



# Standard Test Method for Determination of Methanol in Crude Oils by Multidimensional Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D7059; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the determination of methanol in crude oils by direct injection multidimensional gas chromatography in the concentration range of 15 to 900 ppm (m/m). The pooled limit of quantification (PLOQ) is 15 ppm (m/m).

1.2 This test method is applicable only to crude oils containing less than or equal to 0.1 % (v/v) water.

1.3 This test method has not been tested with crude oil samples that are solid or waxy, or both, at ambient temperatures.

1.4 The values stated in SI units are to be regarded as standard. Alternate units, in common usage, are also provided to increase clarity and aid the users of this test method.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

[D4006 Test Method for Water in Crude Oil by Distillation](#)

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

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

[D4928 Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration](#)

[D6596 Practice for Ampulization and Storage of Gasoline and Related Hydrocarbon Materials](#)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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

## 3. Terminology

### 3.1 Definitions:

3.1.1 *analytical column, n*—porous layer open tubular (PLOT) column with a stationary phase selective for oxygenates. It is used to resolve methanol from 1-propanol to provide accurate quantitative results.

3.1.2 *cool-on-column injector, n*—an injection port that allows controlled injection of the sample at a temperature close to or lower than the boiling point of the solvent into the gas chromatographic column or a liner within the injection port connected to the column.

3.1.2.1 *Discussion*—After the injection, the injection port is heated at a fixed rate to a temperature sufficiently high enough to allow the transfer of sample components of interest from the injection port to the part of the column located in the gas chromatograph (GC) oven.

3.1.3 *electronic pressure control, n*—electronic pneumatic control of carrier gas flows. It can be flow or pressure programmed to speed up elution of components.

3.1.4 *low-volume connector, n*—a special union for connecting two lengths of tubing 1.6-mm inside diameter and smaller; sometimes referred to as a zero dead-volume union.

3.1.5 *pre-column, n*—a polydimethylsiloxane WCOT column used to isolate the methanol and 1-propanol and several light hydrocarbons from the higher boiling portion of the crude oil sample for transfer to the analytical column for further separation and quantification.

3.1.6 *programmable temperature vaporizer (PTV), n*—a temperature programmable injector similar to a cool-on-column injector except that the sample is injected cool into a glass liner or insert instead of the WCOT (3.1.5) column and then the temperature is programmed in a manner similar to the on-column injector.

3.1.6.1 *Discussion*—The liner may be replaced, as necessary, to remove non-volatile materials. This injector may be operated in low split mode or direct (no splitting) mode.

3.1.7 *split/splitless injector, n*—a heated capillary inlet or sample introduction system that allows controlled splitting of the injected sample into two unequal portions, the smaller of which goes to the capillary column, and the greater to a vent.

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

**TABLE 1 Operating Conditions for Configuration A**

Injector	On-column. Temperature program: 50°C (0.1 min) 30°C/min to 300°C until end of oven program; 1.0 microlitre injected with autosampler
Oven temperature program	40°C at 2°C/min to 70°C (0 min); 4°C/min to 190°C; 30°C/min to 250°C (13.0 min)
Detectors	Two flame ionization detectors (FID) at 325°C. Hydrogen at 30 mL/min; air at 300 mL/min; helium make-up gas at 30 mL/min
Columns	60 m × 0.53 mm ID 5.0 µm film polydimethylsiloxane (pre-column) 10 m × 0.53 mm ID 10 µm film CP-Lowox The two columns are coupled through a four-port Valco valve as shown in Fig. 1 When analyses are not being performed, the GC oven temperature should be kept at 250°C, and the pre-column carrier head pressure kept at 60 psi. This procedure conditions the CP-Lowox column, which may trap carrier gas contaminants at the normal 40°C starting temperature, and also elutes residual heavy material from the pre-column.
Carrier gas	Pre-column: 10 psi (20 min) 99 psi/min to 60 psi (until end of oven temperature program) CP-Lowox column flow: constant flow of 10 mL/min
Valve temperature	260°C
Valve timing	1. Valve on at 2.80 min and off at 4.00 min to transfer the methanol from the polydimethylsiloxane column to the CP-Lowox column 2. Valve on at 6.80 min and off at 8.00 min to transfer the internal standard, 1-propanol

3.1.7.1 *Discussion*—When the vent is closed, the entire sample enters the capillary column and the inlet is operated as a *splitless* injector. When the vent is open, the inlet is operated in the *split* mode and only a portion of the sample reaches the capillary column. The ratio of the split between the capillary column and the vent is calculated as described in 3.1.7.2.

