



Designation: D4492 – 10

Standard Test Method for Analysis of Benzene by Gas Chromatography¹

This standard is issued under the fixed designation D4492; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 is applicable for benzene purities of 99.80 weight % or higher.

1.3 The lower limit for detection for non-aromatic impurities is 50 mg/kg. The lower limit of detection for individual aromatic hydrocarbon impurities 10 mg/kg. The lower limit of detection for 1,4-dioxane is 5 mg/kg.

1.4 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.

1.5 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 hazard statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*²

D852 Test Method for Solidification Point of Benzene

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

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.

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

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 Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200³

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 for purity and total impurities, individual impurities are reported in units of mg/kg.

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 D852 is generally used as a criteria for determining the absolute purity.

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

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 5 mg/kg impurity three times 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 (nC₉) 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 identifi-

TABLE 2 Typical Calibration Blend, g

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

cation 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 [D3437](#).

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 [E260](#), [E1510](#) and [E355](#) 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. This standard may be purchased if desired.

11.2 Using the exact weight for each impurity, calculate the mg/kg concentration of each impurity in the calibration blend.

11.3 Partially fill a 50-mL volumetric flask with the calibration blend, add 50 µL of nC₉, dilute to the mark with 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 nC₉, the resulting nC₉ concentration will be 825 mg/kg. Alternate volumes of solutions may be prepared so long as the preparation meets the concentration specified.

11.4 Inject 0.5 µL, or other appropriate volume, 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:

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

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
Makeup gas	helium or nitrogen
Sample size	0.5 µL
Recorder	electronic integration required