



Designation: **D5797–07 D5797 – 13**

## Standard Specification for Fuel Methanol (M70-M85) for Automotive Spark-Ignition Engines<sup>1</sup>

This standard is issued under the fixed designation D5797; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope—Scope\*

1.1 This specification covers a fuel blend, nominally 70 to 85 volume % methanol and 30 to 14 volume % hydrocarbons for use in ground vehicles with automotive spark-ignition engines. **Appendix X1** discusses the significance of the properties specified. **Appendix X2** presents the current status in the development of a luminosity test procedure for M70-M85.

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

1.3 The following precautionary caveat pertains only to the test method portions—**Annex A1**, **Annex A2**, **Annex A3**, and **Appendix X2** of this specification. *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:*<sup>2,3</sup>

[D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure](#)

[D130 Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test](#)

[D381 Test Method for Gum Content in Fuels by Jet Evaporation](#)

[D512 Test Methods for Chloride Ion In Water](#)

[D525 Test Method for Oxidation Stability of Gasoline \(Induction Period Method\)](#)

[D872 Test Method for Test for Sulfonation Index of Road Tars \(Withdrawn 1991\)<sup>4</sup>](#)

[D1193 Specification for Reagent Water](#)

[D1266 Test Method for Sulfur in Petroleum Products \(Lamp Method\)](#)

[D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products](#)

[D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry](#)

[D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry](#)

[D3231 Test Method for Phosphorus in Gasoline](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination](#)

[D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards](#)

[D4626 Practice for Calculation of Gas Chromatographic Response Factors](#)

[D4814 Specification for Automotive Spark-Ignition Engine Fuel](#)

[D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C<sub>1</sub> to C<sub>4</sub> Alcohols in Gasoline by Gas Chromatography](#)

[D4929 Test Methods for Determination of Organic Chloride Content in Crude Oil](#)

[D4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends \(Dry Method\)](#)

<sup>1</sup> This specification is under the jurisdiction of ASTM Committee **D02** on Petroleum Products and Lubricants and is under the direct responsibility of Subcommittee **D02.A0.02** on Oxygenated Fuels and Components.

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<sup>2</sup> Reference to the following documents is to be the latest issue unless otherwise specified.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>4</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

\*A Summary of Changes section appears at the end of this standard

- D5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy  
D5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method) (Withdrawn 2012)<sup>4</sup>  
D5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)  
D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence  
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products  
D7757 Test Method for Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry  
E203 Test Method for Water Using Volumetric Karl Fischer Titration  
E355 Practice for Gas Chromatography Terms and Relationships  
E1145 Specification for Denatured Ethyl Alcohol, Formula 3a (Withdrawn 1993)<sup>4</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *methanol, n*—methyl alcohol, the chemical compound CH<sub>3</sub>OH.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *aliphatic ether*—an oxygen-containing, ashless, organic compound in which the oxygen atom is interposed between two carbon atoms (organic groups), has the general formula C<sub>n</sub>H<sub>2n+2</sub>O with n being 5 to 8, and in which the carbon atoms are connected in open chains and not closed rings.

##### 3.2.1.1 Discussion—

Aliphatic compounds can be straight or branched chains and saturated or unsaturated. The term aliphatic ether, as used in this specification, refers only to the saturated compounds.

3.2.2 *fuel methanol (M70-M85)*—a blend of methanol and hydrocarbons of which the methanol portion is nominally 70 to 85 volume %.

3.2.3 *higher alcohols*—aliphatic alcohols of the general formula C<sub>n</sub>H<sub>2n+1</sub>OH with n being 2 to 8.

3.2.4 *hydrocarbon*—those components in a methanol-hydrocarbon blend that contain only hydrogen and carbon.

