Designation: D7920 – 15ε1

Standard Test Method for Determination of Fuel Methanol (M99) and Methanol Fuel Blends (M10 to M99) by Gas Chromatography[1]

This standard is issued under the fixed designation D7920; 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.

ε[1] NOTE—Section 16 was corrected editorially in September 2015.

1. Scope

1.1 This test method covers the determination of the methanol content, by gas chromatography, of M10 to M99 in methanol fuel blends, including fuel methanol (M99).

1.1.1 Methanol may be determined from 10 % to 99 % by volume.

1.2 This test method is designed to measure not only methanol in the blended gasoline but also the impurities in fuel methanol (M99) itself in the range of 5 mg/kg to 1000 mg/kg. However, not all impurities are measured nor detected by this test method.

1.2.1 Water cannot be determined by this test method and shall be measured by a procedure such as Test Method D1364 and the result used to correct the concentrations determined by this test method.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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]

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants

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

D4814 Specification for Automotive Spark-Ignition Engine Fuel

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D5797 Specification for Fuel Methanol (M70-M85) for Automotive Spark-Ignition Engines

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

3. Terminology

3.1 This test method makes reference to many common chromatographic procedures, terms, and relationships. Detailed definitions can be found in Terminology D4175 and Practices D4626, E355, and E594.

3.2 *Definitions:*

3.2.1 *analyte, n*—a specific compound to be measured quantitatively in a mixture of compounds.

3.2.2 *analytical column, n*—a chromatographic column used to further separate a specific analyte from a mixture of compounds which can coelute in the primary column.

3.2.3 *analytical detector, n*—a device used to quantify the compounds of interest after they elute from the analytical column.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

Current edition approved Aug. 1, 2015. Published September 2015. DOI: 10.1520/D7920-15E01.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.4 *fuel methanol (M99), n*—methyl alcohol produced for the purpose of blending with gasoline to make a fuel for spark-ignition internal combustion engines.

3.2.4.1 *Discussion*—Fuel methanol is typically produced with 99 % by volume methyl alcohol.

3.2.5 *gasoline, n*—a 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 *heart-cut, n—in gas chromatography*, a procedure in which the analyte in question is transferred from one column to a different column, usually of the opposite polarity.

3.2.7 *internal standard (IS), n*—a high purity compound not present in the sample which is added to the sample and used to calculate quantitatively the component of interest.

3.2.7.1 *Discussion*—The internal standard is added in a constant amount to all calibration standards, see 7.4.2.1.

3.2.8 *mass response factor (MRF), n*—a constant of proportionality that converts area percent to mass percent.

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

3.2.10 *methanol fuel blend, n*—a fuel consisting primarily of a mixture of methanol with gasoline.

3.2.10.1 *Discussion*—Typically methanol fuel blends are 70 % to 85 % by volume, identified as M70 to M85.

3.2.11 *microfluidic device, n*—a chromatographic switching valve constructed with micro channels, usually having five ports and to which the columns, restrictors and auxiliary pressure devices are connected in order to carry out a heart-cut.

3.2.11.1 *Discussion*—An auxiliary carrier gas is fed to the device which has two ports of entry such that switching the carrier gas from one port to the other results in changing the direction of the flow of the primary column to either a restrictor or to the analytical column.

3.2.12 *monitor detector, n*—a device used to measure the elution of the analyte from the primary column.

3.2.12.1 *Discussion*—The monitor detector is used to determine the heart-cut time (see 6.1.1), that is, the time where the peak of interest begins and where the peak of interest ends.

3.2.13 *MXX, n*—an abbreviation that represents a fuel consisting primarily of methanol (methyl alcohol) and hydrocarbons in which 'XX' is the percent by volume of methanol in the blended fuel.

3.2.14 *primary column, n*—in chromatography, a device used to perform a primary separation of a mixture of compounds.