3.1.7.2 *split ratio, n*—in capillary gas chromatography, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column, expressed by:

$$\text{split ratio} = (S + C)/C \quad (1)$$

where:

*S* = flow rate at the splitter vent, and

*C* = flow rate at the column outlet.

## 4. Summary of Test Method

4.1 An internal standard, 1-propanol, is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a flow switching system between the two columns. The sample first passes through the polydimethylsiloxane WCOT column that performs a pre-separation of the methanol and 1-propanol and eliminates unwanted hydrocarbons. The methanol and 1-propanol are transferred to the analytical PLOT column for oxygenates. While the methanol and 1-propanol are eluting from the analytical PLOT column for oxygenates, auxiliary carrier gas is used to elute higher boiling crude oil hydrocarbons from the pre-column, either in the forward or backflush mode, to yield a stable baseline for the next analysis.

## 5. Significance and Use

5.1 Methanol is used in production of crude oil to prevent formation of gas hydrates. The presence of residual methanol in crude oils can lead to costly problems in refinery operations.

## 6. Apparatus

6.1 *Chromatograph*—A multidimensional two-WCOT column gas chromatographic system, capable of adequately resolving methanol and the 1-propanol internal standard and of eliminating hydrocarbon and other interferences, is required for this analysis. Flow switching between the two specified WCOT columns may be accomplished by either using a valve or pneumatic (pressure) switching to redirect flows. The unwanted higher boiling hydrocarbons may be removed from the pre-column either by forward flush or backward flush. The system requires that carrier gas flow controllers must be capable of precise control for the typical pressures required. Such flow controllers are available on gas chromatographs. The precision of this test method was obtained using several instrument configurations described in 6.1.1-6.1.5. Other multidimensional configurations may be used, provided that they meet all of the requirements of this test method.

6.1.1 *Configuration A*—Cool-on-column injection (no back-flush of pre-column) with two separate selective heartcuts for the methanol and 1-propanol internal standard. The chromatographic instrument can be operated at the approximate conditions given in Table 1 and Fig. 1. Figs. 2-5 give chromatograms and a calibration curve.

6.1.2 *Configuration B*—Heated split injection with a single heartcut of methanol, 1-propanol and several C<sub>9</sub> minus hydrocarbons transferred to the PLOT column for oxygenates using a six-port valve. The pre-column, located in a separate auxiliary oven, is backflushed to a vent using the six-port valve. Table 2 and Fig. 6 give details of the configuration.

6.1.3 *Configuration C*—Heated split injection with a single heartcut for the methanol, 1-propanol and C<sub>9</sub> minus hydrocarbons, followed by backflush of the pre-column through the injection port to remove the high boiling hydrocarbons retained on the pre-column. The chromatographic instrument can be operated at the approximate conditions given in Table 3 and

