



Standard Test Method for Determination of Aromatics in Finished Gasoline by Gas Chromatography¹

This standard is issued under the fixed designation D 4420; 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.

^{ε1} NOTE—Warning statements were made part of the text in November 1999.

1. Scope

1.1 This test method provides for the determination of benzene, toluene, C₈, C₉ and heavier aromatics, and total aromatics in finished motor gasoline. It is also applicable to gasoline blending components.

NOTE 1—For analysis of gasolines for benzene and toluene, solely, Test Method D 3606 can be used.

1.2 This test method is applicable to the following concentration ranges, in liquid volume percent, for the individual aromatics listed above: benzene, 0.1 to 5; toluene, 1 to 20; C₈, 3 to 25; C₉ and heavier, 5 to 30, and total aromatics, 10 to 80.

1.3 It has not been determined whether this test method is applicable to gasoline containing oxygenates; for example, ethers and alcohols.

1.4 Results are reported to the nearest 0.1 % by liquid volume.

1.5 The values stated in SI units are to be regarded as the 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 precautionary statements see Sections 6.1 through 6.8 and 7.1.

2. Referenced Documents

2.1 ASTM Standards:

D 3606 Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products²

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards²

E 260 Practice for Packed Column Gas Chromatography³

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.04 on Gas Chromatography.

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² *Annual Book of ASTM Standards*, Vol 05.02.

³ *Annual Book of ASTM Standards*, Vol 14.02.

3. Summary of Test Method

3.1 A two-column chromatographic system connected to a dual-filament thermal conductivity detector (or two single-filament detectors) is used. A reproducible volume of sample is injected into the column containing a polar liquid phase. The nonaromatics are directed to the reference side of the detector (or single-filament Detector B) and vented to the atmosphere as they elute. The column is backflushed immediately before the elution of benzene, and the aromatic portion is directed into the second column containing a nonpolar liquid phase. The aromatic components elute in the order of their boiling points and are detected on the analytical side of the detector (or single-filament Detector A). Immediately after the C₈ aromatics have eluted, the flow through the nonpolar column is reversed to backflush the C₉ and heavier aromatics from the column through the detector. Quantitative results are obtained from the measured areas of the recorded aromatic peaks by utilizing factors obtained from the analysis of a blend of known aromatic content.

4. Significance and Use

4.1 A knowledge of aromatics in gasolines is helpful in assessing product quality. Such knowledge can also be an aid in evaluating the health hazard to persons handling and using gasoline.

5. Apparatus

5.1 *Chromatograph*—Any chromatographic instrument that has a direct vaporizing injector, backflush system, and a thermal conductivity detector, and that can be operated at the conditions given in Table 1, can be employed. Two backflush systems are shown. Fig. 1 is a flow diagram employing an eight port rotary valve, and Fig. 2 is a flow diagram using an eleven port linear valve. Either flow pattern may be used.

5.1.1 *Thermal Conductivity Detector*—Either one dual-filament or two single-filament detectors can be used. With dual-filament detectors, both the analytical side and the reference side are used separately to detect eluting components. Proper detection is achieved by manual or automatic switching of the signal polarity. Newer gas chromatographs equipped with single-filament detectors usually have the capability to automatically switch from one signal output to the other so that

TABLE 1 Operating Conditions

Carrier gas	helium
Carrier gas flow rate	60 cm ³ /min
Detector type	thermal conductivity
Detector temperature	150°C
Injection port temperature	200°C
Column oven temperature	135°C
Sample size	3 μL

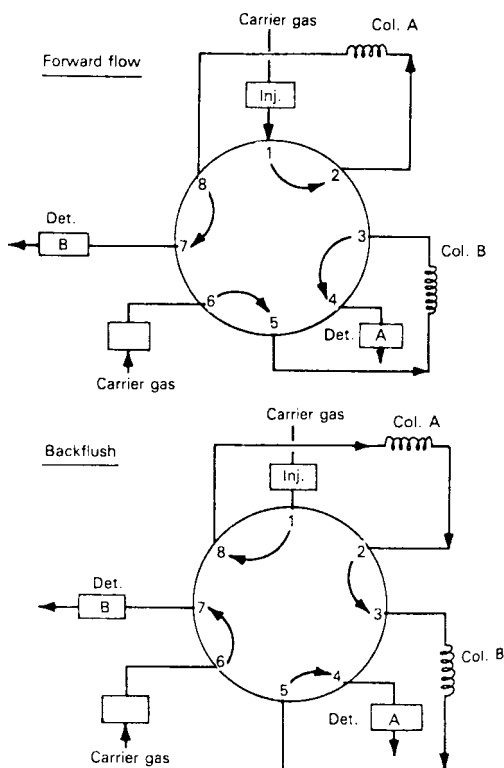


FIG. 1 Flow Pattern with Eight Port Rotary Valve

they also require only a single recorder or single channel of integration.