3.2.14.1 *Discussion*—The primary column, also known as a monitor column, is used to separate the analyte of interest and to determine the start time and the end time of the heart-cut.

4. Summary of Test Method

4.1 The sample is injected in to the gas chromatograph where components are separated in the primary column and subsequently are eluted through the restrictor and detected by the monitor detector. The methanol is identified and the heart-cut window is determined. The instrument settings are set to transfer the methanol from the primary column to the analytical column. A further separation takes place in the analytical polar column suitable for the polarity of methanol. After elution from the secondary column, the methanol is analyzed by the analytical detector. Fuel methanol (M99) is analyzed by the primary column only without the execution of a heart-cut. Analysis is made in the monitor detector. In the case of fuel methanol (M99) the mass percent is determined by difference.

5. Significance and Use

5.1 Methanol is used in blends with gasoline at levels of 70 % to 85 % by volume, as specified in Specification D5797. This test method provides a quantitative approach to measure the methanol content in methanol fuel blends, from 10 % to 99 % by volume. The usual concentration is 70 % to 85 % by volume (M70 to M85). The method is also used to analyze fuel methanol (M99) prior to blending.

6. Apparatus

6.1 *Gas Chromatograph,* capable of operating at the conditions listed in Table 1 and Table 2. A heated flash vaporizing inlet, also known as a split inlet, is designed to provide a linear sample split injection (for example, 500:1). This inlet is required for proper sample introduction. Carrier gas controls shall be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. Pressure and flow control devices used shall be designed to attain the linear velocity required for optimum operation of the columns. Two separate flame ionization detectors are required for this test method. The use of one detector alone is not possible as the setting of the heart-cut times will be difficult and the reliability of the exact cut time determination may be compromised. Detectors should meet the sensitivity criteria of Practice E594.

6.1.1 A heart-cut is a technique which utilizes a switching device to which the following five (5) components are connected: (*1*) a primary column, usually non-polar which spans from the inlet to the device, (*2*) an analytical column, usually

TABLE 1 Conditions for Analysis of Methanol Fuel Blend—Carrier Helium

Valve ON interval, min	2.37–2.60	3.25–3.36
Inlet temperature, °C	250	
Split ratio	500/1	
Primary column pressure, kPa	259.2	
Primary column flow, mL/min	2	
Analytical column pressure, kPa	190.1	
Analytical column, flow, mL/min	3	
Oven, initial T °C	50	
Initial hold time, min	5.5	
Oven temperature rate, °C /min	15	
Final oven temperature, °C	190	
Final hold time, min	3	
Analytical FID, T °C	300	
Hydrogen, mL/min	45	
Air, mL/min	450	
Make up, N_2 mL/min	25	
Monitor, FID, T °C	300	
Hydrogen, mL/min	45	
Air, mL/min	450	
Make up, N_2 mL/min	25	
Volume injected, µL	0.2	

TABLE 2 Conditions for Analysis of Methanol Fuel Blend—Carrier Hydrogen

Valve ON interval, min	1.42-1.52	1.94–2.06
Inlet temperature, °C	250	
Split ratio	500/1	
Primary column pressure, kPa	172.6	
Primary column flow, mL/min	2.5	
Analytical column pressure, kPa	120.7	
Analytical column, flow, mL/min	3.5	
Oven, initial T °C	50	
Initial hold time, min	5.5	
Oven temperature rate, °C /min	15	
Final oven temperature, °C	190	
Final hold time, min	3	
Analytical FID, T °C	300	
Hydrogen, mL/min	45	
Air, mL/min	450	
Make up, N_2 mL/min	25	
Monitor, FID, T °C	300	
Hydrogen, mL/min	45	
Air, mL/min	450	
Make up, N_2 mL/min	25	
Volume injected, µL	0.2	

a polar column, that spans from the device to the analytical detector, (*3*) a restrictor or a tubing of small diameter which connects from the device to a second detector whose function is to serve as the monitor detector, (*4*) an external pressure device which controls the pressure at the point where the two columns coincide, and finally, (*5*), a solenoid that directs the pressure to the two points of the device. By switching the applied pressure, the components eluting from the primary column can either be sent to the monitor detector or to the analytical column where further separation occurs and thus the compounds of interest elute at the analytical detector.

