Designation: D7875 − 14

Standard Test Method for Determination of Butanol and Acetone Content of Butanol for Blending with Gasoline by Gas Chromatography[1]

This standard is issued under the fixed designation D7875; 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 the butanol content of butanol for blending with gasoline by gas chromatography.

1.2 Butanol is determined from 95 % to 99.9 % by mass, acetone is determined from 0.02 % to 1.5 % by mass, ethanol is determined from 0.02 % to 1.5 % by mass, and methanol is determined from 0.02 % to 1.5 % by mass. Equations used to convert these individual components from mass percent to volume percent are provided.

1.3 This test method identifies and quantifies acetone, ethanol, and methanol, but does not purport to identify all individual components that may be present in butanol for gasoline blending.

1.4 Water cannot be determined by this test method and shall be measured by a procedure such as Test Method D1364 and the result used to correct the chromatographic values.

1.5 This test method is inappropriate for impurities that boil at temperatures higher than 225 °C or for impurities that cause poor or no response in a flame ionization detector, such as water.

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

1.7 *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:*[2]

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D7862 Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions can be found in Practices E355 and E594.

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[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 D02.04.0L on Gas Chromatography Methods.

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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.

3.1.1 *butanol, n—for the purposes of this method*, butanol or butyl alcohol refers to one of three structural isomers of butanol—1-butanol, 2-butanol, and 2-methyl-1-propanol. This test method has not been evaluated for use with the butanol isomer 2-methyl-2-propanol.

4. Summary of Test Method

4.1 A representative aliquot of the butanol sample is introduced into a gas chromatograph equipped with a polydimethylsiloxane bonded phase capillary column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The butanol, acetone, ethanol, and methanol components are identified by comparing their retention times to the ones identified by analyzing standards under identical conditions. The concentrations of all components are determined in mass percent area by normalization of the peak areas.

5. Significance and Use

5.1 Butanol is being approved for blending with gasoline in accordance with Specification D7862. This test method provides a method of determining the percentage of butanol (purity) of the butanol for blending with gasoline.

6. Apparatus

6.1 *Gas Chromatograph,* capable of operating at the conditions listed in Table 1. A heated flash vaporizing injector designed to provide a linear sample split injection (for example, 200:1) is required for proper sample introduction. Carrier gas controls shall be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. Pressure control devices and gauges shall be designed to attain the linear velocity required in the column used. A hydrogen flame ionization detector with associated gas controls and electronics, designed for optimum response with open tubular columns, is required.

TABLE 1 Typical Operating Conditions

Column Temperature Program	
Column length	150 m
Initial temperature	75 °C
Initial hold time	7 min
Program rate	15 °C/min
Final temperature	250 °C
Final hold time	15 min
Injector	
Temperature	300 °C
Split ratio	200:1
Sample size	0.1
Detector	
Type	Flame ionization
Temperature	300 °C
Fuel gas	Hydrogen (≈30 mL/min)
Oxidizing gas	Air (≈300 mL/min)
Make-up gas	Nitrogen (≈30 mL/min)
Carrier Gas	
Type	Helium
Average linear velocity	18 cms to 20 cm/s

6.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 1.0 µL injections are suitable. It should be noted that inadequate splitter design, poor injection technique, and overloading the column can result in poor resolution. Avoid overloading, particularly of the butanol peak(s), and eliminate this condition during analysis.

6.3 *Column*—This test method utilizes a fused silica open tubular column with non-polar polydimethylsiloxane bonded (cross-linked) phase internal coating. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.1 can be used.

6.3.1 Open tubular column with a non-polar polydimethylsiloxane bonded (cross-linked) phase internal coating; a 150 m long by 0.25 mm internal diameter column with a 1.0 µm film thickness has been found to be suitable.

