Designation: D7266 – 13$^{\varepsilon 1}$

Standard Test Method for Analysis of Cyclohexane by Gas Chromatography (External Standard)[1]

This standard is issued under the fixed designation D7266; 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.

ε[1] NOTE—The number of samples in Section 15.1 was corrected editorially in April 2013.

1. Scope*

1.1 This test method covers the determination of the purity of cyclohexane by gas chromatography. Calibration of the gas chromatography system is done by the external standard calibration technique.

1.2 This test method has been found applicable to the measurement of impurities such as those found in Table 1, which are impurities that may be found in cyclohexane. The impurities can be analyzed over a range of 3 to 200 mg/kg by this method, but may be applicable to a wider range.

1.3 The limit of detection is 1 mg/kg.

1.4 In determining the conformance of the test results using this test method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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 Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E355 Practice for Gas Chromatography Terms and Relationships

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

2.2 *Other Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200 [3]

3. Terminology

3.1 See Terminology D4790 for definitions of terms used in this test method.

4. Summary of Test Method

4.1 Cyclohexane is analyzed using a gas chromatograph (GC) equipped with a flame ionization detector (FID). A precisely repeatable volume of the sample to be analyzed is injected onto the gas chromatograph. The peak areas of the impurities are measured and converted to concentrations via an external standard methodology. Purity by GC (the cyclohexane content) is calculated by subtracting the sum of the impurities from 100.00. Individual impurities are reported in mg/kg. The cyclohexane purity is reported in weight percent.

5. Significance and Use

5.1 This test method is suitable for setting specifications on the materials referenced in Table 1 and for use as an internal

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

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[2] 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.

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

***A Summary of Changes section appears at the end of this standard**

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

	C_4
(1)	*n*-butane
(2)	isobutene
	C_5
(3)	*n*-pentane
(4)	isopentane
(5)	cyclopentane
	C_6
(6)	*n*-hexane
(7)	2-methylpentane
(8)	3-methylpentane
(9)	methylcyclopentane
(10)	benzene
(11)	cyclohexene
(12)	2,2-dimethylbutane
(13)	2,3-dimethylbutane
	C_7
(14)	3,3-dimethylpentane
(15)	2,2-dimethylpentane
(16)	2,3-dimethylpentane
(17)	2,4-dimethylpentane
(18)	1,1-dimethylcyclopentane
(19)	*trans*-1,3-dimethylcyclopentane
(20)	*trans*-1,2-dimethylcyclopentane
(21)	*cis*-1,2-dimethylcyclopentane
(22)	2,2-dimethylcyclopentane
(23)	2,4-dimethylcyclopentane
(24)	*cis*-1,3-dimethylcyclopentane
(25)	ethylcyclopentane
(26)	methylcyclohexane
(27)	3-ethylpentane
(28)	3-methylhexane
(29)	2-methylhexane
(30)	*n*-heptane
(31)	toluene
	C_8
(32)	*iso*-octane
(33)	*p*-xylene
	C_9
(34)	isopropylcylohexane

quality control tool where cyclohexane is produced or is used in a manufacturing process. It may also be used in development or research work involving cyclohexane.

5.2 This test method is useful in determining the purity of cyclohexane with normal impurities present. If extremely high boiling or unusual impurities are present in the cyclohexane, this test method would not necessarily detect them and the purity calculation would be erroneous.

6. Apparatus

6.1 *Gas Chromatograph*—Any instrument 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 1 mg/kg benzene of twice the height of the signal background noise.

6.2 *Columns*—The choice of column is based on resolution requirements. Any column may be used that is capable of resolving all significant impurities from cyclohexane. The column described in Table 2 has been used successfully.

6.3 *Recorder*—Electronic integration is required.

6.4 *Injector*—The specimen must be precisely and repeatably injected into the gas chromatograph. An automatic sample injection device is highly recommended. Manual injection can

TABLE 2 Instrumental Parameters

Detector	flame ionization
Injection Port	capillary splitter
Column A:	
Tubing	fused silica
Stationary phase	bonded and crosslinked 100 % dimethylpolysiloxane†
Film thickness, µm	0.5
Length, m	100
Diameter, mm	0.25
Temperatures:	
Injector, °C	230
Detector, °C	250
Oven, °C	32 hold for 12 min Ramp 1 = 8°C/min to 64°C, hold for 10 min Ramp 2 = 10°C/min to 200°C, hold for 5 min
Carrier gas	Hydrogen
Flow rate, mls/min	3
Split ratio	100:1
Sample size, µl	1.0

† Corrected editorially.

be employed if the precision stated in Tables 3–7 can be reliably and consistently satisfied.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Gases*—Helium, hydrogen, nitrogen, or other as carrier. Carrier, makeup, and detector gases (except air) 99.999 % minimum purity. Oxygen in carrier gas less than 1 ppm, less than 0.5 ppm is preferred. Purify carrier, makeup, and detector gases to remove oxygen, water, and hydrocarbons. Purify air to remove hydrocarbons and water, and the air used for an FID should contain less than 0.1 ppm total hydrocarbons.

