



# Standard Test Method for Analysis of High-Purity *n*-Heptane and *Isooctane* by Capillary Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D2268; 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.

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

## 1. Scope

1.1 This test method covers and provides for the analysis of high-purity (greater than 99.5 % by volume) *n*-heptane and *isooctane* (2,2,4-trimethylpentane), which are used as primary reference standards in determining the octane number of a fuel. Individual compounds present in concentrations of less than 0.01 % can be detected. Columns specified by this test method may not allow separation of all impurities in reference fuels.

1.2 The values stated in SI units are to be regarded as the standard. The values given 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.*

## 2. Summary of Test Method

2.1 The sample is injected into a capillary gas chromatographic column consisting of at least 61 m (200 ft) of stainless steel tubing (0.25-mm (0.010-in.) inside diameter), the inner walls of which are coated with a thin film of stationary liquid. An inert gas transports the sample through the column, in which it is partitioned into its individual components. As each component is eluted from the column, it is detected with a hydrogen flame ionization detector and recorded on a conventional strip-chart recording potentiometer. The detector response from each impurity is then compared with that of a known quantity of an internal standard. After determining the total impurity concentration, the *n*-heptane, or *isooctane* purity is obtained by difference.

## 3. Significance and Use

3.1 This test method is used for specification analysis of high-purity *n*-heptane and *isooctane*, which are used as ASTM

Knock Test Reference Fuels. Hydrocarbon impurities or contaminants, which can adversely affect the octane number of these fuels, are precisely determined by this method.

## 4. Apparatus

4.1 *Chromatograph*—Gas chromatograph should be equipped with a split-stream inlet device for introducing minute quantities of sample without fractionation, a capillary column, and a hydrogen flame ionization detector. An electrometer to amplify the low output signal of the hydrogen flame ionization detector, and a strip-chart recorder for recording the detector signal are needed. The time constant of neither the electrometer nor the recorder should exceed 1 s. A ball and disk integrator or electronic integrator for peak area measurements should be used. The detection system must have sufficient sensitivity to produce a recorder deflection for cyclohexane of at least 8 divisions on a standard 0–100 scale chart using 0.10 volume percent of cyclohexane in *n*-heptane as defined in 7.1.

4.2 *Microsyringe*—A microsyringe is needed for injecting the sample into the split-stream inlet device.

4.3 *Volumetric Pipet*, 0.1-mL capacity.

4.4 *Analytical Balance*, 200-g capacity.

## 5. Reagents and Materials

5.1 *Carrier Gas*—Argon, Nitrogen, or Helium; 99.99% or greater purity. (**Warning**—Compressed gases under high pressure.)

5.2 *Fuel Gas*—Hydrogen; 99.99% or greater purity. (**Warning**—Compressed gas under high pressure. Extremely flammable gas.)

5.3 *Oxidant Gas*—Air; 99.99% or greater purity. (**Warning**—Compressed gases under high pressure.)

5.4 *Cyclohexane*—At least 99 mol % pure, to be used as internal standard. (**Warning**—Flammable liquid and harmful if ingested or inhaled.)

5.5 *n*-Pentane—Commercial grade. (**Warning**—Volatile and flammable liquid, and harmful if ingested or inhaled.)

5.6 *Isooctane (2,2,4-trimethylpentane)*— (**Warning**—Flammable liquid and harmful if ingested or inhaled.)

<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 D02.04.0L on Gas Chromatography Methods.

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5.7 *Squalane*—Liquid phase for gas chromatographic columns.

5.8 *Tubing*—Type 316, 321, or 347 stainless steel; 0.25 mm (0.010 in.) inside diameter.

## 6. Preparation of Resolving Column

NOTE 1—There are many different procedures for coating capillary columns. A suitable procedure is given in 6.1 through 6.3. Other columns may be used provided they meet resolution and repeatability requirements of the method.

