Designation: D7920 – 15$^{\varepsilon 1}$

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.

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[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.

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[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

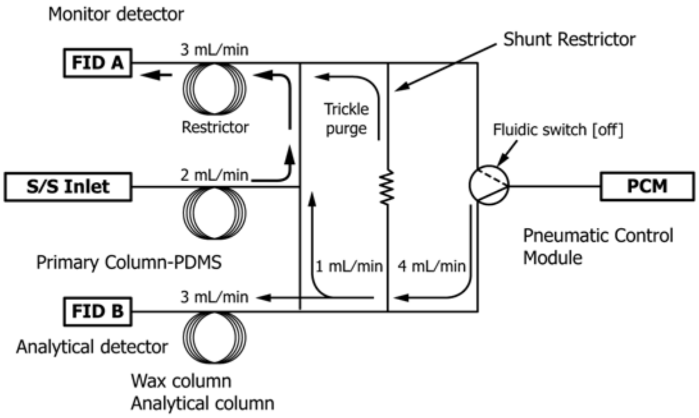

FIG. 1 (a) Heart-cut System Flow to Monitor Detector

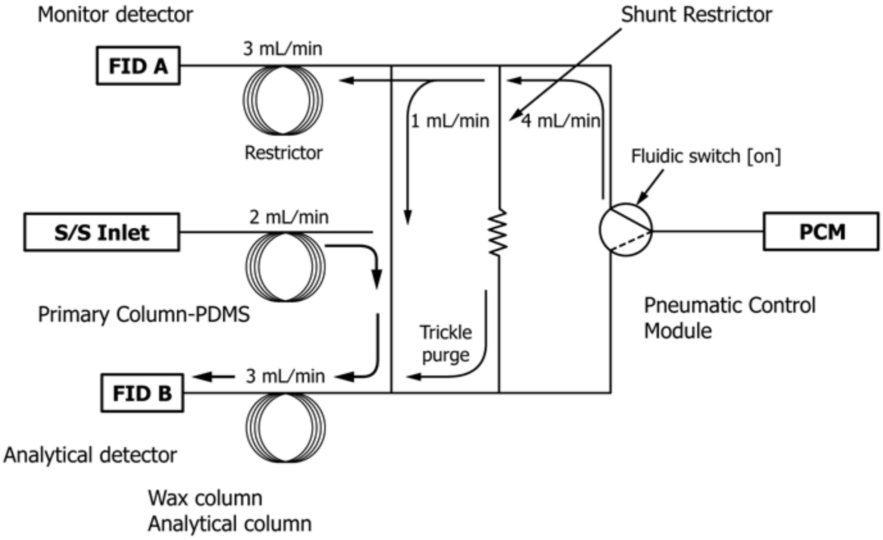

FIG. 1 (b) Heart-cut System Flow to Analytical Detector *(continued)*

conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Consult Practice D4307 in the preparation of standard blends.

7.2 *Carrier Gas*—Helium or hydrogen having at least a minimum purity of 99.95 % can be used as carrier gas. Oxygen removal systems and gas purifiers should be used. (**Warning—**Helium and hydrogen are compressed gases under high pressure). (**Warning—**Hydrogen carrier gas requires additional safety considerations due to its high flammability and potential for explosions. The use of hydrogen sensors for the detection of hydrogen leaks in the GC oven is highly recommended. These devices should be capable of shutting the hydrogen flow to the gas chromatograph.)

7.3 *Detector Gases*—Hydrogen, air, and nitrogen. The minimum purity of the gases used should be 99.95 % for the hydrogen and nitrogen. The air should be hydrocarbon-free grade. Gas purifiers are recommended for the detector gases.

7.4 *Standards for Calibration and Identification*—Standards of all components to be analyzed are required for establishing identification by retention time as well as for the preparation of calibration standards for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed.

7.4.1 *Methanol*—(**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.) Minimum purity required of at least 99 % by volume and free of ethanol. It is recommended that the methanol used in calibration blends be stored over anhydrous sodium sulfate. Water content of the methanol is required for the analysis. Refer to Test Method E1064.

7.4.2 *Ethyl Acetate*—(**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.) This compound is used as the internal standard.

7.4.2.1 The internal standard is added in a constant amount to all calibration standards containing the analyte of interest. A

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[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

plot of the ratio of the area of analyte to internal standard versus the amount of analyte to internal standard yields a linear relationship. The ensuing linear relationship is used to determine the concentration of the analyte in the sample.

7.4.3 *Diluent*—1,2-Dimethoxy ethane (>99 % and anhydrous), methanol free, is used for preparation of calibration standards. This diluent shall be free of any compounds that coelute with methanol and ethyl acetate. (**Warning—**Flammable and may be harmful or fatal, if ingested or inhaled.)

7.4.4 *Gasoline*—Used alternatively as a diluent and as verification of the absence of interfering compounds. The gasoline shall be free of methanol and ethyl acetate. This can be accomplished by analyzing the diluent gasoline as a sample. Verify that the chromatograms do not show the presence of any other component that coelutes with methanol or ethyl acetate.