6.4 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantification of these analyses must meet or exceed these minimum requirements:

6.4.1 Capacity for at least 80 peaks/analysis,

6.4.2 Normalized percent calculation based on peak area and using response factors,

6.4.3 Identification of individual components based on retention time,

6.4.4 Noise and spike rejection capability,

6.4.5 Sampling rate for narrow (<1 s) peaks,

6.4.6 Positive and negative sloping baseline correction,

6.4.7 Peak detection sensitivity compensation for narrow and broad peaks, and

6.4.8 Non-resolved peaks separated by perpendicular drop or tangential skimming as needed.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3]

7.2 *Carrier Gas,* helium, with a minimum purity of 99.95 % by mol. Oxygen removal systems and gas purifiers should be used to attain such purity or method performance. (**Warning—**Helium, compressed gas under high pressure.)

7.3 *Detector Gases,* hydrogen, air, and nitrogen. The minimum purity of the gases used should be 99.95 % by mol for the hydrogen and nitrogen. The air should be hydrocarbon-free grade. Gas purifiers are recommended for the detector gases to attain required purity or method performance. (**Warning—**Hydrogen, extremely flammable gas under high pressure.) (**Warning—**Air and nitrogen, compressed gases under high pressure.)

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.4 *Standards for Calibration and Identification*—Standards of all components to be analyzed are required for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed.

7.4.1 *2-Methyl-1-propanol or isobutanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.2 *1-Butanol or normal butanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.3 *2-Butanol or secondary butanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.4 *Acetone* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.5 *3-Methyl-1-butanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.6 *2-Propanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.7 *2-Butanone* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.8 *Ethanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.9 *Methanol* (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

NOTE 1—Two grades of ethanol are available. Only absolute ethanol 99.5 minimum percent meets the requirements of this test method.

8. Sampling

8.1 Butanol may be sampled into an open container since a vapor pressure of less than 21 kPa is expected. Refer to Practice D4057 for instruction on manual sampling from bulk storage into open containers. Stopper the container immediately after drawing the sample.

8.2 Transfer an aliquot of the sample into a septum vial and seal. Obtain the test sample for analysis directly from the sealed septum vial, for either manual or automatic syringe injection.

9. Preparation of Apparatus

9.1 Install and condition column in accordance with manufacturer's or supplier's instructions. After conditioning, attach column outlet to flame ionization detector inlet and check for leaks throughout the system. When leaks are found, tighten or replace fittings before proceeding.

9.2 Adjust the carrier gas flow rate so that the average linear gas velocity, at the initial temperature of the run, is between 18 and 20 cm/s, as determined by the following equation:

$$\bar{\mu} = \frac{L}{t_m} \tag{1}$$

where:

$\bar{\mu}$ = average linear gas velocity (cm/s),
L = column length (cm), and
t_m = retention time of methane.

Flow rate adjustment is made by raising or lowering the carrier gas pressure (head pressure) to the injector.

9.3 Adjust the operating conditions of the gas chromatograph (Table 1) and allow the system to equilibrate.

9.4 *Linearity*—The linearity of the gas chromatograph system shall be established prior to the analysis of samples.

9.4.1 The split ratio used is dependent upon the split linearity characteristics of the particular injector and the sample capacity of the column. The capacity of a particular column for a sample component is proportional to the amount of liquid phase (loading or film thickness) and the ratio of the column temperature to the component boiling point (vapor pressure). Overloading of the column may cause loss of resolution for some components and, since overloaded peaks are skewed, variance in retention times. This can lead to erroneous component identification. During column evaluations and split linearity studies, be aware of any peaks that may appear *front skewed*, indicating column overload. Note the component size and avoid conditions leading to this problem during actual analysis. Refer to Practice E594 for further guidance.

9.4.2 Splitting injector linearity must be established to determine proper quantitative parameters and limits. Use a standard mixture of known mass percentages of butanol, acetone, and six or more of the following compounds: methanol, ethanol, isopropanol, isobutyraldehyde, 1-propanol, 2,3-butanedione, 2-butanone, 3-hydroxy-2-butanone, 3-methyl-1-butanol, 2-methyl-1-butanol, isobutyl acetate, isobutyl isobutyrate, 2,3,5-trimethylpryazine, 2,3,5,6-tetramethylpryazine, phenylethanol, and phenethyl acetate. The determined mass percent for each component shall match the gravimetric known concentration within ±3 % relative.

