquid air be protected with a suitable metal shield. The mixing of a hydrocarbon or other



- A—Standard-taper, ground-glass joint, 24/40, borosilicate glass.
B—Distilling flask, round bottom, 200-mL capacity, borosilicate glass.
C—Tubing, 10 mm in outside diameter, borosilicate glass.
D, D'—Spherical ground-glass joints, 18/7, borosilicate glass.
E—Dewar flask, 1-qt capacity, borosilicate glass.
F—Receiver, same as J in Fig. 2.

FIG. 3 Simple Distilling Apparatus for Normally Liquid Substances

combustible compound with liquid air due to the breaking of a glass container would almost certainly result in a violent explosion. If liquid nitrogen is used as a refrigerant, no hydrocarbon sample should ever be permitted to cool below the condensation temperature of oxygen (-183°C at atm). This would not be likely to occur in normal operation, but might occur if the apparatus were left unattended for some time.

7. Procedure

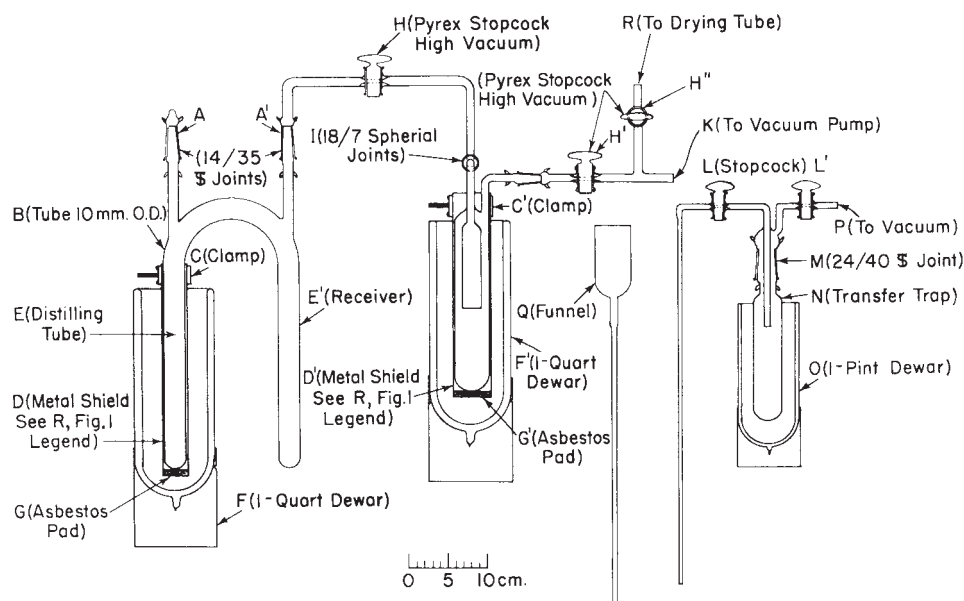
7.1 Measure the freezing point as described in Test Method D 1015, using the modifications and constants given in Sections 8-26 of this test method for the specific compounds being examined.

NOTE 3—The estimated uncertainty in the calculated value of the purity as referred to in Sections 8-26 is not equivalent to the precision defined in RR D-2-1007.

8. *n*-Butane⁶ (**Warning:** Extremely flammable liquefied gas under pressure. Vapor reduces oxygen available for breathing.)

8.1 Determine the freezing point from freezing curves, with the cage stirrer, with a cooling bath of liquid nitrogen (or liquid

⁶ For further details, see Glasgow, Jr., A. R., et al. "Determination of Purity by Measurement of Freezing Points of Compounds Involved in the Production of Synthetic Rubber," *Analytical Chemistry*, ANCHA, Vol 20, 1948, p. 170.



A, A'—Standard-taper ground-glass joints, 14/35 borosilicate glass.

B—Tubing, 27 mm in outside diameter, borosilicate glass.

C, C'—Clamp.