7.4.5 *Impurities in Fuel Methanol (M99)*—The following additional chemicals are required to determine the response factors of the impurities in the fuel methanol. These chemicals should be at least of the purity defined in 7.1: ethanol, acetone, isopropanol, n-propanol, 2-butanol, isobutanol, and 1-butanol. (**Warning—**All of these chemicals are flammable and may be harmful or fatal, if ingested or inhaled.)

7.5 *Calibration Mixtures*—There are two types of calibration procedures required. One set of calibration mixtures is used for the analysis of fuel methanol (M99). The other calibration mixtures are used for the analysis of methanol in the methanol fuel blends.

7.5.1 *Glassware*—Volumetric flasks 25 mL and 100 mL class A are required. In addition, a 25 mL burette (tolerance 0.03 mL class A TD) with 0.1 mL divisions is needed to prepare the calibration standards. A 10 mL burette (graduated in 0.05 mL) is required to pipette the ethyl acetate.

7.5.2 Check for other impurities such as water. Water cannot be determined with sufficient accuracy by most GC methods and shall be measured by other procedures such as Test Methods D1364 or E1064 and the result used to normalize the chromatographic value. If any of the impurities found are components which are also present in the blend, determine their concentrations and make the appropriate corrections.

7.6 *Preparation of Standards for Methanol in Fuel Analysis*—A guide for the preparation of the methanol fuel blend calibration standards is provided in Table 3. The solutions are prepared in 25 mL volumetric flasks. Final volume is fixed to 25 mL by the addition of 1,2-dimethoxyethane or gasoline (described in 7.4.4) as the diluent.

7.6.1 In a separate 25 mL volumetric flask, pipette 1.0 mL of ethyl acetate and dilute to the mark with the solutions prepared in 7.6. These solutions are used to determine the calibration curve.

7.7 *Preparation of Standards for Fuel Methanol (M99):*

7.7.1 *Response Factor Solution*—For the analysis of fuel methanol, prepare a standard solution containing the components in 7.4.5 at approximately 50 mg/kg. First prepare a stock solution by weighing, to the nearest 0.1 mg, approximately 0.100 g of each component listed in 7.4.5 into a 100 mL volumetric flask. Add reagent grade methanol as the solvent and record the mass of methanol. This will yield a stock solution of approximately 1260 mg/kg of each component. Further prepare a second solution by pipetting 1.0 mL of the stock solution and diluting with methanol in a 25 mL volumetric flask. Record the mass in each step so as to determine the concentrations by mass. The second solution is approximately 50 mg/kg and is used to determine the response factors of the impurities. Calculate the concentration of the impurity in the final solution (C_i) in mg/kg using the following equation:

$$(C_i) = ([w_1 / (w_1 + wm_1)] \times w_2 \times 10^6)/(w_2 + wm_2) \quad (1)$$

where:

w_1 = mass of the impurity in the first solution,
wm_1 = the mass of methanol in the first solution,
w_2 = the mass of the aliquot of the first solution, and
wm_2 = is the mass of methanol of the second solution.

8. Sampling

8.1 Fuel methanol may be sampled into an open container since a vapor pressure of less than 21 kPa (3 psi) is expected. Refer to Practice D4057 for instructions on manual sampling from bulk storage into open containers. Stopper the container immediately after drawing the sample.

8.2 To minimize loss of hydrocarbon light ends, chill the sample (4 ºC or less) before transferring an aliquot into an auto sampler vial. Seal immediately

9. Preparation and Verification of Apparatus

9.1 *Column Installation*—Install the primary column, from the inlet to the microfluidic device. Install the analytical column (wax column) from the device to the analytical detector. Consult Practice E1510, which contains information for installing capillary columns.

9.2 *Restrictor Installation*—Install the restrictor, (0.1 mm I.D. fused silica tubing), from the device to the monitor detector. Use a software calculator (available from the web and called "Dean Switch Calculator") to determine the exact length of the restrictor. The length will be approximately 78 cm. This restrictor has an equivalent pneumatic resistance as the analytical column and its length and diameter is selected to minimize the analyte's holdup time.

TABLE 3 Guidefor the Preparation of the Calibration Standards by Volume for the Analysis of Methanol Fuel Blends

Percent Methanol	10	30	40	50	85	90	95	97	99
Methanol (mL)	2.5	7.5	10	12.5	21.25	22.5	23.75	24.25	24.75
1,2 Dimethoxyethane	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Total Volume (mL)	25	25	25	25	25	25	25	25	25

9.2.1 Use software (see 9.2) to determine the pressures required for helium or hydrogen carriers at 50 °C oven temperature. For helium carrier, set the flows in the software to 2 mL/min for the primary column and for the analytical column set the flow to 3 mL/min which will yield the pressures in Table 1. For hydrogen carrier, set the flows in the software to 2.5 mL/min and 3.5 mL/min for the primary and analytical respectively. These settings will yield the pressure settings in Table 2.