8. Hazards

8.1 Consult current OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials listed in this test method.

9. Sampling and Handling

9.1 Sample the material in accordance with Practice D3437.

10. Preparation of Apparatus

10.1 Follow manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the conditions described in Table 2 allowing

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

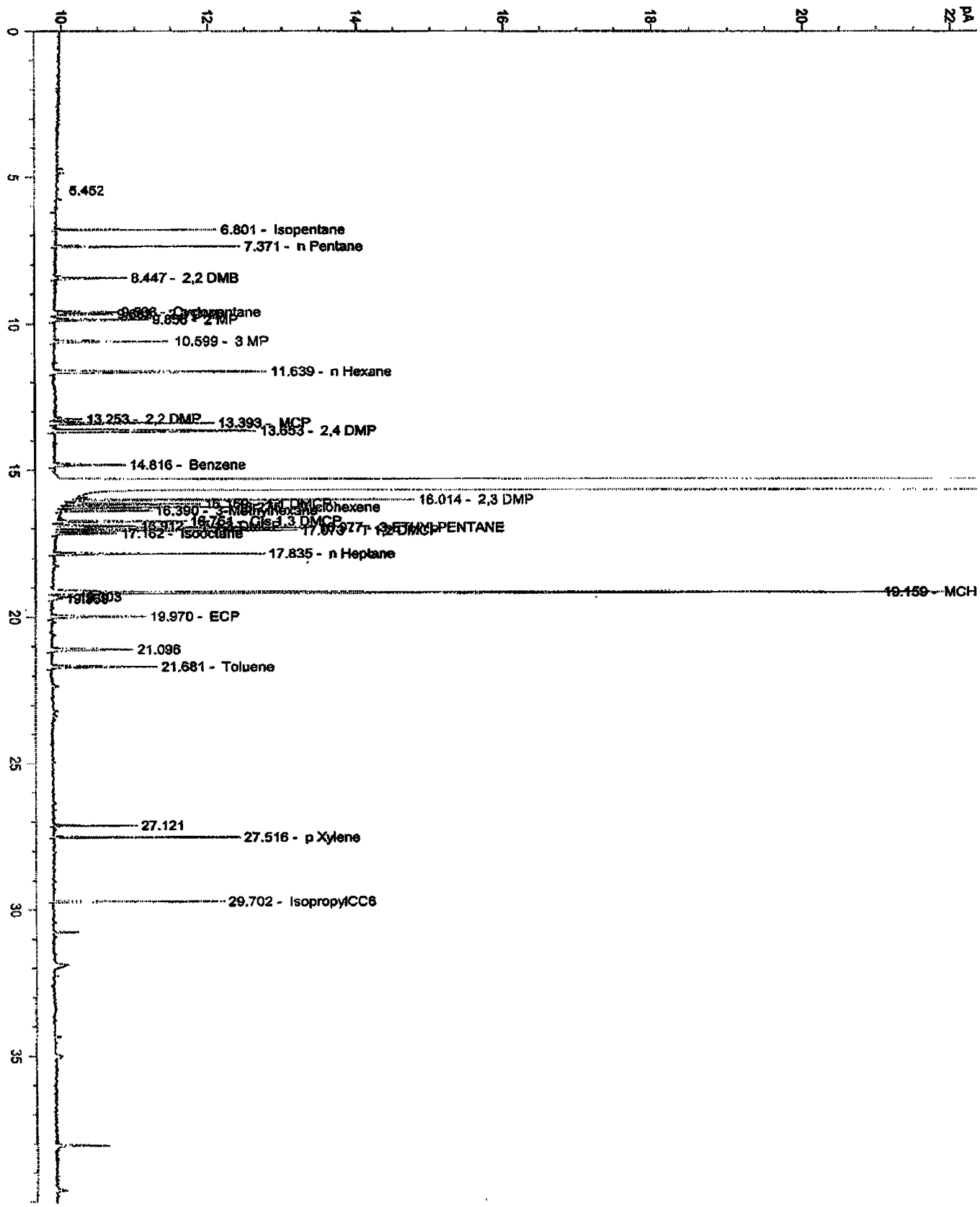

FIG. 1 Typical Chromatogram of Calibration Mixture Using Conditions in Table 2

sufficient time for the equipment to reach equilibrium. See Practices E1510 and E355 for additional information on gas chromatography practices and terminology.

11. Calibration

11.1 Prepare a synthetic mixture of high purity cyclohexane containing impurities at concentrations representative of those expected in the samples to be analyzed in accordance with Practice D4307. The weight of each hydrocarbon impurity must be measured to the nearest 0.1 mg. Because the availability of stock cyclohexane with a purity higher than 99.97 % is problematic, the method of standard additions may be required for impurities such as methycyclohexane and methylcyclopentane, as well as for a number of the other impurities listed in Table 1 that are commonly present.

