Designation: D7871 – 13

Standard Test Method for Analysis of Cyclohexane by Gas Chromatography (Effective Carbon Number)[1]

This standard is issued under the fixed designation D7871; 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 This test method covers the determination of the purity of cyclohexane by gas chromatography.

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 1 to 400 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 hazards statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

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 Standards:*[3]

OSHA Regualtions, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Terminology

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

4. Summary of Test Method

4.1 The specimen to be analyzed is injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column. The peak area of each component is measured and adjusted using effective carbon number (ECN)[4] response factors. The concentration of each component is calculated based on its relative percentages of total adjusted peak area and normalized to 100.0000 %.

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.

[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.

[4] Scanlon, J. T. and Willis, D. E., "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Concept," *Journal of Chromatographic Science*, Vol. 23, August 1985, ppl. 333-339.

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

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.

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

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 may be employed if the precision stated in Tables 4–8 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.[5] 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.

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

11. Calibration and Standardization

11.1 Prior to implementation of the ECN method, a laboratory should demonstrate that acceptable precision and bias can be obtained using a synthetic mixture of known composition (calibration check sample). (Fig. 1)

12. Procedure

12.1 Bring the sample to room temperature.

12.2 Check the chromatography performance to make sure that the column is properly resolving peaks.

[5] *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.