6.1 Connect a 229 mm (9-in.) section of stainless steel tubing 6.4 mm (1/4-in.) outside diameter, total volume of approximately 5 mL) to a high-pressure cylinder of argon, helium, or nitrogen through a pressure regulator. Connect at least 61 m (200 ft) of Type 316, 321, or 347 stainless steel tubing (0.25-mm (0.010-in.) inside diameter) to the 229-mm section of 64 mm tubing which is to be used as a reservoir for the coating solution. The capillary column is generally coiled on a suitable mandrel before coating. To the other end of the capillary column, connect an additional 30 to 9 to 12 m (40 ft) of capillary tubing through a 1.6 mm (1/16-in.) Swagelok union.

6.2 Clean the tubing by passing 25 to 30 mL (5 to 6 reservoir volumes) of *n*-pentane through the tubing with about 1.7 to 2.1 MPa (250 to 300 psig gage) of inert gas. After the column has been cleaned, disconnect the upstream end of the reservoir tube and allow the pressure in the tubing to return to atmospheric.

6.3 Prepare a solution containing 6 volume percent of squalane in *n*-pentane. Fill the reservoir tube with the coating solution and promptly connect to the gas cylinder. Pass the coating solution through the column at 500 psig (3.5 MPa gage) until the solution begins issuing from the end of the capillary tubing; gradually reduce the inlet pressure in order to keep the flow of the solution at a relatively even rate of 40 to 60 drops/min. When the coating solution has been expelled from the column, reduce the inlet pressure to 345 kPa (50 psig gage) and allow gas to pass through the column for 1 to 2 h. Disconnect the 9 to 12-m (30 to 40-ft) tail section and then mount the column in the chromatograph.

6.4 To test column resolution use Fig. 1 and calculate  $R$ , from the distance between the cyclohexane and *n*-heptane peaks at the peak maxima,  $d$ , and the widths of the peaks at the baseline,  $Y_1$  and  $Y_2$ .

$$R = 2(d_1 - d_2)/(Y_1 + Y_2) \quad (1)$$

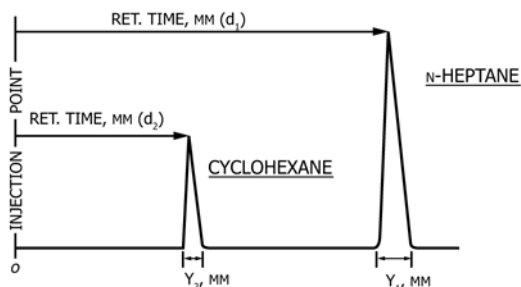


FIG. 1 Column Resolution ( $R$ ).

Resolution ( $R$ ), using the above equation, must exceed a value of 10.

## 7. Sample Preparation

7.1 Place 20 to 30 mL of the reference fuel (*n*-heptane or *isooctane*) into a 100-mL volumetric flask which has been previously weighed.

7.2 Weigh the sample. Using a 0.10-mL volumetric pipet, add 0.10 mL of the internal standard cyclohexane (99 mol %, min) and reweigh. Dilute to the mark with the *n*-heptane or *isooctane* sample and weigh. Use a 200-g analytical balance accurate to  $\pm 0.0002$  g. From these weights (masses) and the relative density (specific gravities) of cyclohexane and *n*-heptane or *isooctane*, calculate the volume percent of the cyclohexane internal standard to the nearest 0.001 volume percent. (Relative density (specific gravity) of cyclohexane at  $20^\circ\text{C} = 0.7786$ ; *n*-heptane = 0.6838, and 2,2,4-trimethylpentane = 0.6919.)

$$\text{Cyclohexane, volume \%} = \text{wt cyclohexane/rel dens cyclohexane} \quad (2)$$

$$\div (\text{wt reference fuel/rel dens reference fuel}) \times 100$$

## 8. Procedure

8.1 Adjust the operating variables to optimum conditions. Temperatures should be as follows: Injection port and splitter 150 to  $250^\circ\text{C}$ , column at optimum temperature and detector greater than  $100^\circ\text{C}$ . Adjust the excess gas flow through the splitter to provide a proper sample size to the column.

8.2 Using the microsyringe, inject sufficient sample containing the internal standard. Both the sample volume and the split ratio must be considered in choosing the correct volume of sample to inject. Volumes entering the column in the range of 0.002 to 0.005  $\mu\text{L}$  have been found satisfactory.