### 4. Fuel Methanol (M70-M85) Performance Requirements

4.1 Fuel methanol (M70-M85) shall conform to the requirements in **Table 1**.

**TABLE 1 Requirements for Fuel Methanol (M70-M85)**

Properties	Class 1 <sup>A</sup>	Class 2	Class 3
Methanol + higher alcohols, min, volume%	84	80	70
Hydrocarbon/aliphatic ether, volume%	14–16	14–20	14–30
Vapor pressure, kPa (psi)	48–62 7.0–9.0	62–83 9.0–12.0	83–103 12.0–15.0
Lead, max, mg/L	2.6	2.6	3.9
Phosphorus, max, mg/L	0.2	0.3	0.4
Sulfur, max, mg/kg	160	200	300
All Classes			
Higher alcohols (C <sub>2</sub> –C <sub>8</sub> ), max, volume %		2	
Acidity, as acetic acid, max, mg/kg		50	
Solvent washed gum content, max, mg/100 mL		5	
Unwashed gum content, max, mg/100 mL		20	
Total chlorine as chlorides, max, mg/kg		2	
Inorganic chloride, max, mg/kg		1	
Water, max, mass%		0.5	
Appearance	This product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at indoor ambient temperatures unless otherwise agreed upon between the supplier and the purchaser.		

<sup>A</sup> See 4.1.1 for volatility class criteria.

NOTE 1—Most of the requirements cited in [Table 1](#) are based on the best technical information currently available regarding the performance of these fuels in current technology vehicles. Requirements for sulfur, phosphorus, and lead are based on the use of gasoline defined in [Specification D4814](#) understanding that control of these elements will affect catalyst lifetime. The lead maximum is limited for Class 1 and Class 2 fuels to the lower limit of the test method. As greater experience is gained from field use of M70-M85 vehicles, and further vehicle hardware developments for the use of higher methanol content fuels occurs, it is expected that many of these requirements will change.

4.1.1 Vapor pressure is varied for seasonal and climatic changes by providing three vapor pressure classes for M70-M85. The seasonal and geographic distribution for the three vapor pressure classes is shown in [Table 2](#). Class 1 encompasses geographical areas with 6-h tenth-percentile minimum ambient temperature of greater than 5°C (41°F). Class 2 encompasses geographical areas with 6-h tenth-percentile minimum temperatures of greater than -5°C (23°F) but less than +5°C. Class 3 encompasses geographical areas with 6-h tenth-percentile minimum ambient temperature less than or equal to -5°C.

4.1.2 The hydrocarbons used shall have a final maximum boiling point of 225°C (437°F) by Test Method [D86](#), oxidation stability of 240-min minimum by Test Method [D525](#), and No. 1 maximum copper strip corrosion by Test Method [D130](#). The hydrocarbons may contain aliphatic ethers as blending components as are customarily used for automotive fuel.

4.1.3 Use of unprotected aluminum in fuel methanol (M70-M85) distribution and dispensing equipment will introduce insoluble aluminum compounds into the fuel causing plugged vehicle fuel filters. Furthermore, this effect can be exaggerated even with protected aluminum by elevated fuel conductivity caused by contact with a nitrile rubber dispensing hose. Therefore, unprotected aluminum and an unlined nitrile rubber dispensing hose should be avoided in fuel methanol (M70-M85) distribution and dispensing systems.<sup>5</sup>

## 5. Workmanship

5.1 Fuel Methanol (M70–M85) shall be visually free of sediment and suspended matter. It shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

5.2 The specification defines only a basic purity for Fuel Methanol (M70–M85). The product shall be free of any adulterant or contaminant that can render the material unacceptable for its commonly used applications.

5.2.1 Manufacturers and blenders of Fuel Methanol (M70–M85) shall avoid methanol (for example, improperly recycled methanol), or hydrocarbon blend components contaminated by silicon-containing materials, or both. Silicon contamination of gasoline, denatured ethanol, and their blends has led to fouled vehicle components (for example, spark plugs, exhaust oxygen sensors, catalytic converters) requiring parts replacement and repairs. Test Method [D7757](#) is a procedure for determining silicon that might be applicable to Fuel Methanol (M70–M85). No specification limits have been established for silicon.

