Designation: ~~D5797 – 15~~ D5797 – 16

Standard Specification for ~~Methanol (M70-M85)~~Methanol Fuel Blends (M51–M85) for Methanol-Capable Automotive Spark-Ignition Engines[1]

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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This specification covers ~~a fuel blend, nominally 70 to 85 volume % methanol and 30 to 14 volume % hydrocarbons~~ the requirements for automotive fuel blends of methanol and gasoline for use in ground vehicles ~~with automotive spark-ignition engines.~~ equipped with methanol-capable flexible-fuel, and dedicated methanol spark-ignition engines. Fuel produced to this specification contains 51 % to 85 % by volume methanol. This fuel is sometimes referred to at retail as "M85." 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.~~(flame visibility) for methanol fuel blends (M51–M85).

1.2 The vapor pressure of methanol fuel blends is varied for seasonal climatic changes. Vapor pressure is increased at lower temperatures to ensure adequate vehicle operability and safety. Methanol content and selection of gasoline blendstocks are adjusted by the blender to meet these vapor pressure requirements.

1.3 The United States government has established various programs for alternative fuels. Many of the definitions of alternative fuel used by these programs can be more or less restrictive than the requirements of this specification. See Annex A1 for additional information on alternative fuels containing methanol.

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

1.4.1 *Exception*—Non-SI units are provided for information only. In most cases, U.S. federal regulations specify non-SI units.

1.5 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:*[2,3]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels 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)[4]~~
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

[1] This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is under the direct responsibility of Subcommittee D02.A0.02 on Oxygenated Fuels and Components.

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[2] Reference to the following documents is to be the latest issue unless otherwise specified.

[3] 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.

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

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination
~~D4307~~D4806 ~~Practice for Preparation of Liquid Blends for Use as Analytical Standards~~Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
~~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_1 to C_4 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)
D5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy
~~D5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method) (Withdrawn 2012)[4]~~
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
D5798 Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D7328 Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection
D7667 Test Method for Determination of Corrosiveness to Silver by Automotive Spark-Ignition Engine Fuel—Thin Silver Strip Method
D7671 Test Method for Corrosiveness to Silver by Automotive Spark–Ignition Engine Fuel–Silver Strip Method
D7757 Test Method for Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
D7920 Test Method for Determination of Fuel Methanol (M99) and Methanol Fuel Blends (M10 to M99) by Gas Chromatography
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)[4]~~

3. Terminology

3.1 For general terminology, refer to Terminology D4175.

~~3.2 *Definitions:*~~

~~3.2.1 *finished fuel, n*—a homogeneous mixture of blendstocks and fuel additives meeting all specification and regulatory requirements for its intended use at the location where sold.~~

~~3.2.2 *methanol, n*—methyl alcohol, the chemical compound CH_3OH.~~

3.2 ~~*Definitions of Terms Specific to This Standard:*~~*Definitions:*

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

~~3.3.1.1 *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.~~

3.2.1.1 *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 *denatured fuel ethanol, n*—ethanol made unfit for beverage use by the addition of denaturants under formula(s) approved by the applicable regulatory agency to prevent the imposition of beverage alcohol tax. **D4806**

3.2.3 *ethanol, n*—ethyl alcohol, the chemical compound C_2H_5OH. **D4806**

3.2.4 *~~fuel methanol~~finished fuel, ~~(M70-M85)~~—n*—a ~~blend~~ homogeneous mixture of ~~methanol and hydrocarbons of which the methanol portion is nominally 70 to 85 volume %.~~blendstocks and fuel additives meeting all specification and regulatory requirements for its intended use at the location where sold.

3.2.5 *fuel methanol (M99), n*—methanol with small/trace alcohol and hydrocarbon impurities.

3.2.6 *gasoline, n*—volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines. **D4814**

3.2.7 *gasoline blendstock, n*—a liquid hydrocarbon component suitable for use in spark-ignition engine fuels.

3.2.7.1 *Discussion*—

Examples of gasoline blendstock include natural gasoline, raffinate, reformate, naphtha, conventional gasoline blendstock for oxygenated blending (CBOB), and reformulated gasoline blendstock for oxygenate blending (RBOB).

3.2.8 *higher alcohols*—aliphatic alcohols of the general formula $C_nH_{2\ n+1}OH$ with *n* being 2 to 8.

3.2.9 *hydrocarbon*—~~those components in a methanol-hydrocarbon blend that contain only~~ a compound composed solely of hydrogen and carbon.

3.2.10 *methanol, n*—methyl alcohol, the chemical compound CH_3OH.

3.2.11 *methanol fuel blend (M51–M85), n*—a blend of methanol and hydrocarbons of which the methanol portion is nominally 51 % to 85 % by volume.

