



Designation: D4815 – 15b (Reapproved 2019)

Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography¹

This standard is issued under the fixed designation D4815; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the determination of ethers and alcohols in gasolines by gas chromatography. Specific compounds determined are methyl *tert*-butylether (MTBE), ethyl *tert*-butylether (ETBE), *tert*-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, *n*-propanol, isobutanol, *tert*-butanol, *sec*-butanol, *n*-butanol, and *tert*-pentanol (*tert*-amylalcohol).

1.2 Individual ethers are determined from 0.20 % to 20.0 % by mass. Individual alcohols are determined from 0.20 % to 12.0 % by mass. Equations used to convert to mass % oxygen and to volume % of individual compounds are provided. At concentrations <0.20 % by mass, it is possible that hydrocarbons may interfere with several ethers and alcohols. The reporting limit of 0.20 % by mass was tested for gasolines containing a maximum of 10 % by volume olefins. It may be possible that for gasolines containing >10 % by volume olefins, the interference may be >0.20 % by mass. Annex A1 gives a chromatogram showing the interference observed with a gasoline containing 10 % by volume olefins.

1.3 This test method includes a relative bias correlation for ethanol in spark-ignition engine fuels for the U.S. EPA regulations reporting based on Practice D6708 accuracy assessment between Test Method D4815 and Test Method D5599 as a possible Test Method D4815 alternative to Test Method D5599. The Practice D6708 derived correlation equation is only applicable for ethanol in fuels in the concentration range from 2.28 % to 14.42 % by mass as measured by Test Method D4815. The applicable Test Method D5599 range for ethanol is from 2.16 % to 14.39 % by mass as reported by Test Method D5599.

1.4 Alcohol-based fuels, such as M-85 and E-85, MTBE product, ethanol product, and denatured alcohol, are specifi-

cally excluded from this test method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

1.5 Benzene, while detected, cannot be quantified using this test method and must be analyzed by alternate methodology (see Test Method D3606).

1.6 The values stated in SI units are to be regarded as standard. Alternate units, in common usage, are also provided to increase clarity and aid the users of this test method.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *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

- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent³
- D3606 Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography
- 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

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.

Current edition approved Dec. 1, 2019. Published December 2019. Originally approved in 1989. Last previous edition approved in 2015 as D4815 – 15b. DOI: 10.1520/D4815-15BR19.

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.

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

D4420 Test Method for Determination of Aromatics in Finished Gasoline by Gas Chromatography (Withdrawn 2004)³

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *low volume connector*—a special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Sometimes this is referred to as zero dead volume union.

3.1.2 *oxygenate*—any oxygen-containing organic compound that can be used as a fuel or fuel supplement, for example, various alcohols and ethers.

3.1.3 *split ratio*—in capillary gas chromatography, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column, expressed by

$$\text{split ratio} = (S + C)/C \quad (1)$$

where:

S = flow rate at the splitter vent, and

C = flow rate at the column outlet.

3.1.4 *tert-amyl alcohol*—*tert*-pentanol.

3.2 Acronyms:

3.2.1 *DIPE*—diisopropylether.

3.2.2 *ETBE*—ethyl *tert*-butylether.

3.2.3 *MTBE*—methyl *tert*-butylether.

3.2.4 *TAME*—*tert*-amyl methylether.

3.2.5 *TCEP*—1,2,3-tris-2-cyanoethoxypropane—a gas chromatographic liquid phase.

3.2.6 *WCOT*—a type of capillary gas chromatographic column prepared by coating the inside of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 An appropriate internal standard, such as 1,2-dimethoxyethane (ethylene glycol dimethyl ether), is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar TCEP column, which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

4.2 After methylcyclopentane, but before DIPE and MTBE elute from the polar column, the valve is switched to backflush the oxygenates onto a WCOT nonpolar column. The alcohols and ethers elute from the nonpolar column in boiling point order, before elution of any major hydrocarbon constituents.

