Designation: ~~D7266 – 13 (Reapproved 2018)$^{\varepsilon 1}$~~ D7266 – 23

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—Section 8 was editorially corrected in January 2018.~~

1. ~~Scope~~ 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~~ is 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.~~. This test method is applicable to samples with concentrations to 400 mg/kg, but may be applicable to a wider range. The limit of detection (LOD) is 1 mg/kg and the limit of quantitation (LOQ) is 3 mg/kg for benzene.

NOTE 1—The LOD and LOQ were calculated from the ILS data for benzene.

~~1.3 The limit of detection is 1 mg/kg.~~

1.3 ~~In~~ The following applies for the purposes of 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.

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty 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.

***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

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.

[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.

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 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~~ and conditions described in Table 2 has been used ~~successfully.~~successfully and shall be used as a referee in cases of dispute.

6.3 ~~*Recorder*—Electronic integration is required.~~Chromatographic data systems are preferred but electronic integration may be used if the user can demonstrate that the results are consistent with the precision statement.

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 be employed if the precision stated in Tables 3–7 can be reliably and consistently satisfied.~~An autoinjector is required.

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

TABLE 2 ~~Instrumental Parameters~~Recommended Operating Conditions

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 1 = 8 °C/min to 64 °C, hold for 10 min ~~Ramp 2 = 10°C/min to 200°C, hold for 5 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

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 *Instrument Setup Check Sample:*

7.2.1 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.

7.2.1.1 Include sufficient n-octane so the standard contains approximately 2 mg/kg n-octane.

7.2.1.2 Below are impurities that may be included.

isopentane CAS 78-78-4
n-pentane CAS 109-66-0
2,2-dimethylbutane CAS 75-83-2
2,3-dimethylbutane CAS 79-29-8
cyclopentane CAS 287-92-3
2-methylpentane CAS 107-83-5
3-methylpentane CAS 96-14-0
n-hexane CAS 110-54-3
2,2-dimethylpentane CAS 590-35-2
methylcyclopentane CAS 96-37-7
2,4-dimethylpentane CAS 108-08-7
benzene CAS 71-43-2
2,3-dimethylpentane CAS 565-59-3
Iso-octane CAS 540-84-1
n-heptane CAS 142-82-5
methylcyclohexane CAS 108-87-2
ethylcyclopentane CAS 1640-89-7
Toluene CAS108-88-3
p-xylene CAS 106-42-3
isopropylcylohexane CAS 696-29-7
1,1-dimethylcyclopentane CAS 1638-26-2
trans-1,3-dimethylcyclopentane CAS 1759-58-6
trans-1,2 dimethylcyclopentane CAS 822-50-4
cis-1,2-dimethylcyclopentane CAS 1192-18-3
cis-1,3-dimethylcyclopentane CAS 2532-58-3
3-ethylpentane CAS 617-78-7
3-methylhexane CAS 589-34-4
2-methylhexane CAS 591-76-4

7.2.1.3 The purpose of this setup sample is to calibrate the instrument, determine retention times of impurities, and determine if setup has the required sensitivity.

7.3 *Gases*—Helium, hydrogen, nitrogen, or other as ~~carrier.~~ carrier are permitted. Hydrogen carrier gas was used to develop this standard. Use of helium or nitrogen require different conditions. The user must conduct the necessary evaluation to determine that equivalent results are obtained. 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' Safety Data Sheets, and local regulations for all materials listed in this test method.

[4] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* 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.

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 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.~~

11.1 Inject the ~~resulting solution~~ instrument set up check sample from ~~11.1~~7.2 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.

