



Standard Test Method for Analysis of High Purity Benzene for Cyclohexane Feedstock by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D 5713; 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 specific impurities in, and the purity of benzene for cyclohexane feedstock by gas chromatography. It is applicable to benzene in the range from 99 to 100 % purity and to impurities at concentrations of 2 to 10 000 mg/kg.

1.2 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.

1.3 *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 a specific hazard statement, see Section 8 and Note 1.

2. Referenced Documents

2.1 ASTM Standards:

D 3437 Practice for Sampling and Handling Cyclic Products²

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³

E 260 Practice for Packed Column Gas Chromatography³

E 355 Practices for Gas Chromatography Terms and Relationships³

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs³

2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁴

3. Terminology

3.1 Definitions:

3.1.1 For definition of terms used in this test method see Terminology D 4790.

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 designed to obtain 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 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

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

Current edition approved June 10, 2000. Published August 2000. Originally published as D 5713 – 95. Last previous edition D 5713 – 96.

² *Annual Book of ASTM Standards*, Vol 06.04.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

background noise for 2 mg/kg of an impurity when operated at recommended conditions.

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 cross-linked methyl silicone (see Table 1 for 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.

7. Reagents and Materials

7.1 *Carrier Gas*—a carrier gas (minimum purity of 99.95 % mol) appropriate to the type of detector used should be employed.

NOTE 1—**Precaution:** 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.

7.2 *Hydrogen and Air* for the flame ionization detector (FID).

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

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 D 3437.

10. Procedure

10.1 Follow the manufacturer's instructions for mounting the column into the chromatograph and adjusting the instru-

ment to the conditions described in Table 1. Allow sufficient time for the equipment to reach equilibrium. See Practices E 260, E 355 and E 1510 for additional information on gas chromatography procedures, terminology, and column installation.

10.2 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 with a Pasteur pipet so that the liquid does not contact the neck.)

10.3 Add approximately 0.1 g of *n*-octane internal standard using a Pasteur pipet 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.)

10.4 Cap the mixture and mix by inverting several times.

10.5 Inject 1.2 μl of the sample containing internal standard and immediately start the recorder, temperature programming sequence, and integrator.

10.6 Determine the areas of all the impurity peaks and *n*-octane. Identify the specific impurities by comparing the chromatogram obtained to the typical chromatogram shown on Fig. 1 (unidentified impurities are summed and reported as a composite).

11. Calculation

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

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

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

where:

B = peak area of a specific impurity or group of impurities,

D = response factor, (see 11.3),

F = mass of *n*-octane added to the sample, g,

G = peak area of the *n*-octane,

H = weight of sample before addition of *n*-octane, g, and

10^6 = factor to convert to weight-mg/kg

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

11.4 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 %.

12. Report

12.1 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 %.

13. Precision and Bias ⁵

13.1 *Precision*—The following criteria should be used to judge the acceptability (95 % probability level) of results

⁵ Supporting data are available from ASTM International Headquarters. Request RR: D16-1018.

TABLE 1 Instrument Typical Parameters

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 methyl silicone fused silica capillary
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

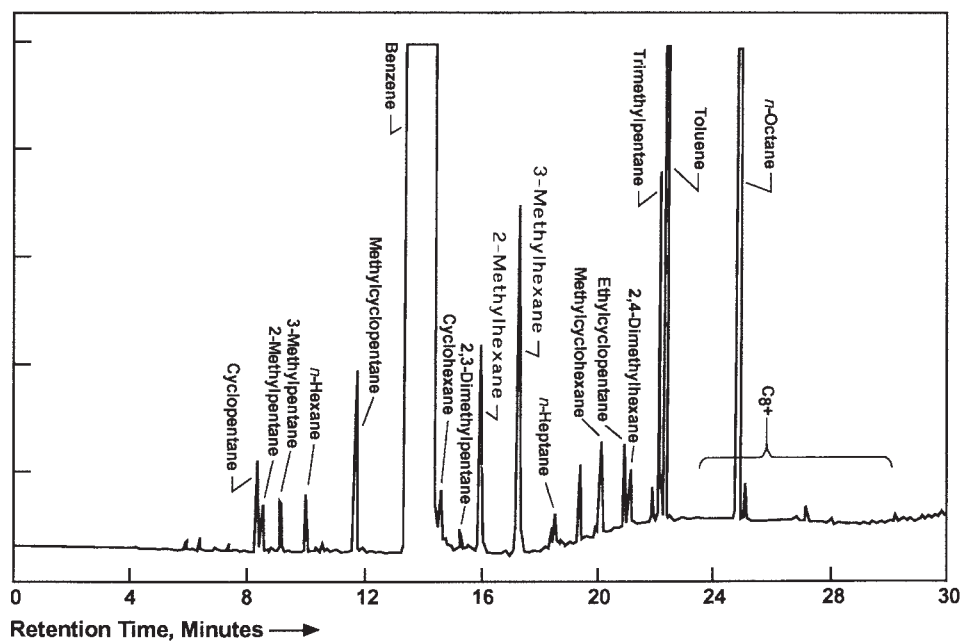


FIG. 1 High Purity Benzene—Typical Chromatogram (See Table 1)

obtained by this test method. The criteria in Table 2 were derived from an interlaboratory study between six laboratories. Three samples were analyzed in duplicate on two days.

13.1.1 *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 Intermediate Precision and Reproducibility

Component	Average Concentration ppm Weight %	Intermediate Precision	Reproducibility
Benzene	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

Table 2. On the basis of test error alone, the difference between two results obtained in the same laboratory on the same material will be expected to exceed this value only 5 % of the time.

13.1.2 *Repeatability*—Results submitted by each of two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 2. 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.

13.2 *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.

14. Keywords

14.1 benzene; cyclohexane feedstock; impurities

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