TABLE 1 Pertinent Physical Constants and Retention Characteristics for TCEP/WCOT Column Set Conditions as in Table 2

Component	Retention Time, Min.	Relative Retention Time		Molecular Mass	Relative Density at 15.56/15.56 °C
		(MTBE = 1.00)	(DME = 1.00)		
Water	2.90	0.58	0.43	18.0	1.000
Methanol	3.15	0.63	0.46	32.0	0.7963
Ethanol	3.48	0.69	0.51	46.1	0.7939
Isopropanol	3.83	0.76	0.56	60.1	0.7899
<i>tert</i> -Butanol	4.15	0.82	0.61	74.1	0.7922
<i>n</i> -Propanol	4.56	0.90	0.67	60.1	0.8080
MTBE	5.04	1.00	0.74	88.2	0.7460
<i>sec</i> -Butanol	5.36	1.06	0.79	74.1	0.8114
DIPE	5.76	1.14	0.85	102.2	0.7282
Isobutanol	6.00	1.19	0.88	74.1	0.8058
ETBE	6.20	1.23	0.91	102.2	0.7452
<i>tert</i> -Pentanol	6.43	1.28	0.95	88.1	0.8170
1,2-Dimethoxyethane (DME)	6.80	1.35	1.00	90.1	0.8720
<i>n</i> -Butanol	7.04	1.40	1.04	74.1	0.8137
TAME	8.17	1.62	1.20	102.2	0.7758

4.3 After benzene and TAME elute from the nonpolar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons.

4.4 The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of each component is calculated with reference to the internal standard.

5. Significance and Use

5.1 Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust, and evaporative emissions are some of the concerns associated with oxygenated fuels.

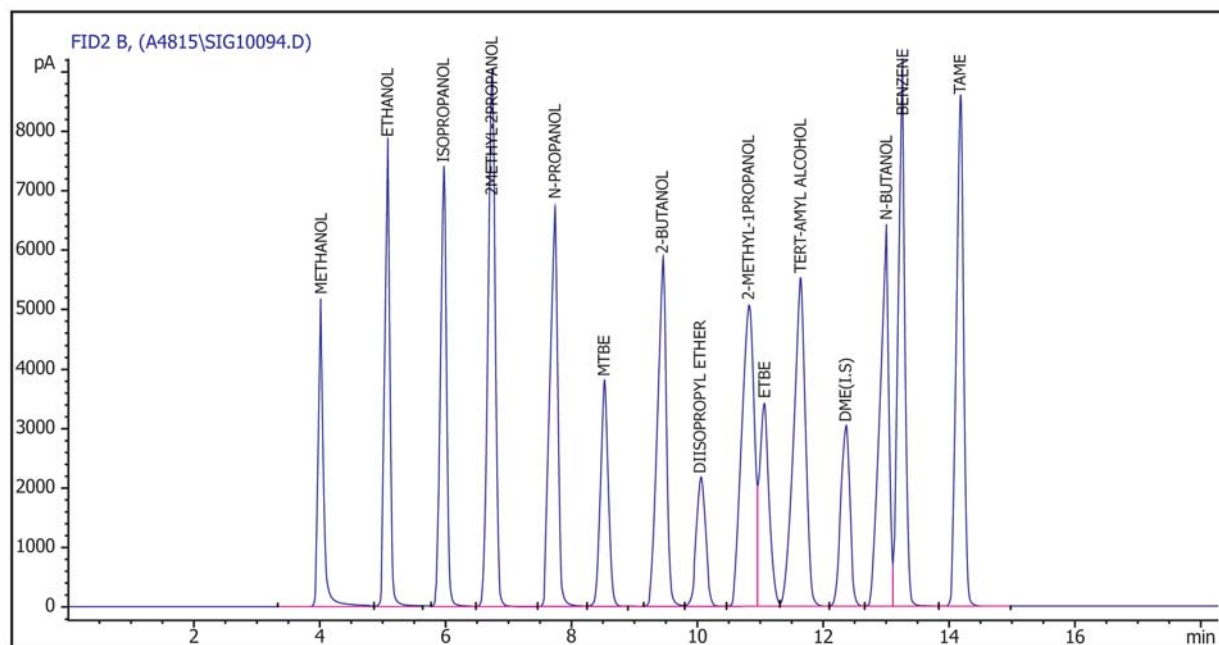
5.2 This test method is applicable to both quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination.