9.4.3 The linearity of the flame ionization detector (FID) shall be verified. Refer to Practice E594 for suggested procedure. A plot of the peak areas versus butanol concentration for prepared standards in the concentration range of interest should be linear. If the plot is not linear, either the split ratio shall be increased or the detector range must be made less sensitive.

10. Calibration and Standardization

10.1 *Identification*—Determine the retention time of the appropriate butanol isomer and the typical by-products associated with butanol isomers (see 10.2) by injecting amounts of each, either separately or in known mixtures, in proportions expected in the final blend.

10.2 *Calibration*—Typical mass relative response factors for the components of interest are found in Table 2. These response factors shall be determined by analyzing a standard suitable for the butanol isomer being analyzed that has been blended according to Practice D4307. This standard is comprised of the proportions of butanol, typical by-products associated with the butanol isomer being evaluated, and acetone expected in the sample. A typical standard blend for 2-methyl-1-propanol would be 97.5 % butanol, 1.0 % 3-methyl-1-butanol, 0.5 % ethanol, and 1.0 % n-Heptane. A typical standard blend for 1-butanol would be 97.5 % butanol, 1.0 % ethanol, 0.5 % 2-propanol, 0.01 % acetone, and 1.0 % heptane. A typical standard blend for 2-butanol would be 97.5 % butanol, 1.0 % ethanol, 0.5 % 2-butanone, 0.01 % acetone, and 1.0 % heptane. Calculate the mass relative response factor according to Practice D4626, using heptane as the standard reference compound.

TABLE 2 Pertinent Component Data

Retention Time (min) relative to 2-Methyl-1-propanol	Typical Mass Relative Response Factors in 2-Methyl-1-propanol	Typical Mass Relative Response Factors in 1-Butanol	Typical Mass Relative Response Factors in 2-Butanol	Relative Density at 15.56 °C
Acetone — 2.83	1.99	1.93	2.12	0.796
Methanol — 4.20	3.20	3.41	3.46	0.796
Ethanol — 3.41	2.23	2.29	2.29	0.794
1-Butanol — 0.82	1.40	1.55	1.71	0.814
2-Butanol — 0.62	1.68	1.81	1.60	0.811
2-Methyl-1-propanol — 0.0	1.41	1.44	1.42	0.806

11. Gas Chromatographic Analysis Procedure

11.1 Set the instrument operating variables. See Table 1 for typical operating conditions.

11.2 Set instrumental sensitivity such that any component of at least 0.002 % by mass can be detected and integrated.

11.3 Inject 0.1 µL of sample into the injection port and start the analysis. Obtain a chromatogram and peak integration report. Sample chromatograms are shown in Figs. 1-4.

12. Calculation

12.1 Multiply the area of each identified peak by the appropriate mass relative response factor. Use those factors determined for individual compounds in 10.2 and use a factor of 1.000 for unknowns or uncalibrated components.

12.2 Determine the relative mass percent of the individual components by using the following equation:

$$RM_i = \frac{AR_i \times 100}{AR_t} \quad (2)$$

where:

RM_i = relative mass percent of the individual components,
AR_i = area of the individual alcohol peak corrected by the appropriate mass relative response factor (see 12.1), and
AR_t = total area of all detected peaks corrected by their appropriate mass relative response factors (see 12.1).

12.3 Obtain the mass percent of water in the sample. Test Methods D1364, E1064, or equivalent, can be used.

12.4 Determine the mass percent of the components of interest by using the following equation:

$$M_i = \frac{RM_i \times (100 - \text{mass \% water in sample})}{100} \quad (3)$$

where:

M_i = mass percent of the individual component being determined, and
RM_i = relative mass percent of the individual component from Eq 2.