## 6. Sampling, Containers, and Sample Handling

6.1 The reader is strongly advised to review all intended test methods prior to sampling to better understand the importance and effects of sampling technique, proper containers, and special handling required for each test method.

6.2 Correct sampling procedures are critical to obtain a sample representative of the lot intended to be tested. Use appropriate procedures in Practice [D4057](#) for manual method sampling and in Practice [D4177](#) for automatic sampling as applicable.

6.3 The correct sample volume and appropriate container selection are important decisions that can impact test results. Refer to Practice [D4306](#) for aviation fuel container selection for tests sensitive to trace contamination. Refer to Practice [D5854](#) for procedures on container selection and sample mixing and handling. Where practical, M70–M85 should be sampled in glass containers. If samples must be collected in metal containers, do not use soldered metal containers. This is because the soldering flux in the containers and the lead in the solder can contaminate the sample. Plastic containers should be avoided.

6.4 A minimum sample size of about 1 L (1 qt) is recommended.

## 7. Test Methods

7.1 Determine the requirements enumerated in this specification in accordance with the following test methods:

NOTE 2—The appropriateness of ASTM test methods cited has not been demonstrated for use with M70-M85. In addition, test methods contained in the annexes and appendixes are in the developmental stages or lack precision and bias determinations.

7.1.1 *Methanol*—A procedure for a test method for methanol content of fuel methanol (M70-M85) is included as [Annex A1](#). Verification of the appropriateness of this test method has indicated that the precision of this method may not be adequate. As work continues to develop a method, this procedure remains the best available.

7.1.2 *Hydrocarbon/Aliphatic Ether*—Use Test Method [D4815](#) to determine higher alcohols, methyl *tert*-butyl ether (MTBE), and other ethers. Water may also be determined if the gas chromatograph is equipped with a thermal conductivity detector. As an alternative, water can be determined by the Karl Fischer test method (see [6.1.97.1.9](#)). The concentration of methanol, other alcohols, and water can be added, and the sum subtracted from 100 to get the percent of hydrocarbons/aliphatic ethers. An alternative test method is contained in [Annex A2](#).

<sup>5</sup> American Automobile Manufacturers Association, “Fuel Methanol Compatibility Standards and Dispensing Equipment List for M85 Fueled Vehicles,” October 1994.

**TABLE 2 Seasonal and Geographical Volatility Specifications for Fuel Methanol (M70-M85)**

NOTE 1—This schedule is subject to agreement between the purchaser and the seller denotes the vapor pressure class of the fuel at the time and place of bulk delivery to fuel dispensing facilities for the end user. Shipments should anticipate this schedule.