9.3 *Conditions for Fuel Methanol (M99)*—Set the conditions for the gas chromatograph as indicated in Table 1 or Table 2, depending on the carrier gas used.

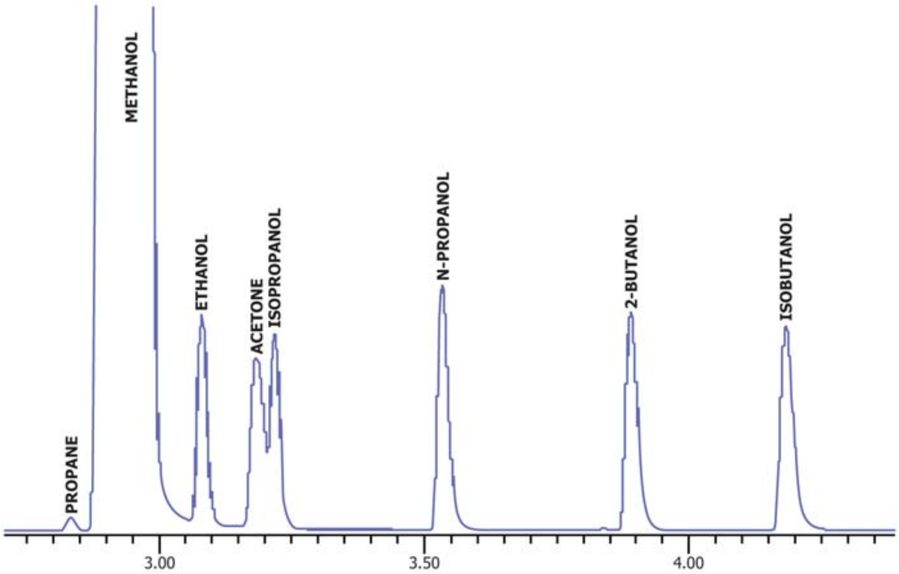
9.3.1 Ensure that the switching valve for the auxiliary gas remains in the off position. Inject 1.0 µL of the calibration standards for the analysis of fuel methanol as prepared in 7.7.1 using the instrument conditions of Table 1 (helium) or Table 2 (hydrogen). The chromatogram is shown in Fig. 2 (helium) and Fig. 3 (hydrogen) where the fuel methanol is analyzed by the primary column. Record the retention times and verify that the retention times are similar to those listed in Table 4. Note that the conditions of Table 1 and Table 2 may yield slightly different retention times.

9.4 *Conditions for Methanol Fuel Blends*—Use the calibrating solution prepared in 7.6.1 containing 85 % methanol and which contains ethyl acetate and 1,2 dimethoxyethane. Prepare the gas chromatograph according to the settings in either Table 1 or Table 2 if using helium or hydrogen carriers. Program the oven to remain isothermal at 50 °C for 5.5 min. Ensure that the valve remains in the off position. The chromatogram obtained from the monitor detector is shown in Fig. 4. A similar chromatogram is obtained when using hydrogen as carrier. The chromatogram is amplified in the data system so as to select the cut windows. Select a time to the left of the methanol peak where the peak begins to rise, at about 0.1 min before the beginning of the rise. Then select the time where the signal has completely returned to the baseline after the methanol peak. The recorded chromatogram can be inspected by using the integration tick marks from the recorded chromatogram as a guide to select the cut window. Select a time 0.1 min larger than the observed baseline time recovery. These two selected times constitute the cut window. Repeat the process for the ethyl acetate. At these two time intervals the solenoid valve is switched on and off as shown in Figures 1A and 1B. It is to be emphasized that the cut times are only given as an example since these values maybe different depending on column dimension values, pneumatic properties, and oven temperature.

9.4.1 Enable the solenoid to turn on and off at the selected cut time as determined in 9.4.

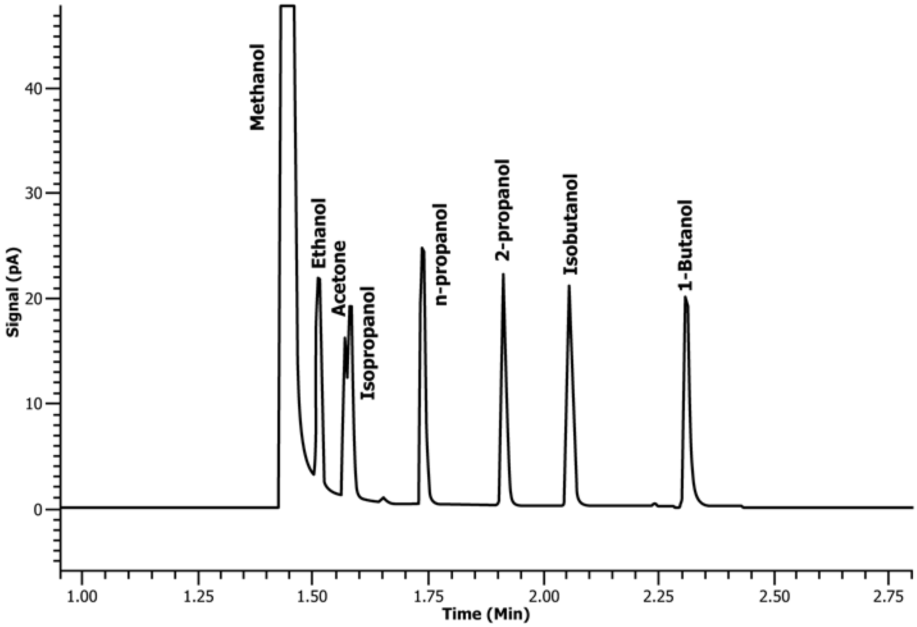
9.4.2 Enable the oven temperature as described in Table 1 or Table 2 but maintained the oven at 50 °C for 5.5 min. Inject the sample prepared in 9.4 containing methanol and ethyl acetate. Record the time necessary for the elution of the ethyl acetate in the analytical column. Add 0.5 min to this time. At this point, the transfer of methanol and ethyl acetate to the analytical column has been completed. Table 4 gives approximate retention times which may differ slightly for different setups.