11.2 Inject the resulting solution from 11.1 into the gas chromatograph, collect and process the data. A typical chromatogram is illustrated in Fig. 1 based on the conditions listed in Table 2.

11.3 Determine the response factor for each impurity in the calibration mixture as follows:

$$Rf_i = \frac{C_i}{A_i} \quad (1)$$

where:

Rf_i = response factor for impurity i,
C_i = concentration of impurity i in the calibration mixture, and
A_i = peak area of impurity i.

11.4 Initially analyze the calibration solution a minimum of three times and calculate an average Rf_i. Subsequent calibrations may be a single analysis as long as the response factors for all components of interest are within ±5 % of the initial validation response factors. A "rolling" average as defined by most modern chromatographic software may also be used. The response factor for *n*-hexane is used for unknowns.

12. Procedure

12.1 Inject into the gas chromatograph an appropriate amount of sample as previously determined in accordance with 6.1 and start the analysis.

12.2 Obtain a chromatogram and peak integration report.

13. Calculations

13.1 Calculate the concentration of each impurity as follows:

$$C_i = (A_i)\,(Rf_i) \quad (2)$$

where:

C_i = concentration of component i in mg/kg,
A_i = peak area of component i, and
Rf_i = response factor for component i.

13.2 Calculate the total concentration of all impurities in wt % as follows:

$$C_t = \frac{\sum C_i}{10\,000} \quad (3)$$

where:

C_t = total concentration of all impurities in wt %.

13.3 Calculate the purity of cyclohexane as follows:

$$\text{Cyclohexane, weight percent} = 100.00 - C_t \quad (4)$$

14. Report

14.1 Report the individual impurities to the nearest mg/kg.

14.2 Report the purity of cyclohexane to the nearest 0.01 wt %.

15. Precision and Bias[5]

15.1 An ILS was conducted which included two laboratories analyzing six samples three times. One lab analyzed the samples on two different instruments. Practice E691 was followed for the design and analysis of the data; this ILS did not meet Practice E691 minimum requirements of six labs, four materials, and two replicates. The details are given in ASTM Research Report No. RR:D16-1045.

15.2 *Repeatability (r)*—Results should not be suspect unless they differ by more than shown in Tables 3-7. Results differing by less than "*r*" have a 95 % probability of being correct.

15.3 *Reproducibility (R)*—Results submitted by two labs should not be considered suspect unless they differ by more than shown in Tables 3-7. Results differing by less than "*R*" have a 95 % probability of being correct.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1045. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Methylcyclopentane (mg/kg)

	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	93	4	12
Sample 1	249	7	24
Sample 2	217	4	28
Sample 3	170	3	22
Sample 4	131	3	13
Sample 5	101	2	14

[A] The average of the laboratories' calculated averages.

TABLE 4 Benzene (mg/kg)

	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	0	0	0
Sample 1	43	1	39
Sample 2	34	1	30
Sample 3	22	1	19
Sample 4	11	0.4	10
Sample 5	3	1	3

[A] The average of the laboratories' calculated averages.

TABLE 5 Methylcyclohexane (mg/kg)

	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	75	3	23
Sample 1	264	7	89
Sample 2	227	5	74
Sample 3	172	4	60
Sample 4	124	3	44
Sample 5	88	15	36

[A] The average of the laboratories' calculated averages.

TABLE 6 Hexane (mg/kg)

	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	212	10	10
Sample 1	410	10	19
Sample 2	369	11	23
Sample 3	307	6	21
Sample 4	258	7	11
Sample 5	220	3	12

[A] The average of the laboratories' calculated averages.

TABLE 7 Cyclohexane (wt %)

	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	99.948	0.003	0.030
Sample 1	99.895	0.005	0.066
Sample 2	99.905	0.003	0.058
Sample 3	99.921	0.002	0.047
Sample 4	99.935	0.002	0.040
Sample 5	99.945	0.001	0.030

[A] The average of the laboratories' calculated averages.

15.4 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method, bias has not been determined.

15.5 The precision statement was determined through statistical examination of 270 results, from two laboratories, on a blank and five samples. The following amounts of impurities were added to the samples:

	Sample 1 mg/kg	Sample 2 mg/kg	Sample 3 mg/kg	Sample 4 mg/kg	Sample 5 mg/kg
hexane	199	159	100	50	10
methylcyclopentane	150	119.9	75	37.5	7.5
benzene	49.9	39.9	25	12.5	2.5
methycyclohexane	201	160	100	50	10

16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.

16.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

16.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

16.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

16.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

17. Keywords

17.1 analysis by gas chromatography; benzene; cyclohexane

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7266 – 07ε1) that may impact the use of this standard. (Approved February 1, 2013.)

(1) The scope was expanded to determine impurities from 3 to 200 mg/kg.
(2) Precision and Bias was replaced with a complete precision statement.
(3) Quality Guidelines was replaced with the current editorial guidelines for quality.