State	January	February	March	April	May	June	July	August	September	October	November	December
Alabama	2	2	2	2	2/1	1	1	1	1	1/2	2	2
Alaska												
Southern Region	3	3	3	3	3/2	2/1	1	1/2	2/3	3	3	3
South Mainland	3	3	3	3	3/2	2/1	1/2	2	2/3	3	3	3
Arizona												
N of 34° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
S of 34° Latitude	2	2	2	2/1	1	1	1	1	1	1/2	2	2
Arkansas	3	3	3/2	2/1	1	1	1	1	1/2	2	2/3	3
California <sup>A</sup>												
North Coast	2	2	2	2	2	2/1	1	1	1	1/2	2	2
South Coast	3/2	2	2	2	2/1	1	1	1	1	1/2	2/3	3
Southeast	3	3/2	2	2	2/1	1	1	1	1/2	2	2/3	3
Interior	2	2	2	2	2	2/1	1	1	1	1/2	2	2
Colorado												
E of 105° Longitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
W of 105° Longitude	3	3	3	3	3/2	2	2/1	1/2	2/3	3	3	3
Connecticut	3	3	3	3/2	2	2/1	1	1	1/2	2	2/3	3
Delaware	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
District of Columbia	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Florida												
N of 29° Latitude	2	2	2	2/1	1	1	1	1	1	1/2	2	2
S of 29° Latitude	2	2/1	1	1	1	1	1	1	1	1	1/2	2
Georgia	3	3/2	2	2/1	1	1	1	1	1	1/2	2	2/3
Hawaii	1	1	1	1	1	1	1	1	1	1	1	1
Idaho	3	3	3	3/2	2	2	2/1	1/2	2	2/3	3	3
Illinois												
N of 40° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
S of 40° Latitude	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Indiana	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Iowa	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
Kansas	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
Kentucky	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Louisiana	2	2	2	2/1	1	1	1	1	1/2	2	2	2
Maine	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Maryland	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Massachusetts	3	3	3	3/2	2	2/1	1	1	1/2	2	2/3	3
Michigan												
Lower Michigan	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Upper Michigan	3	3	3	3	3/2	2/1	1	1/2	2	2/3	3	3
Minnesota	3	3	3	3	3/2	2/1	1	1/2	2	2/3	3	3
Mississippi	2	2	2	2/1	1	1	1	1	1/2	2	2	2
Missouri	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Montana	3	3	3	3	3/2	2	2/1	1/2	2/3	3	3	3
Nebraska	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Nevada												
N of 38° Latitude	3	3	3	3/2	2	2	2/1	1/2	2	2/3	3	3
S of 38° Latitude	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
New Hampshire	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
New Jersey	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
New Mexico												
N of 34° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
S of 34° Latitude	3	3	3/2	2/1	1	1	1	1	1/2	2/3	3	3
New York												
N of 42° Latitude	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
S of 42° Latitude	3	3	3	3/2	2/1	1	1	1	1/2	2	2/3	3
North Carolina	3	3	3/2	2	2/1	1	1	1	1/2	2/3	3	3
North Dakota	3	3	3	3	3/2	2/1	1	1/2	2	2/3	3	3
Ohio	3	3	3	3/2	2/1	1	1	1	1/2	2/3	3	3
Oklahoma	3	3	3	3/2	2/1	1	1	1	1/2	2	2/3	3
Oregon												
E of 122° Longitude	3	3	3	3/2	2	2	2/1	1/2	2	2/3	3	3
W of 122° Longitude	3	3/2	2	2	2	2/1	1	1	1/2	2	2	2/3
Pennsylvania												
N of 41° Latitude	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
S of 41° Latitude	3	3	3	3/2	2	2/1	1	1	1/2	2	2/3	3
Rhode Island	3	3	3	3/2	2/1	1	1	1	1	2	2/3	3
South Carolina	2	2	2	2/1	1	1	1	1	1	1/2	2	2
South Dakota	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Tennessee	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Texas												
N of 31° Latitude	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
S of 31° Latitude	2	2	2	2/1	1	1	1	1	1	1/2	2	2

**TABLE 2** *Continued*

State	January	February	March	April	May	June	July	August	September	October	November	December
Utah	3	3	3	3/2	2	2/1	1	1	1/2	2/3	3	3
Vermont	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Virginia	3	3	3/2	2	2/1	1	1	1	1/2	2	2/3	3
Washington												
E of 122° Longitude	3	3	3/2	2	2	2/1	1	1	1/2	2/3	3	3
W of 122° Longitude	3	3/2	2	2	2	2/1	1	1	1/2	2	2	2/3
West Virginia	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Wisconsin	3	3	3	3/2	2	2/1	1	1/2	2	2/3	3	3
Wyoming	3	3	3	3	3/2	2	2/1	1/2	2	2/3	3	3

<sup>A</sup> Details of State Climatological Division by county as indicated:

California, North Coast—Alameda, Contra Costa, Del Norte, Humboldt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity

California, Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (except that portion lying east of Los Angeles County Aqueduct), Kings, Madera, Mariposa, Marced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada

California, South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct)

California, Southeast—Imperial, Riverside, San Bernadino, Los Angeles (that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct)

7.1.3 *Vapor Pressure*—Test Methods [D4953](#), [D5190](#), or [D5191](#).