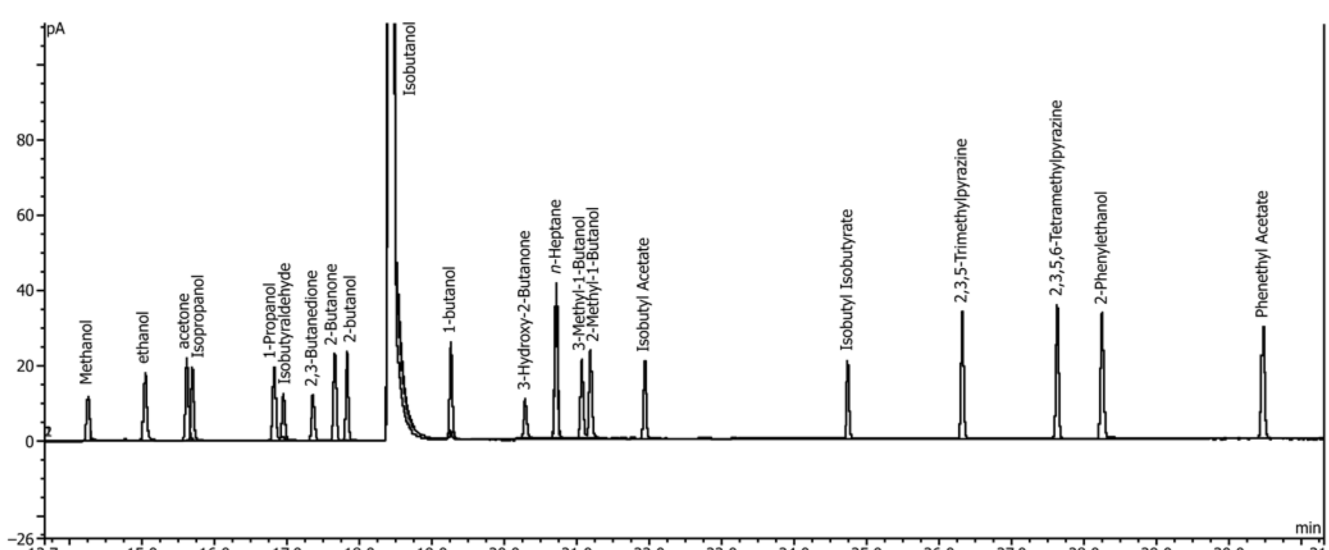

FIG. 1 Sample Chromatogram (1 % Impurities in isobutanol)

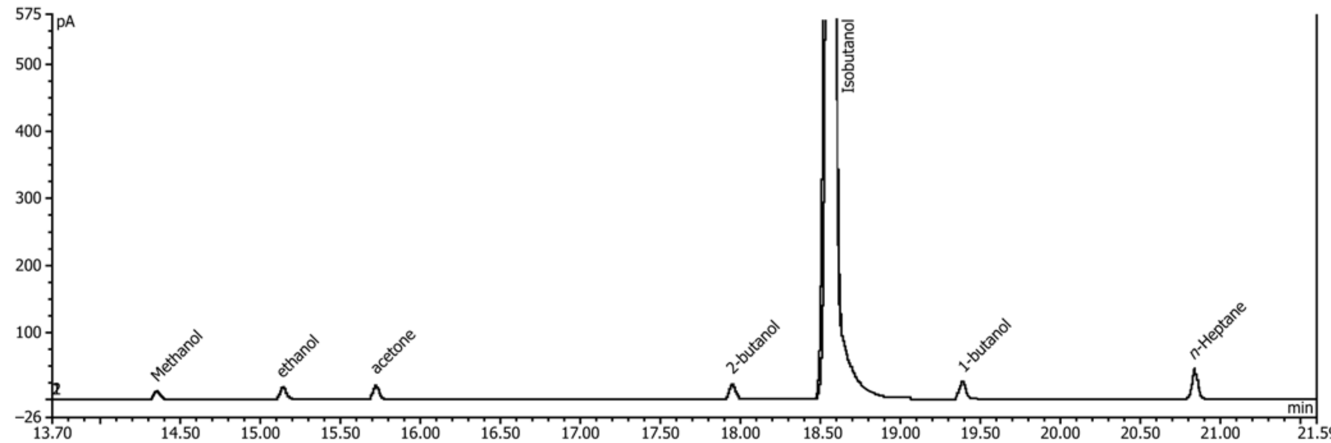

FIG. 2 Sample Chromatogram (1 % Impurities in isobutanol)

