Designation: D4424 – 09 (Reapproved 2014)

Standard Test Method for Butylene Analysis by Gas Chromatography[1]

This standard is issued under the fixed designation D4424; 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 gas chromatographic analysis of commercial butylenes, butylene concentrates, and butane-butylene mixtures.

1.2 This test method does not cover high-purity butene-1 or high-purity isobutene streams, or both. However, it is possible that one or more columns listed in Appendix X3 may be capable of the separation necessary for high-purity analyses.

1.3 This test method is designed to cover the components listed below at about 0.05 % or greater. It is not intended for trace hydrocarbon analysis. Components to be determined are: propane, propylene, isobutane, *n*-butane, butene-1, isobutene, *trans*-butene-2, *cis*-butene-2, 1,3-butadiene, isopentane, *n*-pentane.

1.4 The values stated in SI units are to be regarded as the standard. The values stated in inch-pound units are for information only.

1.5 *This standard does not purport to address all of the safety concerns 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 warning statements, see 5.3.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E260 Practice for Packed Column Gas Chromatography

3. Summary of Test Method

3.1 The sample is separated in a gas chromatograph system using a packed chromatographic column with either helium or hydrogen as the carrier gas. The separated components of the sample are detected by either a thermal conductivity detector or by a flame ionization detector. Calibration data are obtained by using either relative response factors or by using a standard calibration blend.

4. Significance and Use

4.1 This test method could be used to determine butylene stream composition for custody transfer payments. It is also capable of providing data necessary to evaluate processing requirements in an operating plant.

5. Apparatus

5.1 *Chromatograph*—Any chromatographic instrument having either a thermal conductivity or flame ionization detector with an overall sensitivity sufficient to detect at least 0.05 % of each of the components listed in 1.3.

5.2 *Detector*—Either a thermal conductivity or flame ionization detector may be used.

5.3 *Sample Valve*—Either a constant-volume gas sampling valve or a liquid sampling valve may be used. If a gas sampling valve is used, greater care must be taken to ensure that the vaporized butylenes that are injected into the chromatograph are a true representation of the sample.

5.3.1 If the liquid sample valve is used, the sample cylinder must be pressured up to at least 1100 kPa (160 psig) with an inert gas, such as nitrogen or helium. (**Warning—**Compressed gas under high pressure. Gas reduces oxygen available for breathing.) Also a valve must be installed in the purge line downstream of the liquid sample valve to ensure the butylenes sample in the sampling valve is entirely in the liquid phase prior to injection into the column. (**Warning—**Extremely flammable liquefied gas under pressure. Vapor reduces oxygen available for breathing.)

5.4 *Column*—Any chromatographic column may be used, providing the components listed in the scope can be separated sufficiently for the accurate determination of component concentration. Resolution between peaks must afford a resolution such that the depth of the valleys between peaks are no less than 50 % of the peak height of the lesser component. A list of satisfactory columns is given in Appendix X3.

5.5 *Recorder*—A recorder with a full-scale response of 2 s or less and a maximum rate of noise of ±0.3 % of full scale.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.D0.04 on C4 Hydrocarbons.

Current edition approved May 1, 2014. Published July 2014. Originally approved in 1984. Last previous edition approved in 2009 as D4424 – 09. DOI: 10.1520/D4424-09R14.

[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.

6. Preparation of Apparatus

6.1 Set up the chromatograph in accordance with the manufacturer's recommendations. Install the analytical column and adjust the carrier gas flow and column temperature so that the components will elute within the time desired for the analysis.

7. Calibration

7.1 A standard blend containing the components to be analyzed may be either made or purchased from a commercial source. Inject the calibration blend under identical conditions as will be used for the samples. Record the chromatogram and calculate the factors to be used for analysis by using the peak areas as measured by either manual, mechanical, or electronic means.

7.2 Relative response factors may be used if they are available.

NOTE 1—Practice E260 procedures may be helpful to those using this test method.

8. Procedure

8.1 If a vapor sample is to be injected using a gas sample valve, a representative portion of the liquid butylenes must be taken and vaporized into a suitable container. As a suggestion, a small, 5 or 10 mL aliquot of liquid butylenes under pressure in a valved, 5 or 10-mL sample cylinder can be expanded into a larger container as a vapor. Then this resultant vapor would be injected into the chromatograph.

8.2 If a liquid sampling valve is used, pressure the sample cylinder to at least 1100 kPa (160 psig) with either helium or nitrogen.