5.1.2 *Sensitivity*—An overall sensitivity sufficient to detect 0.1 volume % of benzene with a peak height of at least 3-mm with a 3-μL injection.

5.2 *Recorder*, strip chart. A0 to 1-mV range recording potentiometer with a response time of 2 s or less and a maximum noise level of ± 0.3 % of full scale.

5.3 *Integrator*, computer or electronic integration.

5.4 *Column*—Two columns, as described in Table 2. Column A (polar) separates aromatics from nonaromatics and Column B (nonpolar) separates the aromatics by carbon number.

5.5 *Microsyringe*, 5-μL capacity.

6. Reagents and Materials

6.1 *Carrier Gas*, helium, 99.99 % pure. (**Warning**—Compressed gas under high pressure.)

6.2 *Solid Support*, crushed firebrick or inert diatomaceous earth, acid-washed, 60–80 mesh.⁴

⁴ Chromosorb P from Manville Corp., Denver, CO has been found satisfactory for this purpose.

6.3 *Liquid phases*, OV-275⁵ and methyl silicone.⁶

6.4 *Isooctane*, 99⁺ mol %. (**Warning**—Extremely flammable. Harmful if inhaled.)

6.5 *Benzene*, 99⁺ mol %. (**Warning**—Poison. Carcinogen. Harmful or fatal if swallowed. Extremely flammable. Vapors may cause flash fires.)

6.6 *Toluene*, 99⁺ mol %. (**Warning**—Flammable. Vapor harmful.)

6.7 *Xylenes, mixed*, reagent grade, (**Warning**—Flammable. Vapor harmful.) Contains ethylbenzene. (**Warning**—Flammable. Vapor harmful.)

6.8 *n-Butylbenzene*, 99⁺ mol %. (**Warning**—Flammable. Vapor harmful.)

7. Sampling

7.1 Gasoline (**Warning**—Extremely flammable. Vapors harmful if inhaled.) Samples to be analyzed by this test method shall be obtained using the procedures outlined in Practice D 4057. After delivery to the laboratory, volatile samples must be cooled before the container is opened.

8. Preparation of Apparatus

8.1 Install the valve and the columns in the column oven in accordance with the flow pattern shown in either Fig. 1 or Fig. 2. Columns can be prepared by any satisfactory method, used in the practice of the art, provided the separation achievable is equivalent to that shown in Figs. 3-5.

NOTE 2—Typical instructions for preparing columns are given in Practice E 260.

8.1.1 Adjust the operating conditions to those listed in Table 1, but do not turn on the detector circuits. Check the system for carrier gas leaks. After confirming no leaks, turn on the detector and allow the system to equilibrate, as indicated by a stable, recorder baseline.

9. Calibration

9.1 *Calibration mixture*—Using the procedure described in Practice D 4307, prepare a calibration blend of aromatics in isooctane at levels approximately those in the sample to be analyzed. *n*-Butylbenzene is used to represent the C₉ + aromatic composite. Using relative densities, convert the calculated mass (weight) percent to liquid volume percent. (**Warning**—see 6.4, 6.5, 6.6, and 6.7.)

NOTE 3—The following aromatics concentrations, in volume percent, are typical: benzene, 3.00; toluene, 10.00; mixed xylenes (C₈ aromatics), 15.00, and *n*-butylbenzene (C₉ + aromatics), 15.00.

NOTE 4—The following relative densities, at 60/60°F,⁷ are used: benzene 0.8845, toluene 0.8719, *n*-butylbenzene 0.8646, and an average of 0.8727 for mixed xylenes.

9.2 Calibration Procedure:

⁵ OV-275, a dicyanoallylsilicone, from Ohio Valley Specialty Chemicals Inc., Rt. 6, Brant Drive, Marietta, OH 45750, has been found satisfactory for this purpose.

⁶ Silicone gum rubber, GE-SE-30, from General Electric Co. and OV-101 from Ohio Valley Specialty Chemicals, Inc., have been found satisfactory for this purpose.

⁷ "Physical Constants of Hydrocarbons, C₁ to C₁₀," Table VI, American Petroleum Institute, July 1961.