9.5 *Pressure and Oven Program for Accelerating the Removal of the Matrix*—Enable pressure programs for both columns in order to backflush the remaining gasoline components still to be eluted from the primary column at a time after the ethyl acetate has eluted from the analytical column as recorded in 9.4. The pressure program is also used to accelerate the elution of gasoline which has entered the analytical column. The time chosen for the beginning is the recorded time in 9.4.2. This backflush mode is achieved by raising the pressure of the analytical column to 414 kPa at a high rate (that is, 414 kPa/min to 620 kPa/min) while simultaneously lowering the primary column pressure to 6.89 kPa at a similarly high rate. Maintain this pressure program until the end of the chromatographic run time. The rise in pressure through the analytical column hastens the elution of the matrix. At the same time that the pressure programs are enabled, ramp the oven at



NOTE 1—Approximate concentration is 1200 mg/kg each impurity.

FIG. 2 Chromatogram of Fuel Methanol Obtained from Monitor Detector Showing Typical Impurities (Helium Carrier Gas)



NOTE 1—Approximate concentration is 1200 mg/kg each impurity.

FIG. 3 Chromatogram of Fuel Methanol Obtained From the Monitor Detector Showing Typical Impurities (Hydrogen Carrier Gas)

TABLE 4 Retention Times Obtained for the Analysis of M85 and M99 Using Helium and Hydrogen Carriers

Retention Time (min) for Methanol and Ethyl Acetate in M85 Fuel Blend at 50 °C and Constant Pressure as per Table 1 (Helium) and Table 2 (Hydrogen)

Component	Monitor Column	Analytical Column	Carrier
Methanol	2.418	4.12	Helium
Ethyl Acetate (I.S.)	3.286	4.903	Helium
Methanol	1.448	2.653	Hydrogen
Ethyl Acetate (I.S.)	1.970	3.142	Hydrogen

Retention Time (min) for the Analysis of Fuel Methanol (M99) Obtained from the Monitor Column

Component	Helium	Hydrogen
Methanol	2.971	1.44
Propane	2.831	1.39
Ethanol	3.183	1.509
Acetone	3.216	1.567
Isopropanol	3.534	1.579
n-Propanol	3.89	1.736
2-Butanol	3.985	1.911
Ethyl Acetate (I.S.)	4.063	1.96
Isobutanol	4.184	2.054
1-Butanol	4.703	2.308

25 °C/min to 190 °C and hold 2 min. These actions will result in a run time of 10 min to 12 min. A blank run with no injection will verify the absence of any residual components.

9.6 *Check of Cut Times with a Methanol Fuel Blend*—Prepare a methanol fuel blend by pipetting 16 mL of methanol and 1.0 mL of ethyl acetate in a 25 mL volumetric flask. Dilute to the mark with gasoline described in 7.4.4. Inject this blend under the conditions of Table 1 or Table 2 (helium or hydrogen carrier). Enable the pressure and temperatures programs described in 9.5. Verify that the methanol and ethyl acetate appear in the analytical detector as shown in Fig. 5 (helium carrier) and Fig. 6 (hydrogen carrier).

9.6.1 Inject the gasoline used as described in 9.6. Verify the absence of signal at the times corresponding to the elution of methanol and ethyl acetate. Inspect the chromatogram to verify that there are no peaks merging prior or after the elution of methanol and the internal standard.