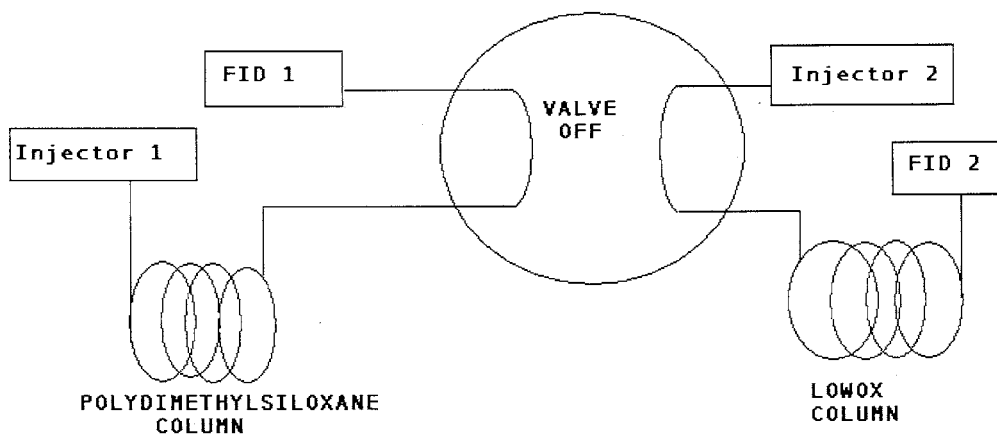
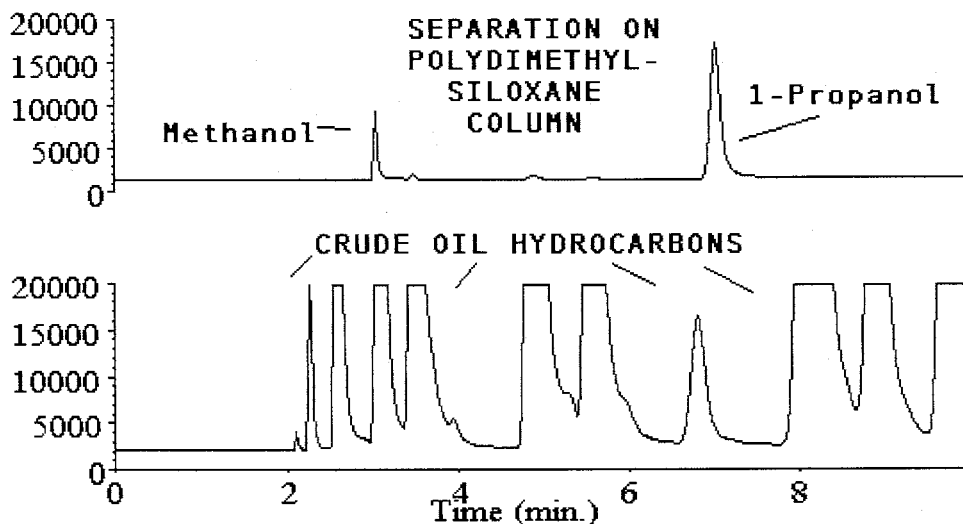


FIG. 1 Valve Diagram for Configuration A



NOTE—Two separate injections: TOP/ methanol/1-propanol internal standard solution and BOTTOM/crude oil only.  
 FIG. 2 Relative Retention Windows on Polydimethylsiloxane Pre-column in Configuration A Using Monitor FID

Fig. 7. The pre-column is located in a separate auxiliary oven. Fig. 8 gives a chromatogram obtained with this system.

6.1.4 *Configuration D*—Direct PTV (no splitting) injection with a single heartcut for the methanol and the 1-propanol internal standard and several low boiling hydrocarbons, followed by backflush of the pre-column through the injector to a vent by pressure switching. Table 4 and Figs. 9 and 10 give flow configurations and operating conditions.

6.1.5 *Configuration E*—Split injection using pressure switching between the pre-column and the analytical column. After transfer to the analytical column, pressure is reduced at the inlet and the pre-column is backflushed to remove high boiling crude components. Table 5 and Fig. 11 give the flow configurations and operating conditions.

6.2 *Detector*—At least one, main flame ionization detector (FID) is required. In a two FID detector configuration, the optional second detector is used to monitor the pre-column elution and aids in setting heartcut or transfer times for the

methanol and 1-propanol. The main detector's response, proportional to the concentrations of the methanol and 1-propanol, is recorded; the peak areas are measured; and the concentration of methanol is calculated with reference to the 1-propanol internal standard and a calibration curve.