6. Apparatus

6.1 *Chromatograph*—While any gas chromatographic system, which is capable of adequately resolving the individual ethers and alcohols that are presented in Table 1, can be used for these analyses, a gas chromatographic instrument, which can be operated at the conditions given in Table 2 and has a column switching and backflushing system equivalent to Fig. 1, has been found acceptable. Carrier gas flow controllers shall be capable of precise control where the required flow rates are low (see Table 2). Pressure control devices and gages shall be capable of precise control for the typical pressures required.

6.1.1 *Detector*—A thermal conductivity detector or flame ionization detector can be used. The system shall have sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1 for 0.005 % by volume concentration of an oxygenate.

³ The last approved version of this historical standard is referenced on www.astm.org.



NOTE 1—Detector B is optional and used to simplify setting cut times.

FIG. 1 Analysis of Oxygenates in Gasoline Schematic of Chromatographic System

TABLE 2 Chromatographic Operation Conditions

Temperatures	Flows, mL/min	Carrier Gas: Helium
Column Oven	60	to injector 75
Injector, °C	200	Column 5
Detector—TCD, °C	200	Auxiliary 3
—FID, °C	250	Makeup 18
Valve °C	60	

^A Sample size must be adjusted so that alcohols in the range of 0.1 % to 12.0 % by mass and ethers in the range of 0.1 % to 20.0 % by mass are eluted from the column and measured linearly at the detector. A sample size of 1.0 µL has been introduced in most cases.

6.1.2 *Switching and Backflushing Valve*—A valve, to be located within the gas chromatographic column oven, capable of performing the functions described in Section 11 and illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.

6.1.2.1 *Valco Model No. A 4C10WP*, 1.6 mm (1/16 in.) fittings. This particular valve was used in the majority of the analyses used for the development of Section 15.

6.1.2.2 *Valco Model No. C10W*, 0.8 mm (1/32 in.) fittings. This valve is recommended for use with columns of 0.32 mm inside diameter and smaller.

6.1.2.3 Some gas chromatographs are equipped with an auxiliary oven, which can be used to contain the valve and polar column. In such a configuration, the nonpolar column is located in the main oven and the temperature can be adjusted for optimum oxygenates resolution.

6.1.3 An automatic valve switching device must be used to ensure repeatable switching times. Such a device should be synchronized with injection and data collection times.

6.1.4 *Injection System*—The chromatograph should be equipped with a splitting-type inlet device if capillary columns

or flame ionization detection are used. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

6.1.4.1 Some gas chromatographs are equipped with on-column injectors and autosamplers, which can inject small samples sizes. Such injection systems can be used provided that sample size is within the limit of the column and detectors optimum efficiency and linearity.

6.1.4.2 Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully for introducing representative samples into the gas chromatographic inlet.

6.2 Data Presentation or Calculation, or Both:

6.2.1 *Recorder*—A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less can be used to monitor detector signal. Full-scale response time should be 1 s or less with sufficient sensitivity and stability to meet the requirements of 6.1.1.

6.2.2 *Integrator or Computer*—Means shall be provided for determining the detector response. Peak heights or areas can be measured by computer, electronic integration, or manual techniques.

6.3 Columns, Two as Follows:

6.3.1 *Polar Column*—This column performs a pre-separation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed onto the nonpolar column in 6.3.2. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.1.1 can be used. The column shall perform at the same temperature as required for the column in 6.3.2, except if located in a separate auxiliary oven as in 6.1.2.3.

