



Designation: D 4492 – 98

Standard Test Method for Analysis of Benzene by Gas Chromatography¹

This standard is issued under the fixed designation D 4492; 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 normally occurring trace impurities in, and the purity of, finished benzene by gas chromatography.

1.2 This test method was judged applicable for nonaromatic impurities at levels from 0.001 to 0.200 weight % and for benzene purities of 99.80 weight % or higher.

1.3 This test method is applicable for aromatic impurities from 0.001 to 0.010 weight % in benzene.

1.4 The following applies to all specified limits in this standard: for purposes of determining conformance with this standard, 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.

1.5 *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 Section 8.

2. Referenced Documents

2.1 ASTM Standards:

D 852 Test Method for Solidification Point of Benzene²

D 3437 Practice for Sampling and Handling Liquid Cyclic Products²

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 Practice for Gas Chromatography Terms and Relationships³

E 691 Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods³

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. Summary of Test Method

3.1 A known amount of an internal standard is added to the specimen. A small volume of this mixture is injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column.

3.2 The peak area of each impurity and the internal standard is measured by an electronic integrator. The concentration of each impurity is calculated from the ratio of the peak area of the internal standard versus the peak area of the impurity. Purity is calculated by subtracting the sum of the impurities found from 100.00 weight %. Results are reported in weight percent.

4. Significance and Use

4.1 This test method is suitable for determining the concentrations of known impurities in finished benzene and for use as an integral quality control tool where benzene is either produced or used in a manufacturing procedure. It is generally applied to impurities such as nonaromatics containing nine carbons or less, toluene, C8 aromatics, and 1, 4-dioxane.

4.2 Absolute purity cannot be determined if unknown impurities are present. Test Method D 852 is generally used as a criteria for determining the absolute purity.

5. Interferences

5.1 Benzene is typically resolved from naturally occurring components with boiling points <138°C. Naturally occurring components include nonaromatic hydrocarbons, toluene, C8 aromatics, and 1, 4-dioxane. An adequate separation of known impurities from benzene should be evaluated for the column selected.

5.2 The internal standard chosen must be sufficiently resolved from any impurity and the benzene peak.

6. Apparatus

6.1 *Gas Chromatograph*—Any chromatograph having a flame ionization detector that can be operated at the conditions given in Table 1. The system should have sufficient sensitivity to obtain a minimum peak height response for a 0.0005 weight

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 *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 Typical Instrumental Parameters

| | |
|------------------|---------------------------------|
| Detector | flame ionization |
| Column: | fused silica |
| Length | 50 m |
| Inside diameter | 0.32 mm |
| Stationary phase | crosslinked polyethylene glycol |
| Film thickness | 0.25 µm |
| Temperatures: | |
| Injector | 200°C |
| Detector | 250°C |
| Column | 70°C isothermal |
| Carrier gas: | helium |
| Linear velocity | 22 cm/s |
| Split ratio: | 200:1 |
| Sample size | 0.5 µL |
| Recorder | electronic integration required |

% impurity twice the height of the signal background noise.

6.2 *Electronic Integrator*, computer-based capable of handling internal standard calculations and peak grouping is recommended.

6.3 *Column*, fused silica capillary column with cross-linked polyethylene glycol stationary phase is recommended. Alternate stationary phases may be used if they produce at least the same aromatic separation and elute C₉ nonaromatic impurities before benzene.

6.4 *Microsyringes*, 10 and 100 µl capacity.

7. Reagents and Materials

7.1 *Carrier Gas*—Chromatographic grade helium is recommended.

7.2 *High Purity Benzene*, 99.99 weight % minimum, prepared by multiple step recrystallization of commercially available 99+ weight % benzene.

7.3 *Internal Standard*, *n*-Nonane (*n*C₉) with a purity of 99 weight % minimum is recommended. Other compounds may be acceptable provided they can be obtained in high purity and meet the requirements of 5.2.