8.3 Take the sample after the proper preparation has been done and inject it into the gas chromatographic column using the appropriate sampling valve. Record the chromatogram using as low an attenuation as possible to insure all peaks are on scale and as large as possible.

8.4 Measure the peak areas after all peaks have eluted. Measurement may be automatic by using either mechanical or electronic integrators or computers.

9. Calculations

9.1 Calculate the concentration of each component using the following equation:

$$C_i = \left(A_i \times F_i \times 100 / \sum A_i \times F_i\right) \quad (1)$$

where:

C_i = concentration of the *i*-th component,
A_i = peak area of the *i*-th component,
F_i = calibration factor for the *i*-th component, and
$\sum A_i \times F_i$ = sum of all products of peak areas times calibration factors.

10. Report

10.1 Report individual hydrocarbon compounds of the test sample using units of mass percent, rounded to the nearest 0.05 mass percent.

11. Precision and Bias

11.1 It is not feasible to provide a complete precision statement covering repeatability and reproducibility for this test method at this time, since a sufficient quantity of repeat tests and samples under the required ASTM protocol are not available. This information is being determined and will be available on or before May 31, 2014.

11.2 The temporary repeatability standard deviation was determined to be as shown in Table 1.

11.3 *Bias*—Since there is no accepted reference material suitable for determining bias for the procedure in this test method, bias cannot be determined.

12. Keywords

12.1 butylene; C_1-C_4 hydrocarbons; gas chromatography

TABLE 1 Repeatability Estimates

	Propylene	Isobutane	*n*-Butane	*trans*-2-Butene	Butene-1	Isobutylene	*cis*-2-Butene	iso-Pentane	*n*-Pentane	1,3-Butadiene
	0.513	0.703	3.040	5.000	14.000	20.000	3.990	0.203	0.102	50.550
	0.510	0.702	3.037	4.993	13.989	19.988	3.984	0.203	0.102	50.448
	0.509	0.702	3.044	4.993	14.001	19.996	4.004	0.205	0.103	50.385
	0.509	0.698	3.025	4.982	13.943	19.920	3.974	0.201	0.102	50.380
	0.508	0.699	3.032	4.981	13.947	19.922	3.981	0.202	0.102	50.451
	0.509	0.698	3.031	4.988	13.961	19.932	3.983	0.202	0.102	50.414
	0.510	0.702	3.045	4.994	14.002	20.015	3.997	.0198	0.102	50.475
	0.508	0.697	3.025	4.978	13.937	19.897	3.973	0.202	0.102	50.360
	0.510	0.699	3.039	5.002	14.002	20.011	3.990	0.203	0.102	50.551
	0.510	0.700	3.033	4.993	13.979	19.972	3.983	0.203	0.102	50.484
	0.508	0.696	3.017	4.956	13.885	19.855	3.963	0.201	0.101	50.253
AVERAGE	0.509	0.700	3.033	4.987	13.968	19.955	3.984	0.202	0.102	50.432
STDDEV	0.001	0.002	0.009	0.013	0.037	0.053	0.011	0.002	0.000	0.087
RSD	0.283	0.334	0.286	0.258	0.267	0.265	0.288	0.870	0.438	0.173

APPENDIXES

(Nonmandatory Information)

X1. GC PARAMETERS KNOWN TO WORK

X1.1 GC Parameters:

Column, GS Alumina—50 m × 0.53 mm
Carrier Gas, Helium—at 5.6 cm^3/min at 60°C
Oven 60°C initial—for 3 min
  5°C/min to 105°C—hold 3 min
  5°C/min to 150°C—hold 20 min
  20°C/min to 180°C—hold 1.5 min
Sample Valve—0.1-µL liquid valve
Split Vent Flow—113 cc^3/min
Septum Purge—2 cc^3/min
Auxiliary Gas, Helium—33 cc^3/min
FID hydrogen—33 cc^3/min
FID air—375 cc^3/min

X2. EXAMPLE CHROMATOGRAM

X2.1 See Fig. X2.1.