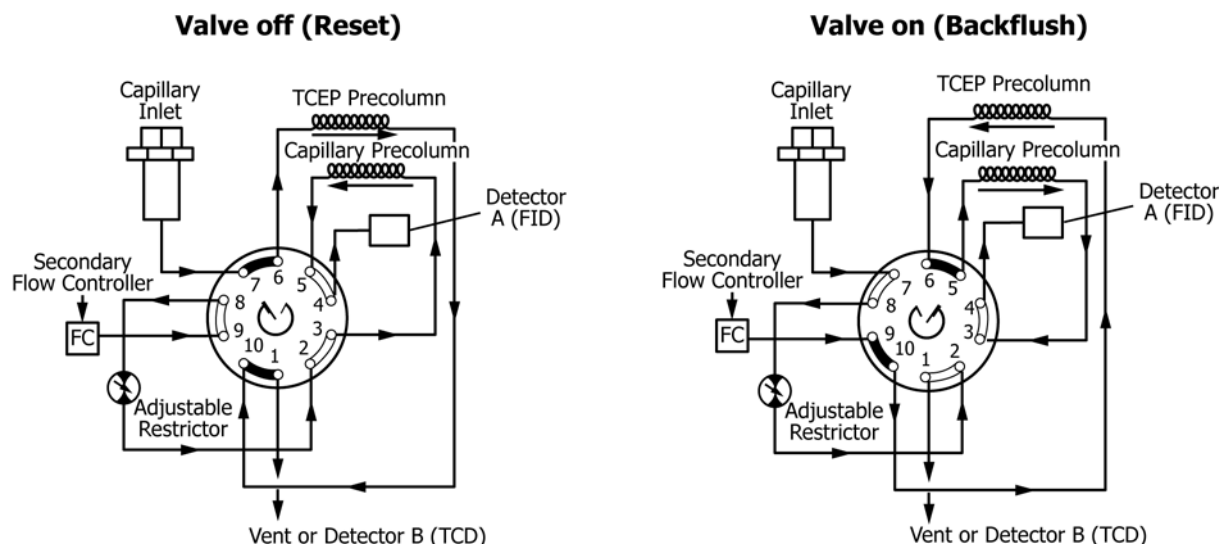


FIG. 2 Analyses of Oxygenates in Gasoline Example Chromatogram Showing Oxygenates

6.3.1.1 *TCEP Micro-Packed Column*, 560 mm (22 in.) by 1.6 mm ($\frac{1}{16}$ in.) outside diameter by 0.76 mm (0.030 in.) inside diameter stainless steel tube packed with 0.14 g to 0.15 g of 20 % (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW). This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

6.3.2 *Nonpolar (Analytical) Column*—Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.2.1 and illustrated in Fig. 2 can be used.

6.3.2.1 *WCOT Methyl Silicone Column*, 30 m (1181 in.) long by 0.53 mm (0.021 in.) inside diameter fused silica WCOT column with a 2.6 μ m film thickness of cross-linked methyl siloxane. This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

7. Reagents and Materials

7.1 *Carrier Gas*—Carrier gas appropriate to the type of detector used. Helium has been used successfully. The minimum purity of the carrier gas used must be 99.95 mol %.

7.2 *Standards for Calibration and Identification*—Standards of all components to be analyzed and the internal standard 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. (**Warning**—These materials are flammable and can be harmful or fatal if ingested or inhaled.)

7.3 *Methylene Chloride*, used for column preparation, reagent grade, free of nonvolatile residue. (**Warning**—Harmful if inhaled. High concentrations may cause unconsciousness or death.)

8. Preparation of Column Packings

8.1 TCEP Column Packing:

8.1.1 Any satisfactory method used in the practice of the art that will produce a column capable of retaining the C1 to C4 alcohols and MTBE, ETBE, DIPE, and TAME from compo-

nents of the same boiling point range in a gasoline sample. The following procedure has been used successfully.

8.1.2 Completely dissolve 10 g of TCEP in 100 mL of methylene chloride. Next add 40 g of 80/100 mesh Chromosorb P(AW) to the TCEP solution. Quickly transfer this mixture to a drying dish, in a fume hood, without scraping any of the residual packing from the sides of the container. Constantly, but gently, stir the packing until all of the solvent has evaporated. This column packing can be used immediately to prepare the TCEP column.

9. Sampling

9.1 Every effort should be made to ensure that the sample is representative of the fuel source from which it is taken. Follow the recommendations of Practice D4057, or its equivalent, when obtaining samples from bulk storage or pipelines.