9.7 Overloading of the column can cause loss of resolution for some components. Overloaded peaks are skewed and produce variances in retention times. This can lead to erroneous component identification. During column evaluations and split linearity studies, be aware of any peaks that appear front skewed, indicating column overload. Note the component size and avoid conditions leading to this problem during actual

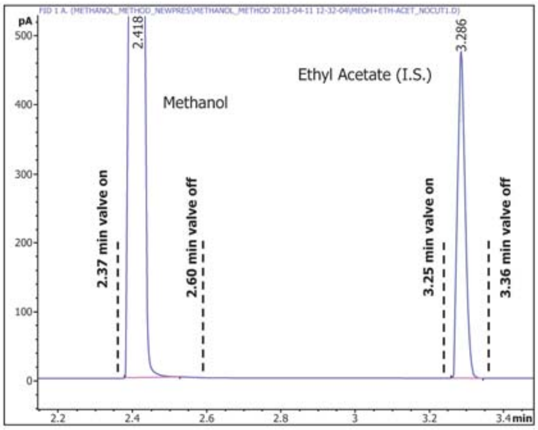


FIG. 4 Chromatogram of Methanol and Ethyl Acetate Mixture for Determining Cut Times (Helium Carrier)

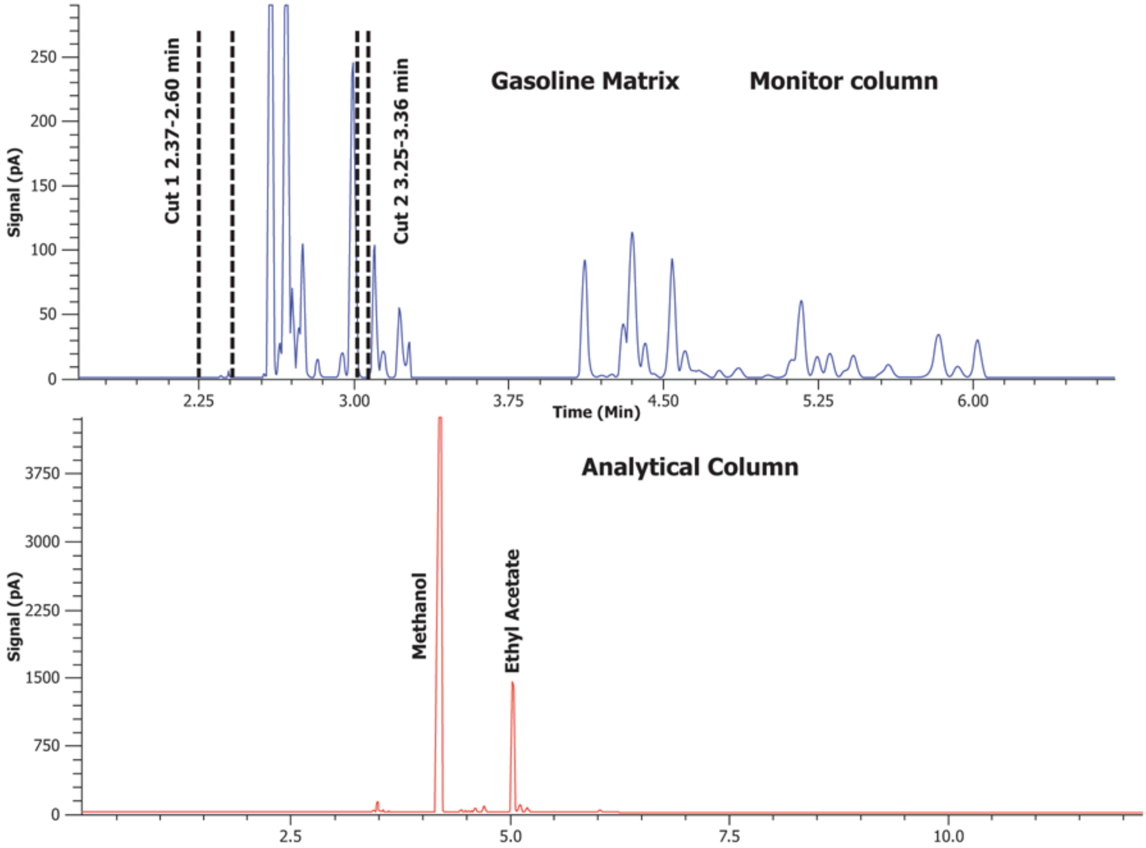


FIG. 5 Chromatogram Obtained from Analytical Detector (Lower Chromatogram) after Executing Heart-cut at Times Indicated in Upper Chromatogram (Helium) Gasoline Matrix

analysis. Refer to Practice E594 for further guidance. Use split ratio of 500:1 for both carriers due to the large concentrations of methanol.

10. Calibration and Standardization

10.1 *Calibration for Analysis of Methanol in Methanol Fuel Blend Analysis,* when preparing standards correct for the percent impurities of the oxygenates used. Whenever possible, use stocks having at least 99.5 % purity or higher.

10.1.1 For the 1,2-dimethoxyethane used in the standard preparation, it is important that the 1,2-dimethoxyethane be examined for the absence of signal where methanol and ethyl acetate elute in the chromatogram. Inject 0.2 µL of the 1,2-dimethoxyethane using the cut times determined in 9.6.

