Designation: D5713 – 14

Standard Test Method for Analysis of High Purity Benzene for Cyclohexane Feedstock by Capillary Gas Chromatography[1]

1. Scope*

1.1 This test method covers the determination of specific impurities in, and the purity of benzene for cyclohexane feedstock by gas chromatography.

1.2 This test method has been found applicable to benzene in the range from 99 to 100 % purity and to impurities at concentrations of 2 to 10 000 mg/kg.

1.3 In determining the conformance of the test results using this 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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 7.2 and 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

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

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 *Definitions:*

3.1.1 See Terminology D4790 for definition of terms used in this test method.

4. Summary of Test Method

4.1 In this test method, the chromatogram peak area for each impurity is compared to the peak area of the internal standard (*n*-octane or other suitable known) added to the sample. From the response factor of toluene relative to that of the internal standard, and using a response factor of 1.00 for nonaromatic impurities and the amount of internal standard added, the concentrations of the impurities are calculated. The benzene content is obtained by subtracting the total amount of all impurities from 100.00.

5. Significance and Use

5.1 This test method is useful for benzene purity on the basis of impurities normally present in benzene and may be used for final product inspections and process control.

5.2 This test method will detect the following impurities: toluene, methylcyclopentane, *n*-hexane, 2-methylhexane, cyclohexane, cyclopentane, 2-methylpentane, 2,3-dimethylpentane, 3-methylhexane, *n*-heptane, methylcyclohexane, ethylcyclopentane, 2,4-dimethylhexane, trimethylpentane, and others where specific impurity standards

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[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**

are available. Absolute purity cannot be accurately determined if unknown impurities are present.

6. Apparatus

6.1 *Gas Chromatograph*—Any gas chromatograph having a temperature programmable oven, flame ionization detector and a splitter injector suitable for use with a fused silica capillary column may be used, provided the system has sufficient sensitivity that will give a minimum peak height of 3 times the background noise for 2 mg/kg of an impurity.

6.2 *Column*—Fused silica capillary columns have been found to be satisfactory. An example is 50 m of 0.20-mm inside diameter fused silica capillary internally coated to a film thickness of 0.50 µm with polydimethylsiloxane (see Table 1 for suggested instrument parameters). Other columns may be used after it has been established that such a column is capable of separating all major impurities (for example, compounds listed in 5.2) and the internal standard from the benzene under operating conditions appropriate for the column. The column must give satisfactory resolution (distance from the valley between the peaks is not greater than 50 % of the peak heights of the impurity) of cyclohexane from benzene as well as other impurity peaks. A poorly resolved peak, such as cyclohexane, will often require a tangent skim from the neighboring peak.

6.3 *Electronic Integration,* with tangent skim capabilities is recommended.

6.4 *Vial.*

6.5 *Microsyringes,* assorted volumes.

6.6 *Injector,* the specimen must be precisely and repeatedly injected into the gas chromatograph. An automatic sample injection device is highly recommended. Manual injection can be employed if the precision stated in Table 2 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 *Carrier Gas*—a carrier gas (99.999 % minimum purity) appropriate to the type of detector used should be employed. (**Warning**—If hydrogen is used as the carrier gas, take special safety precautions to ensure that the system is free of leaks and that the effluent is properly vented or burned.)

7.3 *Hydrogen,* for the flame ionization detector (FID) minimum purity of 99.999 % and <0.5 ppm total hydrocarbons is preferred.

7.4 *Air,* for the flame ionization detector, <0.1 ppm total hydrocarbons is preferred.

7.5 *n-octane,* 99.0 % minimum purity, or other internal standard (99.0 % minimum purity), such as *iso*-octane, previously analyzed to be free of compounds coeluting with impurities in the sample.