7.1.4 *Acidity*—Test Method [D1613](#).

7.1.5 *Gum Content, Solvent Washed and Unwashed*—Test Method [D381](#).

7.1.6 *Total Chlorine as Chloride* —Test Methods [D4929](#), Method B.

7.1.7 *Lead*—Test Method [D5059](#). With Test Method [D5059](#), prepare the calibration standards using methanol (reagent grade) as the solvent to prevent errors caused by large differences in carbon-hydrogen ratios.

7.1.8 *Phosphorus*—Test Method [D3231](#).

7.1.9 *Water*—Test Method [E203](#).

7.1.10 *Sulfur*—Test Methods [D1266](#), [D2622](#), [D3120](#), or [D5453](#). With Test Method [D2622](#), prepare the calibration standards using methanol (reagent grade) as the solvent to prevent errors caused by large differences in carbon-hydrogen ratios.

7.1.11 *Inorganic Chloride*—Inorganic chloride can be determined by Test Methods [D512–81](#)(1985)<sup>E1</sup> (Method C). Also, see the test method in [Annex A3](#). Another test method is under development.

## 8. Keywords

8.1 acidity; alcohol; automotive spark-ignition engine fuel; chloride; copper corrosion; ether; fuel methanol (M70-M85) for automotive spark-ignition engines; gum content; hydrocarbon; inorganic chloride; lead; MTBE; M70-M85; methanol; oxidation stability; oxygenates; phosphorus; solvent washed; sulfur; total chlorine; vapor pressure; volatility; water

## ANNEXES

### (Mandatory Information)

#### A1. TEST METHOD FOR DETERMINATION OF METHANOL IN FUEL METHANOL (M70-M85) FOR AUTOMOTIVE SPARK-IGNITION ENGINES

##### A1.1 Scope

A1.1.1 This test method covers a procedure for determination of methanol in fuel methanol (M70-M85) by gas chromatography. This test method is appropriate for fuels containing 70 to 95 volume % methanol.

A1.1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

##### A1.2 Referenced Documents

A1.2.1 *ASTM Standards*<sup>2,3</sup>: [D4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products

[D4177](#) Practice for Automatic 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

**E355** Practice for Gas Chromatography Terms and Relationships

### **A1.3 Terminology**

#### *A1.3.1 Definitions of Terms Specific to This Standard:*

**A1.3.1.1** *low-volume connector*—special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Also referred to as a zero dead-volume union.

**A1.3.1.2** *split ratio*—in gas chromatography using capillary columns the ratio of the total flow of the carrier gas to the sample inlet versus the flow of carrier gas to the capillary column.

**A1.3.1.3** TCEP—1,2,3-tris-2-cyanoethoxypropane. A gas chromatographic liquid phase.

**A1.3.1.4** WCOT—abbreviation for a type of capillary column, wall-coated open tubular, used in gas chromatography. This type of column is prepared by coating the inside of the capillary with a thin film of stationary phase

### **A1.4 Summary of Test Method**

**A1.4.1** An internal standard, *tert*-amyl alcohol, is added to the sample that is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample passes into the first column, a polar TCEP column that elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

**A1.4.2** After methylcyclopentane, but before methanol elutes from the polar column, the valve is switched to backflush the oxygenates onto a WCOT nonpolar column. The methanol and internal standard elute from the nonpolar column in boiling point order, before elution of any major hydrocarbon constituents.

**A1.4.3** After the internal standard elutes from the non-polar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons. 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 methanol is calculated with reference to the internal standard.

