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

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D1088 Method of Test for Boiling Point Range of Polymerization-Grade Butadiene (Withdrawn 1983)[3]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

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

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 weight % of impurity.

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.

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.
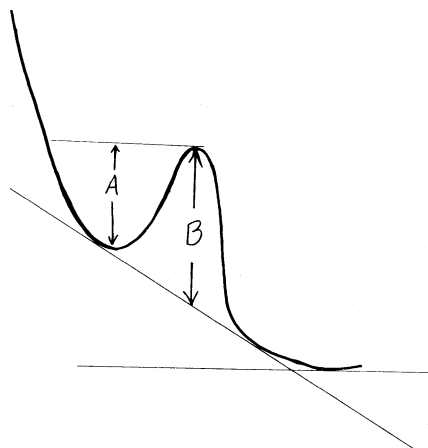

FIG. 1 Illustration of A/B Ratio for Small-Component Peak

6.3 *Hydrocarbons for Calibration and ~~Identification~~ —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 occurs during a 2-min period. Remove a small amount of packing from the open end, plug with glass wool, and shape the column to fit the chromatograph.

7.2 *Chromatograph*—Mount the column in the chromatograph and establish the operating conditions required to give the desired separation (Appendix X1). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable base line. Control the oven temperature so that it is constant to within 0.5°C without thermostat cycling which causes an uneven base line. Set the carrier-gas flow rate, measured with a soap film meter, so that it is constant to within 1 mL/min of the selected value.

8. Calibration

8.1 *Identification*—Select the conditions of column temperature and carrier gas flow that will give the necessary separation. Determine the retention time for each compound by injecting small amounts of the compound either separately or in mixtures. Recommended sample sizes for retention data are 1 μL for liquids and 1 cm^3 or less for gases.

8.2 *Standardization*—The area under the peak of the chromatogram is considered a quantitative measure of the amount of the corresponding compound. The relative area is proportional to the concentration if the detector responses of the sample components are equal. The recommended procedure for quantitative calibration is as follows: with all equipment at equilibrium at operating conditions, inject constant volume samples of high-purity components. Each compound should be injected at least three times. The areas of the corresponding peaks should agree within 1 %. When a recorder is used, adjust the attenuation in all cases to keep the peak on-scale and with a height of at least 50 % of full scale. Measure the area of the peaks by any reliable method (Note 7). To obtain component weight % response data from the area response of the volume injections, it is necessary to consider the density and purity of the compounds used for calibration. The average volume area response of each component is divided by the density multiplied by the weight percent purity of the component as follows:

$$\text{Weight percent response of component} \tag{1}$$

$$= \frac{\text{average component peak area}}{\text{density} \times \text{weight percent purity of component}}$$

Component weight percent detector correction factors are then obtained by selecting a reference component such as butadiene, and dividing the individual component weight responses into the reference weight response.

8.2.1 Factors derived on a thermal-conductivity detector using helium-carrier gas are as follows:

Component	Mol wt	Thermal Response	Weight Factor	Weight Factor, Butadiene-1,3 = 1.00
Butadiene-1,3	54	80	0.68	1.00
Propane	44	65	0.68	1.00
Propylene	42	63	0.67	0.98
Isobutane	58	82	0.71	1.04
n-Butane	58	85	0.68	1.00
Butene-1	56	81	0.69	1.01
Isobutylene	56	82	0.68	1.00

Component	Mol wt	Thermal Response	Weight Factor	Weight Factor, Butadiene-1,3 = 1.00
trans-Butene-2	56	85	0.66	0.97
cis-Butene-2	56	87	0.64	0.94
Propadiene	40	53	0.75	1.10
Methyl acetylene	40	58	0.69	1.01

NOTE 5—Response based on data represented by Messner, A. E., Rosie, D. M., and Argabright, P. A., *Analytical Chemistry*, Vol 31, 1959, pp. 230–233, and Dietz, W. A., *Journal of Gas Chromatography*, Vol 5, No. 2, 1967, pp. 68–71.