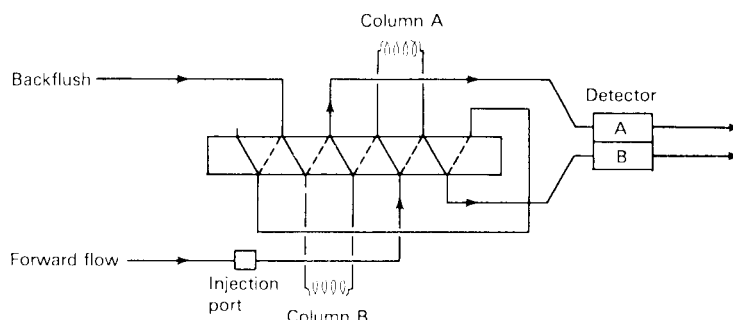


FIG. 2 Flow Pattern with Eleven Port Linear Valve

TABLE 2 Columns

	Column A	Column B
Liquid phase	OV-275	SE-30 or OV-101
Length (stainless steel), m	3	3
Diameter, mm (in.)		
Inside	1.8 (0.07)	1.8 (0.07)
Outside	3.2 (1/8)	3.2 (1/8)
Loading Mass, %	33	25
Solid support	Chromosorb P	Chromosorb P
Mesh	60-80	60-80
Treatment	acid-washed	acid-washed

h Eleven Port Linear Valve

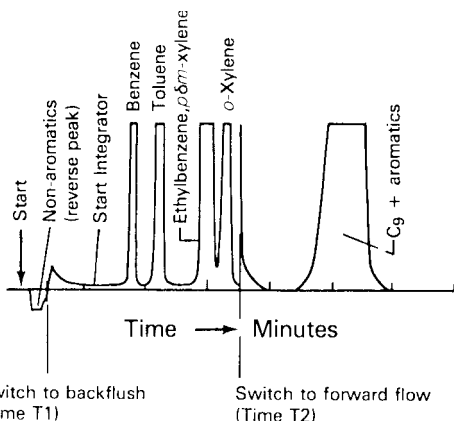


FIG. 3 Illustrative Chromatogram Showing Valve Switching Positions

9.2.1 Inject 3 μL of the calibration mixture with the valve in the forward flow position and the detector on polarity B. If a single-filament detector is being used, monitor the signal from Detector B. Determine the time, in seconds, at which benzene begins to elute, and subtract 6 s from this value. Call this time T_1 .

9.2.2 Chromatograph the calibration mixture with the detector on polarity A. If a single-filament detector is being used, monitor the signal from Detector A. At time T_1 , switch the valve to the backflush position. When the *o*-xylene peak returns to baseline, switch the valve to the forward flow position. Call this time T_2 . An illustrative chromatogram is given in Fig. 3.

9.2.3 Measure the areas of the benzene, toluene, C_8 aromatic composite and *n*-butyl benzene peaks. Calculate the response factor (volume percent per unit of area) for each of these components or groups from the following equation:

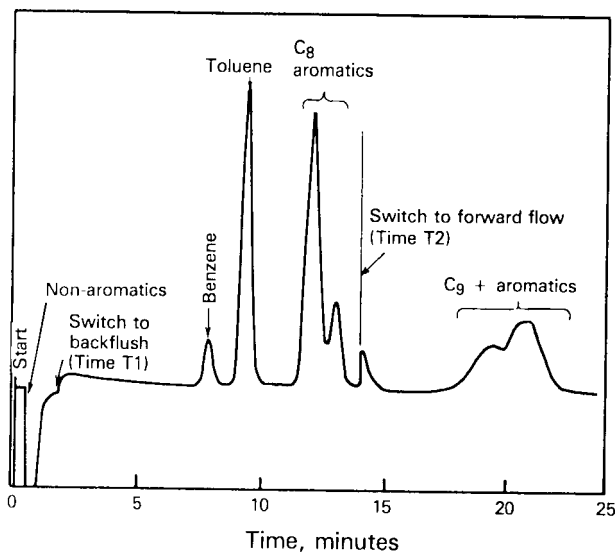


FIG. 4 Illustrative Chromatogram of a Gasoline

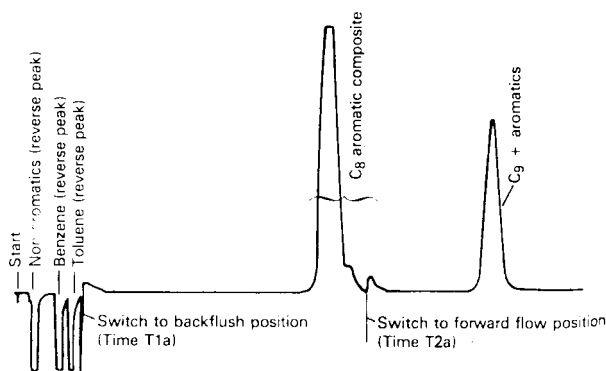


FIG. 5 Illustrative Chromatogram Showing Valve Switching Positions for a Second Analysis