3.2.11.1 *Discussion*—

In the abbreviation, MXX, the XX represents the volume percentage of methanol in the fuel blend.

4. Ordering Information

4.1 The purchasing agency shall:

4.1.1 Indicate the season and locality in which the fuel is to be used,

4.1.2 If requested, ensure that the methanol concentration meets the requirements for an alternative fuel for United States federal fleets.

4.1.3 For further information, see Annex A1 of this specification.

5. ~~Fuel~~ Methanol ~~(M70-M85)~~ Fuel Blends Performance Requirements

5.1 Methanol fuel blends shall conform to the requirements in Table 1.

NOTE 1—Most of the requirements cited in Table 1 are based on the best technical information currently available. As greater experience is gained from field use of methanol-capable vehicles, some of these requirements will change.

5.1.1 The components used to produce methanol fuel blends are limited to methanol and gasoline blendstock as defined in 5.2.

TABLE 1 Requirements for Methanol Fuel Blends (M51–M85)

Properties	Class 1[A]	Class 2	Class 3	Test Methods Annex A1 D4953 or D5191
Vapor pressure, kPa[B] (psi)	48–62 (7.0–9.0)	62–83 (9.0–12.0)	83–103 (12.0–15.0)	
		All Classes[C]		
Methanol Content, % by volume, min		51–85		D7920
Lead, mg/L, max		2.6		D5059[D]
Phosphorus, mg/L, max		0.2		D3231
Sulfur, mg/kg, max		80		D5453
Acidity, as acetic acid, mg/kg, max		50		D1613
Unwashed gum content, mg/100 mL, max		20		D381
Solvent washed gum content, mg/100 mL, max		5		D381
Total Inorganic Sulfate, mg/kg, max		4		D7328
Water, % by mass, max		0.5		E203
Total Inorganic Chloride, mg/kg, max		1		D7328

[A] See 5.3 for volatility class criteria.
[B] The vapor pressure overlap is intentional to cover changes associated with seasonal changes.
[C] Methanol content and selection of gasoline blendstock are adjusted by the blender to meet vapor pressure requirements. See X1.3.3 for additional information and guidance for blending.
[D] With Test Methods D5059, prepare the calibration standards using methanol (reagent grade) as the solvent to prevent errors caused by large differences in carbon-hydrogen ratios.

5.1.2 The intentional addition of lead or phosphorus compounds to methanol fuel blends is not permitted.

5.2 Gasoline blendstocks used shall meet the requirements of Table 2. The gasoline blendstock may contain aliphatic ethers as blending components that are used in automotive fuels in some countries outside of North America.

5.3 Vapor pressure is varied for seasonal and climatic changes by providing three vapor pressure classes for methanol fuel blends as follows:

(1) Class 1 encompasses geographical areas with 6 h tenth-percentile minimum ambient temperature of greater than 5 °C (41 °F).

(2) Class 2 encompasses geographical areas with 6 h tenth-percentile minimum temperatures of greater than –5 °C (23 °F) but less than or equal to 5 °C (41 °F).

(3) Class 3 encompasses geographical areas with 6 h tenth-percentile minimum ambient temperature less than or equal to –5 °C (23 °F).

5.3.1 There is a 10 % probability that the highest temperature of the six coldest consecutive hourly temperature readings of a 24 h day will be colder than the 6 h tenth percentile minimum ambient temperature.

5.3.2 See 5.4.2 for seasonal and geographical distributions in the United States.

5.4 *Regulatory and Other Requirements in the United States:*

5.4.1 Methanol content and other requirements for methanol alternative fuel blends in the United States can be found in Annex A1 of this standard.

5.4.2 The United States seasonal and geographical distribution for the three vapor pressure classes is shown in Annex A1, Table A1.1.

5.5 *Regulatory and Other Requirements Outside the United States:*

5.5.1 Users of this specification are advised to consult with the applicable regulatory agency for specific requirements for their jurisdictions.

5.5.2 Users of the specification in geographical areas outside the United States need to determine the 6 h tenth percentile minimum ambient temperatures for their geographic areas and times of year in order to select the appropriate classes of fuel.

