Designation: D 6229 – 01

Standard Test Method for
Trace Benzene in Hydrocarbon Solvents by Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D 6229; 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 capillary gas chromatography of trace benzene in hydrocarbon solvents at levels from 1.0 to 2400 vppm.

NOTE 1—Lower levels of benzene may be determined by this test method. However the gas chromatography (GC) will have to be modified from those specified in this test method. The precision of the method may not apply to these lower benzene levels.

1.2 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

1.3 The values stated in SI units are to be regarded as the statement. The values in parenthesis are given for information only and are not necessarily the exact equivalent of the SI unit values.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*
D 4367 Test Method for Benzene in Hydrocarbon Solvents by Gas Chromatography[2]
E 300 Practice for Sampling Industrial Chemicals[3]

3. Summary of Test Method

3.1 A given volume of the sample is introduced into a gas chromatograph equipped with two capillary columns connected in series by switching valve. The specimen passes first through a short capillary column with a bounded nonpolar phase where the components are separated by boiling point. After octane has eluted from the first column, the components heavier than octane are back-flushed to vent. The octane and lighter components then pass through a second capillary column with bounded polar phase where the aromatic and nonaromatic components are separated. The eluted components are detected by a flame ionization detector, and the peak areas are integrated electronically. The concentration of benzene is calculated by a data processor using a response factor determined by external standard technique.

4. Significance and Use

4.1 This test method is similar to Test Method D 4367 with the exception that capillary columns are used and intended for trace level of benzene in hydrocarbon solvents. The need for trace benzene analysis in hydrocarbon solvents arose because of the increase of more stringent regulation of benzene level in these materials.

5. Apparatus

5.1 *Chromatograph*—Any gas chromatographic instrument that has a backflush system operated by a switching valve automatically, flame ionization detector, and can be operated at the conditions given in Table 1.

5.2 *Detector*—The flame ionization detector shall have sufficient sensitivity to detect 0.1 vppm of benzene at a peak height of 3 times the noise level.

5.3 *Columns*—one 2–m (6.5–ft), 0.53 mm inside diameter fused silica capillary with 5-μm thick bounded methyl silicone column and one 30–m (98.5–ft), 0.53-mm inside diameter fused silica capillary with 0.5-μm thick bounded polyethylene glycol column.

5.4 *Switching Valve*— A 6–port switching valve 175°C (347 °F) maximum temperature, housed in a separate, temperature-controlled oven, that can be activated automatically by the gas chromatograph.

5.5 *Sample Inlet System*—The sample inlet system shall be capable of split injection typically at a 1:10 split ratio.

NOTE 2—An auto injector was used in the generation of the repeatability value of this test method, and is recommended. Manual injection with a syringe is acceptable; however, the observed precision may not apply.

5.6 *Data Acquisition System*:
5.6.1 *Recorder*—A 0 to 1 mv range recorder or equivalent, with a full-scale response time of 2 s shall be used.

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

TABLE 1 Instrument Conditions Found Satisfactory for Measuring Trace Concentrations of Benzene in Hydrocarbon Solvents

GC Parameter	Values
Detector	Flame ionization detector (FID)
Columns:	
Length, m	(A) 2; (B) 30
Inside diameter, mm	(A) 0.53; (B) 0.53
Liquid phase, bonded	(A) methyl silicone; (B) polyethylene glycol
Liquid phase thickness	(A) 5 μm; (B) 0.5 μm
Switching value temperature	150°C (302°F)
Temperature programme:	
Initial temperature	40°C (104°F)
Initial time hold	8 min
Ramp rate	20°C (68°F)/min
Final temperature	200°C (392°F)
Final time hold	5 min
Sample size	1 μL
Split ratio	1:10
Column flow (He carrier gas)	5.0 mL/min
Backflush to vent activation time	3.0 min

5.6.2 *Integrator*—Means shall be provided for determining the area of the benzene peak. This can be done by means of an electronic integrator or a computer based chromatography data system. The integrator/computer system shall have standard chromatographic software for determining the retention times and areas of eluting peaks.

5.7 *Microsyringe*— 5 μL capacity.

5.8 *Pipets*—measuring 1 and 2 mL, graduated in 0.01 mL: 5, 10, and 20 mL capacity.

5.9 *Pipets*—delivery 0.5, 1, 2, 5, 10, 25 mL capacity.

