Designation: D4367 – 02 (Reapproved 2007)

StandardTest Method for Benzene in Hydrocarbon Solvents by Gas Chromatography[1]

This standard is issued under the fixed designation D4367; 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 by gas chromatography of benzene at levels from 0.01 to 1 volume % in hydrocarbon solvents.

NOTE 1—For benzene levels lower than 0.01 volume %, use Test Method D6229.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 For purposes of determining conformance of an observed or a calculated value using this test method to relevant specifications, test result(s) 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 E29.

1.4 *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.*

1.5 For hazard information and guidance, see the supplier's Material Safety Data Sheet. For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D6229 Test Method for Trace Benzene in Hydrocarbon Solvents by Capillary Gas Chromatography

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E300 Practice for Sampling Industrial Chemicals

3. Summary of Test Method

3.1 An internal standard, methyl ethyl ketone (MEK), is added to the material and then introduced into a gas chromatograph equipped with two columns connected in series. The specimen passes first through a column packed with the nonpolar phase, methyl silicone, which separates the components by boiling point. After octane has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than octane. The octane and lighter components then pass through a column with the highly polar phase, 1,2,3-tris(2-cyanoethoxy)propane, that separates the aromatic and nonaromatic compounds. The eluted components are detected by a conventional detector and recorded on a strip chart. The peak areas are measured and the concentration of each component is calculated by reference to the internal standard.

4. Significance and Use

4.1 Benzene is classed as a toxic and carcinogenic material. A knowledge of the concentration of this compound may be an aid in evaluating the possible health hazards to persons handling and using hydrocarbon solvents, but this test method is not intended to evaluate such hazards.

5. Apparatus

5.1 *Chromatograph*—Any gas chromatographic instrument that has a backflush system and flame ionization detector and that can be operated at the conditions given in Table 1. The detector-recorder combination must produce a 4-mm deflection for a 1-μL specimen containing 0.05 volume % MEK when operated at maximum sensitivity.

5.2 *Columns,* one 0.8-m (2.5-ft) length of 3.2-mm (⅛-in.) outside diameter stainless steel tubing and one 4.6-m (15-ft) length of 3.2-mm (⅛-in.) outsider diameter stainless steel tubing.

5.3 *Recorder, Strip Chart*—Potentiometer with a full-scale deflection of 1 mV, a full-scale response time of 2 s or less, and a maximum noise level of ±0.3 % of full scale.

5.4 *Microsyringe,* 5-μL capacity.

5.5 *Pipets,* measuring 1 and 2 mL, graduated in 0.01 mL; 5, 10, and 20-mL capacity.

5.6 *Flasks,* volumetric, 25 and 100-mL capacity.

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

Current edition approved June 1, 2007. Published June 2007. Originally approved in 1984. Last previous edition approved in 2002 as D4367 – 02. DOI: 10.1520/D4367-02R07.

[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.

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

TABLE 1 Instrument Conditions Found Satisfactory for Measuring Low Concentrations of Benzene in Hydrocarbon Solvents (Note 2)

Detector	flame ionization
Columns	two, stainless steel
Length, m	(A) 0.8; (B) 4.6
Outside diameter, mm	3.2
Stationary phases	(A) methyl silicone, 10 weight % (B) TCEP, 25 weight %
Support	(A) acid-washed calcined diatomite, 60 to 80-mesh (B) acid-washed pink diatomaceous earth, 80 to 100-mesh
Reference column	any column or restriction may be used
Temperature, °C	
Injection port	150
Column, isothermal	100
Detector block	150
Carrier gas	helium
Flow rate, mL/min	approximately 30
Recorder range, mV	0 to 1
Chart speed, mm/min	10
Specimen size, µL	1.0
Time to backflush, min	approximately 2
Total cycle time, min	approximately 30

5.7 *Vibrator,* electric.

5.8 *Vacuum Source.*

5.9 *Evaporator,* vacuum, rotary.

5.10 *Flask,* boiling, round-bottom, short-neck, with 24/40 T joint, 500-mL capacity. Suitable for use with the evaporator (see 5.9).

5.11 *Lamp,* infrared.

5.12 *Burets,* automatic, with integral reservoir, 25-mL capacity.

NOTE 2—Suppliers of stationary phases and supports can be found in Research Report RR:D01-1038, available from ASTM International Headquarters.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Acetone.*

6.3 *Chloroform.*

6.4 *Diatomaceous Earth*[4]—Acid-washed, 60 to 80 mesh and 80 to 100 mesh.