(1)

where:

F = response factor of the component or group for a 3- μL volume,

M = concentration of the component, volume percent, and

A = peak area for the component

9.2.4 Calculate response factors to at least three significant figures.

10. Procedure

10.1 *Chromatographic Analysis*—Chromatograph the sample using the procedure described for the calibration mixture in 9.2. The volume of sample injected must be exactly the same as the volume used for calibration.

10.1.1 A sample that contains heavy non-aromatics, which interfere with the determination of C₉ + aromatics, is indicated on the chromatogram by the non-aromatics reverse peak not returning to near-baseline by time T₁. If a single-filament detector is being used, the nonaromatics peak will appear positive. For quantitation of the C₉ + aromatics composite, times T_{1a} and T_{2a} are determined and utilized for a second analysis of this same sample that determines C₉ + aromatics only.

10.1.2 Time T_{1a} is determined by chromatographing the calibration blend with the valve in forward flow position and the detector on polarity “B.” If a single-filament detector is being used, monitor the signal from Detector B. Determine the time in seconds at which the mixed xylenes composite begins to elute and subtract 6 s from this value. Call this time T_{1a}.

10.1.3 Chromatograph the blend with the detector on polarity A. If a single-filament detector is being used, monitor the signal from Detector A. At time T_{1a}, switch the valve to the backflush position. When the *o*-xylene peak returns to baseline, switch the valve to the forward flow position. Call this time T_{2a}. This is illustrated in Fig. 5.

10.1.4 If the non-aromatics peak for the sample containing heavy non-aromatics returns to a near baseline condition before time T_{1a}, the C₉ + aromatic composite can be determined from this second analysis. If a near-baseline condition is still not achieved, the C₉ + aromatics composite cannot be determined.

10.2 *Measurement of Area*—Measure the areas of the benzene, toluene, C₈ aromatics composite and C₉ + composite. Units must be consistent with 9.2.3 above.

NOTE 5—The precision statement in Section 13 was developed from data obtained using electronic integrators or on-line computers. The precision statement need not apply if other methods of integration or peak area measurement is used.

11. Calculation

11.1 Calculate the liquid volume percent (LV-%) of each aromatic hydrocarbon component or group present in the sample using the following equation:

$$\text{Component, LV-\%} = FC \quad (2)$$

where:

F = response factor, previously defined in 9.2.3 and

C = peak area for that component

12. Report

12.1 Report the concentration of the individual aromatics or

aromatics groups on an absolute basis to the nearest 0.1 liquid volume percent.

13. Precision and Bias

13.1 *Precision*—The precision of the test method as determined by a statistical examination of interlaboratory test results is as follows:

13.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty:

	Liquid Volume Percent
Benzene	0.171 × measured value
Toluene	0.089
C ₈ aromatics	0.121
C ₉ + aromatics	0.092
Total aromatics	0.078

13.1.2 *Reproducibility*—The difference between two, single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

	Liquid Volume Percent
Benzene	0.408 × measured value
Toluene	0.156
C ₈ aromatics	0.190
C ₉ + aromatics	0.196
Total aromatics	0.141

NOTE 6—The precision was determined using conventional motor gasolines purchased on the open market and representative gasoline blending components. Benzene concentrations, in most of the samples, were less than 2 liquid volume percent. For more precise benzene analysis, at low concentration levels, Test Method D 3606 should be used.

13.2 *Bias*—Since there is no accepted reference gasoline containing known concentrations of individual aromatics, the bias for the procedure in Test Method D 4420 for measuring aromatics in finished gasoline can not be determined.

13.2.1 This test method uses purposely prepared calibration blends to establish the relationship between absolute detector response and known concentration for each of the individual aromatics or group of aromatics listed in the scope. The response factors so determined effectively compensate for any instrumental bias. The calibration blends used, however, are much simpler in composition than gasoline; thus matrix effects can not be adequately addressed and can be a source of bias.

14. Keywords

14.1 aromatics; benzene; gas chromatography; gasoline; toluene

 **D 4420**

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