Designation: D1016 – 05 (Reapproved 2010)

Standard Test Method for Purity of Hydrocarbons from Freezing Points[1]

This standard is issued under the fixed designation D1016; 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.)

n-butane	1,3-butadiene
isobutane	isoprene(2-methyl-1,3-butadiene)
n-pentane	benzene
isopentane	toluene (methylbenzene)
n-hexane	ethylbenzene
n-heptane	*o*-xylene (1,2-dimethylbenzene)
n-octane	*m*-xylene (1,3-dimethylbenzene)
2,2,4-trimethylpentane	*p*-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:*[3]

D1015 Test Method for Freezing Points of High-Purity Hydrocarbons

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]

$$-1n\,N_1 = -1n\,(1 - N_2) = A(t_{f0} - t_f)[1 + B(t_{f0} - t_f) + ...] \quad (1)$$

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 D1015),

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.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0D on Physical and Chemical 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 C_1 to C_{10}*, or both, prepared by the American Petroleum Institute, Research Project 44.

[3] 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.

[4] For a more complete discussion of this test method, see Glasgow, A. R., Jr., 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.

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

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

where:

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

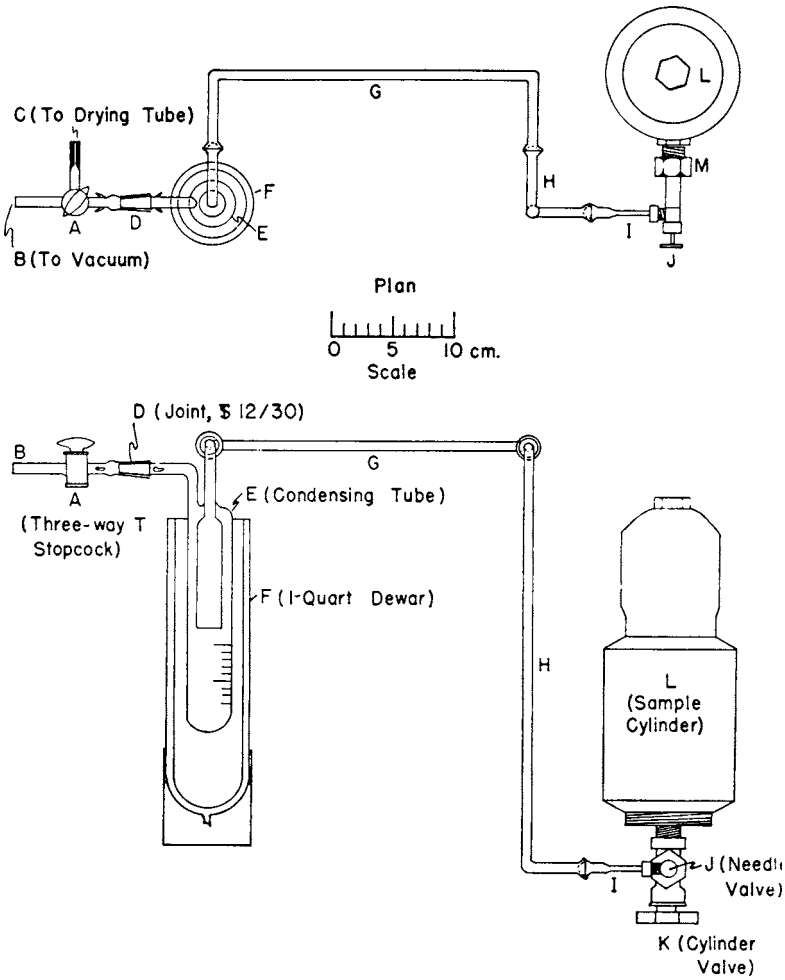
4. Significance and Use

4.1 The experimental procedures and physical constants provided by this test method, when used in conjunction with Test Method D1015, 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

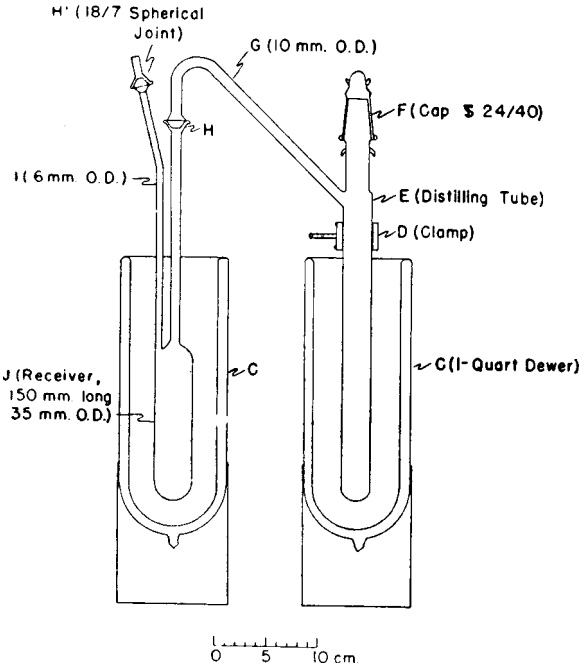
5.1 *Sampling Apparatus*, as shown in Fig. 1, for withdrawing liquefied gases (for example, 1,3-butadiene) from pressure storage cylinders.

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.



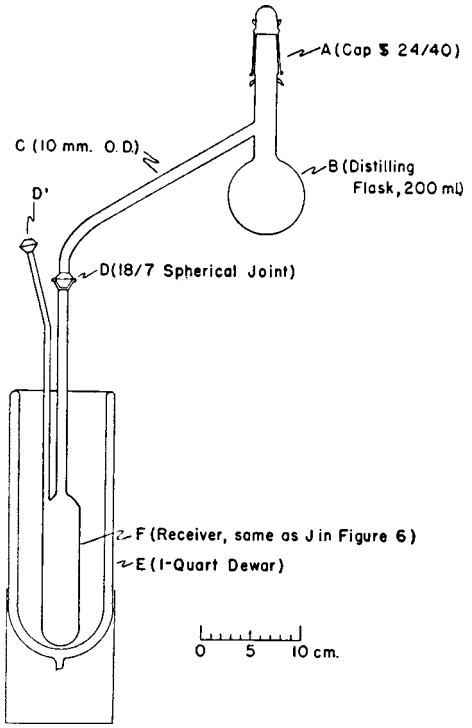
A—Three-way T stopcock, borosilicate glass (similar to Corning Pyrex No. 7420).
B—Connection to vacuum for purging and for evacuating system *CDEGHI*.
C—Capillary tube for venting, to which drying tube is also connected.
D—Joint, standard taper, 12/30, borosilicate glass.
E—Condensing tube, borosilicate 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



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

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.

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. (**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 is recommended.(**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 causes 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 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 D1015, using the modifications and constants given in Sections 8-26 of this test method for the specific compounds being examined.

NOTE 2—The estimated uncertainty in the calculated value of the purity