



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 D 4815; 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 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 0.1 to 20.0 mass %. Individual alcohols are determined from 0.1 to 12.0 mass %. Equations used to convert to mass % oxygen and to volume % of individual compounds are provided.

1.3 Alcohol-based fuels, such as M-85 and E-85, MTBE product, ethanol product, and denatured alcohol, are specifically excluded from this test method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

1.4 Benzene, while detected, cannot be quantified using this test method and must be analyzed by alternate methodology (see Test Method D 3606 or D 4420).

1.5 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.

1.6 *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 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method²

D 1744 Test Method for Water in Liquid Petroleum Prod-

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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

ucts by Karl Fischer Reagent²

D 3606 Test Method for the Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography³

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter³

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards³

D 4420 Test Method for Aromatics in Finished Gasoline by Gas Chromatography³

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 *MTBE*—methyl *tert*-butylether.

3.1.3 *ETBE*—ethyl *tert*-butylether.

3.1.4 *TAME*—*tert*-amyl methylether.

3.1.5 *DIPE*—diisopropylether.

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

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

3.1.8 *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.

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

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

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

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.

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 volume % concentration of an oxygenate.

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:

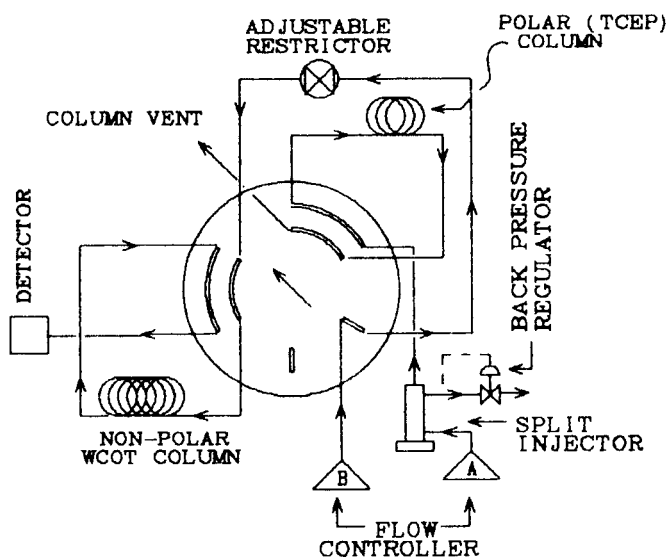
TABLE 1 Pertinent Physical Constants and Retention Characteristics for TCEP/WCOT Column Set Conditions as in Table 2

Component	Retention Time, Min.	Relative Retention Time		Molecular Weight	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

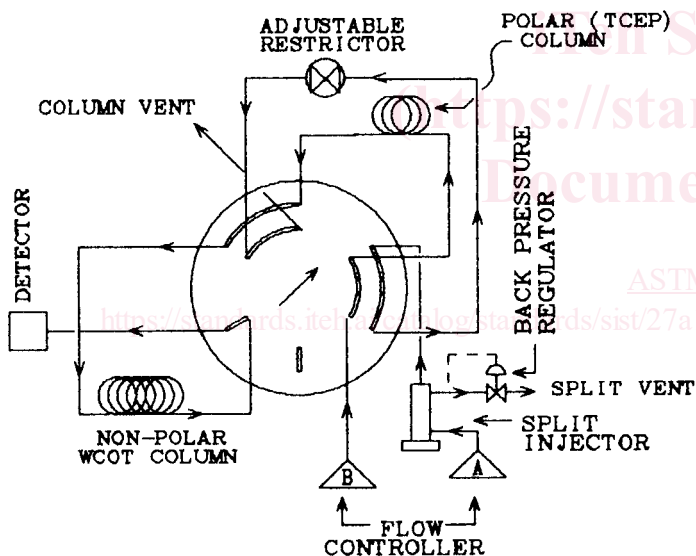
TABLE 2 Chromatographic Operation Conditions

	Temperatures	Flows, mL/min	Carrier Gas: Helium
Column Oven	60	to injector	75
Injector, °C	200	Column	5
Detector—TCD, °C	200	Auxillary	3
—FID, °C	250	Makeup	18
Valve °C	60		
		Sample size, μL^A	1.0–3.0
		Split ratio	15:1
		Backflush, min	0.2–0.3
		Valve reset time	8–10 min
		Total Analysis time	18–20 min

^ASample size must be adjusted so that alcohols in the range of 0.1 to 12.0 mass % and ethers in the range of 0.1 to 20.0 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.



Valve in RESET Position



Valve in BACKFLUSH Position

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

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.

6.3.1.1 *TCEP Micro-Packed Column*,⁴ 560 mm (22 in.) by 1.6-mm (1/16-in.) outside diameter by 0.76-mm (0.030-in.) inside diameter stainless steel tube packed with 0.14 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 components 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

⁴ Available from Hewlett Packard Co., Avondale, PA.

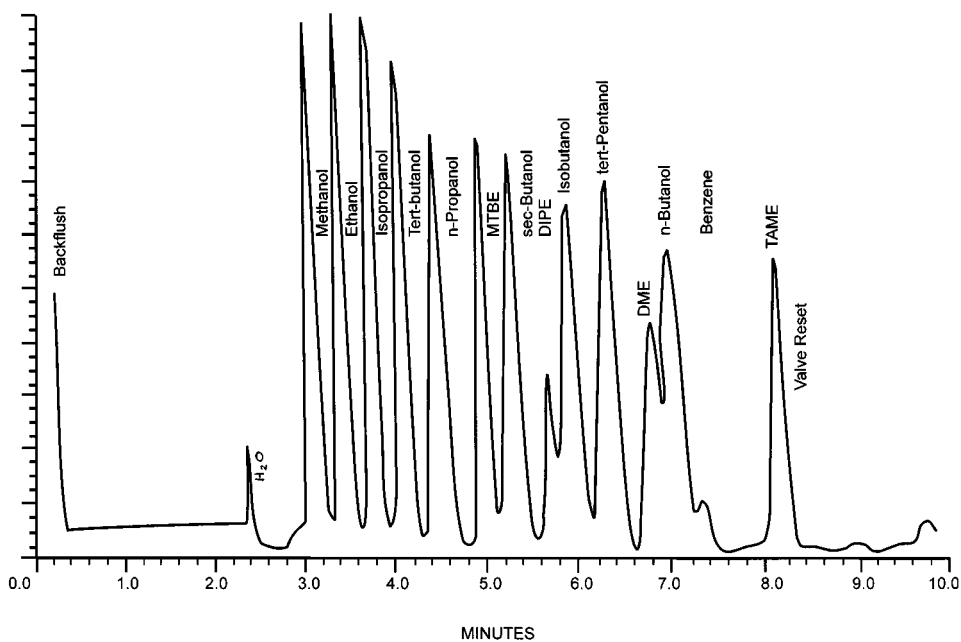


FIG. 2 Analyses of Oxygenates in Gasoline Example Chromatogram Showing Oxygenates

representative of the fuel source from which it is taken. Follow the recommendations of Practice D 4057, 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 to 5°C (32 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 to 5°C (32 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 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 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 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