7.4 Pure compounds for calibration should include toluene, benzene, ethylbenzene, cyclohexane, and 1, 4-dioxane of a purity not less than 99%. If the purity of the calibration compounds is less than 99%, the concentration and identification of impurities must be known so that the composition of the final weighed blends can be adjusted for the presence of the impurities.

8. Hazards

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

8.2 Benzene is considered a hazardous material. The sampling and testing of benzene should follow safety rules in order to adhere to all safety precautions as outlined in current OSHA regulations.

9. Sampling

9.1 Sample the material in accordance with Practice D 3437.

10. Preparation of Apparatus

10.1 Follow manufacturer's instructions for mounting the column into the chromatograph and adjusting the instrument to

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

11. Calibration

11.1 Prepare a synthetic mixture of high purity benzene and representative impurities by direct weighing. Weigh each impurity to the nearest 0.1 mg. Table 2 contains a typical calibration blend. Cyclohexane is used for the nonaromatic portion and ethylbenzene for the C₈ aromatic portion.

11.2 Using the exact weight for each impurity, calculate the weight % concentration of the calibration blend.

11.3 Into a 50-mL volumetric flask, add 50 µL of *n*C₉ to 49.95 mL of the calibration blend and mix well. Using a density of 0.874 g/mL for the calibration blend and a density of 0.718 g/mL for the *n*C₉, the resulting *n*C₉ concentration will be 0.0825 weight %.

11.4 Inject 0.5 µL of the blend with internal standard into the chromatograph and integrate the area under each peak, excluding benzene.

11.5 Calculate the relative response factors (RRF) as follows:

$$RRF_i = (A_s)(C_i)/(C_s)(A_i) \quad (1)$$

where:

- RRF_i = RRF for impurity *i*,
- A_s = peak area of internal standard,
- A_i = peak area of impurity *i*,
- C_i = weight % for impurity *i*, from 11.2,
- C_s = concentration of internal standard, weight % from 11.3.

12. Procedure

12.1 Into a 50-mL volumetric flask, add 50 µL of *n*C₉ internal standard and dilute to the mark with specimen. Mix well.

12.2 Inject 0.5 µL of mixture into the chromatograph.

12.3 Integrate the area under all peaks except for benzene. Sum the nonaromatic fraction up to *n*C₉ for reporting as a single component. See Fig. 1 for a typical chromatogram.

13. Calculation

13.1 Calculate the amounts of each individual impurity as required. Sum the areas of all the nonaromatic peaks.

13.2 Calculate the weight % concentration of each impurity as follows:

$$C_i = (A_i)(RRF_i)(C_s)/(A_s) \quad (2)$$

13.3 Calculate the benzene purity as follows:

$$\text{Benzene, weight \%} = 100.00 - C_t \quad (3)$$

TABLE 2 Typical Calibration Blend, g

| | |
|--------------|---------|
| Benzene | 99.0000 |
| Toluene | 0.0500 |
| Cyclohexane | 0.0500 |
| Ethylbenzene | 0.0500 |
| 1, 4 Dioxane | 0.0200 |