6.3 *Valve or Pneumatic (pressure) Switching*, for systems using valve switching (for example, Configurations A, B in 6.1), a high temperature and low volume valve, located within the gas chromatographic column oven or in a separate oven, capable of performing the functions described in 6.1. The valve connections shall not contribute significantly to chromatographic deterioration. Refer to Fig. 2, Fig. 3, and Fig. 8 for compound peak performance, manufacturer's guidelines and examples given in 6.1 as a guide in assembling the GC system. For example, Valco Model No. A 4C10WP, 1.6-mm (1/16-in.) fittings was used in Configuration A (6.1). Other equivalent valves may be used. Alternatively, pneumatic or pressure

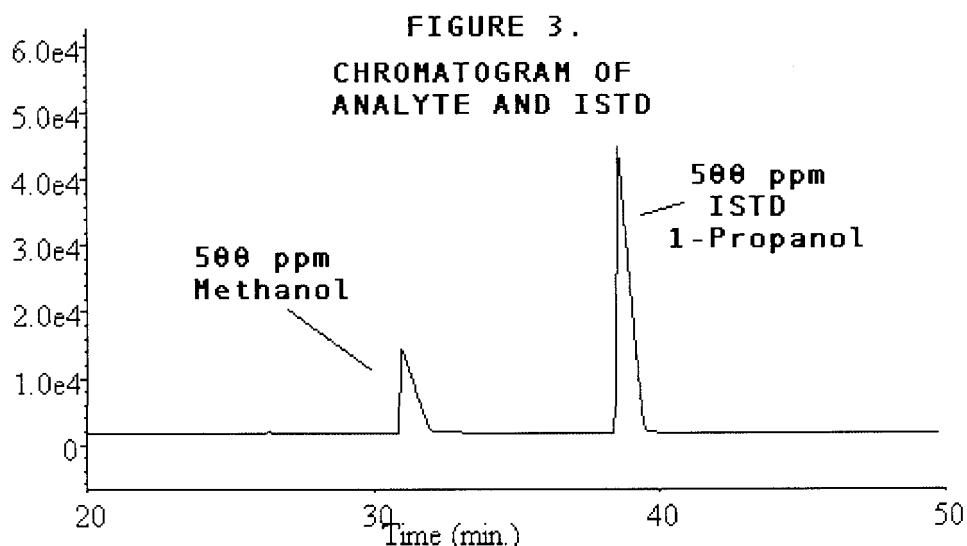


FIG. 3 Chromatogram of Methanol and 1-propanol Internal Standard with Configuration A

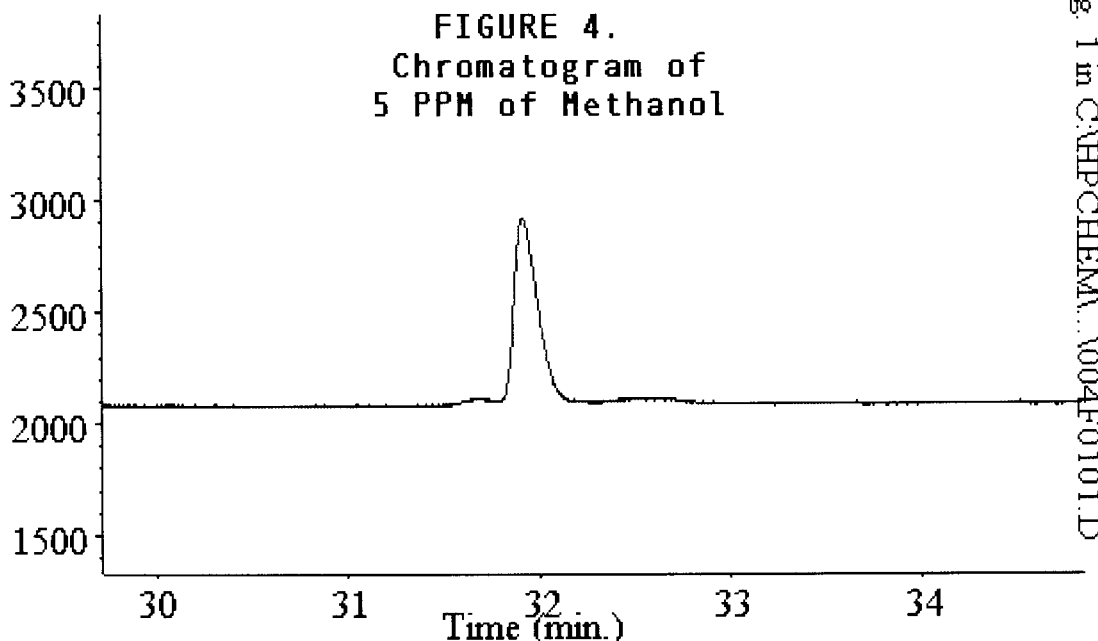


FIG. 4 Chromatogram of 5 ppm Methanol with Configuration A

Fig. 1 in C:\HP\CHEM\...004F0101.D

switching may be used instead of a valve (for example, Configurations C, D, and E in 6.1).

6.3.1 When using valve switching for heart-cutting, an automatic valve-switching device must be used to ensure repeatable switching times. Such a device must be synchronized with injection and data collection times. For the pressure switching (Configurations C, D, and E) approach, automatic precise and stable pressure control must be used to yield stable retention times.

6.4 *Injection System*—Several sample injection systems have been used successfully with the configurations in 6.1. Generally, splitless or direct injection types allow detection of lower levels (1 ppm or less) of methanol. The splitless or direct

injection systems include: (A) a cool-on-column temperature programmable vaporizer, and appropriate autosampler to allow such injections (Configuration A in 6.1); and (B) PTV (Configuration D in 6.1). Alternatively, heated, splitting type injectors may be used with low split ratios (Configurations B, C, and E in 6.1). The splitting type of injection generally is applicable for concentrations greater than or equal to 2 ppm methanol. With splitting type injectors, the replaceable glass deactivated liner (single-taper style with deactivated glass wool at the bottom to retain unvaporized components) was used successfully (for example, as in Configuration C in 6.1).

6.4.1 Automatic microlitre syringe injectors must be used for introducing representative samples into the GC inlet.

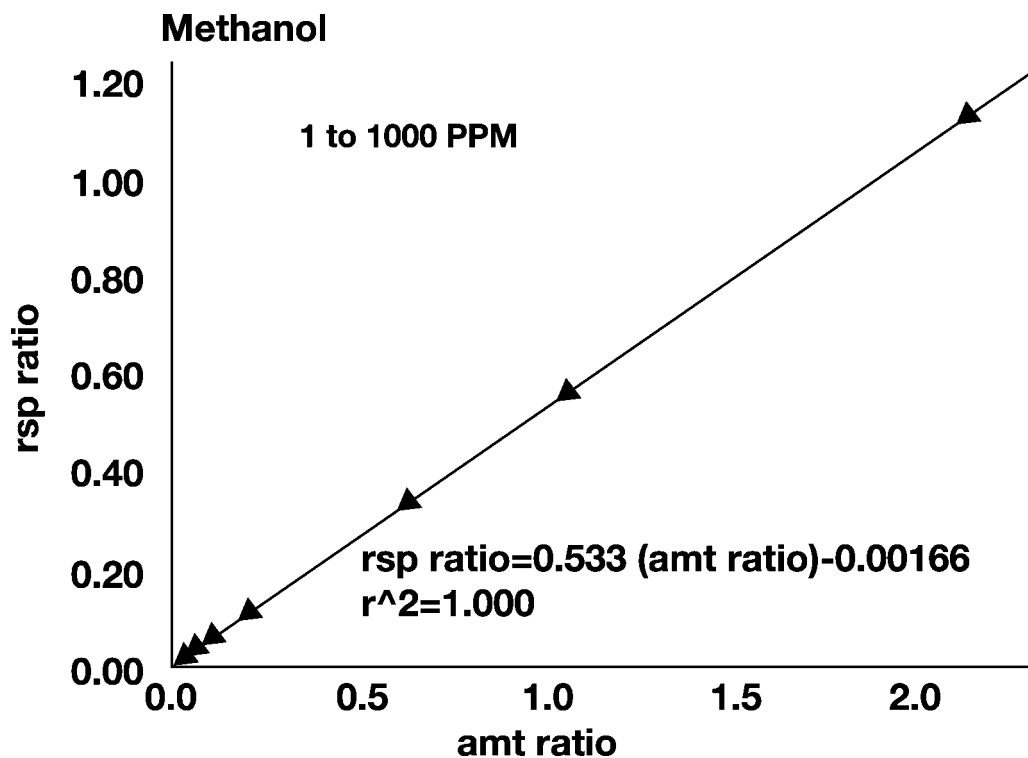


FIG. 5 Calibration Curve of 1 to 1000 ppm Methanol with Configuration A

TABLE 2 Operating Conditions for Configuration B

Column 1 (pre-column)	10 m x 0.53 mm polydimethylsiloxane (5 µm film)
Column 2	10 m x 0.53 mm CP-Lowox (10 µm film)
Injector type	Capillary Split
Injector split ratio	5:1
Injection size	2 µL (with autosampler)
Injector temperature	350°C
Pre-column oven	300°C
Detector temperature	300°C
Oven temperature	125°C (2 min) 20°C/min to 300°C (4.25 min)
Carrier gas	Helium
Carrier gas flow rate	10 mL/min

Cool-on-column automated injectors may need special syringe needles, and so forth. Follow the manufacturer's instructions.

#### 6.5 Data Presentation or Calculation:

6.5.1 *Recorder*—A data system is used for recording and evaluating the chromatograms.

