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An American National Standard

Standard Guide for Analysis of 1,3–Butadiene Product[1]

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1. Scope

1.1 This guide covers the analysis of 1,3–butadiene products produced in North America. It includes possible components and test methods, both ASTM and other, either actually used or believed to be in use, to test for these components. This guide is not intended to be used or construed as a set of specifications for butadiene products.

1.2 The values given in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1025 Test Method for Nonvolatile Residue of Polymerization Grade Butadiene[2]

D 1157 Test Method for Total Inhibitor Content (TBC) of Light Hydrocarbons[2]

D 1550 ASTM Butadiene Measurement Tables[2]

D 2384 Test Methods for Traces of Volatile Chlorides in Butane-Butene Mixtures[2]

D 2426 Test Method for Butadiene Dimer and Styrene in Butadiene Concentrates by Gas Chromatography[2]

D 2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography[2]

D 3246 Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry[3]

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder[3]

D 4178 Practice for Calibrating Moisture Analyzers[3]

D 4423 Test Method for Determination of Carbonyls in C_4 Hydrocarbons[3]

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry[4]

D 4629 Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection[3]

D 4864 Test Method for Determination of Traces of Methanol in Propylene Concentrates by Gas Chromatography[3]

D 5799 Test Method for Determination of Peroxides in Butadiene[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *1,3-butadiene*—hydrocarbon product containing more than 99 % 1,3-butadiene.

3.2 *Symbols:*

3.2.1 *BHT*—butyl hydroxy toluene.

3.2.2 *GC*—gas chromatography.

3.2.3 *pTBC*—paratertiary butyl catechol.

3.2.4 *4VCH-1*—4-vinyl cyclo hexene (1,3-butadiene dimer).

4. Significance and Use

4.1 This guide is intended to provide information on the possible composition of 1,3-butadiene products and possible ways to test them. Since there are currently not enough ASTM standards for determining all components of interest, this guide provides information on other potentially available test methods.

4.2 Although this guide is not to be used for specifications, it can provide a starting point for parties to develop mutually agreed-upon specifications that meet their respective requirements. It can also be used as a starting point in finding suitable test methods for 1,3-butadiene components.

5. Sampling

5.1 *General*:

5.1.1 1,3-butadiene is a very reactive hydrocarbon. It reacts with oxygen to form peroxides and to polymerize. It also dimerizes at a rate that is temperature dependent. Below 10°C (50°F), the dimerization rate is less than 1 mg/kg by mass/h; but, at 20°C (77°F), it increases to 3 to 4 mg/kg mass/h; and at 40°C (104°F), to 14 to 20 mg/kg mass/h. 1,3-butadiene is also

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 05.06.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

TABLE 1 1,3-Butadiene Test Methods (ASTM)

Property	Units	Test Method	Concentration Range
Amines	mg/kg	See Table 2	<1 to 25
Ammonia	mg/kg	See Table 2	<1 to 25
Benzene	mg/kg	See Table 2	<0.1 to 10
1,2-butadiene	mg/kg	D 2593	<1 to 100
1,3-butadiene dimer (4VCH-1)	mg/kg	D 2426	<100 to 200
C_5 hydrocarbons	mg/kg	D 2593	<1 to 1000
C_{6+} hydrocarbons	mg/kg	See Table 2	<1 to 1000
Carbonyls	mg/kg	D 4423	<1 to 100
Chlorides	mg/kg	See Table 2	<1 to 25
Ethylene glycol	mg/kg	See Table 2	<1 to 100
Inhibitor (p-TBC)	mg/kg	D 1157 See Table 2	<1 to 500
Methanol and other alcohols	mg/kg	D 4864 See Table 2	<1 to 25
Moisture	mg/kg	D 4178 See Table 2	<1 to saturated
Nonvolatile residue	mass %	D 1025	<0.001 to 0.2
Oxygen in vapor space	mass %	See Table 2	<0.001 to 0.3
Peroxides	mg/kg	D 5799	<1 to 10
Propadiene	mg/kg	D 2593	<1 to 25
Propane	mg/kg	D 2593	<1 to 25
Propylene	mg/kg	D 2593	<1 to 25
Purity of 1,3-butadiene	mass %	D 2593	99.0 min
Relative density	15.6/15.6	D 1550	0.625 to 0.630
Toluene	mg/kg	See Table 2	<1 to 500
Total acetylenes	mg/kg	D 2593	<1 to 100
Total nitrogen	mg/kg	See Table 2	<1 to 25
Total sulfur	mg/kg	See Table 2	<1 to 25

