



Standard Test Method for Butadiene Dimer and Styrene in Butadiene Concentrates by Gas Chromatography¹

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1. Scope

1.1 This test method covers the determination of butadiene dimer (4-vinylcyclohexene-1) and styrene in butadiene concentrates, both recycle and specification grade.

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 precautionary statements see Sections 6 and 8.

2. Referenced Documents

2.1 ASTM Standards:²

D1657 Test Method for Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer

D1945 Test Method for Analysis of Natural Gas by Gas Chromatography

D2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography

2.2 Other Documents:²

STP 109A Physical Constants of Hydrocarbons C₁ to C₁₀

3. Summary of Test Method

3.1 The sample is introduced into a gas-liquid partition column. The components of interest are separated as they are transported through the column by a carrier gas, and their presence in the effluent is detected and recorded as a chromatogram. Packed columns are used, and either thermal conductivity or ionization detectors are permissible. The quantity of the

components of interest present in the sample is determined from the chromatogram by comparing their peak areas or heights with those obtained from a synthetic sample.

4. Significance and Use

4.1 Butadiene dimer and styrene may be present as impurities in commercial butadiene. This test method is suitable for use in internal quality control and in establishing product specifications.

5. Apparatus

5.1 *Chromatograph*—Any chromatograph having either a thermal conductivity or flame ionization detector may be used. The detector system shall have sufficient sensitivity to obtain a deflection of at least 2 mm at a signal-to-noise ratio of at least 5:1 for 0.01 weight % of butadiene dimer and styrene under the operating conditions prescribed in this test method.

5.2 *Recorder*—A 0 to 1-mV, 0 to 5-mV, or 0 to 10-mV recorder with a full-scale response time of 2 s or less, and with sufficient sensitivity to meet the requirements of 5.1.

5.3 *Column*—Any column may be used that is capable of resolving the butadiene dimer and styrene as discrete peaks, quantitatively proportional to concentration and within an elapsed time sufficiently short to be practical.

5.4 *Liquid Sampling Valve*—Any liquid sampling valve may be used that will permit the reproducible introduction of the butadiene concentrate as a liquid under its vapor pressure or higher and in a quantity sufficient to meet the sensitivity and resolution requirements in 5.1 and 5.3, respectively.

NOTE 1—Suitable valves are commercially available

6. Reagents and Materials

6.1 *4-vinylcyclohexene-1 and Styrene*, for calibration, purity of not less than 99 %.

6.2 *Carrier Gas*—Helium or hydrogen for use on thermal conductivity detector units; or nitrogen, helium, or argon for use on ionization detector units. (**Warning**—Compressed gas. Hazardous pressure.) (**Warning**—Hydrogen gas is flammable. Hazardous pressure.)

6.3 *Liquid Phase*, for column.

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.

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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.

TABLE 1 Columns and Conditions Used Successfully

	Dow Silicone 200	Carbowax 1500	Carbowax 1540	Silicone SE-30	Carbowax 20M + Dow Corning Hi Vac	Polyethylene Glycol-6000	Barecowax 1035
Column length, m	1.5	4.6	3.7	15.2	3.1	3.7	6.1
Column diameter, mm	3.2	4.8	6.4	0.5	6.4	4.8	6.4
Column temperature, °C	85	110	100	75	100–128	155	140
Liquid phase, wt %	10	15	16	...	0.75 each	30	20
Support material	Chromosorb P	TFE-fluorocarbon	Chromosorb P	(Coated)	Silica	Chromosorb P	Chromosorb P
Mesh	80–100	40–60	100–120	30–50	60–80
Carrier flow, mL/min	19	60	60	15	30	171	60
Detector	HFI ^A	T.C. ^B	HFI	HFI	T.C.	T.C.	T.C.
Sample size, µL	0.77	20	0.07	1.54	1.03	8.69	3.0
Peak measurement	triangulation	triangulation	integrator	triangulation	triangulation	peak height	planimeter

^A HFI = hydrogen flame ionization.

^B T.C. = thermal conductivity.

NOTE 2—The following materials have been used successfully as liquid phases (see Table 1)³:

Carbowax 400, 1500, 1540

General Electric SE-30 silicone gum rubber

Polyethylene glycol 6000

Barecowax 1035

Dow Corning silicone oil

Carbowax 20M + Dow Corning Hi Vac.

6.4 *Solid Support*, for use in packed column, usually crushed fire brick or diatomaceous earth. Sieve size will depend on the diameter of the column used and support loading and should be such as to give optimum resolution and analysis time.

7. Preparation of Apparatus

7.1 *Column Preparation*—Any satisfactory method, used in the practice of the art, that will produce a column meeting the requirements of 5.3. See Appendix X2, Sample Calculations, of Test Method D1945, also see 6.1, Carrier Gas, of Test Method D2593.

7.2 *Chromatograph*—Put in service in accordance with the manufacturer's instructions. The injector temperature shall be no greater than 5°C above the column oven temperature. The column oven temperature shall not exceed 185°C. See Table 1 for typical operating conditions.

7.3 *Synthetic Blends*—Prepare a synthetic mixture from 99 mol % minimum pure 4-vinylcyclohexene-1 and styrene in a suitable matrix in approximately the same concentration expected in the sample. The matrix may be any one of the normal paraffin hydrocarbons from butane to heptane, inclusive. In preparing the blend, weigh each compound added with sufficient precision to result in a mixture accurate to 5 % relative or 0.02 % absolute, whichever is greater. Transfer the blend to a container of the type to be used for the sample and pressure with a suitable gas.

8. Procedure

8.1 Using the liquid sampling valve, inject into the column the desired volume of synthetic blend and record the peaks at a sensitivity setting that allows the maximum peak height.

³ If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

Pressure the sample cylinder with a suitable gas to a pressure sufficient to ensure no flashing in the line to the sampling valve or in the valve itself. Using the same sample size and instrument conditions, inject the sample into the column and record the peaks. (See Table 1 for typical operating conditions.) (**Warning**—Butadiene gas is flammable under pressure.)

9. Calculation

9.1 *Peak Measurement*—Measure the peak area or height of each component of interest in both the synthetic blend and the sample. Measurement may be accomplished by any method that meets the precision requirements of Section 10. Area methods found to be acceptable include planimetry, integration, and triangulation (multiplying the peak height by the width at the half-height). In peak area or height methods care must be taken so that chromatograph operating parameters such as column temperature and carrier gas flow rate are kept at the same conditions on both the synthetic standard and the sample. Calculate the percentage by weight of each component as follows:

$$\text{Concentration, weight \%} = (A_s/A_o) \times S \times (G_o/G_s) \quad (1)$$

where:

- A_s = peak area or height of component in the sample,
- A_o = peak area or height of component in the synthetic blend,
- S = weight % of component in the synthetic blend,
- G_s = relative density 60/60 of the sample, and
- G_o = relative density 60/60 of the synthetic blend.

NOTE 3—The specific gravity of the sample may be determined in accordance with Test Method D1657 and the specific gravity of the synthetic may be assumed to be equal to the gravity of solvent used to prepare the blend. A list of such gravities is found in STP 109A.

10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *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, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

	Concentration	Repeatability
Dimer, wt %	0.15	0.005
Styrene, wt %	1.49	0.044

10.1.2 *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, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

	Concentration	Reproducibility
Dimer, wt %	0.15	0.018
Styrene, wt %	1.49	0.051

10.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring dimer and styrene, bias has not been determined.

11. Keywords

11.1 butadiene concentrate; butadiene dimer; gas chromatography; styrene

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