TABLE 1 Recommended Operating Conditions

Carrier gas	hydrogen
Linear velocity at 40°C, cm/s	40
Detector	flame ionization
Detector temperature, °C	250°C
Injection port temperature, °C	250°C
Split ratio	40:1
Split flow, mL/min	60
Column	50 m by 0.20 mm ID by 0.5 µm bonded polydimethylsiloxane capillary column
Initial column temperature, °C	40
Initial time, min	17
Programming rate	10°C/min
Final temperature, °C	250°C
Final time, min	10
Sample size, µL	1.2

TABLE 2 Summary of Precision Data

Component	Average Concentration mg/kg	Intermediate Precision	Reproducibility
Benzene (weight %)	99.96	0.006	0.022
	99.97	0.007	0.020
	99.96	0.008	0.025
Methylcyclopentane	104	8.3	27.9
	43	12.2	19.4
	54	2.5	15.1
Toluene	64	5.1	22.0
	63	3.0	16.6
	28	1.8	9.1
Methylcyclohexane	132	7.4	34.8
	43	1.4	5.4
	79	3.2	17.0
Methylcyclohexane + Toluene	196	7.9	54.9
	106	12.9	33.6
	106	4.4	20.4
n-Hexane	4	2.2	3.7
	3	1.5	2.2
	2	1.8	2.5
n-Heptane	6	2.7	11.1
	16	1.5	5.6
	15	4.0	23.4
Ethylcyclopentane	7	1.8	3.7
	6	1.9	11.0
	11	1.5	6.1
Total Other Impurities	99	22.5	163.0
	107	44.6	190.6
	185	55.5	233.0

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[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*, BHD, Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

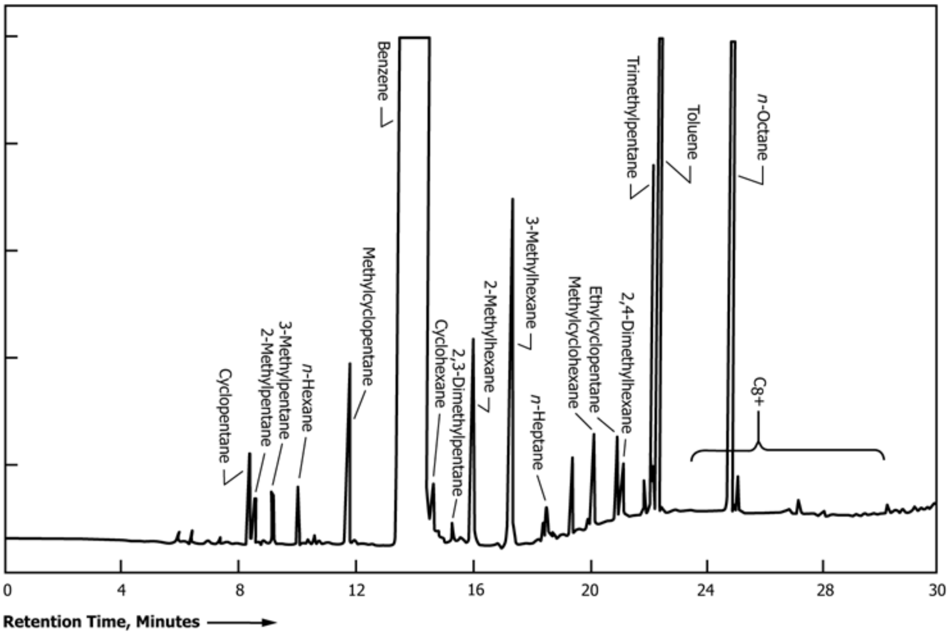

FIG. 1 High Purity Benzene—Typical Chromatogram (See Table 1 for Operating Conditions)

NOTE 1—It is highly recommended the carrier, make-up and detector gases be purified to remove oxygen (to less than 1 ppm, less than 0.5 ppm is preferred), water and hydrocarbons. It is also recommended the air be purified to remove hydrocarbons and water.

8. Hazards

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

9. Sampling

9.1 Sample in accordance with Practice D3437.

10. Preparation of Apparatus

10.1 Follow the manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the desired conditions. Allow sufficient time for the equipment to reach equilibrium. See Practices E260, E355 and E1510 for additional information on gas chromatography procedures, terminology, and column installation. The column and conditions in Table 1 were used to develop this analysis. If there is a dispute, the column and conditions should be agreed upon between the parties or use Table 1 as a referee.