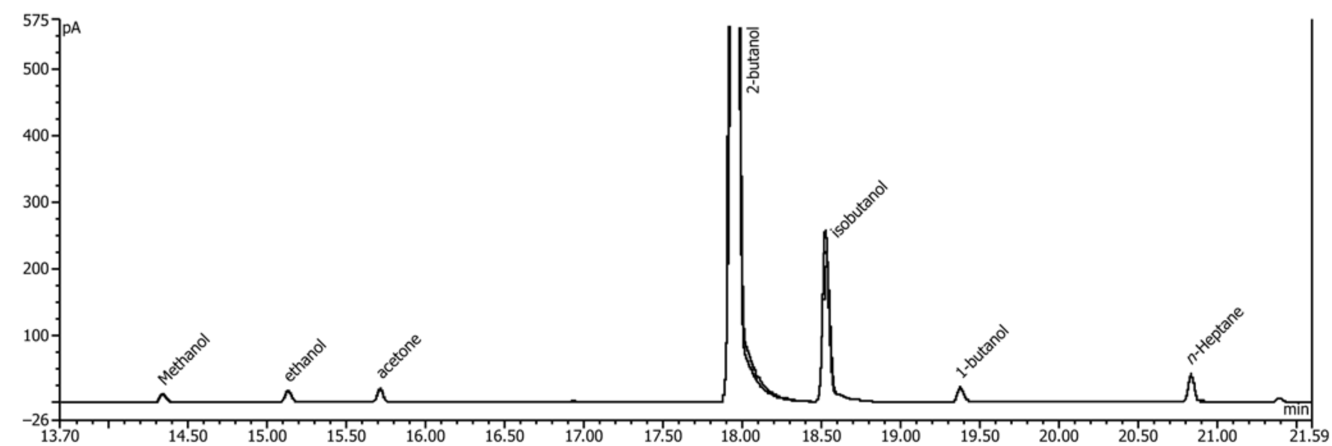

FIG. 3 Sample Chromatogram (1 % Impurities in 2-butanol)