9.2 Upon receipt in the laboratory, chill the sample in its original container to 0 °C to 5 °C (32 °F to 40 °F) before any subsampling is performed.

9.3 If necessary, transfer the chilled sample to a vapor tight container and store at 0 °C to 5 °C (32 °F to 40 °F) until needed for analysis.

10. Preparation of Micro-Packed TCEP Column

10.1 Wash a straight 560 mm length of 1.6 mm outside diameter (0.76 mm inside diameter) stainless steel tubing with methanol and dry with compressed nitrogen.

10.2 Insert six to twelve strands of silvered wire, a small mesh screen, or stainless steel frit inside one end of the tube. Slowly add 0.14 g to 0.15 g of packing material to the column and gently vibrate to settle the packing inside the column. When strands of wire are used to retain the packing material inside the column, leave 6.0 mm (0.25 in.) of space at the top of the column.

10.3 *Column Conditioning*—Both the TCEP and WCOT columns are to be briefly conditioned before use. Connect the

columns to the valve (see 11.1) in the chromatographic oven. Adjust the carrier gas flows as in 11.3 and place the valve in the RESET position. After several minutes, increase the column oven temperature to 120 °C and maintain these conditions for 5 min to 10 min. Cool the columns below 60 °C before shutting off the carrier flow.

11. Preparation of Apparatus and Establishment of Conditions

11.1 *Assembly*—Connect the WCOT column to the valve system using low volume connectors and narrow bore tubing. It is important to minimize the volume of the chromatographic system that comes in contact with the sample; otherwise, peak broadening will occur.

11.2 Adjust the operating conditions to those listed in Table 2, but do not turn on the detector circuits. Check the system for leaks before proceeding further.

11.2.1 If different polar and nonpolar columns or capillary columns of smaller ID, or both, are used it can be necessary to use different optimum flows and temperatures.

11.3 Flow Rate Adjustment:

11.3.1 Attach a flow measuring device to the column vent with the valve in the RESET position and adjust the pressure to the injection port to give 5.0 mL/min flow (14 psig). Soap bubble flow meters are suitable.

11.3.2 Attach a flow measuring device to the split injector vent and adjust the flow from the split vent using the A flow controller to give a flow of 70 mL/min. Recheck the column vent flow set in 11.3.1 and adjust if necessary.

11.3.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same column vent flow set in 11.3.1. This is necessary to minimize flow changes when the valve is switched.

11.3.4 Switch the valve to the inject position RESET and adjust the B flow controller to give a flow of 3.0 mL/min to 3.2 mL/min at the detector exit. When required for the particular instrumentation used, add makeup flow or TCD switching flow to give a total of 21 mL/min at the detector exit.

11.4 When a thermal conductivity detector is used, turn on the filament current and allow the detector to equilibrate. When a flame ionization detector is used, set the hydrogen and air flows and ignite the flame.

11.5 *Determine the Time to Backflush*—The time to backflush will vary slightly for each column system and must be determined experimentally as follows. The start time of the integrator and valve timer must be synchronized with the injection to accurately reproduce the backflush time.

11.5.1 Initially assume a valve BACKFLUSH time of 0.23 min. With the valve RESET, inject 1 µL to 3 µL of a blend containing at least 0.5 % or greater oxygenates (see 7.3), and simultaneously begin timing the analysis. At 0.23 min, rotate the valve to the BACKFLUSH position and leave it there until the complete elution of TAME is realized. Record this time as the RESET time, which is the time at which the valve is returned to the RESET position. When all of the remaining hydrocarbons are backflushed, the signal will return to a stable

baseline and the system is ready for another analysis. The chromatogram should appear similar to the one illustrated in Fig. 2.

11.5.1.1 Ensure that the BACKFLUSH time is sufficient to quantitatively transfer the higher concentrations of the ethers, specifically MTBE, into the nonpolar column.

11.5.2 It is necessary to optimize the valve BACKFLUSH time by analyzing a standard blend containing oxygenates. The correct BACKFLUSH time is determined experimentally by using valve switching times between 0.20 min and 0.35 min. When the valve is switched too soon, C5 and lighter hydrocarbons are backflushed and are co-eluted in the C4 alcohol section of the chromatogram. When the valve BACKFLUSH is switched too late, part or all of the ether component (MTBE, ETBE, or TAME) is vented, resulting in an incorrect ether measurement.