TABLE 2 1,3-Butadiene Test Methods (Non-ASTM Methods)[A]

Property	Possible Test Method
Amines	Adaption of Test Method D 4629
Ammonia	Acid absorption with Nessler finish Acid absorption with specific ion finish
Benzene	Capillary gas chromatography
Chlorides	Organic chlorides by GC, with hall detector; also, Test Methods D 2384
Ethylene glycol	Capillary gas chromatography
Inhibitor (BHT)	Capillary gas chromatography or titration method
Inhibitor (pTBC)	Test Method D 1157; also, gas chromatography and titration methods using ceric ammonium sulfate
Methanol and other alcohols	Adaption of Test Method D 4864
Moisture	Panametrics moisture instrument; adaption of Karl Fisher titration
Oxygen	Adaption of Panometric or Teledyne oxygen analyzers
Toluene	Capillary gas chromatography
Total sulfur	Adaption of Test Methods D 3246 or D 4468
Total nitrogen	Adaption of Test Method D 4629; also, micro-coulometry

[A]The above are possible butadiene test methods or techniques which are believed to be in use in the industry for testing. Inclusion of any test method in this list is not to be construed as a recommendation by ASTM for its use. Some of the test methods in this list are ASTM test methods that are specified for other products but are being used by some labs for butadiene analysis. However, use of ASTM test methods beyond their scope is not recommended by ASTM. Precision and bias may be adversely affected.

classified as toxic and as a potential health hazard, having been found carcinogenic to laboratory animals. Therefore, sampling of 1,3-butadiene must adhere to the following three principles:

5.1.1.1 Minimize personnel exposure. See the appropriate OSHA Material Safety Data Sheet for guidance,

5.1.1.2 Eliminate or keep to an absolute minimum the inclusion of oxygen during and after sampling, and

5.1.1.3 Sample the product at as low a temperature as possible, maintain the sample at a low temperature, and analyze it as soon as possible. Do not allow it to sit outdoors in the sun after sampling.

5.1.2 In addition to 5.1.1.1-5.1.1.3, 1,3-butadiene to be analyzed for trace components should be sampled by a technique that minimizes or eliminates loss of light components and concentration of heavy ones. The subsections below list some different sampling methods and principles. However, it is not the intent of this guide to list procedures that are applicable to all sampling situations. It is strongly recommended that samples be obtained under the supervision of a person with wide knowledge and experience in sampling 1,3-butadiene.

5.1.3 Also, even though this guide does not address the location of a sampling point in a line or vessel, the importance of the proper sampling location cannot be overemphasized.

5.2 *Floating Piston Cylinder*—Test Method D 3700 meets the criterion of minimizing or elimination of loss of light components and concentration of heavy ones. However, some labs have safety codes preventing use of rupture-disc piston containers. Alternative procedures must be used in these labs.

5.3 *Conventional "Outaging" Method*—The widely used "outaging" techniques (that is, the practice of removing a portion of the fluid contents from a conventional sampling cylinder after filling in order to provide expansion room) causes a partial loss of light components into the vapor space. Subsequent handling to recapture these light ends in the liquid phase of the sample, such as repressurization of the cylinder contents with an inert gas, is usually successful, since 1,3-butadiene seldom contains noncondensables. However, if permanent gases are present and are to be determined, an alternate procedure may be required.

5.4 *Vaporization Methods*—Vaporization of the sample, either at the source or in the lab prior to analysis, may cause loss of heavier components, if present, and concentration of lighter ones. Also, since 1,3-butadiene is so reactive, the heat required to vaporize may cause undesirable changes in the composition of the sample. For these reasons, vaporization is not recommended for 1,3-butadiene.

5.5 *Reactive Components*—Determination of reactive components, such as certain sulfur compounds, is generally believed to require special sample containers, such as TFE-fluorocarbon-lined cylinders.

6. Composition and Test Methods

6.1 Table 1 indicates possible composition ranges and ASTM methods for 1,3-butadiene product. Table 2 lists other test methods known or believed to be in use.

7. Keywords

7.1 1,3-butadiene; 1,3-butadiene product; 1,3-butadiene test methods