D—Brass cylinder, 273 mm (10¾ in.) in length, 28.6 mm (1½ in.) in inside diameter; for precautions in use of liquid nitrogen and liquid air, see R in legend to Fig. 1 of Test Method D 1015 and Notes 2 and 3 of Test Method D 1015.

D'—Brass cylinder, 254 mm (10 in.) in length, 47.6 mm (1⅞ in.) in inside diameter, (see D above).

E—Original sample.

E'—Distilled sample.

F, F'—Dewar flask, 0.0009-m³ (1-qt) capacity, borosilicate glass.

G and G'—Asbestos pad.

H, H', H''—Stopcock, ground for high vacuum, borosilicate glass.

I—Spherical ground-glass joint, 18/7, borosilicate glass.

J—Condensing tube, used as trap (see E in Fig. 1).

K—Connection to vacuum system.

L, L'—Stopcock, ground for high vacuum, borosilicate glass.

M—Standard-taper ground-glass joint, 24/40 borosilicate glass.

N—Receiver withdrawal, 36 mm in outside diameter, borosilicate glass.

O—Dewar flask, 0.0005-m³ (1-pt) capacity, borosilicate glass.

P—Connection to vacuum.

Q—Funnel with extension, 4 mm in inside diameter, borosilicate glass.

R—Connection to drying tube, borosilicate glass.

FIG. 4 Apparatus for Simple Vacuum Distillation

air), with a cooling rate of 0.3 to 0.8°C/min for the liquid near the freezing point, and with crystallization induced immediately below the freezing point by means of a cold rod.

8.2 The method of obtaining the samples shall be as follows: Assemble the apparatus for obtaining the sample as shown in Fig. 1, but with no lubricant on the ground-glass joints and with the valve at the bottom of the cylinder, so that sampling is from the liquid phase. Attach to C an absorption tube containing anhydrous calcium sulfate or other suitable desiccant (except magnesium perchlorate) so that water is not introduced into the system (Note 4). Fill the flask F with the carbon dioxide refrigerant to within about 51 mm (2 in.) of the top. After about 20 or 30 min, when the system will have cooled sufficiently, remove the absorption tube and begin the collection of liquid *n*-butane by opening the valve K and adjusting the needle valve J so that the sample is collected at a rate of 1 to 2 mL (liquid)/min in the condensing tube E.

NOTE 4—However, if some water does condense with the hydrocarbon, the freezing point will not be affected significantly because of the extremely low solubility of water in the hydrocarbon at the freezing point of the latter.

8.3 Assemble the freezing point apparatus. Place the cooling bath in position around the freezing tube (O in Fig. 1 of Test Method D 1015), letting the temperature as read on the platinum thermometer reach about -80°C when all the sample has been collected.

8.4 When 50 mL of liquid (temperature about -80°C) has been collected in the condensing tube, close the valve K (Fig. 1) and allow the liquid which has collected at I to warm and transfer to the condensing tube (Note 5). Replace the attaching tubes G and D on the condensing tube by caps. The liquid sample is now ready for introduction into the freezing tube (O in Fig. 1 of Test Method D 1015).

NOTE 5—In case the original sample contained water, there will remain at I some water that may be discarded after the hydrocarbon portion has been collected as outlined above.

8.5 When the temperature of the platinum thermometer is near -80°C, remove the condensing tube (E in Fig. 1) from the Dewar flask. Wrap a cloth around the upper portion of the condensing tube (for ease of handling and for preventing the refrigerating liquid from contaminating the sample on pouring), and after removing the caps on the condensing tube, raise the stopper holding the platinum thermometer, and pour the sample through the tapered male outlet of the condensing tube into the freezing tube (O in Fig. 1 of Test Method D 1015). Quickly replace the stopper holding the platinum thermometer and start the stirrer, with dry air flowing into the upper portion of the freezing tube through M (Fig. 1 of Test Method D 1015).

8.6 Because the material is normally gaseous at room temperature, care should be taken in disposing of the sample safely.