



Standard Test Method for Benzene Content of Cyclic Products by Gas Chromatography¹

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1. Scope

1.1 This test method covers the determination of the benzene content of specific cyclic hydrocarbon products.

1.2 Benzene may be determined over a range from 5 to 300 mg/kg.

1.3 The products in which benzene can be determined include cyclohexane, toluene, individual C₈ aromatics, cumene, and styrene.

1.4 *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.* A specific hazard statement is given in Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 3437 Practice for Sampling and Handling Liquid Cyclic Products²

E 260 Practice for Packed Column Gas Chromatography³

E 355 Practice for Gas Chromatography Terms and Relationships³

2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁴

3. Summary of Test Method

3.1 A gas chromatograph with a flame ionization or other detector and a column containing a supported polar liquid phase is used. A reproducible volume of sample is injected. Quantitative results are obtained from the measured area of the recorded benzene peak by using a factor obtained from the

analysis of a blend of known benzene content.

4. Significance and Use

4.1 Knowledge of the benzene content is typically required for cyclic products used as chemical intermediates and solvents. This test method may be used for final product inspections, process control, establishing specifications, and research work.

5. Apparatus

5.1 *Gas Chromatograph*—Any chromatograph having either a flame ionization or other detector that is capable of providing a minimum peak height response of 0.1 mV for 20 mg/kg benzene using a maximum sample injection of 2 μ L.

5.2 *Chromatographic Column*—The choice of column is based on resolution requirements. Any column may be used if it is capable of resolving benzene from the major component and other impurities. The column described in Table 1 has been found satisfactory.

5.3 *Integrator*—Electronic integration is recommended.

5.4 *Recorder, Strip Chart*, 0 to 1-mV range recording potentiometer with a response time of 1 s or less and maximum noise level of 0.3 % of full scale. If electronic integration is not used, a minimum chart width of 200 mm and a minimum chart speed of 1 cm/min is required.

5.5 *Microsyringe*, 10- μ L capacity.

5.6 *Volumetric Flask*, 50-mL capacity.

6. Reagents and Materials

6.1 *Carrier Gas*, helium or nitrogen, chromatographic grade.

6.2 *Hydrogen*, zero grade.

6.3 *Compressed Air*, oil free.

6.4 *Benzene*, 99 % minimum purity.

6.5 *Specific Cyclic Hydrocarbon*, high-purity (best grade obtainable) benzene content not to exceed 10 % of the level expected in the sample.

7. Hazards

7.1 Consult current OSHA regulations, supplier's Material

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 D16.04 on Instrumental Analysis.

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

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

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

TABLE 1 Instrument Parameters

| | |
|---------------------|---------------------------------------------------|
| Detector | Hydrogen flame ionization |
| Column | Copper |
| Length | 3.7 m (12 ft) |
| Outside diameter | 3.175 mm (1/8 in.) |
| Stationary phase | TCEPE (Tetracyanoethylated pentaerythritol), 10 % |
| Support | Chromosorb P, ^A 60–80 mesh |
| Temperature, °C | |
| Sample inlet system | 200 |
| Column | 75–85 ^B |
| Detector | 200 |
| Carrier gas | Helium or nitrogen |
| Flow rate | 20 mL/min ^A |
| Sample size | 0.5–2 µL, reproducible |

^AChromosorb P is a registered trademark of Johns-Manville Corp.

^BApproximate values, see 10.1.

Safety Data Sheets, and local regulations for all materials used in this test method.

8. Sampling

8.1 Guidelines for taking samples from bulk are given in Practice D 3437.

9. Calibration

9.1 Prepare a calibration blend or blends of benzene in the specific cyclic hydrocarbon at the level or levels approximating those in the samples to be analyzed. A separate blend must be made for each specific cyclic hydrocarbon.

9.2 Calculate the benzene content of the calibration blend using the following equation and the densities listed in Table 2.

$$\text{Benzene, mg/kg} = \frac{(B_1)(B_2)}{(S_1)(S_2)} (10^3) \quad (1)$$

where:

B_1 = density of benzene,

B_2 = volume of benzene added to the cyclic hydrocarbon, µL,

S_1 = density of cyclic hydrocarbon, and

S_2 = volume of cyclic hydrocarbon, mL.