### **A1.5 Significance and Use**

**A1.5.1** The production of fuel methanol (M70-M85) requires knowledge of the methanol content to ensure acceptable commercial fuel quality. The methanol content of fuel methanol (M70-M85) affects the performance of an automobile designed to run on such fuel.

**A1.5.2** This test method is applicable to both quality control in the production of fuel methanol (M70-M85) and for the determination of fuel contamination.

### **A1.6 Apparatus**

**A1.6.1** *Chromatograph*— See Practice **E355** for specific descriptions and definitions.

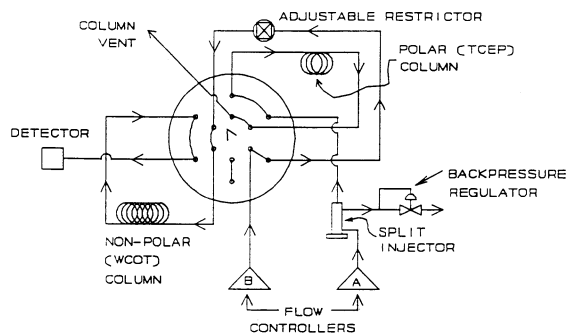
**A1.6.1.1** *Gas Chromatographic Instrument*, operable at the conditions given in **Table A1.1** and having a column switching and backflushing system equivalent to **Fig. A1.1**. Carrier gas flow controllers must be designed for use at the required flow rates (see **Table A1.1**). Pressure control devices and gages must be designed for use at the pressures required.

**A1.6.1.2** *Detector*, either a thermal conductivity detector (TCD) or flame ionization detector (FID) may be used. The system must have sufficient sensitivity and stability to sense absolute concentration changes of 0.01 volume % of methanol or internal standard at the 50 volume % level.

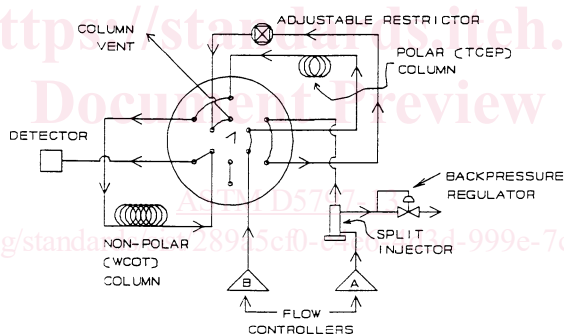


TABLE A1.1 Chromatographic Operating Conditions

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



Valve in RESET Position



Valve in BACKFLUSH Position

FIG. A1.1 Schematic of Chromatographic System

TABLE A1.2 Retention Characteristics for TCEP/WCOT Column Set Conditions as in Table A1.1

Component	Retention Time, min	Relative Retention Time ( $t_{\text{Amyl Alcohol}} = 1.00$ )
Methanol	3.21	0.44
<i>t</i> -Amyl Alcohol	7.30	1.00

A1.6.1.3 *Switching and Backflushing Valve*, a ten-port valve, to be located within the gas chromatographic column oven, capable of performing the functions described in A1.10 and illustrated in Fig. A1.1. The valve must be of low volume design and not contribute significantly to chromatographic deterioration.<sup>6</sup>

<sup>6</sup> A Valco Model No. CM-VSV-10-HT valve with 1.6-mm (1/16-in.) fittings has been found satisfactory for this purpose. This is the valve being used in the majority of the analyses for the development of the data for A1.15. A Valco Model No. C10W with 0.8-mm (1/31-in.) fittings is recommended for use with columns of 0.32-mm inside diameter and smaller. The sole source of supply of the apparatus known to the committee at this time is VICI Valco, 7806 Bobbitt, Houston, TX 77055. 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,<sup>1</sup> which you may attend.

A1.6.1.4 *Automatic Valve Switching Device*, (strongly recommended to ensure repeatable switching times) a device synchronized with injection and data collection times. If no such device is available, a stopwatch, started at the time of injection, should be used to indicate the proper valve switching time.

