Designation: D7360 − 16

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

This standard is issued under the fixed designation D7360; 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 with external calibration. A similar test method, using the internal standard technique of calibration is Test Method D4492.

1.2 This test method is applicable for nonaromatic hydrocarbon impurities at levels from 5 to 2000 mg/kg and for benzene purities of 99.80 weight % or higher.

1.3 This test method is applicable for aromatic impurities from 5 to 2000 mg/kg in benzene.

1.4 This test method has been found applicable to heteroatomic species such as 1,4-dioxane, from 10 to 2000 mg/kg in benzene.

1.5 The limit of detection for aromatic impurities is 0.9 mg/kg, 2.7 mg/kg for 1,4-dioxane and 1.1 mg/kg for methyl cyclohexane.

1.6 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.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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 9.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D3798 Test Method for Analysis of *p*-Xylene by Gas Chromatography (Withdrawn 2009)[3]

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4492 Test Method for Analysis of Benzene by Gas Chromatography

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

2.2 *Other Document:*[4]

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Terminology

3.1 See Terminology D4790 for definition of terms used in this test method.

---

[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 Nov. 1, 2016. Published January 2017. Originally approved in 2011. Last previous edition approved in 2011 as D7360 – 11. DOI: 10.1520/D7360-16.

[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] The last approved version of this historical standard is referenced on www.astm.org.

[4] 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**

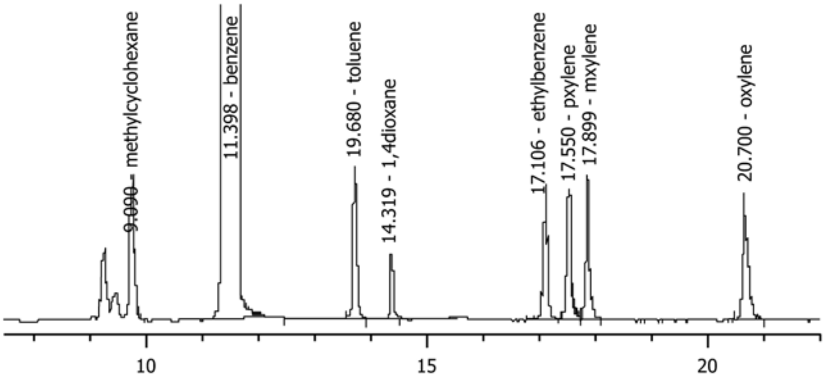

FIG. 1 Typical Chromatogram

4. Summary of Test Method

4.1 A repeatable volume of the specimen to be analyzed is precisely injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column.

4.2 The peak area of each impurity is measured. The concentration of each impurity is determined using response factor or the linear calibration curve of peak area versus concentration. Purity is calculated by subtracting the sum of the impurities found from 100.00 weight %. The concentration of impurities are reported in mg/kg. Purity of benzene is reported in weight percent.

5. Significance and Use

5.1 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.

5.2 Absolute purity cannot be determined if undetected impurities are present.

6. Interferences

6.1 Benzene is typically resolved from components with boiling points <138°C that normally are found in purified benzene. Components normally found in purified benzene 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.

7. Apparatus

7.1 *Gas Chromatograph,* any chromatograph having a flame ionization detector that can be operated at the conditions given in Table 1.

7.2 *Electronic Integrator* chromatography data system.

7.3 *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 as achieved in the chromatogram in Fig. 1 and elute C_9 nonaromatic impurities before benzene.

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:	100:1
Sample size	2.0 µL
Recorder	electronic integration required

7.4 *Automatic Injector*—The sample must be precisely and repeatably injected into the gas chromatograph. An automatic sample injection device is highly recommended.

8. Reagents and Materials

8.1 *Carrier Gas,* 99.999 % helium or hydrogen. Concentration of oxygen in the carrier should be <1 ppm, <0.5 ppm is preferred.

8.2 *Detector Gases, 99.999 %*—Nitrogen is recommended for make up 99.999 %. Hydrogen with THC <0.5 mg/kg. Air with CO2, CO and THC <1 mg/kg and oxygen between 20 and 22 %, is recommended.