9.3 For example, to prepare an 81-mg/kg blend of benzene in toluene, fill a 50-mL volumetric flask to the mark with high-purity toluene. With a microsyringe, carefully add 4.0 µL of benzene to the toluene and mix well.

9.4 Analyze both the blend and the pure cyclic hydrocarbon used to prepare the blend as described in Section 10. Subtract the area of the benzene found in the pure cyclic hydrocarbon from the area of the benzene in the blend to determine the area represented by the concentration of benzene added to the blend, as shown in 11.1.

10. Procedure

10.1 Install the chromatographic column, and establish stable instrument operation at the proper operating conditions

as shown in Table 1. Adjust column temperature and flow rate to achieve sufficient resolution. A retention time of 5 to 6 min for benzene has been found to yield sufficient resolution with the recommended column. Refer to instructions provided by the manufacturer of the chromatograph and to Practices E 260 and E 355.

10.2 Inject a repeatable volume of sample, typically 2 µL or less, into the chromatograph. The volume of sample injected must be exactly the same as the volume of blend injected. Start the recorder or integration device, or both, and obtain the chromatogram.

NOTE 1—Some samples may contain components significantly heavier than benzene that may have a long retention time. If desired, the column temperature may be raised after the elution of benzene to shorten the retention time of these components. If this is done, the column must be reequilibrated at the analysis temperature before each subsequent analysis.

10.3 Measure the area of the benzene peak. Units must be consistent with 9.4.

11. Calculation

11.1 Calculate the concentration of benzene in mg/kg in the cyclic hydrocarbon using the following equation:

$$\text{Benzene, mg/kg} = AB/(C - D) \quad (2)$$

where:

A = area of benzene peak in the sample,

B = concentration of benzene added to the blend. **Important:** Blend must be made in the same cyclic hydrocarbon as is being analyzed as the sample,

C = area of benzene peak in the blend, and

D = area of benzene in the pure cyclic hydrocarbon.

12. Report

12.1 Report the concentration of benzene in the sample on an absolute basis to the nearest 1 mg/kg.

13. Precision and Bias⁵

13.1 *Precision*—The following criteria should be used to judge the acceptability (95 % probability level) of results obtained by this method. The criteria were derived from a round robin among five laboratories.

13.1.1 *Repeatability*—Results in the same laboratory should not be considered suspect, unless they differ by more than the amount shown in Table 3.

13.1.2 *Reproducibility*—It is estimated that results on the same sample run in two laboratories should be considered suspect if they differ by more than the reasonable range shown in Table 3. Because of the round-robin results from this method, these values were taken straight from the research report without statistical reduction.

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

14. Keywords

14.1 benzene; cumene; cyclohexane; cyclic products; gas

⁵ Supporting data are available from ASTM International Headquarters. Request RR: D16-1006.

TABLE 2 Density of Cyclic Hydrocarbons at 15.56°C, g/mL

| | |
|-------------|--------|
| Benzene | 0.8838 |
| Cumene | 0.8655 |
| Cyclohexane | 0.7826 |
| Styrene | 0.9102 |
| Toluene | 0.8711 |

TABLE 3 Precision

| Major Component | Benzene Concentration, mg/kg | Repeatability, mg/kg | Reasonable Range, mg/kg |
|-----------------|------------------------------|----------------------|-------------------------|
| Cumene | 5 | 1 | 0–11 |
| Cumene | 27 | 2 | 22–33 |
| Cumene | 222 | 19 | 206–256 |
| Cyclohexane | 64 | 4 | 35–90 |
| Cyclohexane | 86 | 5 | 55–115 |
| Cyclohexane | 277 | 28 | 244–310 |
| Styrene | 15 | 2 | 0–35 |
| Styrene | 38 | 6 | 25–67 |
| Styrene | 204 | 11 | 120–250 |
| Toluene | 20 | 2 | 14–23 |
| Toluene | 190 | 16 | 147–206 |

chromatography; styrene; toluene

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