A1.6.1.5 *Injection System*, a splitting-type inlet device. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

A1.6.1.6 *Sample Introduction System*, any system capable of introducing a representative sample into the split inlet device.

NOTE A1.1—Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully.

#### A1.6.2 *Data Presentation or Calculation System:*

A1.6.2.1 *Recorder*, a recording potentiometer or equivalent with a full-scale deflection of 1 mV or less, and full-scale response time of 1 s or less, with sufficient sensitivity and stability to meet the requirements of A1.6.1.2.

A1.6.2.2 *Integrator or Computer Devices*, capable of meeting the requirements of A1.6.1.2, and providing graphic and digital presentation of the chromatographic data. Peak heights or areas can be measured by computer, electronic integration, or manual techniques.

#### A1.6.3 *Columns*—Two columns are used as follows:

A1.6.3.1 *Polar Column*— Any column with equivalent or better chromatographic efficiency and selectivity to that described in A1.6.3.1(I) can be used. The column must perform at the same temperature as required for the column in A1.6.3.2. 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 A1.6.3.2.

(1) *TCEP Micro-Packed Column*,<sup>7</sup> 560-mm (22-in.) by 1.6-mm (1/16-in.) outside diameter by 0.38-mm (0.015-in.) inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20 % by mass TCEP on 80/100 mesh Chromosorb P(AW). This column is being used to develop precision and bias data for A1.15.

A1.6.3.2 *Nonpolar (Analytical) Column*—Any column with equivalent or better chromatographic efficiency and selectivity to that described in A1.6.3.2(I) and illustrated in Fig. A1.2 can be used.

(1) *WCOT Methyl Silicone Column*, 30-mm (1.181-in.) long by 0.53-mm (0.021-in.) inside diameter fused silica WCOT column with a 2.65- $\mu$ m film thickness of crosslinked methyl siloxane. This column is being used to develop precision and bias data for A1.15.

### A1.7 Reagents and Materials

A1.7.1 *Carrier Gas*, carrier gas appropriate to the type of detector used. The minimum purity of the carrier gas shall be 99.995 mol %.

NOTE A1.2—Helium has been used successfully.

A1.7.2 *Methanol, 99.9 % Purity*, required to establish identification by retention time and for calibration. Shall be of known purity and free of the other components to be analyzed. (**Warning**—Flammable. Health hazard.)

A1.7.3 *Methylene Chloride*, used for column preparation. Reagent grade, free of nonvolatile residue. (**Warning**—Health hazard.)

A1.7.4 *Nitrogen, 99.998 mol %*, used to prepare tubing for the micro-packed TCEP column. (**Warning**—Gas under pressure.)

<sup>7</sup> The sole source of supply of the apparatus known to the committee at this time is Hewlett-Packard Company, Wilmington, DE 19808. 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,<sup>1</sup> which you may attend.