8.3 The various impurities present in the primary reference standards can be identified from retention time data obtained at the same gas chromatographic conditions. Typical chromatograms of ASTM *n*-heptane and ASTM *isooctane* are shown in Fig. 2. Relative retention time data for a number of hydrocarbons over squalane at  $30^\circ\text{C}$  are given in Table 1. The retention time data of Table 1 are corrected for the gas holdup of the column and are relative to *n*-heptane. Argon was used as the carrier gas.

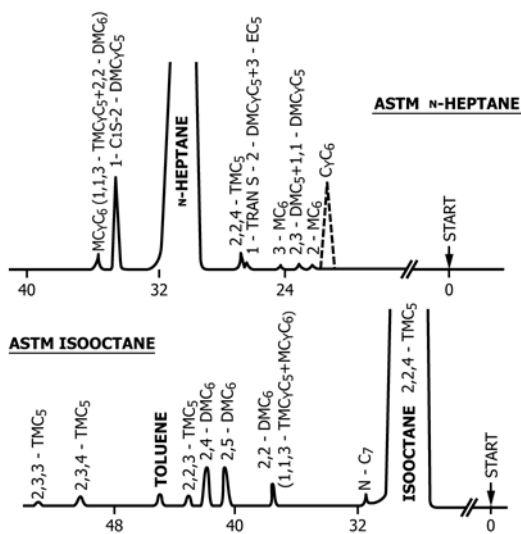
8.4 Hydrocarbons that are commonly found as impurities in ASTM *n*-heptane and ASTM *iso octane* are listed in Table 2.

## 9. Calculation

9.1 After identifying the various impurities, measure the peak area of each impurity peak and that of the internal standard, cyclohexane, by ball and disk integrator or electronic integrator. Calculate the volume percent of each impurity as follows:

$$V_I = \frac{V_s \times PA_I}{PA_s \times S_I \times (100 - V_s)} \times 100 \quad (3)$$

where:



Column: 0.25 mm (0.010-in.) inside diameter by 61-m (200-ft) stainless steel  
 Coating: squalane  
 Temperature: 30°C  
 Inlet Pressure: 110 kPa (16 psi gage) argon  
 Flow Rate: 0.85/min  
 Linear Velocity: 150 mm  
 Detector: hydrogen flame ionization  
 Sample Size: 0.2 µL split 100 to 1

FIG. 2 Chromatogram of ASTM *n*-Heptane and ASTM *Isooctane*

$V_I$  = volume percent of the impurity to be determined,  
 $V_S$  = volume percent of the internal standard, cyclohexane,  
 $PA_I$  = peak area of the impurity to be determined,  
 $PA_S$  = peak area of the internal standard, cyclohexane, and  
 $S_I$  = the response per unit volume of the hydrogen flame ionization detector to the impurity relative to the response per unit volume to cyclohexane.

9.2 Hydrogen flame ionization detector response is given for several hydrocarbons relative to cyclohexane in Table 3. Report the volume percent of each impurity.

9.3 Total the concentrations of the individual impurities and then calculate the purity of the *n*-heptane or *isooctane* sample by difference.

## 10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *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 the following values only one case in twenty:

$$0.010 \text{ volume \% at levels } > 99.5 \text{ volume \%} \quad (4)$$

10.1.2 *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 the following values only one case in twenty:

$$0.054 \text{ volume \% at levels } > 99.5 \text{ volume \%} \quad (5)$$

TABLE 1 Relative Retention Data for Various Hydrocarbons Over Squalane at 30°C (*n*-Heptane = 1.00)