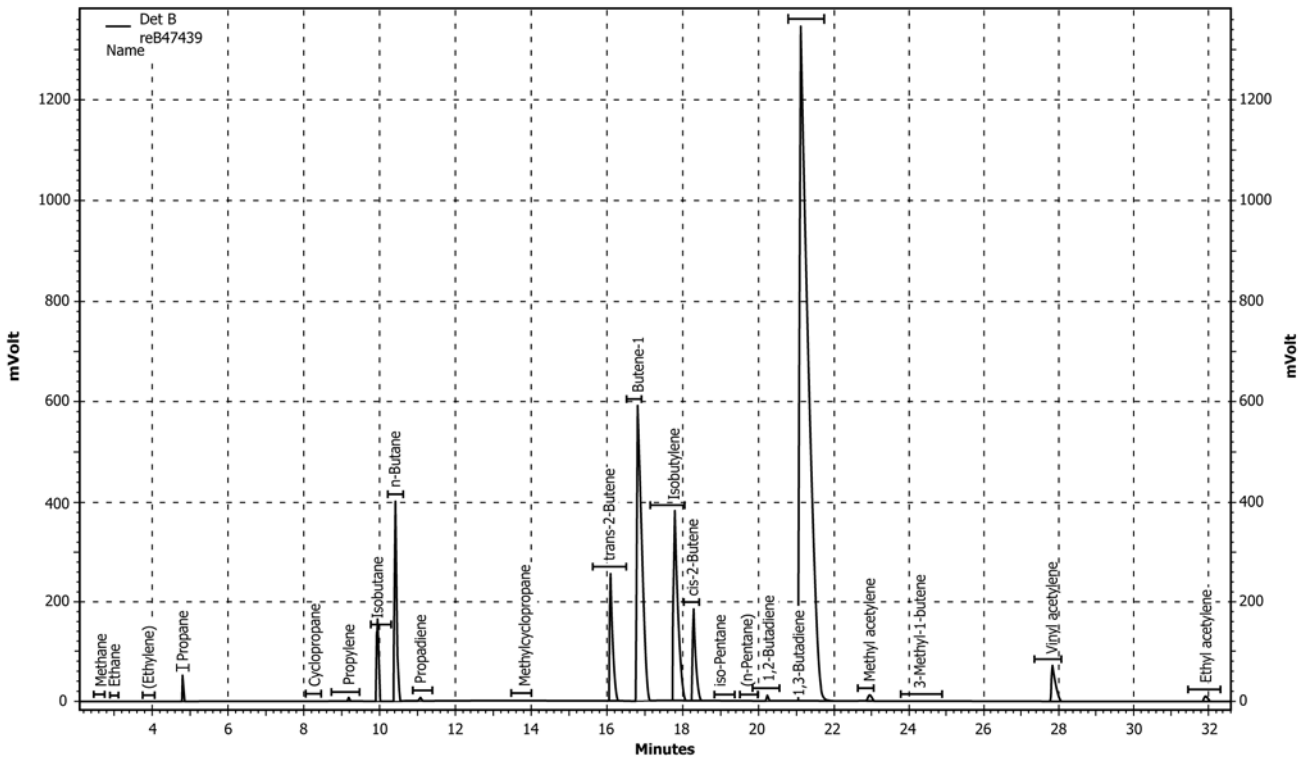

FIG. X2.1 Example Chromatogram

X3. SUGGESTED COLUMNS

X3.1 Column A

X3.1.1 *Column*—2.1 m by 3.2-mm (7 ft by ⅛-in.) outside diameter steel packed with 20 % diisopropyl phthalate on 60/80 mesh NAW Chromosorb P; followed by 15.2 m by 3.2-mm (50 ft by ⅛-in.) outside diameter stainless steel packed with 20 % dimethyl sulfolane on 60/80 mesh NAW Chromosorb P.

X3.1.2 *Carrier Gas*—helium at 30 cm^3/min.

X3.1.3 *Column Oven Temperature*—ambient.

X3.1.4 *Sample Valve*—1-µL liquid valve.

X3.2 Column B

X3.2.1 *Column*—12.2 m by 3.2-mm (40 ft by ⅛-in.) outside diameter stainless steel packed with 16 % sebaconitrile on 80/100 mesh AW Chromosorb P; followed by 1.8 m by 3.2-mm (6 ft by ⅛-in.) outside diameter stainless steel packed with 80/100 mesh OPN/Porasil C Durapak; followed by 1.2 m by 3.2-mm (4 ft by ⅛-in.) outside diameter stainless steel packed with 80/100 mesh phenylisocyanate on Porasil C Durapak.

X3.2.2 *Carrier Gas*—hydrogen at 30 cm^3/min.

X3.2.3 *Column Oven Temperature*—40°C.

X3.2.4 *Sample Valve*—1-µL liquid valve.