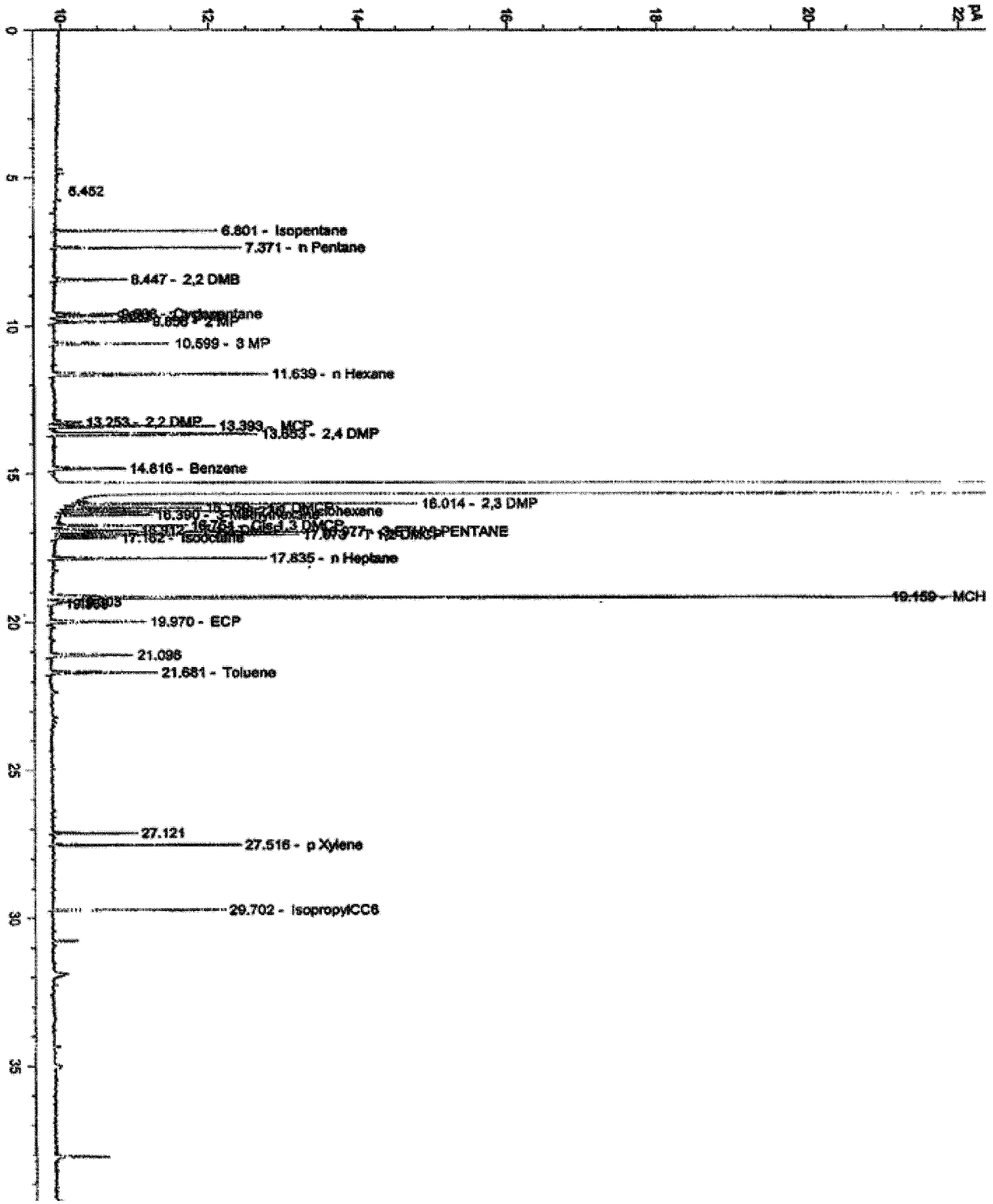

FIG. 1 Typical Chromatogram of Calibration Mixture Using Conditions in Table 2

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

12.4 Obtain a chromatogram and peak integration report.

13. Calculations

13.1 Using the ECN weight response factors listed in Table 3, calculate the concentration of each component as follows:

$$C_i = (A_i \times R_i) \times 1{,}000{,}000 / \Sigma (A_i \times R_i) \quad (1)$$

where:

C_i = concentraion for component i, mg/kg,
A_i = peak area of component i, and
R_i = ECN response factor for component i.

13.2 Calculate the purity of cyclohexane as follows:

$$\text{Cyclohexane, weight percent} = C_i / 10{,}000 \quad (2)$$

where C_i is mg/kg of cyclohexane.

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 %.

TABLE 3 Effective Carbon Number Response Factors

Component	Response Factor (Weight)[A]
benzene	0.91
butane	1.015
cyclohexane	0.98
cyclopentane	0.98
2-methylpentane	1.003
3-methylpentane	1.003
2,2-dimethylpentane	1.00
2,3-dimethylpentane	1.00
2,4-dimethylpentane	1.00
2,2-demethylbutane	1.003
2,3-dimethylbutane	1.003
1,1-dimethylcyclopentane	0.98
3-ethylpentane	0.98
hexane	1.003
methylcyclopentane	0.98
2-methylhexane	1.00
n-pentane	1.008
toluene	0.92
o-xylene	0.9275
m,p-xylene	0.9275
unidentified peaks	1.000

[A] Response factors are relative to *n*-heptane.

15. Precision and Bias[6]

15.1 An ILS was conducted which included two laboratories analyzing six sample three times. 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: RR:D16-1046.

15.2 *Repeatability (r)*—Results should not be suspect unless they differ by more than shown in Tables 4-8. 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 4-8. Results differing by less than "*R*" have a 95 % probability of being correct.

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 180 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

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1046. Contact ASTM Customer Service at service@astm.org.

TABLE 4 Methylcyclopentane (mg/kg)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	86	2	2
Sample 1	232	3	3
Sample 2	202	3	3
Sample 3	159	2	2
Sample 4	123	2	2
Sample 5	93	4	4

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

TABLE 5 Benzene (mg/kg)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	0	0.9	0.9
Sample 1	50	2	2
Sample 2	40	2	2
Sample 3	26	2	2
Sample 4	13	2	2
Sample 5	4	0.5	1

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

TABLE 6 Methylcyclohexane (mg/kg)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	85	3	22
Sample 1	290	8	44
Sample 2	249	10	42
Sample 3	188	3	36
Sample 4	136	4	27
Sample 5	95	4	23

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

TABLE 7 Hexane (mg/kg)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	205	5	7
Sample 1	403	8	9
Sample 2	362	7	7
Sample 3	303	2	4
Sample 4	255	7	7
Sample 5	215	7	7

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

TABLE 8 Cyclohexane (wt %)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Blank	99.939	0.001	0.009
Sample 1	98.879	0.001	0.012
Sample 2	99.891	0.004	0.011
Sample 3	99.908	0.001	0.009
Sample 4	99.923	0.002	0.010
Sample 5	99.935	0.001	0.009

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