Designation: D2593 – 23

Standard Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography[1]

This standard is issued under the fixed designation D2593; 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 butadiene-1,3 purity and impurities such as propane, propylene, isobutane, *n*-butane, butene-1, isobutylene, propadiene, *trans*-butene-2, *cis*-butene-2, butadiene-1,2, pentadiene-1,4, and, methyl, dimethyl, ethyl, and vinyl acetylene in polymerization grade butadiene by gas chromatography. Impurities including butadiene dimer, carbonyls, inhibitor, and residue are measured by appropriate ASTM procedures and the results used to normalize the component distribution obtained by chromatography.

NOTE 1—Other impurities present in commercial butadiene must be calibrated and analyzed. Other impurities were not tested in the cooperative work on this test method.

NOTE 2—This test method can be used to check for pentadiene-1,4 and other C_5s instead of Test Method D1088.

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

1.3 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 6.1 and 9.3.

1.3.1 *The user is advised to obtain LPG safety training for the safe operation of this test method procedure and related activities.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1088 Method of Test for Boiling Point Range of Polymerization-Grade Butadiene (Withdrawn 1983)[3]

2.2 *Energy Institute Standards:*[4]

IP 194 Analysis of Butadiene-1,3 Polymerization Grade

3. Summary of Test Method

3.1 A representative sample is introduced into a gas-liquid partition column. The butadiene and other components are separated as they are transported through the column by an inert carrier gas. Their presence in the effluent is measured by a detector and recorded as a chromatogram. The chromatogram of the sample is interpreted by applying component attenuation and detector response factors to the peak areas or peak heights and the relative concentration determined by relating individual peak response to total peak response. Impurities including butadiene dimer, carbonyls, inhibitor, and residue are measured by appropriate ASTM procedures and the results used to normalize the distribution obtained by gas chromatography.

4. Significance and Use

4.1 The trace hydrocarbon compounds listed can have an effect in the commercial use of butadiene. This test method is suitable for use in process quality control and in setting specifications.

5. Apparatus

5.1 *Chromatograph*—Any chromatograph having either a thermal-conductivity or flame ionization detector can be used provided the system has sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at signal-to-noise ratio of at least 5:1 for 0.01 % by mass of impurity.

[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 and C5 Hydrocarbons.

This test method was adopted as a joint ASTM-IP Standard, IP 194, in 1972.

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[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] Obsolete. Contact Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

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

5.2 *Column*—Any column can be used that is capable of resolving the components listed in 1.1 with the exception of butene-1 and isobutylene, which can be eluted together. The components should be resolved into distinct peaks such that the ratio *A/B* will not be less than 0.5 where *A* is the depth of the valley on either side of peak *B* and *B* is the height above the baseline of the smaller of any two adjacent peaks. In the case where the small component peak is adjacent to a large one, it can be necessary to construct a baseline of the small peak tangent to the curve as shown in Fig. 1.

5.2.1 A description of columns that meet the requirements of this test method is tabulated in the Appendix. Persons using other column materials must establish that the column gives results that meet the precision requirements of Section 11.

5.3 *Sample Inlet System*—Means shall be provided for introducing a measured quantity of representative sample into the column. Pressure-sampling devices can be used to inject a small amount of liquid directly into the carrier gas. Introduction can also be accomplished by use of a gas valve to charge the vaporized liquid.

5.4 *Recorder*—A recording potentiometer with a full-scale deflection of 10 mV or less is suitable for obtaining the chromatographic data. Full-scale response time should be 2 s or less, and with sufficient sensitivity to meet the requirements of 5.1.

NOTE 3—Other methods of recording detector output such as computer-teletype systems can be used instead of a recorder, provided precision requirements of Section 11 are met.

6. Reagents and Materials

6.1 *Carrier Gas*—A carrier gas appropriate to the type of detector used should be employed. Helium or hydrogen may be used with thermal conductivity detectors. Nitrogen, helium, or argon may be used with ionization detectors. The minimum purity of any carrier should be 99.95 mol %. (**Warning—** Compressed gas. Hazardous pressure.) (**Warning—**Hydrogen flammable gas. Hazardous pressure.)

6.1.1 If hydrogen is used, special safety precautions must be taken to ensure that the system is free from leaks and that the effluent is properly vented.

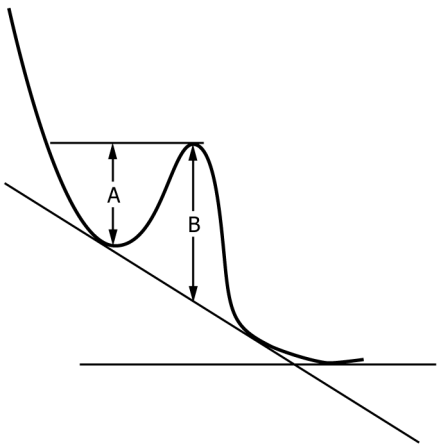

FIG. 1 Illustration of A/B Ratio for Small-Component Peak

6.2 *Column Materials:*

6.2.1 *Liquid Phase*—The materials that have been used successfully in cooperative work as liquid phases are listed in Table X1.1.

6.2.2 *Solid Support*—The support for use in the packed column is usually crushed firebrick or diatomaceous earth. Sieve size will depend on the diameter of the column used and liquid-phase loading, and should be such as would give optimum resolution and analysis time. Optimum size ranges cannot be predicted on purely theoretical grounds. For some systems it has been found that a ratio of average particle diameter to column inside diameter of 1:25 will result in minimum retention time and minimum band widths.

6.2.3 *Tubing Material*—Copper, stainless steel, Monel, aluminum, and various plastic materials have been found to be satisfactory for column tubing. The material must be nonreactive with respect to substrate, sample, and carrier gas and of uniform internal diameter.

6.3 *Hydrocarbons for Calibration and Identification*—Hydrocarbon standards for all components present are needed for identification by retention time and for calibration for quantitative measurements.

NOTE 4—Mixtures of hydrocarbons can be used provided there is no uncertainty as to the identity or concentration of the compounds involved.

7. Preparation of Apparatus

7.1 *Column Preparation*—The technique used to prepare the column is not critical as long as the finished column produces the desired separation. Preparation of the packing is not difficult once the support, partitioning liquid, and loading level have been determined. The following general directions have been found to produce columns of acceptable characteristics.

7.1.1 Weigh out the desired quantity of support, usually twice that required to fill the column.

7.1.2 Calculate and weigh out the required quantity of partitioning agent. Dissolve the partitioning agent in a volume of chemically inert, low-boiling solvent equal to approximately twice the volume of support.

7.1.3 Gradually add the support material to the solution with gentle stirring.

7.1.4 Slowly evaporate the solvent while gently agitating the mixture until the packing is nearly dry and no free liquid is apparent.

7.1.4.1 Some stationary phases such as benzyl cyanide silver nitrate are susceptible to oxidation and must be protected from excessive exposure to air during the evaporation and drying steps.

7.1.5 Spread the packing in thin layers on a nonabsorbent surface and air- or oven-dry as required to remove all traces of solvent.

7.1.6 Resieve the packing to remove fines and agglomerates produced in the impregnation step.

7.1.7 Fill the column tubing with packing by plugging one end with glass wool and pouring the packing into the other end through a small funnel. Vibrate the tubing continuously over its entire length while filling. When the packing ceases to flow, tap the column gently on the floor or bench-top while vibrating is continued. Add packing as necessary until no further settling