6.5 *Helium,* 99.99 % pure.

6.6 *Methanol.*

6.7 *Methylene Chloride.*

6.8 *Methyl Ethyl Ketone (MEK),* 99.9 mol %.

6.9 *Methyl Silicone.*[4]

6.10 *1,2,3-Tris(2-Cyanoethoxy) Propane (TCEP).*[4]

6.11 *Calibration Standards.*

6.11.1 *Benzene,* 99$^+$ mol %.

6.11.2 *Isooctane,* 99$^+$ mol %.

6.11.3 *n-Nonane,* 99$^+$ mol %.

7. Hazards

7.1 Many hydrocarbon solvents are flammable and hazardous; use special precautions when handling them. Of the reagents used in this procedure, methanol, chloroform, methylene chloride, acetone, methyl ethyl ketone, benzene (see 4.1), and *n*-nonane are hazardous.

7.2 Benzene is volatile and highly flammable. Exercise care to prevent accidental ignition. Benzene is also carcinogenic and toxic; acute or chronic poisoning may result from inhalation of benzene vapor, absorption of benzene through the skin, or drinking benzene.

8. Sampling

8.1 Take samples of solvents to be analyzed by this test method using the procedures described in Practice E300.

9. Preparation of Columns

9.1 *Column Packing Preparation*—Prepare the two packing materials, one containing 10 % methyl silicone and the other 25 % TCEP, as follows:

9.1.1 Weigh 45 g of the acid-washed calcined diatomite support 60 to 80 mesh, into a 500-mL flask (see 5.10). Dissolve 5 g of the methyl silicone in approximately 50 mL of chloroform. (**Warning**—Chloroform is a toxic material and inhalation must be avoided.) Pour the methyl silicone–chloroform solution into the flask containing the support. Attach the flask to the evaporator (see 5.9), connect the vacuum, and start the motor. Turn on the infrared lamp and allow the packing to mix thoroughly until dry.

9.1.2 Weigh 75 g of acid-washed pink diatomaceous earth, 80 to 100 mesh, into a 500-mL flask (see 5.10). Dissolve 25 g of TCEP in 200 mL of methanol and pour into the flask containing the support. Attach the flask to the evaporator (see 5.9), connect the vacuum, and start the motor. Turn on the infrared lamp and allow the packing to mix thoroughly until dry, but do not heat the packing above 180°C.

9.2 *Column Preparation:*

9.2.1 Clean the stainless steel tubing as follows: Attach a metal funnel to one end of the steel tubing. Hold or mount the stainless steel tubing in an upright position and place a beaker under the outlet end of the tubing. Pour about 50 mL of methylene chloride into the funnel and allow it to drain through the steel tubing into the beaker. Repeat the washing with 50 mL of acetone. Remove the funnel and connect the steel tubing to

[3] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] See Note 2.

an air line, by means of vinyl tubing. Remove all solvent from the steel tubing by blowing filtered, oil-free air through or applying a vacuum.

9.2.2 Pack the 0.8-m (2.5-ft) tubing (Column A) with the methyl silicone packing (see 9.1.1) and the 4.6-m (15-ft) tubing (Column B) with the TCEP packing (see 9.1.2) as follows: Preform Columns A and B separately to fit the chromatographic instrument. Close one end of each tubing with a small, glass wool plug and connect this end to a vacuum source by means of a glass-wool packed tube. To the other end connect a small polyethylene funnel by means of a short length of vinyl tubing. Start the vacuum and pour the appropriate packing into the funnel until the column is full. While filling each column, vibrate the column with the electric vibrator to settle the packing. Remove the funnel and shut off the vacuum source. Remove the top 6 mm (¼ in.) of packing and insert a glass wool plug in this end of the column.

9.3 Prepacked columns conforming to specifications listed in Table 1, and in 5.2, 9.1, and 9.2 may be obtained from any reputable chromatography supply company.

10. Preparation of Chromatographic Apparatus and Establishment of Conditions

10.1 *Column Conditioning*—Join Columns A and B as shown in Fig. 1. Connect the inlet of Column A to the injection port of the chromatograph. Pass helium gas through the column at approximately 40 mL/min. Condition the columns in accordance with the following time-temperature schedule.