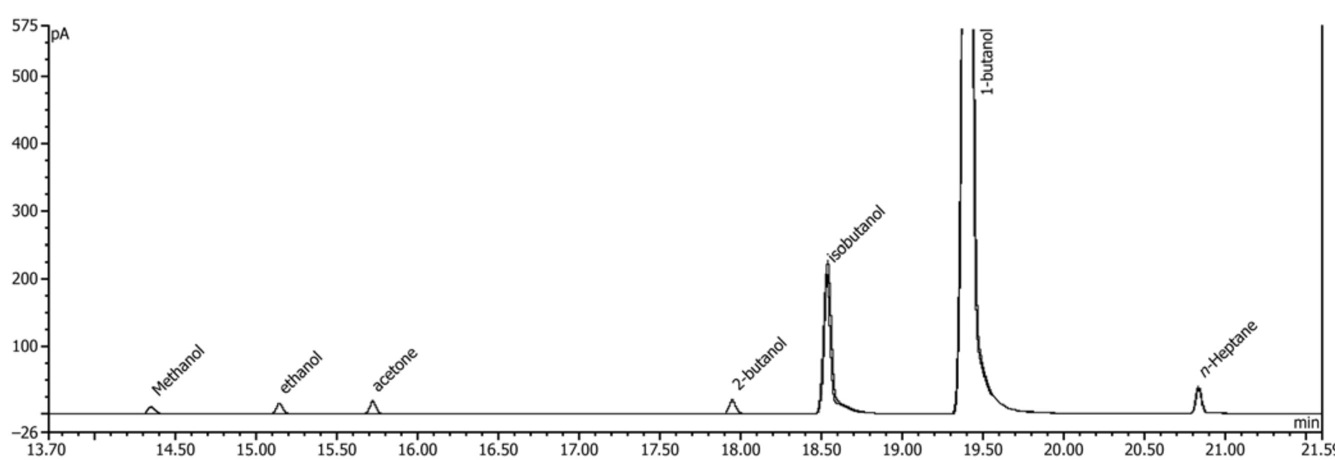

FIG. 4 Sample Chromatogram (1 % Impurities in 1-butanol)

12.5 For the volumetric concentration of the component, calculate as follows:

$$V_i = \frac{M_i \times D_s}{D_i} \tag{4}$$

where:

V_i = volume percent of component i,
M_i = mass percent of component i from Eq 3,
D_i = relative density at 15.56 °C of component i as found in Table 2, and
D_s = sample under study as determined by Test Method D1298 or D4052.

13. Quality Control

13.1 Conduct a regular statistical quality assurance (quality control) program, monitoring both precision and accuracy, in accordance with the techniques of Practice D6299 or equivalent. Measure the butanol concentrations using the procedure outlined in Section 11. Confirm the performance of the instrument or the test procedure after each calibration and on each day of use thereafter. Include at least one quality control sample of known butanol content.

13.1.1 Standard(s) of known concentration may be supplied from a vendor, cross-check program, or may be prepared gravimetrically. If possible, use of a certified reference material is recommended. Test at least one standard for each class of butanol routinely analyzed (such as fuel butanol (>96 % butanol).

13.1.2 Prepare standard(s) in sufficient volume to allow for a minimum of 30 quality control measurements to be made on one batch of material. Properly package and store the quality control samples to ensure that all analyses of quality control samples from a given lot are performed on essentially identical material. Use of the Q-procedure in Practice D6299 is recommended when switching between batches of control sample.

14. Report

14.1 Report the purity of butanol as the sum of the amounts of 1-butanol, 2-butanol, and 2-methyl-1-propanol to the nearest 0.01 % by mass using Eq 3 or nearest 0.01 % by volume using Eq 4. Report individually acetone, ethanol, and methanol to the nearest 0.01 % by mass.

15. Precision and Bias

15.1 The precision of this test method was determined by statistical examination of limited laboratory results. The precision data are provisional, and further data are to be developed in an interlaboratory cooperative test program before the five-year reapproval (2018) required by the society.

15.2 *Precision*—The precision of this test method as determined by the statistical examination of gas chromatographic test results from a single laboratory using Practice D6300 for the design and analysis of the data as follows:

15.2.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

Butanol Repeatability[A]

Component	Range, Mass Percent	Repeatability, Mass percent
2-methyl-1-propanol	95 to 99.9	0.205
1-butanol	95 to 99.9	0.350
2-butanol	95 to 99.9	0.366
acetone	0.02 to 1.5	$0.000185^*(X)^{1/2}$
methanol	0.02 to 1.5	$0.000199^*(X)^{1/2}$
ethanol	0.02 to 1.5	$0.000202(X)^{1/2}$

[A] where X is the mass percent.

NOTE 2—The data below shows the repeatability for butanols and several acetone values obtained using the formula given in 15.2.1.