Isopentane	0.08
<i>n</i> -Pentane	0.11
2,2-Dimethylbutane	0.16
Cyclopentane	0.22
2,3-Dimethylbutane	0.23
2-Methylpentane	0.24
3-Methylpentane	0.27
<i>n</i> -Hexane	0.33
2,2-Dimethylpentane	0.43
Methylcyclopentane	0.43
2,4-Dimethylpentane	0.46
Benzene	0.48
2,2,3-Trimethylbutane	0.50
3,3-Dimethylpentane	0.62
Cyclohexane	0.63
2-Methylhexane	0.69
2,3-Dimethylpentane	0.72
1,1-Dimethylcyclopentane	0.71
3-Methylhexane	0.76
1- <i>cis</i> -3-Dimethylcyclopentane	0.81
1- <i>trans</i> -3-Dimethylcyclopentane	0.84
3-Ethylpentane	0.85
1- <i>trans</i> -2-Dimethylcyclopentane	0.85
2,2,4-Trimethylpentane ( <i>isooctane</i> )	0.87
<i>n</i> -heptane	1.00
1- <i>cis</i> -2-Dimethylcyclopentane	1.20
2,2-Dimethylhexane	1.22
1,1,3-Trimethylcyclopentane	1.24
Methylcyclohexane	1.25
2,5-Dimethylhexane	1.36
Ethylcyclopentane	1.39
2,4-Dimethylhexane	1.42
2,2,3-Trimethylpentane	1.48
1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane	1.52
Toluene	1.54
3,3-Dimethylhexane	1.56
1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane	1.63
2,3,4-Trimethylpentane	1.71
2,3,3-Trimethylpentane	1.81

TABLE 2 Hydrocarbon Impurities Commonly Found in ASTM *n*-Heptane and *Isooctane*

Impurities in ASTM <i>n</i> -Heptane	
Major	Minor
1- <i>cis</i> -2-Dimethylcyclopentane	2-Methylhexane 2,3-Dimethylpentane
Methylcyclohexane	1,1-Dimethylcyclopentane
2,2,4-Trimethylpentane ( <i>isooctane</i> )	3-Methylhexane 1- <i>trans</i> -2-Dimethylcyclopentane 3-Ethylpentane
Impurities in ASTM <i>Isooctane</i>	
Major	
<i>n</i> -Heptane	
	2,2-Dimethylhexane 2,5-Dimethylhexane 2,4-Dimethylhexane 2,2,3-Trimethylpentane 2,3,4-Trimethylpentane 2,3,3-Trimethylpentane Toluene

10.2 The above precision values are based on cooperative data from seven laboratories using five samples. Calculations were performed using peak area. Both electronic integration and triangulation were employed.

10.3 Since there are no acceptable reference test methods for comparison, no statement of bias can be made.

**TABLE 3 Hydrogen Flame Ionization Detector Relative Response Data (Response per Unit Volume Relative to Cyclohexane)**

Compound	Relative Response per Unit Volume
Isopentane	0.84
<i>n</i> -Pentane	0.84
2,2-Dimethylbutane	0.87
Cyclopentane	1.00
2,3-Dimethylbutane	0.88
2-Methylpentane	0.87
3-Methylpentane	0.89
<i>n</i> -Hexane	0.87
2,2-Dimethylpentane	0.88
Methylcyclopentane	0.97
2,4-Dimethylpentane	0.88
Benzene	1.27
2,2,3-Trimethylbutane	0.91
3,3-Dimethylpentane	0.92
Cyclohexane	1.00
2-Methylhexane	0.89
2,3-Dimethylpentane	0.88
1,1-Dimethylcyclopentane	1.00
3-Methylhexane	0.90
1- <i>cis</i> -3-Dimethylcyclopentane	0.96
1- <i>trans</i> -3-Dimethylcyclopentane	0.96
3-Ethylpentane	0.92
1- <i>trans</i> -2-Dimethylcyclopentane	0.98
2,2,4-Trimethylpentane ( <i>isooctane</i> )	0.89
<i>n</i> -heptane	0.88
1- <i>cis</i> -2-Dimethylcyclopentane	0.99
2,2-Dimethylhexane	0.90
1,1,3-Trimethylcyclopentane	1.00
Methylcyclohexane	1.00
2,5-Dimethylhexane	0.90
Ethylcyclopentane	0.99
2,4-Dimethylhexane	0.89
2,2,3-Trimethylpentane	0.94
1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane	0.94
Toluene	1.19
3,3-Dimethylhexane	0.91
1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane	0.97
2,3,4-Trimethylpentane	0.92
2,3,3-Trimethylpentane	0.94

## 11. Keywords

11.1 ASTM knock test reference fuels; capillary column; gas chromatography; *isooctane*; *n*-heptane

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