5.10 *Flasks*—volumetric, 25, 50, 100, and 500 mL capacity.

6. Reagents

6.1 *Purity of Reagents*—All reagents shall be reagent grade chemicals with a minimum purity of 99 + mol %.

6.1.1 *Benzene*.

6.1.2 *n-Hexane*, benzene-free.

6.1.3 *n-Octane*, benzene-free.

6.1.4 *n-Nonane*, benzene-free.

7. Sampling

7.1 Take samples of solvents to be analyzed by this test method using the procedures described in Practice E 300.

8. Preparation and Conditioning of Capillary Columns

8.1 Both columns prescribed by this procedure shall be obtained ready to use from reputable chromatographic suppliers.

8.2 Columns shall be conditioned following column supplier recommended procedures before use.

9. Preparation of Gas Chromatograph

9.1 Connect columns A and B to the 6–port switching valve by referring to Fig. 1.

9.1.1 Adjust the operating conditions to those listed in Table 1, but do not turn on the detector. Check the system for leaks.
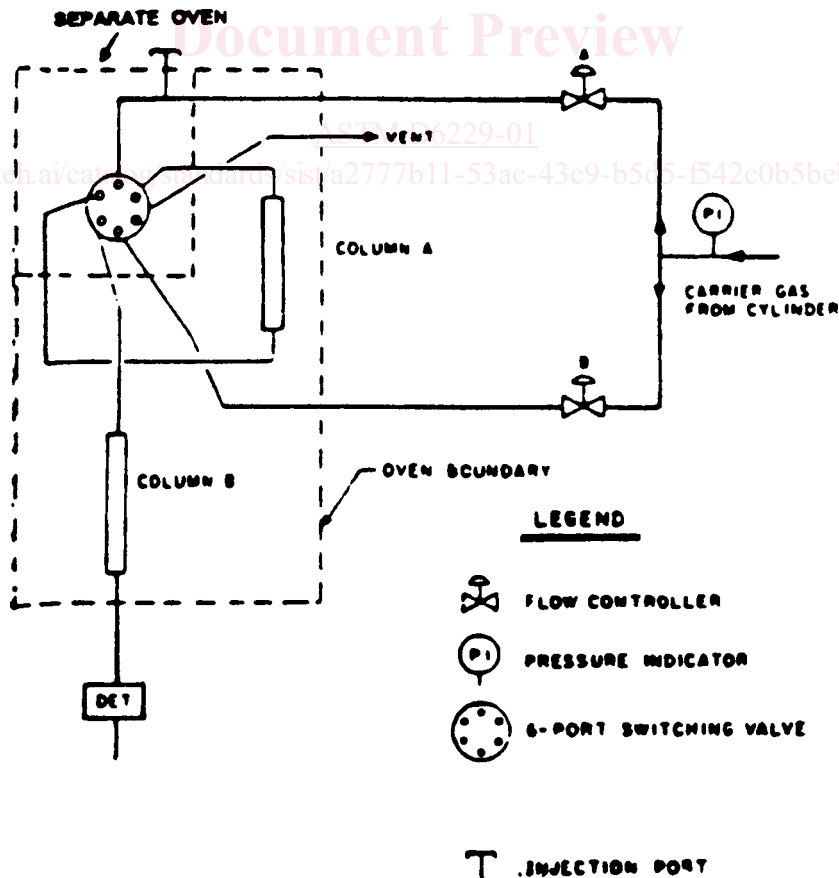

FIG. 1 Columns Connections to Switching Valve

9.2 Adjust the column flow rate as follows:

9.2.1 Set the switching valve in the *forward flow* mode (Fig. 2 (a)) and adjust the flow controller to give the required column flow rate.

9.2.2 Set the switching valve in the *backflush* mode (Fig. 2 (b)) and check that the column flow is as required.

9.2.3 Turn on the detector. Change the switching from the *forward flow* to the *backflush* mode several times and observe the baseline. There shall be no baseline shift resulting from the pressure surge when the switching valves are changed. (A persistent drift indicates leaks somewhere in the system).