6.2 *Sample Introduction System*—Automated liquid injection to the split inlet is required. Devices capable of 0.2 µL to 2.0 µL injections is suitable.

6.3 *Columns*—The precision for this test method was developed utilizing fused silica open tubular columns with non-polar polydimethylsiloxane bonded (cross-linked) phase coating and a polyethylene glycol coated fused silica column.

6.3.1 *Primary Column*—An open tubular column with a non-polar polydimethylsiloxane bonded (cross-linked) phase coating, having 30 m by 0.25 mm with a 0.25 µm film thickness, is used as primary column. This column is installed from the split inlet to the microfluidic device. Follow Practice E1510 for column installation at the split inlet. The column is also inserted to the proper port of the microfluidic device with an appropriate ferrule. Follow the instructions of the manufacturer of the microfluidic device when inserting the column and setting the ferrule to the column. Utmost care is required when making the connection of the ferrule to the device in order not to crack the fused silica column.

6.3.2 *Analytical Column*—A second open tubular column, 30 m by 0.25 mm with a film thickness 0.25 µm, containing a polyethylene glycol phase which is a polar phase. One end of this analytical column is inserted into the microfluidic device and the opposite end is connected to the analytical detector. Observe the same precautions in making the connections as described in 6.3.1.

6.3.3 A *balance restrictor* is required; composed of inert deactivated fused silica whose dimensions provide the same flow resistance as that of the analytical column while minimizing the holdup time of peaks eluting from the primary column to the monitor detector. A typical sized restrictor will be of approximately 1 m in length and 0.1 mm internal diameter. It is connected from the device to the monitor detector. This length is sufficient to accommodate the equivalent pneumatic resistance of the analytical column. The dimensions of the restrictor facilitate the fast transfer of the eluents from the primary column so as to provide negligible delay in reaching the monitor detector. Thus accurate cut times can be determined.

6.4 *Microfluidic Device*—The microfluidic device shall be treated to become inert in order to avoid adsorption of any components in the sample. It shall be manufactured with extremely small volumes and grooves so as not to introduce peak broadening or dead volumes. These devices are available from several manufacturers.

6.5 *Electronic Pressure Control*—An electronic means of controlling the auxiliary pressure is required to cause the transfer of the components from the primary column to the analytical column. This controller is connected to the microfluidic device through a solenoid. The pressure controller must be capable of controlling pressures to within at least 0.069 kPa.

6.6 *Solenoid*—Device required to switch the direction of the flow from the restrictor point to the analytical column point. Typical solenoids should be capable of executing more than one million cycles. The solenoid should be free of components that may interfere with the analysis. When the solenoid is in the off position the flow of the primary column is sent to the monitor detector (Fig. 1(a)). When the solenoid is in the on position, the flow of the primary column is sent to the analytical column and subsequently to the analytical detector (Fig. 1(b)). A shunt restrictor is placed across the output of the solenoid which provides a trickle of flow to the unswept section.

6.7 The gas chromatograph requires a means to program the pressures required for the transfer of components from the primary to the analytical column as well as to control the inlet pressure during the analysis so as to perform backflush. It is essential that the gas chromatograph be provided with accurate and reproducible oven temperature control. Control may be through hardware or software of the gas chromatograph. In addition software is required to integrate the signals and perform internal standard and or external standard calculations as required.

6.8 A data system is required to acquire data and to control the gas chromatograph's operational variables. A data system is required to perform calibrations and analysis in the internal standard mode. The data systems require that sample mass and internal standard mass be entered. The calculation of response factors are described in Practice D4626.

7. Reagents and Materials

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall