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Standard Specification for Methanol Fuel Blends (M51–M85) for Methanol-Capable Automotive Spark-Ignition Engines¹

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1. Scope*

1.1 This specification covers the requirements for automotive fuel blends of methanol and gasoline for use in ground vehicles 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 (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.

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

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards*:^{2,3}

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

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
 D525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)
 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
 D3231 Test Method for Phosphorus in Gasoline
 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
 D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
 D4814 Specification for Automotive Spark-Ignition Engine Fuel
 D4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)
 D5059 Test Methods for Lead and Manganese in Gasoline by X-Ray Fluorescence Spectroscopy
 D5191 Test Method for Vapor Pressure of Petroleum Products and Liquid Fuels (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
 D7923 Test Method for Water in Ethanol and Hydrocarbon Blends by Karl Fischer Titration
 E203 Test Method for Water Using Volumetric Karl Fischer Titration

3. Terminology

3.1 For general terminology, refer to Terminology **D4175**.

3.2 Definitions:

3.2.1 *aliphatic 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.

3.2.1.1 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.

3.2.1 *denatured fuel ethanol, n*—fuel 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**

3.2.2 *ethanol, n*—ethyl alcohol, the chemical compound CH_3CH_2OH . **D4806**

3.2.3 *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.

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

3.2.5 *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**

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

3.2.6.1 *Discussion*—

Examples of gasoline blendstock include natural gasoline, raffinate, reformat, 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 $C_nH_{2n+1}OH$ with n being 2 to 8.

3.2.7 *hydrocarbon*—a compound composed solely of hydrogen and carbon.

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

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

3.2.9.1 *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. Methanol Fuel Blends Performance Requirements

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

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)	
Methanol Content, % by volume, min		All Classes ^C 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		D7923 or 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.

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.

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 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

TABLE 2 Requirements for Gasoline Blendstock

Properties	Test Methods	
Distillation, end point, °C(°F), max	225 (437)	D86
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.

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 methanol fuel blend distribution and dispensing systems.^{4,5}

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.

6.2 The specification defines only a basic purity for 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 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 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, 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. 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) 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 M51–M85. In addition, test methods contained in the annexes and appendixes are in the developmental stages or lack precision and bias determinations.

8.1.1 *Vapor Pressure*—Test Methods **D4953** or **D5191**.

8.1.2 *Methanol Content*—Test Method **D7920**.

8.1.3 *Lead*—Test Methods **D5059**. 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.

8.1.4 *Phosphorus*—Test Method **D3231**.

⁴ 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 California Air Resources Board, Methanol Fuel Additive Demonstration, <http://arb.ca.gov/research/apr/past/a832-123a>

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 **D7923** or **E203**.

8.1.10 *Total Inorganic Chloride*—Total inorganic chloride may be determined by a modification of Test Method **D7328**, 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** 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** is also the standard test method for determination of existent and potential inorganic sulfate in 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 (M99); gasoline blendstock; gum content; hydrocarbon; hydrocarbon blendstock; inorganic chloride; lead; methanol; methanol fuel blends (M51–M85); MTBE; oxidation stability; oxygenates; phosphorus; solvent washed; sulfur; vapor pressure; volatility; water

(Mandatory Information)**A1. INFORMATION SPECIFIC TO THE UNITED STATES**

A1.1 The composition of alternative fuels in the United States is regulated by various government agencies and regulations including the U.S. Department of Energy (DOE) and U.S. Environmental Protection Agency (EPA). With regard to fuel properties including volatility, this specification can be more or less restrictive than DOE or EPA rules, regulations and waivers. To qualify as an alternative fuel for federal fleet use in the United States, methanol fuel blends are required to meet the U.S. Department of Energy’s definition of alternative fuels, enacted under the Energy Policy Act of 1992 (Title III, Sec. 301). For methanol, the Act defines “alternative fuel” as “mixtures containing 85 % or more (or such other percentage, but not less than 70 %, as determined by the Secretary, by rule, to provide for requirements to cold start, safety, or vehicle functions) by volume of methanol.” The U.S. government has other programs and definitions for alternative fuels. Users of this specification are advised to check with the applicable regulatory agency for specific alternative fuel requirements.

A1.2 Methanol fuel blends of any volatility class shall meet the same limits for lead and phosphorus as required by U.S. Environmental Protection Agency (EPA) regulations for unleaded gasoline. EPA regulations limit “the maximum concentration of lead in unleaded gasoline to 0.013 g/L(0.05 g lead/US gal) and the maximum concentration of phosphorus in unleaded gasoline to 0.0013 g/L (0.005 g/US gal), respectively.” Details of the EPA regulations and test methods are available in the United States Code of Federal Regulations, Title 40, Part 80.

A1.3 **Table A1.1** provides the United States seasonal and geographical volatility specifications for methanol fuel blends.

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