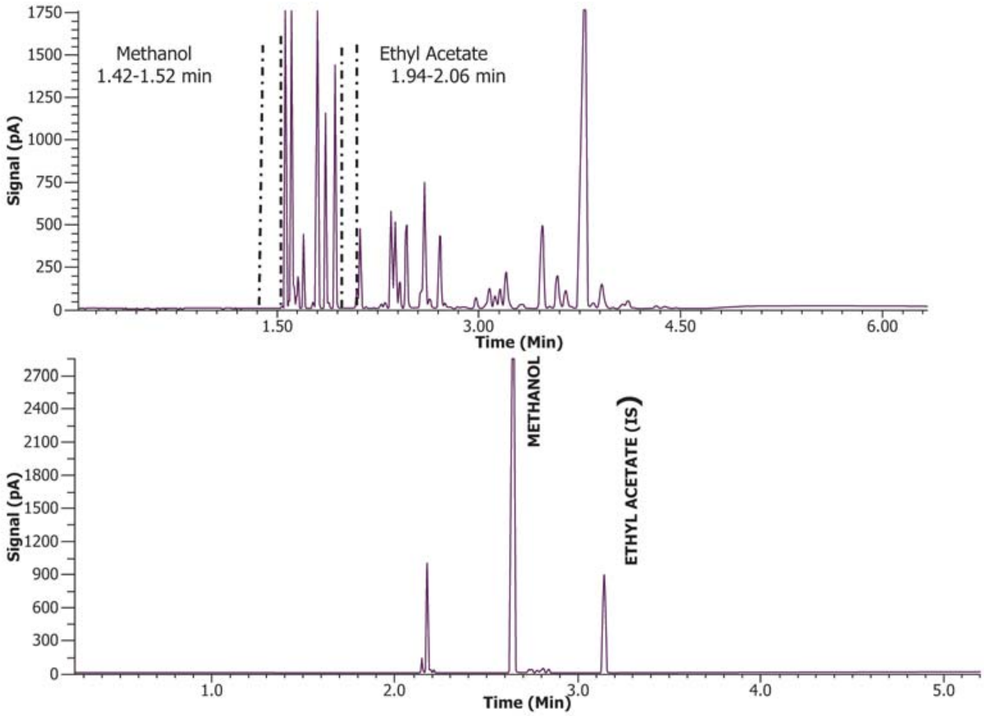


FIG. 6 Chromatogram Obtained from Analytical Detector (Lower Chromatogram) of Methanol Fuel Blend Injection after Executing Heart-cut at Times Indicated in Upper Chromatogram (Hydrogen Carrier)

Verify the absence of peaks at the corresponding times of methanol and ethyl acetate in the analytical column.

10.2 Use the standard solutions prepared in 7.6.1. These standards cover the range from 10 % to 99 % methanol by volume.

10.3 Inject 0.2 µL from the calibration solutions prepared in 7.6.1 in ascending order of the methanol content and verify that the solenoid valve is switched as per the established cut times in 9.4 causing the transfer of the methanol and ethyl acetate to the analytical column.

10.4 Record the areas for the methanol and the internal standard.

10.5 Obtain from the data system, the area ratio of the methanol to the ethyl acetate. Obtain the ratio of the amount of methanol to ethyl acetate from the data of the preparation of the calibration standards (Table 3).

10.6 A plot of the area ratios versus the amount ratios is a linear relationship as seen in Fig. 7 (seven levels) using helium as carrier and Fig. 8 (9 levels) using hydrogen as carrier. Verify

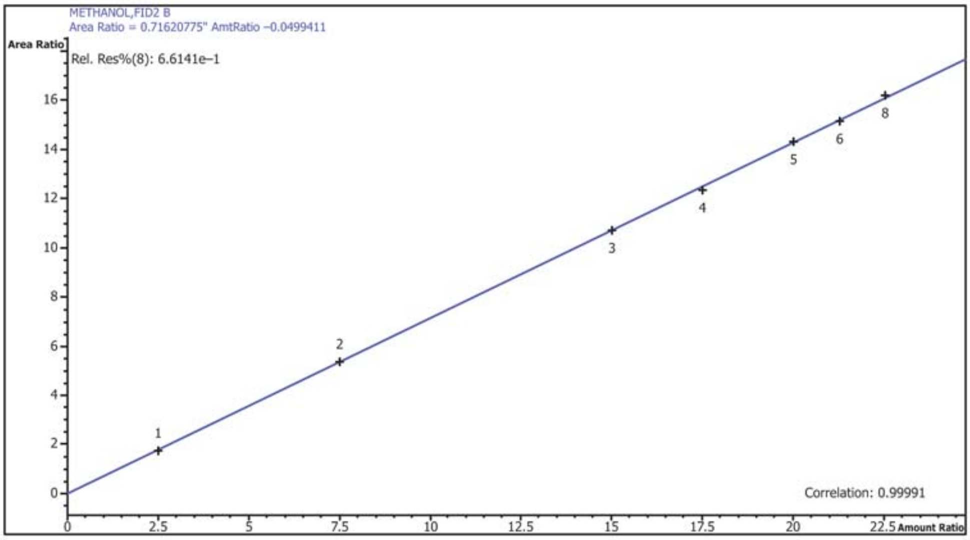


FIG. 7 Linear Plot of Area Ratios versus Volume Amount Ratios for Methanol (Helium Carrier))