11.5.2.1 DIPE may require a BACKFLUSH time slightly shorter than the other ethers. The system may require reoptimization if the analysis of DIPE is required.

11.5.3 To facilitate setting BACKFLUSH time, the column vent in Fig. 1 can be connected to a second detector (TCD or FID), as described in Test Method D4420, and used to set BACKFLUSH TIME based on the oxygenates standard containing the ethers of interest.

12. Calibration and Standardization

12.1 *Identification*—Determine the retention time of each component either by injecting small amounts separately, in known mixtures, or by comparing the relative retention times with those in Table 1.

12.1.1 To ensure minimum interference from hydrocarbons, it is strongly recommended that a fuel devoid of oxygenates be chromatographed to determine the level of any hydrocarbon interference.

12.2 *Preparation of Calibration Samples*—Prepare multi-component calibration standards of the oxygenates and concentration ranges of interest, *by mass*, in accordance with Practice D4307.

12.2.1 For each oxygenate, prepare a minimum of five calibration standards spanning the range of the oxygenate in the samples. As an example, for full range calibration, 0.1 %, 0.5 %, 2 %, 5 %, 10 %, 15 %, and 20 % by mass of each oxygenate may be used.

12.2.2 Before preparing the standards, determine the purity of the oxygenate stocks and make corrections for the impurities found. Whenever possible, use stocks of at least 99.9 % purity. Correct the purity of the components for water content, determined by Test Method D1744.

12.2.3 To minimize evaporation of light components, chill all chemicals and gasoline used to prepare standards.

12.2.4 Prepare standards by transferring a fixed volume of oxygenates, using pipettes or eye droppers (for volumes below 1 % by volume), to 100 mL volumetric flasks or septum capped vials as follows. Cap and record the tare weight of the volumetric flask or vial to 0.1 mg. Remove the cap and carefully add the oxygenate to the flask or vial. Do not contaminate with sample the part within the flask or vial that contacts the cap. Cap and record the net mass (W_i) to 0.1 mg of

TABLE 3 Example Calculation of Correlation Coefficient

X_i	Y_i	$x = X_i - \bar{x}$	$y = Y_i - \bar{y}$	xy	x^2	y^2
1.0	0.5	-2.0	-1.0	2.0	4.0	1.0
2.0	1.0	-1.0	-0.5	0.5	1.0	0.25
3.0	1.5	0.0	0.0	0.0	0.0	0.0
4.0	2.0	+1.0	0.5	0.5	1.0	0.25
5.0	2.5	+2.0	1.0	2.0	4.0	1.0
$\bar{x} = 3.0$	$\bar{y} = 1.5$			$(\sum xy) = 25.0$	$\sum x^2 = 10.0$	$\sum y^2 = 2.5$
				$n = 25.0$		

$$r^2 = \frac{(\sum xy)^2}{(\sum x^2)(\sum y^2)} = \frac{25.0}{(10.0)(2.5)} = 1.0$$

the oxygenate added. Repeat the addition and weighing procedure for each oxygenate of interest. Similarly, add 5 mL of the internal standard (DME) and record its net mass (W_s) to 0.1 mg.

12.2.5 Dilute each standard to 100.0 mL with oxygenate-free gasoline or a mixture of hydrocarbons, such as *isooctane*/mixed xylenes (63.35 % by volume). Do not exceed 30 % by volume for all oxygenates, including the internal standard added. Store the capped calibrations standards below 5 °C (40 °F) when not in use.