8.2.1.1 Although not determined with standards, weight factors of 1.00 (compared to butadiene 1,3 as 1.00) were used for pentadiene-1,4 butadiene-1,2, dimethyl acetylene, ethyl and vinyl acetylene in this study to obtain the precision listed in Section 11. It is permissible to use the above established response factors instead of calibration when using thermal-conductivity detectors with helium-carrier gas. With other detectors or carrier gas, or both, it is necessary to calibrate (Note 5).

8.2.2 Measurements can be made using peak heights as criteria for calculations instead of peak areas. If peak heights are used, care must be taken so that chromatograph-operating parameters such as column temperature and carrier-gas flow rate are kept at the same conditions as when the unit was calibrated. The chromatograph can be calibrated using known blends or by establishing relative-response data using peak heights in the same manner as listed above.

NOTE 6—Use of a hydrogen-flame detector gives essentially equal relative response to hydrocarbons. On a weight basis, the sensitivity of the flame detector for hydrocarbons is essentially independent of the hydrocarbons structure. On a molar basis, the sensitivity appears to be a function of the carbon content, giving essentially equal relative response to hydrocarbons containing the same number of carbon atoms.

8.2.3 Because detector or amplifier output need not be linear with component concentration, this must be checked by injecting constant volumes of pure butadiene at a series of decreasing pressures from ambient down to 20 mm Hg (torr) or by using synthetic standards with vapor sample valves at ambient or at decreasing pressures or by using synthetic standards with liquid sample valves. If on plotting the results the response is linear, then the calibration procedure given above is satisfactory. If not, the relative responses of the minor components must be determined in the linear response region.

9. Procedure

9.1 Attach the sample cylinder to the instrument-sampling valve so that the sample is obtained from the liquid phase. If introduction is through a liquid valve the sample cylinders should be pressured with a suitable gas, such as helium, to a pressure sufficient to ensure that sample flashing does not occur in the line to the sampling valve or in the valve itself. If a vapor valve is used, care must be taken to completely vaporize a small liquid sample, allowing the vapor to flow through the sample loop at a flow rate of 5 to 10 mL/min until at least ten times the volume of the sample loop has been flushed through. If a vacuum-sampling system is used with a vapor valve, the sample loop should be filled and evacuated at least twice before introduction of sample.

9.2 Charge sufficient sample to ensure a minimum of 10 % recorder deflection for 0.1 % concentration of impurity at the most sensitive operating setting of the instrument (for trace impurities, such as acetylenes, greater sensitivity is needed).

9.3 Using the same conditions as were used for calibration, record the peaks of all compounds at attenuation or sensitivity settings that allow maximum peak heights. (**Warning—**Butadiene flammable gas under pressure.)

10. Calculation

10.1 Measure the area or heights of all peaks (Note 7) and multiply by the appropriate attenuation factor to express the peak area or heights on a common sensitivity basis. Apply the appropriate calibration factors to the peak areas or heights to correct for the differences in response to the components. Make area calculations by relating the individual component corrected area to the total corrected area of all peaks. If peak heights are used, multiply the peak heights, calibration factors, and component attenuations for each component and normalize the resulting products to give percentages. Make corrections to account for the dimer, carbonyl, inhibitor residue (and acetylene if not determined chromatographically) concentration as determined by separate ASTM procedures. Calculations are as follows:

$$\frac{\text{Corrected peak response}}{\text{Sum of corrected peak responses}}$$

$$\times [100 - \text{sum of dimer, carbonyl, inhibitor, and residual}$$

$$\text{impurities (and acetylene if not determined}$$

$$\text{chromatographically)}] \qquad (2)$$

NOTE 7—The area can be determined by any method that meets the precision requirements of Section 11. Methods found to be acceptable include planimetering, integration (electronic or mechanical or computer processing), and triangulation (multiplying the peak height by the width at the half height).