11. Procedure

11.1 Transfer approximately 10 g of the sample to be analyzed to a tared vial and weigh to the nearest 0.1 mg. (Make sure that the sample is deposited in the center of the vial so that the liquid does not contact the neck.)

11.2 Add approximately 0.1 g of internal standard (*n*–octane was used in Fig. 1) and quickly reweigh to the nearest 0.1 mg. (The internal standard is added to the vial while on the balance pan and deposited into the center of the liquid—not on the side of the vial.)

11.3 Cap the mixture and mix by inverting several times.

11.4 Inject into the gas chromatograph an appropriate amount of the mixture as previously determined in accordance with 6.1 and 6.2 and immediately start the analysis. (1.2 µL was used in Fig. 1.)

11.5 Determine the areas of all the impurity peaks and the internal standard. Identify the specific impurities by comparing the chromatogram obtained to a typical chromatogram. (Unidentified impurities are summed and reported as a composite.) The chromatogram shown in Fig. 1 can be used for the column and conditions specified in Table 1.

12. Calculation

12.1 Measure the areas of all peaks, including the internal standard, except the benzene peak.

12.2 Calculate the weight to milligram per kilogram—mg/kg of the individual impurities, C_i as follows:

$$C_i = 10^6 \frac{BDF}{GH} \qquad (1)$$

where:

B = peak area of a specific impurity or group of impurities
D = response factor, (see 12.3)
F = mass of internal standard added to the sample, g
G = peak area of the internal standard
H = weight of sample before addition of internal standard, g
10^6 = factor to convert to weight-mg/kg

12.3 A response factor of 1.000 should be used for all hydrocarbon impurities except toluene which will be 0.935.

12.4 Calculate the benzene content by subtracting the sum of the impurities from 100.000. Benzene weight % = 100.000 − (sum of impurities in weight %). Total impurities are converted from mg/kg to weight percent by multiplying by 0.0001 %.

13. Report

13.1 Report the concentration of impurities to the nearest mg/kg and the benzene content to the nearest 0.01 %. For conversion purposes, 1 mg/kg equals 0.0001 %.

14. Precision and Bias[5]

14.1 *Precision*—The criteria in Table 2 should be used to judge the acceptability at the 95 % probability level of the results obtained by this test method (95 % confidence level). The criteria were derived from an interlaboratory study of three samples analyzed in duplicate on two days between six laboratories. Details of the design and analysis of the data is given in ASTM Research Report RR: RR:D16-1018.

14.1.1 *Intermediate Precision (formerly Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than the amounts shown in Table 2. Results differing by less than "*r*" have a 95 % probability of being correct.

14.1.2 *Reproducibility*—Results submitted by each of two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 2. Results differing by less than "*R*" have a 95 % probability of being correct.

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

15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

15.2 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.

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

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

15.5 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.

16. Keywords

16.1 benzene; cyclohexane feedstock; impurities

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D5713–09) that may impact the use of this standard. (Approved February 15, 2014.)

(1) Modified Table 1 title to reflect D16 Editorial Guidelines dated February 12, 2013.
(2) Modified Table 2 title to reflect D16 Editorial Guidelines dated February 12, 2013.
(3) Changed ppm in Table 2 to mg/kg to reflect D16 Editorial Guidelines dated February 12, 2013.
(4) Added new Section 7.1 and renumbered all other listings in this section to reflect D16 Editorial Guidelines dated February 12, 2013.
(5) Added revised footnote 4 to reflect D16 Editorial Guidelines dated February 12, 2013.
(6) Added wording to Figure 1 for clarification.
(7) Added wording to Section 10.1 for clarification.
(8) Modified wording in Sections 14.1, 14.1.1, and 14.1.2 to reflect D16 Editorial Guidelines dated February 12, 2013.
(9) Added new Section 15.1 and renumbered all other listings in this section to reflect D16 Editorial Guidelines dated February 12, 2013.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1018. Contact ASTM Customer Service at service@astm.org.

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