Designation: D 3054 – 98

Standard Test Methods for Analysis of Cyclohexane by Gas Chromatography[1]

This standard is issued under the fixed designation D 3054; 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 These test methods cover the determination of the hydrocarbon impurities typically found in cyclohexane and the purity of cyclohexane by difference by gas chromatography. Typical impurities in high purity cyclohexane are listed in Table 1.

1.2 These test methods are applicable to impurity concentrations in the range of 0.0001 to 0.1000 wt% and for cyclohexane purities of 98 % or higher when using the internal standard procedure.

1.3 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, an observed value or a calculated value shall be rounded off to the nearest unit in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.4 *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 Note 2 and Section 7.

TABLE 1 Impurities Known or Suggested to be Present in Commercial Cyclohexane

C_4
(1) *n*-butane
(2) isobutane
C_5
(3) *n*-pentane
(4) isopentane
(5) cyclopentane
C_6
(6) *n*-hexane[A]
(7) 2-methylpentane
(8) 3-methylpentane
(9) methylcyclopentane[A]
(10) benzene[A]
(11) 2,2-dimethylbutane
(12) 2,3-dimethylbutane
C_7
(13) 3,3-dimethylpentane
(14) 2,3-dimethylpentane
(15) 1,1-dimethylcyclopentane
(16) 1,t3-dimethylcyclopentane
(17) 1,t2-dimethylcyclopentane
(18) 1,c2-dimethylcyclopentane
(19) 2,2-dimethylpentane
(20) 2,4-dimethylpentane
(21) 1,c3-dimethylcyclopentane
(22) ethylcyclopentane
(23) methylcyclohexane[A]
(24) 3-ethylpentane
(25) 3-methylhexane
(26) 2-methylhexane
(27) *n*-heptane

[A] These components were used to prepare the standards used in the round robin program.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3437 Practice for Sampling and Handling Liquid Cyclic Products[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

E 260 Practice for Packed Column Gas Chromatography[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[3]

2.2 *Other Document:*

OSHA Regulations, 29 CFR, Paragraphs 1910.1000 and 1910.1200[4]

3. Summary of Test Methods

3.1 *Test Method A: Internal Standard Procedure*—This procedure is used when the impurities are at 0.00010 to 0.1000 wt% levels. A known amount of internal standard is added to the sample. A portion of the sample is injected into the chromatograph and the levels of impurities are calculated relative to the amount of internal standard added. The amount

[1] These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and are the direct responsibility of Subcommittee D16.01 on Benzene, Toluene, Xylenes, Cyclohexane, and Their Derivatives.

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[2] *Annual Book of ASTM Standards*, Vol 06.04.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20004.

of measured impurities, including benzene, is subtracted from 100.00 to establish the purity of the cyclohexane samples.

3.2 *Test Method B: Straight Normalization Procedure*—A portion of the sample is injected into the chromatograph using a microlitre syringe at the specified conditions of the test method. The area of all the peaks and main component are electronically integrated. These areas are normalized to 100.00 %.

4. Significance and Use

4.1 These test methods are suitable for establishing contract specifications on cyclohexane and for use in internal quality control where cyclohexane is either produced or used in a manufacturing process. They may also be used in development or research work. Purity is commonly reported by subtracting the determined impurities from 100.00. However, a gas chromatographic analysis can not determine absolute purity if unknown components are contained within the material being examined.

NOTE 1—In case of dispute, the internal standard procedure will be the correct procedure to use.

5. Apparatus

5.1 *Gas Chromatograph (GC) (for a Fused Silica Column)*—A multi-ramp temperature, programmable GC built for capillary column chromatography. It must have a flame ionization detector and a split injection system that will not discriminate over the boiling range of the samples analyzed.

5.1.1 *Gas Chromatograph*—Any chromatograph having a flame ionization detector that can be operated at the conditions given in Table 2. The system should have sufficient sensitivity to obtain a minimum peak height response for a 0.0001 wt% impurity twice the height of the signal background noise.

5.2 *Chromatographic Column*—The recommended column is a methyl silicone-fused silica capillary column. Any other column used must be capable of resolving all significant impurities from cyclohexane. The internal standard peak must be individually resolved without interference from cyclohexane or any other impurities. A typical chromatogram with the identified impurities is found in Fig. 1.

TABLE 2 Typical Instrument Conditions for Cyclohexane Analysis (See Chromatogram Fig. 1)

Instrument:	
Range	3
Attenuation	1
Inlet, °C	200
Detector,° C	275
Sample size, µL	1.2
Column:	
Carrier gas	helium
Linear velocity, cm/sec	20.0
Split ratio	45:1
Tubing	fused silica
Stationary phase	methyl silicone
Solid support	cross-linked
Film thickness, µm	0.50
Length, m	60
Inside diameter, mm	0.32
Temperature Program:	
Initial, °C	32
Time, min	6
Rate No. 1, °C/min	5
Intermediate, °C	52
Time, min	5
Rate No. 2,° C/min	20
Final, °C	230
Time, min	9
Internal Standard:	
2,2-Dimethylbutane	

5.2.1 *Cross-Linked Methyl Silicone Fused Silica Capillary Column*, 60 m by 0.50 µm film thickness by 0.32 mm inside diameter.

5.3 *Integrator or Data Handling System*— Electronic or equivalent equipment for obtaining peak areas. This device must integrate areas at a rate of 15 readings per second so that very narrow peaks resulting from fused silica capillary columns can be accurately measured.

5.4 *Microsyringes*, capacities 1.0 or 10 µL, and 50 µL.

5.5 *Volumetric Flasks*, 100-mL capacity.

6. Reagents and Materials

6.1 *2,2-Dimethylbutane*, 99.0 % minimum purity (internal standard).

6.2 *Helium*.

6.3 *Hydrogen and Air*, for FID detector.

7. Hazards

7.1 Consult current OSHA regulations, suppliers' Material Safety Data Sheets (MSDS), and local regulations for all materials used in this test method.

8. Sampling

8.1 Take samples in accordance with Practice D 3437.

9. Procedures

9.1 *Test Method A*:

9.1.1 *Internal Standard Procedure*—Install the chromatographic column and establish stable instrument operation at the proper operating conditions shown in Table 2. The selected column and conditions must satisfy the resolution requirements as stated in 5.2. Make reference to instructions provided by the manufacturer of the chromatograph, and to Practices E 260 and E 1510.

9.1.2 Place 50 to 60 mL of the cyclohexane sample to be analyzed into a 100-mL volumetric flask. Accurately add, using a micropipet or microsyringe, 25 µL of the internal standard to the flask and then fill to the calibration mark with additional sample. Based on using 2,2-dimethylbutane as the internal standard with a density of 0.649 g/mL (C20°C) and cyclohexane with a density of 0.778 g/mL, the concentration of the internal standard will be 0.021 wt%. Similar calculations must be made for any alternative internal standard that may be used. Mix the above, blend thoroughly, and analyze using the chromatographic conditions stated in Table 2.

9.2 *Test Method B*:

9.2.1 *Straight Normalization Procedure*— Proceed as in 9.1.1. Then, inject a proper specimen size directly into the gas chromatograph. Integrate all peaks, impurities, and cyclohexane.

NOTE 2—**Caution:** A smaller specimen size might be required so as not to exceed the dynamic range of the instrument used.