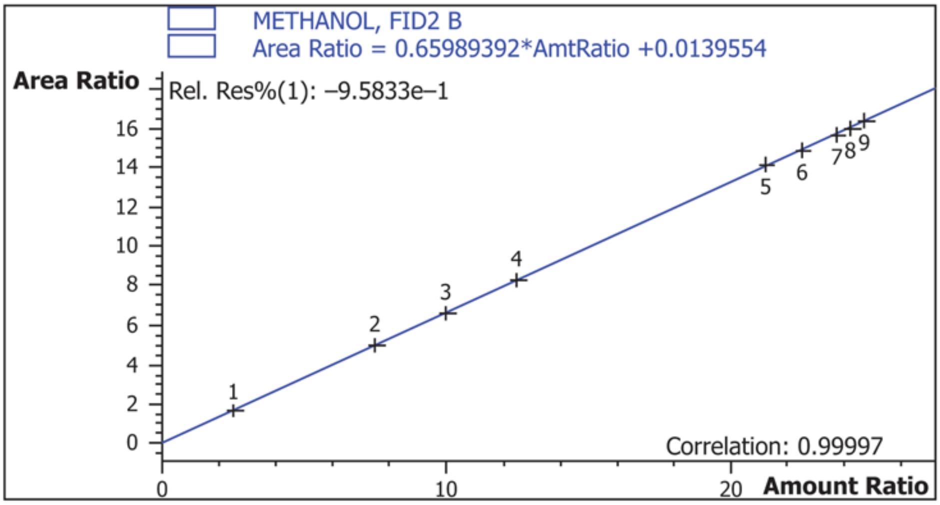


FIG. 8 Linear Plot of Area Ratios versus Amount Ratios (V/V) for Methanol (Hydrogen Carrier) Covering Range 10 % to 99 % Methanol

that the calibration has a correlation coefficient of at least 0.999. Force the calibration through the origin.

10.7 In the event that an electronic data acquisition system is not available use spreadsheet or other software to carry out the calculations as shown below. The spreadsheet will aid in determining a linear regression analysis which yields a linear equation as described in 10.6.

$$\frac{Ai}{As} = \left(\frac{mi}{ms}\right)\left(\frac{1}{RRF}\right) \qquad (2)$$

where:

Ai = area of the methanol standard,
As = area of the ethyl acetate,
mi = volume percent of methanol in the standard, and
ms = the volume percent of the ethyl acetate.

The constant 1/RRF is the slope. RRF is the relative response factor for methanol relative to ethyl acetate.

10.8 *Calibration for Fuel Methanol*—Prepare the calibration standards as described in 7.7.1. Set the instrument to the conditions in Table 1 (helium) or Table 2 (hydrogen). Ensuring that the valve remains in the off position, inject the response factor solution containing the possible impurities. A typical chromatogram is shown in Fig. 2 and Fig. 3 for helium and hydrogen, respectively. Record all the areas for the impurities added to the methanol. Using a data acquisition system or utilizing Eq 3below determine the response factors for the components added to the methanol. This calibration is carried out on a mass basis.

$$(RF)_I = (m_i) \, / \, (A_i) \qquad (3)$$

where:

$(RF)_I$ = response factor of the impurity,
m_i = concentration of the impurity in mg/kg, and
A_i = area of the impurity.

11. Quality Control

11.1 Conduct a regular statistical quality assurance (quality control) program, monitoring both precision and accuracy, in accordance with the techniques of Practice D6299 or equivalent. Measure the ethanol and methanol concentrations using the procedure outlined in Section 12. Confirm the performance of the instrument or the test procedure after each calibration and on each day of use thereafter. Include at least one quality control sample of known ethanol and methanol content.

11.1.1 Standard(s) of known concentration may be obtained from vendor, a cross-check program, or may be prepared gravimetrically as shown in Table 3; use the density of methanol to determine the volume.

12. Gas Chromatographic Analysis Procedure

12.1 *Analysis of Fuel Methanol*—Set the instrument operating conditions depending on the carrier gas used. See Table 1 or Table 2. Ensure that the valve will not be switched.

12.1.1 Inject 1.0 µL of the sample of fuel methanol with identical conditions as the injection of the calibration standards. The chromatograms obtained should be similar to the ones shown in Fig. 2 and Fig. 3. Record the areas of the impurities and the retention time of the impurities for identification. Note the retention time of any peak which cannot be identified.

12.2 *Analysis of Methanol Fuel Blends*—Into a 25 mL volumetric flask pipette 1.0 mL of ethyl acetate. Fill to the mark with the methanol fuel blend to be analyzed. Inject 0.2 µL of the sample under the conditions of Table 1 or Table 2 (helium or hydrogen carrier). Record the area of methanol and ethyl acetate in order to calculate percent methanol in the sample.

13. Calculation

13.1 *Fuel Methanol*—Obtain the areas for the identified impurities in the fuel methanol. Utilizing the data system in the external standard mode, calculate the percent of each impurity identified. For those impurities not identified apply the relative response factor of the nearest identified impurity.