6.5.2 *Integrator or Computer*—A computer or electronic integrator is used to obtain peak areas.

6.6 *Pre-column WCOT*, containing a 5 µm film thickness of cross-linked polymethylsiloxane, or equivalent, to meet all of the requirements in this test method. This column performs a pre-separation of the methanol and 1-propanol internal standard from hydrocarbons in the same boiling point range. The column shall perform at the same temperature as required for the column in 6.7, except if located in a separate auxiliary oven. The configurations in 6.1 give examples of columns used successfully.

6.7 *Analytical Column*, a PLOT column for oxygenates, 10 m long by 0.53 mm I.D., with a stationary phase coated onto a fused silica capillary or equivalent. At a minimum, the column shall have sufficient retention for methanol that it elutes after

n-tridecane (retention index >1300) at 150°C, and have sufficient efficiency and capacity to resolve methanol from 1-propanol to provide accurate quantitative results. Ensure that acetone does not interfere with the methanol analysis by analyzing a 1000 ppm mixture of acetone in crude oil containing the 1-propanol internal standard after the system has been optimized.

## 7. Reagents and Materials

7.1 *Carrier Gas*—Helium and ultrapure nitrogen have been used successfully. The minimum purity of the carrier gas used must be 99.95 mole %. Oxygen scrubbers are recommended to safeguard the WCOT columns.

7.2 *Methanol*, >99.9 % pure (**Warning**—Flammable; vapor harmful).

7.3 *1-Propanol*, >99.9 % pure, and containing <500 ppm methanol (**Warning**—Flammable; vapor harmful).

7.4 *Toluene*, >99.9 % pure, and containing <0.5 ppm methanol (**Warning**—Flammable; vapor harmful).

7.5 *Quality Control Standards*, containing known concentrations of methanol in crude oils (**Warning**—Flammable; vapor harmful).

## 8. Sampling

8.1 Ensure that the sample is representative of the crude oil from which it is taken. The use of multiple samples which are mixed or composite sampling is recommended when sampling from a large source of the crude oil. Follow the recommendations of Practice D4057, or its equivalent, when obtaining samples from bulk storage or pipelines. The use of epoxy-lined cans is recommended for storage or shipping, or both, of the sample.