8.3 *High Purity Benzene,* 99.999 weight % minimum, prepared by multiple step recrystallization of commercially available 99 + weight % benzene. See Annex A1. The benzene must be recrystalized a minimum of three times and then analyzed using this test method. Continue recrystalizing the benzene until no impurity greater than three times the noise level is detected.

8.4 Pure compounds for calibration should include toluene, *o*-, *m*-, and *p*-xylene, ethylbenzene, methylcyclohexane, 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.

9. Hazards

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

9.2 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.

10. Sampling

10.1 Sample the material in accordance with Practice D3437.

11. Preparation of Apparatus

11.1 Follow manufacturer's instructions for installing the column into the chromatograph and adjusting the instrument to the conditions described in Table 1. Other conditions may be used as long as the same level of precision is achieved. Allow sufficient time for the equipment to reach equilibrium. See Practices E260, E1510 and E355 for additional information on gas chromatography practices and terminology.

12. Calibration

12.1 Prepare synthetic mixtures 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. Methylcyclohexane is used for the nonaromatic portion.

12.1.1 It has been determined that the detector is linear to 2000 mg/kg.

12.2 Using the exact weight for each impurity, calculate the mg/kg concentration of the calibration blends, in accordance with Practice D4307, being sure to correct for impurities in the benzene as described therein. This standard may be purchased if desired.

12.3 Inject 2 µL, or other appropriate volume, that will give precision stated in precision statement, into the chromatograph and integrate the area under each peak, excluding benzene.

12.4 Determine the response factor for each impurity in the calibration mixture as follows:

$$Rf_i = C_i / A_i \quad (1)$$

where:

Rf_i = response factor for impurity i,
C_i = concentration of the impurity i in the calibration mixture, (mg/kg), and
A_i = peak area of impurity i.

TABLE 2 Typical Calibration Blend, mg/kg

Benzene	99.8 (wt %)
Toluene	250
Methylcyclohexane	250
Ethylbenzene	250
p-Xylene	250
m-Xylene	250
o-Xylene	250
1,4-Dioxane	250

12.5 Initially analyze the calibration solution a minimum of three times and calculate an average Rf_i.

13. Procedure

13.1 Inject 2 µL, or other appropriate volume of sample into the chromatograph. The size and conditions of the sample injection shall be the same as the injected standard used for calibration.

13.2 Integrate the area under all peaks except for benzene. Sum the nonaromatic fraction eluting before benzene for reporting as a single component. See Fig. 1 for a typical chromatogram.

14. Calculation

14.1 Calculate the concentration of each impurity as follows:

$$C_i = A_i \times Rf_i \quad (2)$$

where:

C_i = concentration of the impurity, mg/kg,
A_i = average peak i area, and
Rf_i = response factor for the impurity i.

14.2 Calculate the benzene purity as follows:

$$Benzene\ weight\ \% = 100 - Ct \quad (3)$$

where:

Ct = total concentration of all impurities, weight %, calculated this way:

$$Ct = \sum_i C_i\,(mg/kg)/10000\,(mg/kg/weight\,\%) \quad (4)$$

15. Quality Assurance/Quality Control (QA/QC)

15.1 Laboratories shall have a quality control system in place.

15.2 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

15.3 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

15.4 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

15.5 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

16. Report

16.1 Report the following information:

16.1.1 Benzene and the total impurities to the nearest 0.01 % and

16.1.2 Individual impurities to the nearest 1 mg/kg.

TABLE 3 Concentration (*mg/kg*) 99.9979 % Benzene

Analyte	Average $\bar{X}$	Repeatability Limit r
Methylcyclohexane	3	1
Toluene	3	1
1,4-Dioxane	4	3
Ethylbenzene	3	1
p-Xlyene	3	1
m-Xylene	3	1
o-Xylene	3	1
Benzene (*wt %*)	99.9979	0.0004

TABLE 4 Concentration (*mg/kg*) 99.77 % Benzene

Analyte	Average $\bar{X}$	Repeatability Limit r
Methylcyclohexane	330	40
Toluene	270	40
1,4-Dioxane	400	80
Ethylbenzene	320	40
p-Xlyene	320	65
m-Xylene	340	64
o-Xylene	320	50
Benzene (*wt %*)	99.77	0.02

17. Precision and Bias[5]

17.1 A single sample with components near the limit of detection was analyzed 20 times by one person using one instrument over the shortest practical time. A second sample near the upper limit of the method was also analyzed 20 times by one person using one instrument over the shortest practical time. Details are given in Research Report No. RR:D16-1042.