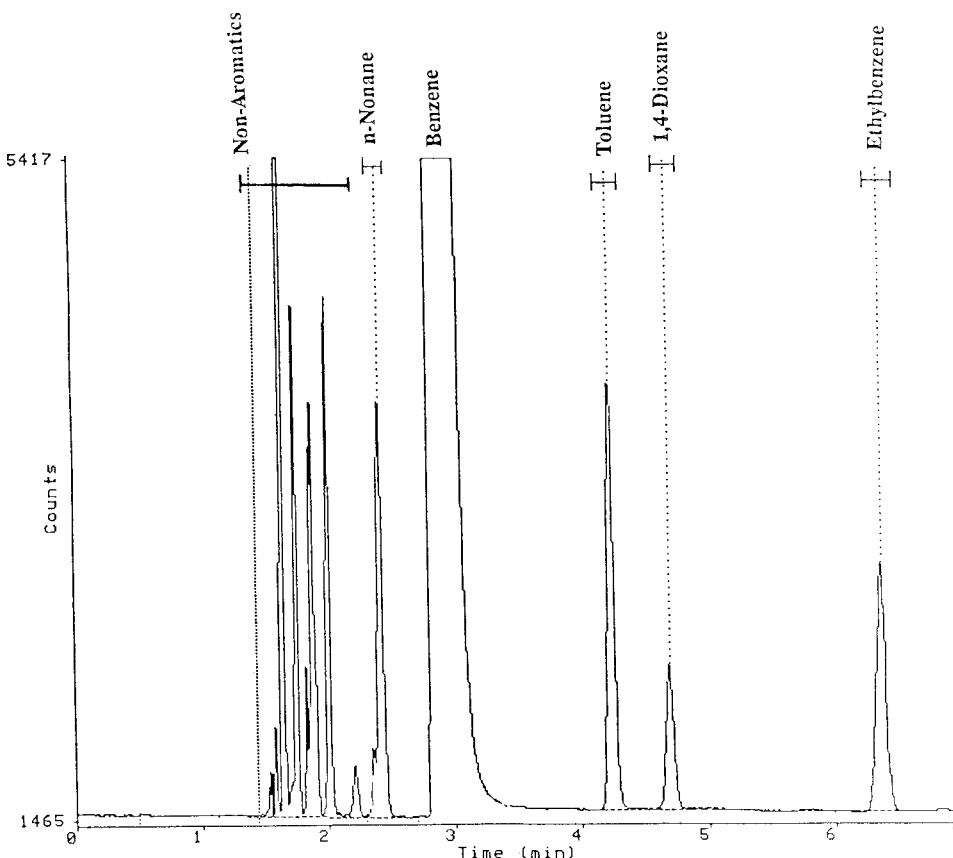


FIG. 1 Typical Chromatogram

where:

C_t = total concentration of all impurities, weight %.

14. Report

14.1 Report the following information:

14.1.1 Benzene and the total impurities to the nearest 0.01 %, and

14.1.2 Individual impurities to the nearest 0.001 %.

15. Precision and Bias⁵

15.1 *Precision*—The following criteria should be used to judge the acceptability of results obtained by this test method (95 % confidence level). The precision criteria was derived from the round-robin data submitted by six different laboratories. Each sample was run twice in two days by two different operators. The precision criteria for 1, 4-Dioxane was derived from the interlaboratory study data submitted by nine different laboratories. Each sample was run twice in two days by two different operators. Results of the round robin data were analyzed in accordance with Practice E 691.

15.2 *Intermediate Precision*—Duplicated results by the same operator should not be considered suspect unless they differ by more than \pm the amount shown in Table 3.

TABLE 3 Benzene Purity Intermediate Precision and Reproducibility

| Component | Concentration (mg/kg) | | |
|------------------|-----------------------|------------------------|-----------------|
| | Average Concentration | Intermediate Precision | Reproducibility |
| Nonaromatics | 22 | 19 | 20 |
| | 737 | 70 | 184 |
| Toluene | 14 | 2 | 6 |
| | 116 | 4 | 54 |
| Ethylbenzene | 14 | 3 | 7 |
| | 121 | 7 | 14 |
| <i>p</i> -Xylene | 13 | 3 | 5 |
| | 110 | 5 | 16 |
| <i>m</i> -Xylene | 44 | 5 | 9 |
| | 162 | 9 | 17 |
| <i>o</i> -Xylene | 14 | 5 | 18 |
| | 89 | 7 | 8 |
| 1, 4 Dioxane | 10 | 2.3 | 4.8 |
| | 5 | 1.9 | 2.5 |
| | 100 | 3.0 | 9.0 |
| Benzene (wt %) | 99.87 | 0.01 | 0.027 |
| | 99.99 | 0.002 | 0.004 |

15.3 *Reproducibility*—The results between two laboratories should not be considered suspect unless they differ by more than \pm the amount shown in Table 3.

15.4 *Bias*—Since there was no accepted reference material available at the time of interlaboratory testing, no statement on bias can be made at this time.

16. Keywords

16.1 benzene; gas chromatography; purity

⁵ Supporting data are available from ASTM International Headquarters. Request RR: D16-1005.

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