12.3 Standardization:

12.3.1 Run the calibration standards and establish the calibration curve for each oxygenate. Plot the response ratio (rsp_i):

$$rsp_i = (A_i/A_s) \tag{2}$$

where:

A_i = area of oxygenate, and
 A_s = area of internal standard.

as the y-axis versus the amount ratio (amt_i):

$$amt_i = (W_i/W_s) \tag{3}$$

where:

W_i = mass of oxygenate, and
 W_s = mass of internal standard.

as the x-axis calibration curves for each oxygenate. Check the correlation r^2 value for each oxygenate calibration. The r^2 value should be at least 0.99 or better. r^2 is calculated as follows:

$$r^2 = \frac{(\sum xy)^2}{(\sum x^2)(\sum y^2)} \tag{4}$$

where:

$$x = X_i - \bar{x} \tag{5}$$

$$y = Y_i - \bar{y} \tag{6}$$

and:

X_i = amt_i ratio data point,
 \bar{X} = average values for all (amt_i) data points,
 Y_i = corresponding rsp_i ratio data point, and
 \bar{y} = average values for all (rsp_i) data points.

12.3.2 Table 3 gives an example on the calculation of r^2 for an ideal data set X_i and Y_i :

12.3.3 For each oxygenate i calibration data set, obtain the linear least-squares fit equation in the form:

$$(rsp_i) = (m_i)(amt_i) + b_i \tag{7}$$

MTBE

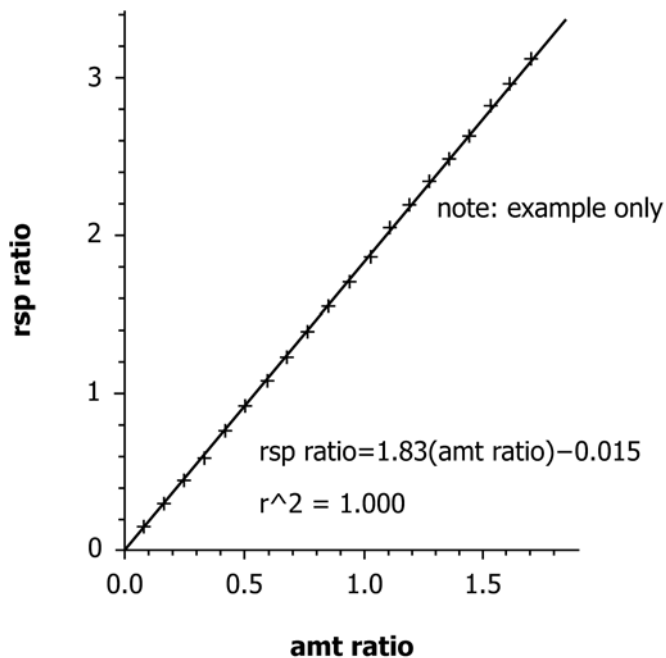


FIG. 3 A Least-Squares Fit Calibration for MTBE

where:

(rsp_i) = response ratio for oxygenate i (y-axis),
 m_i = slope of linear equation for oxygenate i ,
 amt_i = amount ratio for oxygenate i (x-axis), and
 b_i = y-axis intercept.

12.3.4 The values m_i and b_i are calculated as follows:

$$m_i = \frac{\sum xy}{\sum x^2} \tag{8}$$

and

$$b_i = \bar{y} - m_i \bar{x} \tag{9}$$

12.3.5 For the example in Table 3:

$$m_i = 5/10 = 0.5 \tag{10}$$

and

$$b_i = \bar{y} - m_i \bar{x} = 1.5 - (0.5)(3) = 0 \tag{11}$$

Therefore, the least-squares fit (see Eq 7) for the above example in Table 3 is:

$$(rsp_i) = 0.5 amt_i + 0 \tag{12}$$

NOTE 1—Normally the b_i value is not zero and may be either positive or negative. Fig. 3 gives an example of a linear least-squares fit for MTBE and the resulting equation in the form of Eq 7.

12.3.6 For an optimum calibration, the absolute value of the y-intercept b_i must be at a minimum. In this case, A_i approaches zero when w_i is less than or equal to 0.1 % by mass. The equation to determine the mass % oxygenate i or w_i , reduces to Eq 13. The y-intercept can be tested using Eq 13:

$$w_i = (b_i/m_i)(W_s/W_g)100 \% \tag{13}$$

where:

w_i = mass % oxygenate i , where w_i is ≤ 0.1 % by mass,