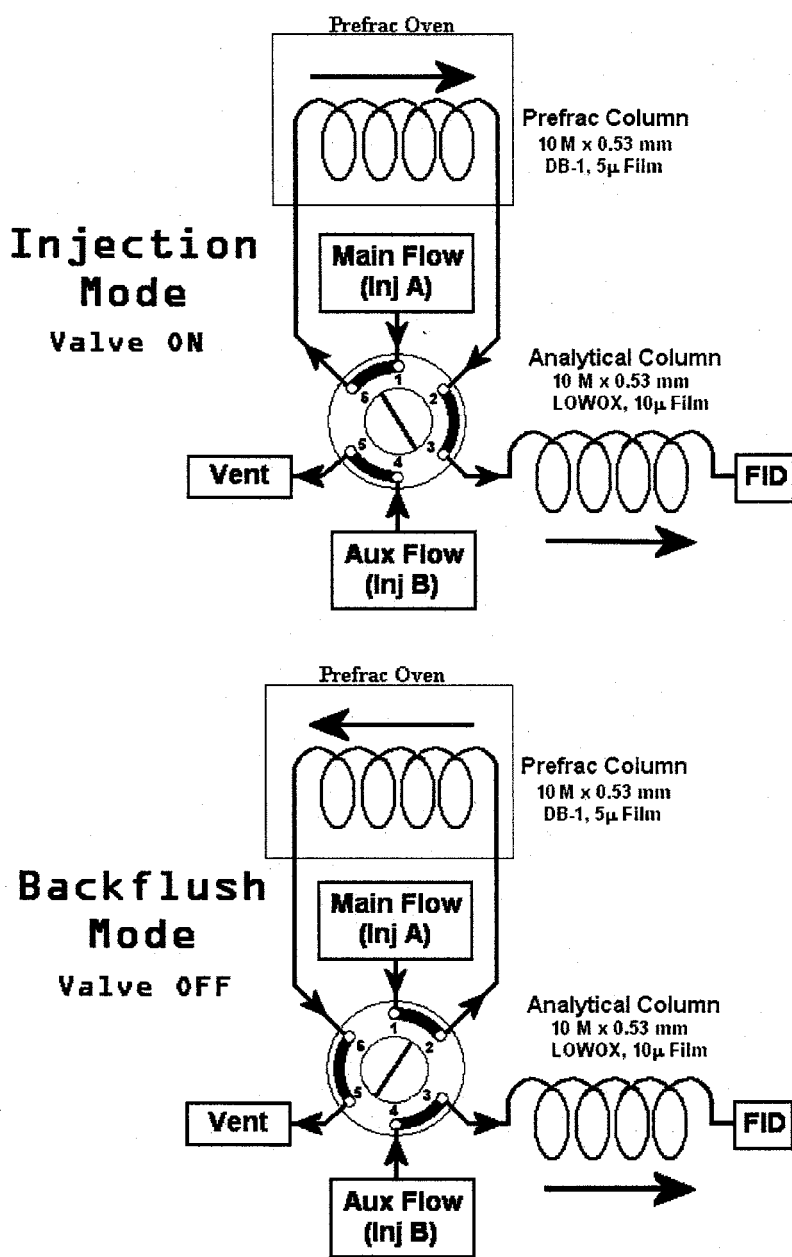


FIG. 6 Valve Diagram for Configuration B

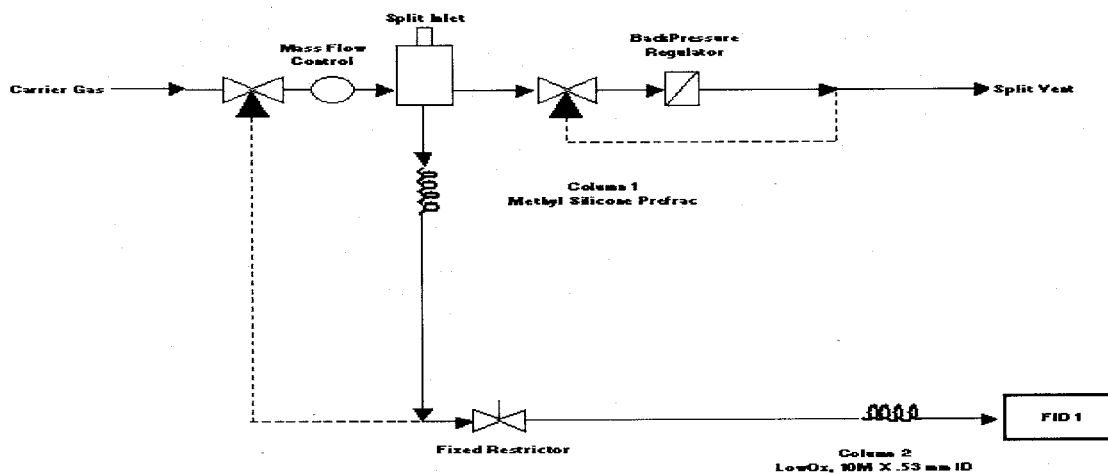
TABLE 3 Configuration C (Pressure Switching and Backflush of Pre-column) Approximate Operating Conditions (Pre-column in Isothermal Second Oven)