Butanol Repeatability

	amount (mass percent	*r*
2-Methyl-1-propanol	95 to 99.9	0.205
1-Butanol	95 to 99.9	0.350
2-Butanol	95 to 99.9	0.366
Acetone in 2-Methyl-1-propanol	1.50	0.000226
Acetone in 2-Methyl-1-propanol	1.00	0.000194
Acetone in 2-Methyl-1-propanol	0.70	0.000154
Acetone in 2-Methyl-1-propanol	0.25	0.000092
Acetone in 2-Methyl-1-propanol	0.10	0.000058
Acetone in 2-Methyl-1-propanol	0.02	0.000026
Acetone in 1-Butanol	1.50	0.000378
Acetone in 1-Butanol	1.00	0.000323
Acetone in 1-Butanol	0.70	0.000258
Acetone in 1-Butanol	0.25	0.000154
Acetone in 1-Butanol	0.10	0.000097
Acetone in 1-Butanol	0.02	0.000044
Acetone in 2-Butanol	1.50	0.000411
Acetone in 2-Butanol	1.00	0.000352
Acetone in 2-Butanol	0.70	0.000281
Acetone in 2-Butanol	0.25	0.000168
Acetone in 2-Butanol	0.10	0.000106
Acetone in 2-Butanol	0.02	0.000047

NOTE 3—The data below shows the repeatability for butanols and several ethanol values obtained using the formula given in 15.2.1.

Butanol Repeatability

	amount (mass percent	*r*
2-Methyl-1-propanol	95 to 99.9	0.205
1-Butanol	95 to 99.9	0.350
2-Butanol	95 to 99.9	0.366
Ethanol in 2-Methyl-1-propanol	1.50	0.000247
Ethanol in 2-Methyl-1-propanol	1.00	0.000212
Ethanol in 2-Methyl-1-propanol	0.70	0.000169
Ethanol in 2-Methyl-1-propanol	0.25	0.000101
Ethanol in 2-Methyl-1-propanol	0.10	0.000064
Ethanol in 2-Methyl-1-propanol	0.02	0.000029
Ethanol in 1-Butanol	1.50	0.000413
Ethanol in 1-Butanol	1.00	0.000354
Ethanol in 1-Butanol	0.70	0.000282
Ethanol in 1-Butanol	0.25	0.000169
Ethanol in 1-Butanol	0.10	0.000107
Ethanol in 1-Butanol	0.02	0.000048
Ethanol in 2-Butanol	1.50	0.000437
Ethanol in 2-Butanol	1.00	0.000375
Ethanol in 2-Butanol	0.70	0.000299
Ethanol in 2-Butanol	0.25	0.000179
Ethanol in 2-Butanol	0.10	0.000113
Ethanol in 2-Butanol	0.02	0.000051

NOTE 4—The data below shows the repeatability for butanols and several methanol values obtained using the formula given in 15.2.1.

Butanol	Repeatability amount (mass percent	r
2-Methyl-1-propanol	95 to 99.9	0.205
1-Butanol	95 to 99.9	0.350
2-Butanol	95 to 99.9	0.366
Methanol in 2-Methyl-1-propanol	1.50	0.000243
Methanol in 2-Methyl-1-propanol	1.00	0.000208
Methanol in 2-Methyl-1-propanol	0.70	0.000166
Methanol in 2-Methyl-1-propanol	0.25	0.000099
Methanol in 2-Methyl-1-propanol	0.10	0.000063
Methanol in 2-Methyl-1-propanol	0.02	0.000028
Methanol in 1-Butanol	1.50	0.000415
Methanol in 1-Butanol	1.00	0.000355
Methanol in 1-Butanol	0.70	0.000284
Methanol in 1-Butanol	0.25	0.000169
Methanol in 1-Butanol	0.10	0.000107
Methanol in 1-Butanol	0.02	0.000048

Butanol	Repeatability amount (mass percent	r
Methanol in 2-Butanol	1.50	0.000458
Methanol in 2-Butanol	1.00	0.000392
Methanol in 2-Butanol	0.70	0.000313
Methanol in 2-Butanol	0.25	0.000187
Methanol in 2-Butanol	0.10	0.000188
Methanol in 2-Butanol	0.02	0.000053

15.2.2 *Reproducibility*—Reproducibility was not determined for this test method.

15.2.3 *Bias*—Bias was not determined for this test method.

16. Keywords

16.1 acetone; bio-butanol; butanol; fuel grade butanol; gas chromatography