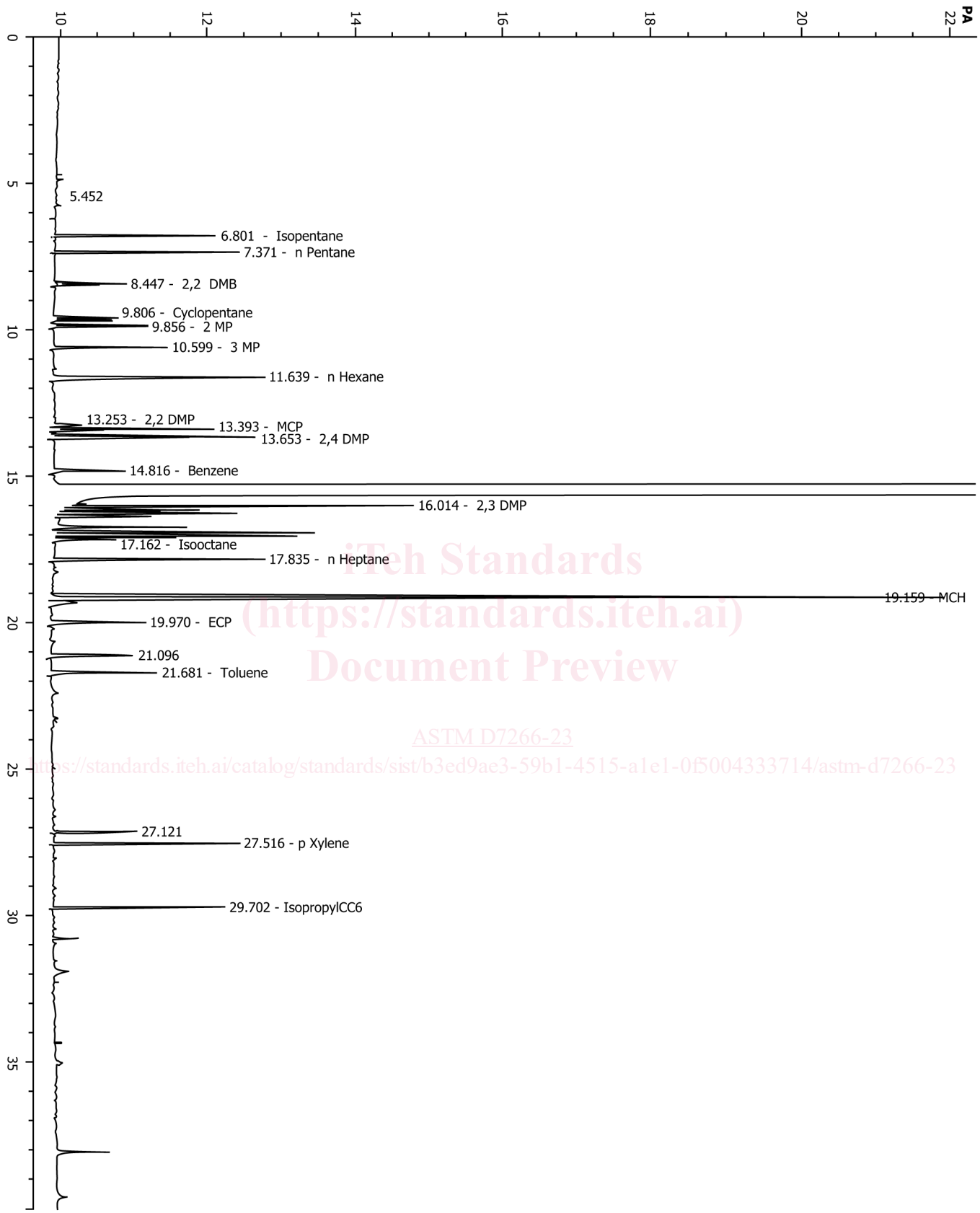

FIG. 1 Typical Chromatogram of Calibration Mixture Using Conditions in Table 2

~~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.~~

11.2 Initially analyze the ~~calibration solution~~ instrument setup check sample a minimum of three times and calculate an average ~~Rf~~Rfi.~~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.

11.3 Determine the response factor for each impurity in the instrument setup check sample 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 instrument setup check sample, and
A_i = peak area of impurity i.

11.4 Calculate instrument sensitivity.

11.4.1 Calculate n-octane using the response factor for n-hexane. Acceptable results are 0.9 mg/kg to 3 mg/kg.

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 %.