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.

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]

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.

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 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

[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.

Current edition approved Aug. 10, 1998. Published October 1998. Originally published as D 3054 – 93. Last previous edition D 3054 – 95.

[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.

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.

10. Calculation

10.1 *Calculation for Internal Standard Procedure*:

10.1.1 For the purposes of this test method the response factors for the impurities and for the internal standard are

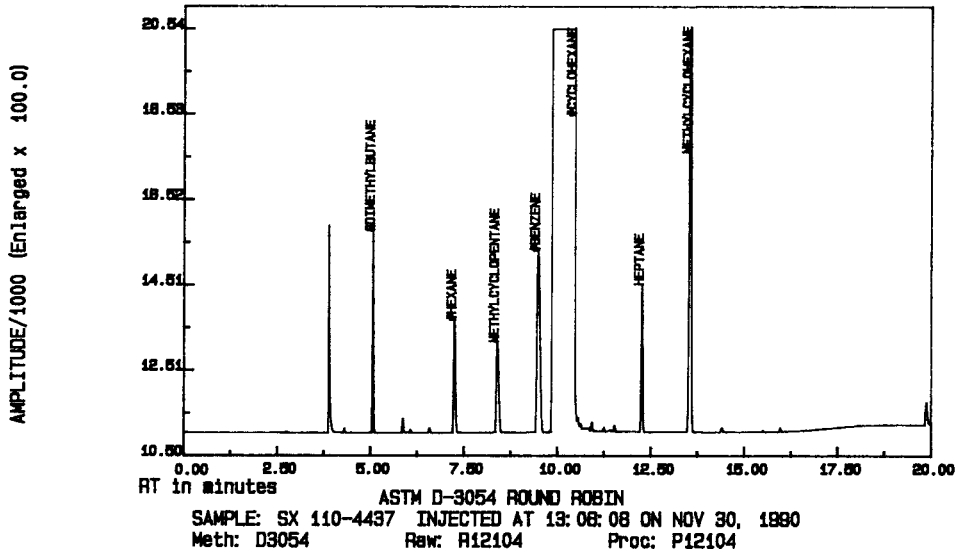

FIG. 1 Sample 110-4437

considered to be unity (=1.00). Calculate the concentration of the impurities as follows:

$$C_i = \frac{(A_s)(C_s)}{(A_s)} \quad (1)$$

where:

A_i = peak area of impurity, *i*,
C_s = concentration of the internal standard, as calculated in 9.1.2
A_s = peak area of internal standard, and
C_i = concentration of impurity, *i*,

and:

10.1.2 Calculate the total concentration of impurities as follows:

$$C_t = \Sigma\ C_{i's} \quad (2)$$

where:

C_t = total concentration of all impurities, weight %.

10.1.3 *Cyclohexane Purity by Difference (Weight Percent)*:

$$Cyclohexane, \% = 100.00 - C_t \quad (3)$$

TABLE 3 Intermediate Precision (Formerly Called Repeatability) and Reproducibility[A]

Internal Standard Method				
Component	Expected Concentration wt %	Average-Reported Concentration wt %	Intermediate Precision	Reproducibility
Purity	99.9755	99.9755	0.0006	0.0017
	99.7866	99.7830	0.0072	0.0175
n-Hexane	0.0050	0.0050	0.0001	0.0003
	0.0207	0.0189	0.0003	0.0015
n-Heptane	0.0049	0.0049	0.0004	0.0007
	0.0208	0.0209	0.0002	0.0016
Methylcyclopentane	0.0047	0.0047	0.0002	0.0009
	0.0208	0.0220	0.0004	0.0017
Benzene	0.0010	0.0009	0.0001	0.0004
	0.0507	0.0534	0.0015	0.0098
Methylcyclohexane	0.0089	0.0089	0.0004	0.0014
	0.1004	0.1016	0.0022	0.0153

[A] Outliers removed from data. All 5 participating laboratories used 1.0 response factors for impurities and the internal standard.

10.2 *Calculation for Straight Normalization Procedure*:

NOTE 3—Detector response factors have been defined to be equal to unity; therefore, area percent is equivalent to weight percent.

10.2.1 *Area Percent Cyclohexane*:

$$Cyclohexane, \% = (A_1/A_2) \times 100 \quad (4)$$

where:

A_1 = integrated area of cyclohexane, and
A_2 = total integrated areas of all peaks.

10.2.2 *Area Percent Impurities*:

$$impurity-i, \% = (A_1/A_2) \times 100 \quad (5)$$

where:

A_1 = integrated area for impurity peak" *i*", and
A_2 = total integrated areas of all peaks.

11. Report

11.1 Report the following information:

11.1.1 The cyclohexane purity of the sample to the nearest 0.01 wt%.

11.1.2 The amount of each impurity in the sample to the nearest 0.0001 wt% for the Internal Standard Procedure and to the nearest 0.0010 wt% for the Straight Normalization Procedure.

12. Precision and Bias [5]

12.1 *Precision*—The following criteria should be used to judge the acceptability (95 % probability level) of results obtained by this test procedure. The criteria were derived from an interlaboratory study among five participating laboratories. The data were determined on two days using different operators and using two samples. The samples were gravimetrically prepared from recrystallized cyclohexane and the individual hydrocarbon impurities to the concentrations listed in Table 3

[5] Supporting data are available from ASTM International Headquarters. Request RR: D16–1016.

and Table 4. The results of the interlaboratory study were calculated and analyzed using Practice E 691.

12.1.1 *Intermediate Precision*, (formerly called Repeatability)—Results in the same laboratory should not be considered suspect unless they differ by more than the amount shown in Table 3 and Table 4. On the basis of test error alone, the difference between two test results obtained in the same laboratory on the same material will be expected to exceed this value only 5 % of the time.

12.1.2 *Reproducibility*—Results obtained by each of two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 3 and Table 4. On the basis of test error alone, the difference between two test results obtained in different laboratories on the same material will be expected to exceed this value only 5 % of the time.

TABLE 4 Intermediate Precision (Formerly Called Repeatability) and Reproducibility[A]

Straight Normalization Method				
Component	Expected Concentration wt %	Average-Reported Concentration wt %	Intermediate Precision	Reproducibility
Purity	99.9755	99.9751	0.0009	0.0021
	99.7866	99.7851	0.0051	0.0113
n-Hexane	0.0050	0.0050	0.0003	0.0006
	0.0207	0.0194	0.0027	0.0038
n-Heptane	0.0049	0.0049	0.0002	0.0007
	0.0208	0.0208	0.0001	0.0011
Methylcyclopentane	0.0047	0.0046	0.0004	0.0009
	0.0208	0.0211	0.0005	0.0029
Benzene	0.0010	0.0010	0.0007	0.0010
	0.0507	0.0518	0.0025	0.0062
Methylcyclohexane	0.0089	0.0088	0.0003	0.0014
	0.1004	0.1018	0.0036	0.0081

[A] Outliers removed from data. All 5 participating laboratories used 1.0 response factors for impurities.

12.2 *Bias*—Although the interlaboratory test utilized a sample prepared gravimetrically from chemicals obtained at the highest purity available, these samples have not been approved as an acceptable reference material and consequently bias has not been determined.

12.2.1 As an aid for the users in determining the possibility of bias, the calculated concentration of each impurity in the two round robin samples is listed in Table 3 and Table 4 as the "expected concentration." The average value for each impurity as reported from the six participating laboratories is listed as "average concentration reported."

13. Keywords

13.1 cyclohexane; gas chromatography; impurities