5.6 ~~Fuel methanol (M70-M85) shall conform to the requirements~~ Use of unprotected aluminum in methanol fuel blend 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 ~~Table 1.~~methanol fuel blend distribution and dispensing systems.[4,5]

~~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~~

[4] ~~The last approved version of this historical standard is referenced on www.astm.org.~~California Energy Commission, "Fifteen Years of Fuel Methanol Distribution," http://www.methanol.org/Energy/Resources/Alternative-Fuel/CEC- 1996-ISAF-Fuel-Meoh-Paper.aspx

[5] ~~American Automobile Manufacturers Association, "Fuel Methanol Compatibility Standards and Dispensing Equipment List for M85 Fueled Vehicles," October 1994.~~

[5] ~~A Valco Model No. CM-VSV-10-HT valve with 1.6-mm (~~California Air Resources Board, Methanol Fuel Additive Demonstration, http://arb.ca.gov/research/apr/past/a832-123a~~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 (1/32 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,[1] which you may attend.~~

TABLE 2 Requirements for Gasoline Blendstock

Properties		Test Methods
Distillation, end point, °C(°F), max	225 (437)	D86
Oxidation stability, minutes, min	240	D525
Copper strip corrosion, max	No. 1	D130
Silver strip corrosion, max	No. 1	D7667, D7671
Vapor pressure, kPa	Report[A]	D4953, D5191

[A] While not a requirement of this specification, the blender will need to know the vapor pressure of the gasoline blendstock in order to choose a suitable blend ratio for the components to meet the vapor pressure requirement of a particular volatility class.

~~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.[5]~~

6. Workmanship

6.1 The finished fuel blend shall be visually free of sediment, suspended, or undissolved matter. It shall be clear and bright at the fuel temperature at the point of custody transfer or at a lower temperature agreed upon by the purchaser and seller.

NOTE 2—Finished fuel should be resistant to phase separation or undissolved matter at the lowest temperatures to which it is likely to be subjected, dependent on the time and place of its intended use. See Specification D4814, Table X7.1 for guidance.

NOTE 3—Solubility is temperature dependent. As this fuel cools, some high molecular weight additives can become insoluble.

~~NOTE 2—Finished fuel should be resistant to phase separation or undissolved matter at the lowest temperatures to which it is likely to be subjected, dependent on the time and place of its intended use. See Specification D4814, Table X7.1 for guidance.~~

~~NOTE 3—Solubility is temperature dependent. As this fuel cools, some high molecular weight additives can become insoluble.~~

6.2 The specification defines only a basic purity for ~~Fuel Methanol (M70–M85).~~ methanol fuel blend (M51–M85). The product shall be free of any adulterant or contaminant that can render the material unacceptable for its commonly used applications.

6.2.1 Manufacturers and blenders of ~~Fuel Methanol (M70–M85)~~ methanol fuel blend (M51–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).~~ methanol fuel blend (M51–M85). No specification limits have been established for silicon.

7. Sampling, Containers, and Sample Handling

7.1 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.

7.2 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.

7.3 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~~ methanol fuel blends should be sampled in amber borosilicate glass containers. If samples must be collected in metal containers, do not use soldered metal containers. ~~This is because the~~ The soldering flux in the containers and the lead in the solder can contaminate the sample. Plastic containers should be avoided.

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

8. Test Methods

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

NOTE 4—The appropriateness of ASTM test methods cited has not been demonstrated for use with ~~M70-M85.~~M51–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 7.1.9). 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.~~

8.1.1 *Vapor Pressure*—Test Methods D4953, ~~D5190,~~ or D5191.

8.1.2 ~~*Acidity*—~~*Methanol Content*—Test Method ~~D1613~~D7920.

~~7.1.5 *Gum Content, Solvent Washed and Unwashed*—Test Method D381.~~

~~7.1.6 *Total Chlorine as Chloride* —Test Methods D4929, Method B.~~

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

8.1.4 *Phosphorus*—Test Method D3231.

8.1.5 *Sulfur*—Test Methods D1266 or D5453.

8.1.6 *Acidity*—Test Method D1613.

8.1.7 *Gum Content, Solvent Washed and Unwashed*—Test Method D381.

8.1.8 *Total Sulfates*—Test Method D7328.

8.1.9 *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.~~

8.1.10 *Total Inorganic Chloride*—~~Inorganic~~ Total inorganic chloride ~~can~~may be determined by ~~Test Methods~~a modification of Test Method ~~D512~~D7328~~–81(1985),~~[ε1] ~~(Method C). Also, see~~ a standard test method for determination of total inorganic chloride in fuel ethanol by ion chromatography using aqueous sample injection. Refer to Test Method D7328~~the~~ for terminology, equipment required, reagents and solutions, calibration procedures, and general procedure for the determination of total inorganic chloride in fuel ethanol. Note that although Test Method D7328~~test method~~ is also the standard test method for determination of existent and potential inorganic sulfate in ~~Annex A3. Another test method is under development.~~fuel ethanol, that determination is addressed separately in Specification D5797, the standard specification for methanol fuel blends. The procedure for total inorganic chloride determination will be summarized:

8.1.10.1 Obtain a well-mixed homogeneous sample of methanol fuel blend in a glass container, equipped with closures that can be well-sealed, and free of any residual or extractable chloride. If containers have been cleaned and rinsed with water, they should be thoroughly rinsed with Type II or better reagent water according to Specification D1193 and dried prior to use.