17.2 *Repeatability:*

17.2.1 Results should not be suspect unless they differ by more than shown in Table 3 and Table 4. Results that differ by less than "*r*" have a 95 % probability of being correct.

17.3 Reproducibility has not been determined and will be determined within five years.

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

18. Keywords

18.1 benzene; gas chromatography; purity

ANNEX

(Mandatory Information)

A1. RECRYSTALIZATION OF BENZENE

A1.1 A schematic of the process is shown in Fig. A1.1: the benzene is frozen slowly overnight at 4°C, just below its melting point of 5.5°C. The result is a bulk of frozen benzene with a liquid cover comprised of a blend of benzene and concentrated contaminants. This liquid is discarded and the benzene is allowed to melt for analysis. This test should give a cleaner chromatogram for the benzene since the contaminants stayed in liquid phase. This process is repeated until no impurity with a peak area three times the noise level is detected. A minimum of three recrystalizations is required and may require up to seven cycles.

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1042. Contact ASTM Customer Service at service@astm.org.

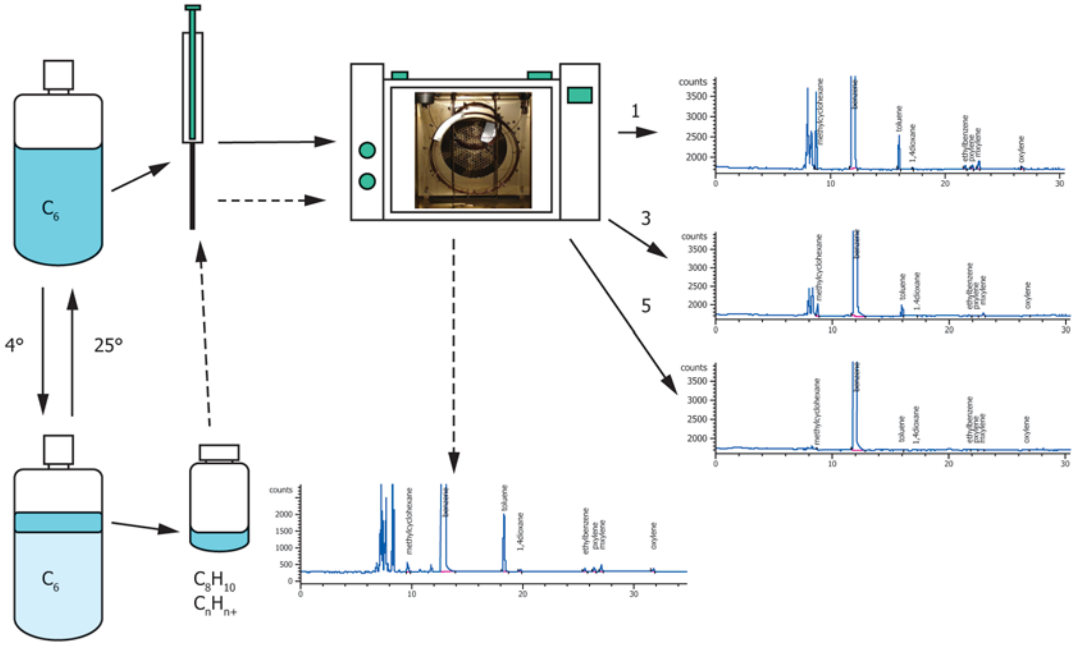

FIG. A1.1 Schematic

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7360–11) that may impact the use of this standard. (Approved November 1, 2016.)

(1) Added Summary of Changes section.
(2) Reference to Material Safety Data Sheet corrected to Safety Data Sheet.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/