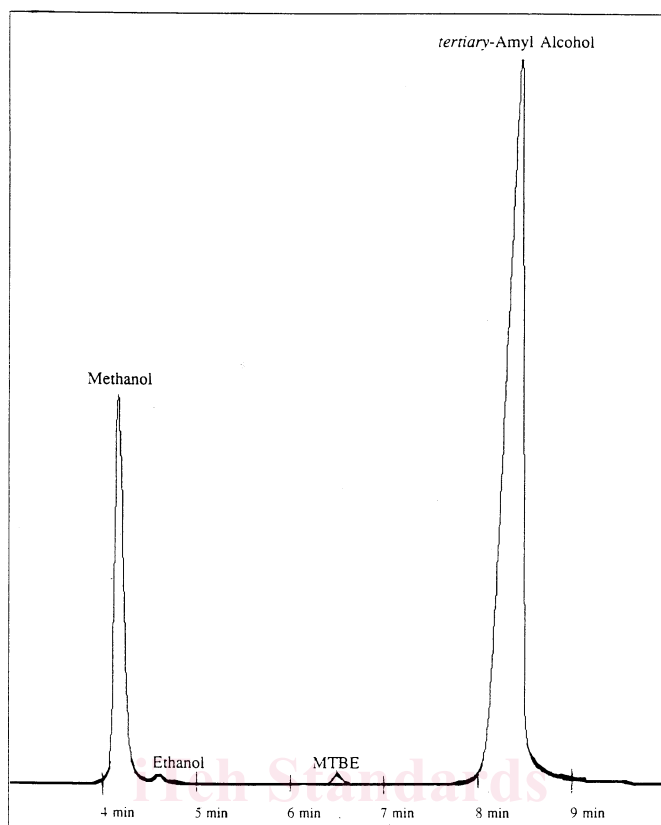


FIG. A1.2 Example of Chromatographic Results

A1.7.5 *Tert-Amyl Alcohol (2-Methyl-2-Butanol)*, 99 % Purity, used as the internal standard. (**Warning**—Flammable. Health hazard.)

## A1.8 Preparation of Column Packing

### A1.8.1 Preparation of TCEP Column Packing:

A1.8.1.1 Any satisfactory method, used in the practice of the art that will produce a column capable of retaining methanol and *tert*-amyl alcohol (internal standard) from hydrocarbon components of the same boiling point range in a fuel methanol (M70-M85) sample, may be used. The following procedure has been used successfully.

A1.8.1.2 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 an evaporating 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.

### A1.8.2 Packing of Micro-Packed TCEP Column:

A1.8.2.1 Wash a straight 560-mm length of 1.6-mm outside diameter (0.38-mm inside diameter) stainless steel tubing with methanol and dry with compressed nitrogen.

A1.8.2.2 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 6.4 mm (0.25 in.) of space at the top of the column. Place wire or screen in the column to retain packing.

A1.8.2.3 *Column Conditioning*—Both the TCEP and WCOT columns are to be briefly conditioned before use. Connect the columns to the valve (see A1.10.1) in the chromatographic oven. Adjust the carrier gas flows as in A1.10.3 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.

## A1.9 Sampling

A1.9.1 To obtain samples for this test method, use the procedures outlined in Practice D4057 or Practice D4177 except that water displacement (see section 10.3.1.8 of Practice D4057) shall not be used.

A1.9.2 Fuel samples shall be stored under refrigeration until the laboratory subsample is taken for analysis. Any laboratory subsamples shall also be refrigerated if they are not to be analyzed immediately.

A1.9.3 Thoroughly shake the sample container prior to withdrawing any subsample for analysis. Allow any particulate matter to settle to the bottom of the subsample container. Inspect the subsample for evidence of phase separation. If phase separation is detected, the sample is invalid and a new sample shall be requested.

## A1.10 Preparation of Apparatus and Establishment of Conditions

A1.10.1 *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.

A1.10.2 Adjust the operating conditions to those listed in Table A1.1. (If a TCD is being used, do not turn on the detector circuits.) Check the system for leaks before proceeding further.

A1.10.3 *Flow Rate Adjustment*—See Fig. A1.1.

A1.10.3.1 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).

NOTE A1.3—Soap-bubble flowmeters are suitable.

A1.10.3.2 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 A1.10.3.1 and adjust, if necessary.

A1.10.3.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same column vent flow set in A1.10.3.1. This is necessary to minimize flow changes when the valve is switched.

A1.10.3.4 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.

A1.10.4 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, ignite the flame, and turn on the electrometer.

A1.10.5 *Valve Switch Times*—The times for switching the valve to the BACKFLUSH position and then back to the RESET position will vary slightly for each column system and shall be determined experimentally as follows. The start time of the integrator and valve timer shall be synchronized with the injection to accurately reproduce the backflush time.

A1.10.5.1 Prepare a blend consisting of approximately, 40 volume % methanol, 10 volume % gasoline (methanol-free), and 50 volume % *tert*-amyl alcohol (internal standard.)