13.1.1 The mass percent of each impurity is calculated by Eq 4.

$$m_i = (R\ F)_1 (A_i) \times 10^{-2} \qquad (4)$$

where:

m_i = percent mass of the impurity,
A_i = area of the impurity, and
$(RF)_1$ = response of the impurity.

13.1.2 The percent mass of methanol is determined by difference from the following equation:

$$A = 100 - \text{percent mass } W_{H20} - [(\Sigma \quad m_i \quad \text{percent})] \qquad (5)$$

where:

A = percent mass methanol,
$(\sum m_i \text{ percent})$ = sum of the percent mass of the impurities determined in 13.1.1, and
W_{H20} = percent mass water in the methanol.

13.1.3 Consult Test Methods D1364 and E1064 for the percent water determination.

13.2 *Methanol Fuel Blend*—For the analysis of methanol in a methanol fuel blend, set the data system in the internal standard mode utilizing the calibration levels as determined in 10.7. From the area obtained from the injection of methanol sample and using the recorded areas of methanol and ethyl acetate obtained in section 12.2, interpolate the percent methanol utilizing Eq 2.

13.3 If a data system is not available use a spread sheet to plot the area ratios versus the amount ratios as shown in 10.7. Use the spreadsheet software to determine the linear regression coefficient and the calibration curve. Solve for the amount of methanol.

13.4 If it is desired to report a percent mass of methanol in the methanol fuel use the following equation:

$$\text{percent w} = (\text{percent} \quad V / D_f) \times 0.7918 \qquad (6)$$

where:

percent w = percent mass of methanol in the fuel,
D_f = relative density of the fuel at 15.5 °C/15.6 °C (60 °F/60 °F), and
percent V = percent volume as determined by the test method.

14. Report

14.1 Report the volume percent of methanol in methanol fuel blends to the nearest 0.01 % as determined in Section 13; report the mass percent of fuel methanol to the nearest 0.01 %. Use the guidelines of Practice E29 for the proper significant figures.

15. Precision and Bias

15.1 *Precision*—The precision of this test method is to be determined by an interlaboratory study (ILS).

15.2 A temporary repeatability standard deviation as defined in ASTM Form and Style Manual (A21.5.1) was obtained by analyzing samples of methanol fuel blends as well as fuel methanol and these interim values are listed in Table 5 and Table 6 using helium and hydrogen as carrier gases, respectively. A proper ILS will be completed by 2020.

TABLE 5 Repeatability Obtained for Analysis of Methanol Fuel Blends Obtained from Three Different Samples using Helium and Hydrogen as Carriers

		Helium Carrier Volume Percent		
Run	Sample 1	Sample 2	Sample 3	
1	71.30	88.96	85.26	
2	70.72	89.48	85.24	
3	71.48	88.60	85.22	
4	71.38	89.39	85.33	
5	71.63	89.41	85.32	
6	71.70	89.38	85.18	
7	71.57	89.04	85.29	
8	71.69	88.76	85.38	
Average	71.43	89.13	85.28	
Std.Dev.	0.30	0.31	0.07	
percent RSD	0.42	0.35	0.08	
Repeatability Std.Dev.	0.74	0.77	0.16	
		H2 Carrier Volume Percent		
Run	Sample 4	Sample 5	Sample 6	Sample 7
1	86.73	85.76	85.43	99.2
2	86.72	85.11	85.45	99.42
3	87.24	85.1	85.48	99.45
4	87.25	85.32	85.53	99.21
5	87.25	84.75	85.51	99.31
6	87.31	85.31	85.6	99.37
7	87.23	85.24	85.52	99.45
8	87.11	85.44	85.41	99.25
Average	87.11	85.25	85.49	99.33
Std.Dev.	0.24	0.27	0.06	0.10
percent RSD	0.28	0.32	0.07	0.11
Repeatability Std.Dev.	0.59	0.67	0.15	0.26

TABLE 6 Repeatability of Fuel Methanol Helium and Hydrogen Carrier

NOTE 1—Fuel methanol made from reagent grade methanol.

NOTE 2—Not corrected for water.

	Repeatability of Fuel Methanol mass percent	
	Helium	Hydrogen
	98.69	97.93
	98.69	98.21
	98.67	98.19
	98.68	98.35
	98.69	98.37
	98.68	97.99
	98.68	98.18
Average	98.68	97.17
Std.Dev.	0.01	0.17
percent STD	0.01	0.17
Rep. Std.	0.02	0.41

15.2.1 In Table 5, the repeatability standard deviation associated with two different instruments (older and newer) are listed and because the difference was determined to be statistically significant the standard deviations (sd), degrees of freedom (df) and ranges are listed in Table 7.

15.3 At present, no bias statement can be made since this test method has not been evaluated using an industry-accepted Certified Reference Material (CRM).

16. Keywords

16.1 fuel methanol; impurities in methanol; methanol content in gasoline; methanol fuel; methanol-gasoline blends

TABLE 7 Statistical Comparison of Data of Table 5

	sd	df	range
new inst.	0.06	49	70–97
old inst.	0.25	21	71–94

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