9.3 Determine the backflush activation time. The backflush activation time varies for each column system and shall be determined experimentally as follows:

9.3.1 Prepare a solution of 0.1 v % *n*–octane and 0.1 v % *n*–nonane in benzene-free *n*–hexane. With the system in the *forward flow* mode, introduce 1μL of the *n*–octane/*n*–nonane in *n*–hexane mixture. Allow the chromatogram to run until the *n*–nonane has eluted from the second column and the chromatographic trace has returned to baseline. Measure the time in minutes from the injection until the signal goes back to baseline after the *n*–octane peak. At this point all of the *n*–octane but essentially none of the *n*–nonane shall have eluted. One half of the measured time approximates the time to backflush (see 9.3.3).

NOTE 3—Some minor adjustment of the backflush activation time may be necessary for some samples.

9.3.2 Repeat the run, including the injection of the *n*–octane/*n*–nonane in a *n*–hexane mixture, but switching the system to the *backflush* mode at the determined backflush

activation time. This should result in a chromatogram showing only *n*–hexane and *n*–octane, with little or no *n*–nonane evident.

9.3.3 If necessary, make additional runs, adjusting the backflush activation time until a chromatogram of all the *n*–octane (evidenced by a repeatable and constant area count) and little or none of the *n*–nonane is obtained. The established backflush activation time for a particular type of sample shall be used in all subsequent calibration and analysis.

10. Calibration and Standardization

10.1 *5000 vppm Stock Solution*—Prepare a 5000-vppm benzene in *n*–hexane stock solution by accurately delivering 0.50 mL of 99+ % purity benzene into a 100–mL volumetric flask by means of a delivery pipet. Dilute to the mark with *n*–hexane. This stock solution can be used to prepare various levels of benzene in *n*–hexane by accurately diluting the required volume of this solution with *n*–hexane in a volumetric flask.

10.2 *Calibration Standard Solution*—Prepare a 10.0 vppm benzene in *n*–hexane calibration standard solution by accurately delivering 1.0 mL of the 5000 vppm stock solution into a 500–mL volumetric flask. Dilute to the mark with *n*–hexane. This calibration standard can be used in calibrate the procedure by external standard technique.

10.3 *Calibration*— If the system has not been used for at least 12 h, condition the system by running the GC method once without injecting any sample. After conditioning, introduce 1 μL of the 10 vppm benzene in *n*–hexane calibration standard by the recommended injection technique and allow the run to be completed. Determine the response factor for the
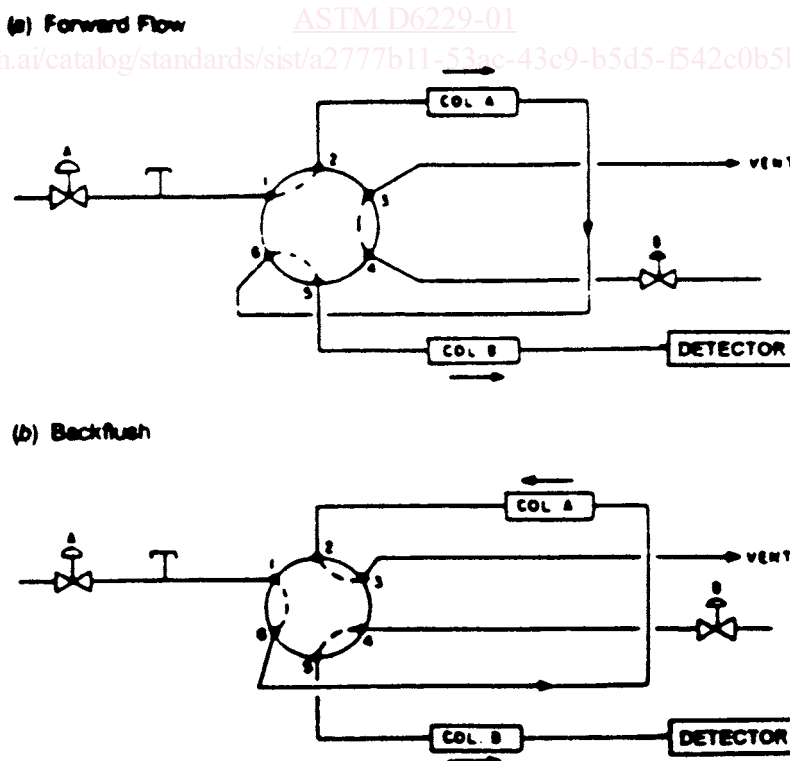

(a) Forward Flow

(b) Backflush

FIG. 2 Flow Switching System