8.1.10.2 Thoroughly mix the sample in its container immediately prior to withdrawal of the test specimen.

8.1.10.3 Set up the ion chromatograph in accordance with the manufacturer's instructions.

8.1.10.4 Equilibrate the system by pumping eluent for 15 min to 30 min, until a stable baseline is obtained.

8.1.10.5 Start the chromatographic run in accordance with manufacturer's instructions.

8.1.10.6 Carefully add 2.00 mL of the methanol fuel blend test specimen into a clean, dry, tared 15 mL glass vial without its screw cap closure.

8.1.10.7 Place the vial with sample in a hot block at 65 °C and blow a steady stream of nitrogen gas over the sample at 2 mL/min to 3 mL/min flowrate. Maintain these conditions for 15 min. Remove the vial from the hot block and allow it to cool to room temperature 15 °C to 27 °C. Note that it is probable that a small amount of liquid remains. Do not worry about this residue since any inorganic chloride will be extracted into the water phase.

8.1.10.8 Carefully add 2.00 mL of Type II or better water to the dried sample. Seal the vial with a screw cap, and shake the vial vigorously to dissolve all of the solid salts.

8.1.10.9 If an emulsion results after these steps, pass the liquid through a column or cartridge designed specifically to remove hydrocarbons from liquids prior to injecting them in an ion chromatograph.

8.1.10.10 Inject 25 µL of the resulting clear solution or eluent into the ion chromatograph, and measure the area of the peak corresponding to chloride ion.

8.1.10.11 Calculate the concentration of inorganic chloride in the original sample according to the procedures shown in Section 12 of Test Method D7328.

9. Keywords

9.1 acidity; alcohol; automotive spark-ignition engine fuel; chloride; copper corrosion; ether; fuel methanol ~~(M70-M85) for automotive spark-ignition engines;~~ (M99); gasoline blendstock; gum content; hydrocarbon; hydrocarbon blendstock; inorganic chloride; lead; ~~MTBE;~~methanol; ~~M70-M85;~~ methanol fuel blends (M51–M85); ~~methanol;~~MTBE; oxidation stability; oxygenates; phosphorus; solvent washed; sulfur; ~~total chlorine;~~ vapor pressure; volatility; water

~~ANNEXES~~ANNEX

(Mandatory Information)

A1. ~~TEST METHOD FOR DETERMINATION OF METHANOL IN FUEL METHANOL (M70-M85) FOR~~INFORMATION SPECIFIC TO THE UNITED STATES ~~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*[2,3]:~~ ~~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.

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.[6]

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(*1*) 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,[7] 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 g 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.

TABLE ~~2~~ A1.1 United States Seasonal and Geographical Volatility Specifications for Methanol Fuel ~~Methanol (M70-M85)~~Blends (M51-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.

NOTE 2—Where alternative classes are listed, either class is acceptable; the option shall be exercised by the seller.

NOTE 3—This schedule was developed using actual (versus altitude-adjusted) 6 h tenth percentile minimum ambient temperatures

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~~
Southern Region	3	3	3	3/2	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~~
South Mainland	3	3	3	3	3/2	2	2/1	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[A]												
~~North Coast~~	~~2~~	~~2~~	~~2~~	~~2~~	~~2~~	~~2/1~~	~~1~~	~~1~~	~~1~~	~~1/2~~	~~2~~	~~2~~
North Coast	2	2	2	2	2/1	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~~
South Coast	2	2	2	2	2/1	1	1	1	1	1/2	2	2
~~Southeast~~	~~3~~	~~3/2~~	~~2~~	~~2~~	~~2/1~~	~~1~~	~~1~~	~~1~~	~~1/2~~	~~2~~	~~2/3~~	~~3~~
Southeast	2	2	2	2	2/1	1	1	1	1	1/2	2	2
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	1/2	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	1/2	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~~
S of 38° Latitude	2	2	2	2	2/1	1	1	1	1	1/2	2	2
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	1/2	2/3	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~~
Ohio	3	3	3	3/2	2	2/1	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												

TABLE A1.1 *Continued*

State	January	February	March	April	May	June	July	August	September	October	November	December
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	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
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~~
E of 122° Longitude	3	3	3	3/2	2	2	2/ 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

[A] Details of State Climatological Division by county as indicated:

California, North Coast—Alameda, Contra Costa, Del Norte, Humbolt, 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)

~~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(*1*) 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 µm 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.)~~

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

A1.1 ~~Preparation of Column Packing~~

~~A1.8.1 *Preparation of TCEP Column Packing:*~~