Temperature, °C	Time, h
50	½
100	½
150	1
170	3

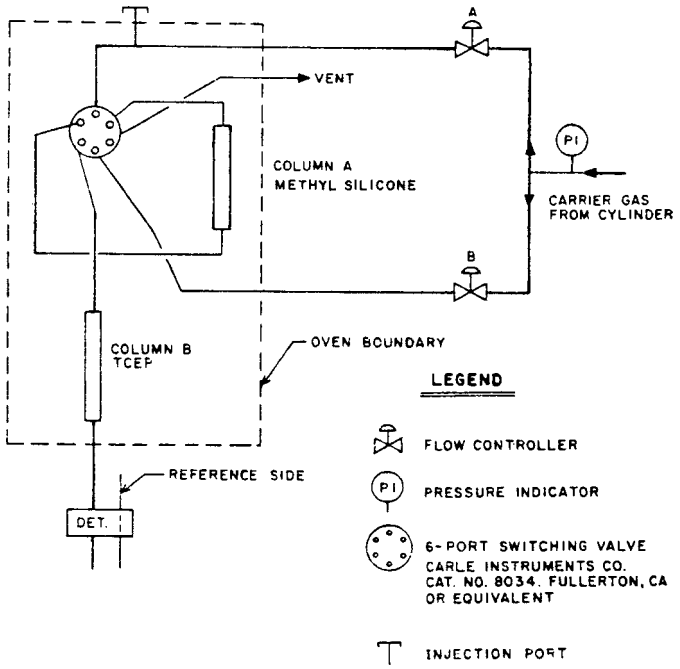

FIG. 1 Tubing Assembly and Instrumentation

10.2 Connect the outlet of Column B to the detector port. Adjust the operating conditions to those listed in Table 1, but do not turn on the detector circuits. Check the system for leaks.

10.3 Adjust the flow rate as follows:

10.3.1 Set the value in the *forward flow* mode (Fig. 2(*a*)) and adjust Flow Controller A to give the required flow rate (Table 1). Measure the flow rate at the detector vent, specimen side.

10.3.2 Set the valve in the *backflush position* (Fig. 2(*b*)) and measure the flow rate at the detector vent, specimen side. If the rate has changed, adjust Flow Controller B to obtain the required flow rate to within ±1 mL/min.

10.3.3 Turn on the detector circuit. Change the valve from *forward flow* to the *backflush* position several times and observe the baseline. There should be no baseline shift or drift after the initial peak resulting from the pressure surge with the valve change. If there is a baseline shift, slightly increase or decrease flow with Controller B to balance the baseline. (A persistent drift indicates leaks somewhere in the system.)

10.4 Determine time before backflushing, which varies for each column system and must be determined experimentally as follows:

10.4.1 Prepare a mixture of 5 volume % *iso*octane in *n*-nonane. Using the injection technique described in 11.3 and with the system in the *forward flow* mode, inject 1 µL of the *iso*octane–*n*-nonane mixture. Allow the chromatogram to run until the *n*-nonane has eluted and the recorder pen has returned to baseline. Measure the time in seconds from the injection until the recorder pen returns to baseline between the *iso*octane and *n*-nonane peaks. At this point all of the *iso*octane but essentially none of the *n*-nonane should have eluted. One half of the measured time approximates the time to backflush and should be from 30 to 120 s.

10.4.2 Repeat the run, including the injection, but switching the system to the *backflush* mode at the determined backflush

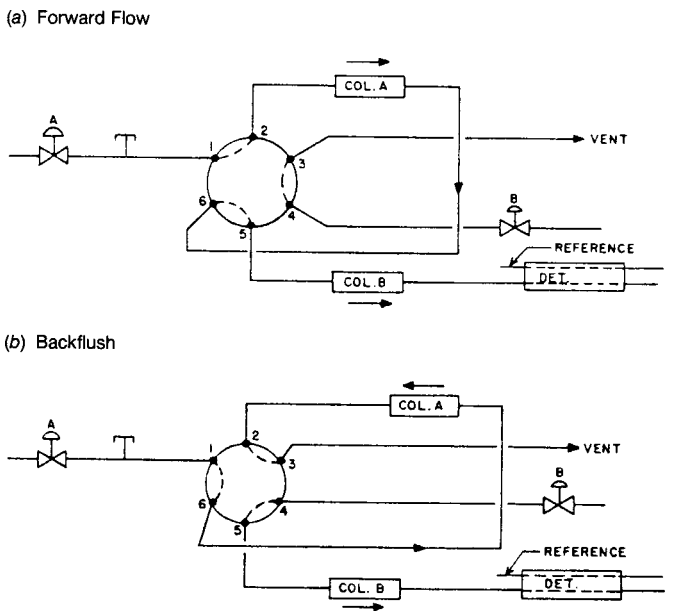

FIG. 2 Flow Switching System