Designation: D 4492 – ~~98~~03

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

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:*

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[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.

Current edition approved ~~Aug.~~ June 10, ~~1998.~~ 2003. Published ~~October 1998.~~ July 2003. Originally ~~published as D 4492 – 85.~~ approved in 1985. Last previous edition approved in 1998 as D 4492 ~~–~~- 9~~6~~8.

***A Summary of Changes section appears at the end of this standard.**

D 852 Test Method for Solidification Point of Benzene[2]
D 3437 Practice for Sampling and Handling Liquid Cyclic Products[2]
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]
E 260 Practice for Packed Column Gas Chromatography[4]
E 355 Practice for Gas Chromatography Terms and Relationships[4]
E 691 Practice for Conducting an Interlaboratory ~~Test Program~~ Study to Determine the Precision of a Test Method~~s~~[3]
E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[4]

2.2 *Other Document:*

OSHA Regulations. 29 CFR, paragraphs 1910.1000 and 1910.1200[5]

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 % 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.

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

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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~~

[4] *Annual Book* of ~~*Documents, U.S. Government Printing Office, Washington DC 20402.*~~ *ASTM Standards*, Vol 03.06.

~~[5] Supporting data are available~~

[5] Available from ~~ASTM International Headquarters. Request RR: D16-1005.~~ U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

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.

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 C_8 aromatic portion. This standard may be purchased if desired.

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 nC_9 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 nC_9, the resulting nC_9 concentration will be 0.0825 weight %.

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:

$$RRF_i = (A_s)(C_i)/(C_s)(A_i) \tag{1}$$

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 nC_9 internal standard and dilute to the mark with specimen. Mix well.

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

TABLE 2 Typical Calibration Blend, g

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

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 weight % concentration of each impurity as follows:

$$C_i = (A_i)(RRF_i)(C_s)/(A_s) \tag{2}$$

13.3 Calculate the benzene purity as follows:

$$\text{Benzene, weight \%} = 100.00 - C_t \tag{3}$$

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 Bias [6]

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 ± the amount shown in Table 3.

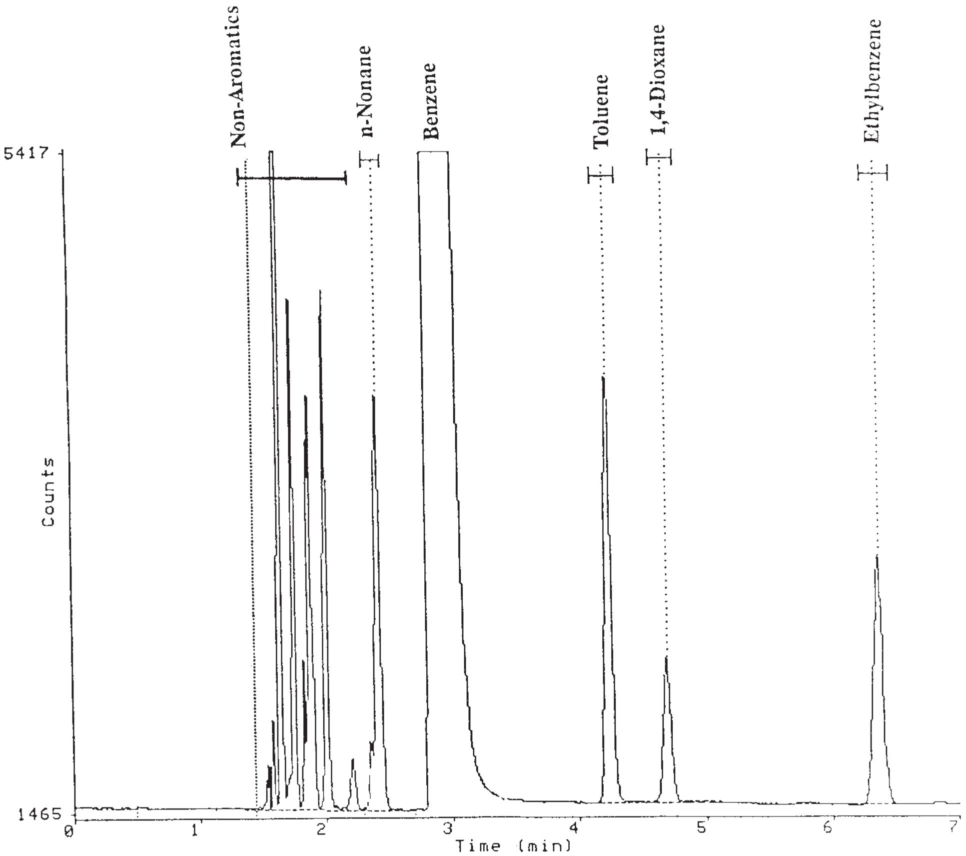

FIG. 1 Typical Chromatogram

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[6] Supporting data are available from ASTM International Headquarters. Request RR: D16-1005.

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

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. Keywords

16.1 benzene; gas chromatography; purity

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D 4492 - 00) that may impact the use of this standard.

(1) Modified 11.1 to allow purchase of standard.
(2) Modified 11.4 and 12.2 to allow an appropriate volume of sample to be injected.

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