Standard Test Method for Analysis of Benzene by Gas Chromatography[1]

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 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 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

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 1910.1200 [3]

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.

[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**

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 C_9 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 (nC_9) 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.

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

TABLE 2 Typical Calibration Blend, g

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

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 C_8 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 nC_9, 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 nC_9, the resulting nC_9 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:

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

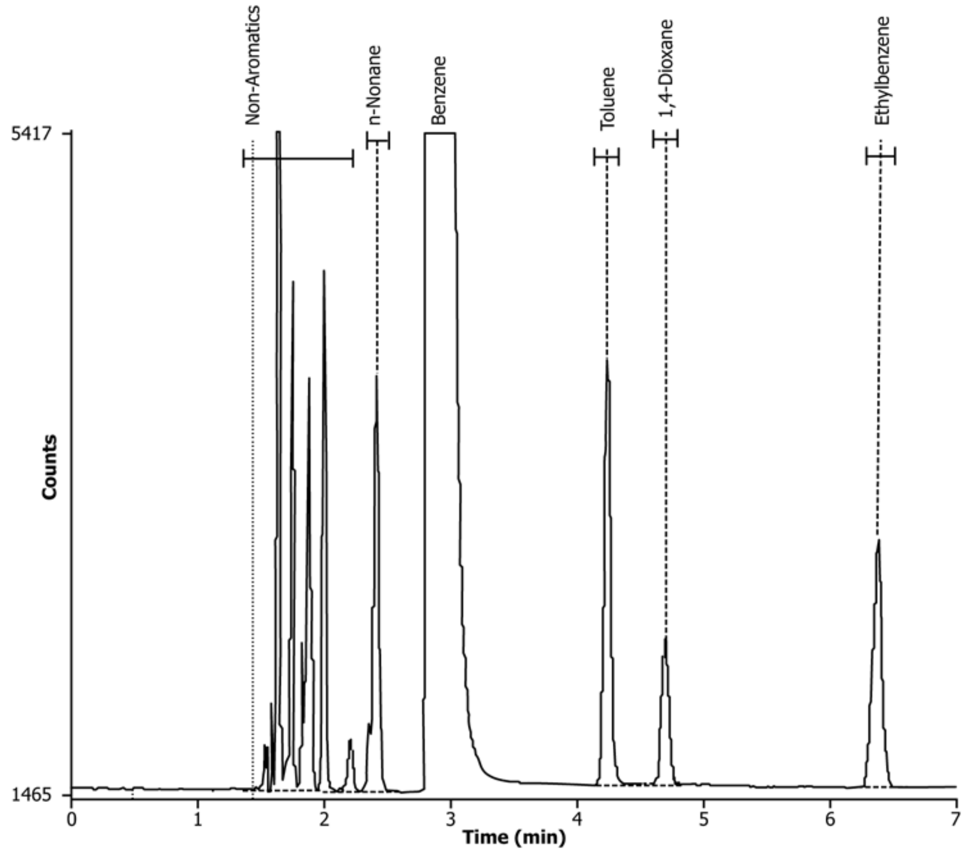

FIG. 1 Typical Chromatogram

where:

RRF_i	=	RRF for impurity *i*,
A_s	=	peak area of internal standard,
A_I	=	peak area of impurity *i*,
C_i	=	mg/kg for impurity *i*, from 11.2,
C_s	=	concentration of internal standard, mg/kg from 11.3.

12. Procedure

12.1 Into a 50-mL volumetric flask, add 50 µL of nC_9 internal standard and dilute to the mark with specimen. Mix well. Alternate volumes of solutions may be prepared so long as the preparation meets the concentration specified.

12.2 Inject 0.5 µL, or other appropriate volume of mixture into the chromatograph.

12.3 Integrate the area under all peaks except for benzene. Sum the nonaromatic fraction up to nC_9 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 mg/kg 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:

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

where:

C_t	=	$(\sum C_I)(0.0001)$, total concentration of all impurities, weight %
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 10 mg/kg. If needed, 1,4-dioxane may be reported down to 5 mg/kg.

15. Precision and Bias[4]

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 an interlaboratory study 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 an interlaboratory study by nine different laboratories. Each sample was run twice in two days by two different

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1005. Contact ASTM Customer Service at service@astm.org.

operators. Results of the interlaboratory study data were analyzed in accordance with Practice E691.

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

15.3 *Reproducibility*—The results between two laboratories should not be considered suspect unless they differ by more than ± 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. Quality Guidelines

16.1 Refer to Guide D6809 for suggested QA/QC activities that can be used as a part of this test method. It is recommended that the operator of this test method select and perform relevant QA/QC activities like the ones in Guide D6809 to help ensure the quality of data generated by this test method.

17. Keywords

17.1 benzene; gas chromatography; purity

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
p-Xylene	13	3	5
	110	5	16
m-Xylene	44	5	9
	162	9	17
o-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

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D4492 - 07) that may impact the use of this standard. (Approved March 15, 2010.)

(1) Modified the method to make calculation and reporting of the individual impurities correspond to the units given in the precision tables.