Injector	Split/splitless, 4:1 split ratio; 325°C; 1.0 microlitre injected with autosampler
Oven temperature program (contains CP-Lowox WCOT column)	125°C (3 min.) 20°C/min. to 300°C (10 min)
Prefrac oven (contains pre-column) temp	300°C
Detectors	Single flame ionization detector (FID) at 350°C. Hydrogen at 35 mL/min; air at 350 mL/min; make-up gas at 20 mL/min
Columns	10 m x 0.53 mm ID 5.0 µm film polydimethylsiloxane (pre-column) 10 m x 0.53 mm ID 10 µm film CP-Lowox The two columns are coupled through a pressure switching coupling as shown in Fig. 6
Carrier gas	Helium at a linear velocity of 120 cm/s
Pre-column backflush timing	15 to 20 s

8.1.1 Methanol content by this test method must be determined on a sample containing less than or equal to 0.1 % (v/v)

water. All of the crude oil samples used in the cooperative study to develop the precision of this test method contained

### Flow Path at Injection



### Flow Path at Backflush Event

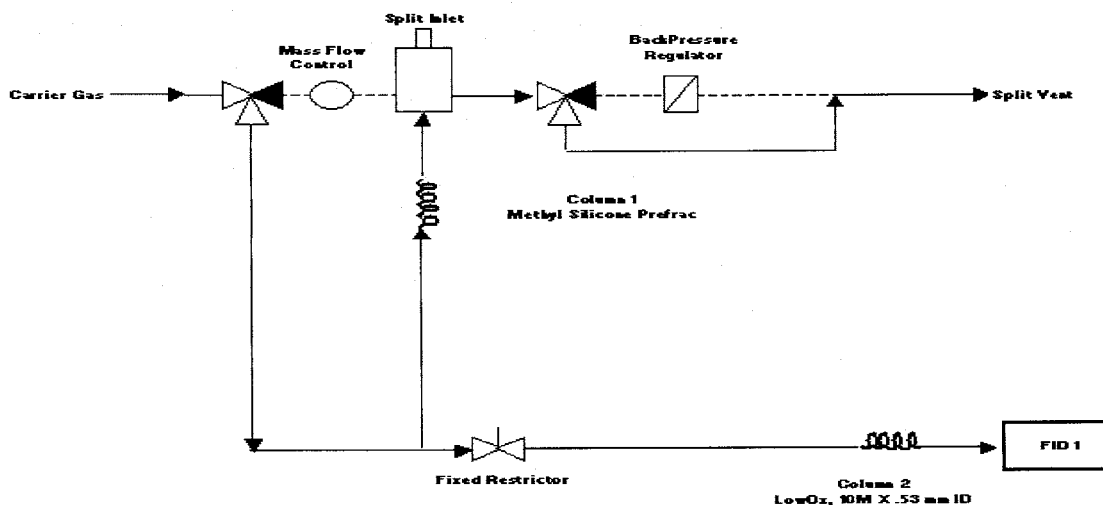


FIG. 7 Schematic of Configuration C (Table 3)

less than or equal to 0.1 % (v/v) water. Determine the water content using Test Method D4928, Test Method D4006, or equivalent.

NOTE 1—The methanol content in crude oils is the combined methanol content in the crude oil and, if present, in the associated water. It is known that some crude oils are associated with high levels of water and in such cases, the water phase may extract a significant amount of the methanol and obscure the true total methanol content in the total sample determined by this test method.

8.2 Prior to analysis, allow the sample container as received to come to ambient temperature. Mix well the entire sample in

the sealed sample container. Waxy or other solid crudes, or both, were not evaluated by this test method. Once mixed in the original sample container, immediately transfer the required aliquot for weighing to avoid potential segregation of the methanol from the crude oil. A poorly mixed sample may lead to erroneous results. Heating samples to attain homogeneity may result in the loss of methanol during sample transfers.

NOTE 2—Waxy and solid samples were not evaluated by this test method. For such samples, it may be necessary to heat the sample to a temperature of 20°C above the expected pour point in the original container. The sample is shaken vigorously to mix the sample. To avoid

ASTM RR Sample 17

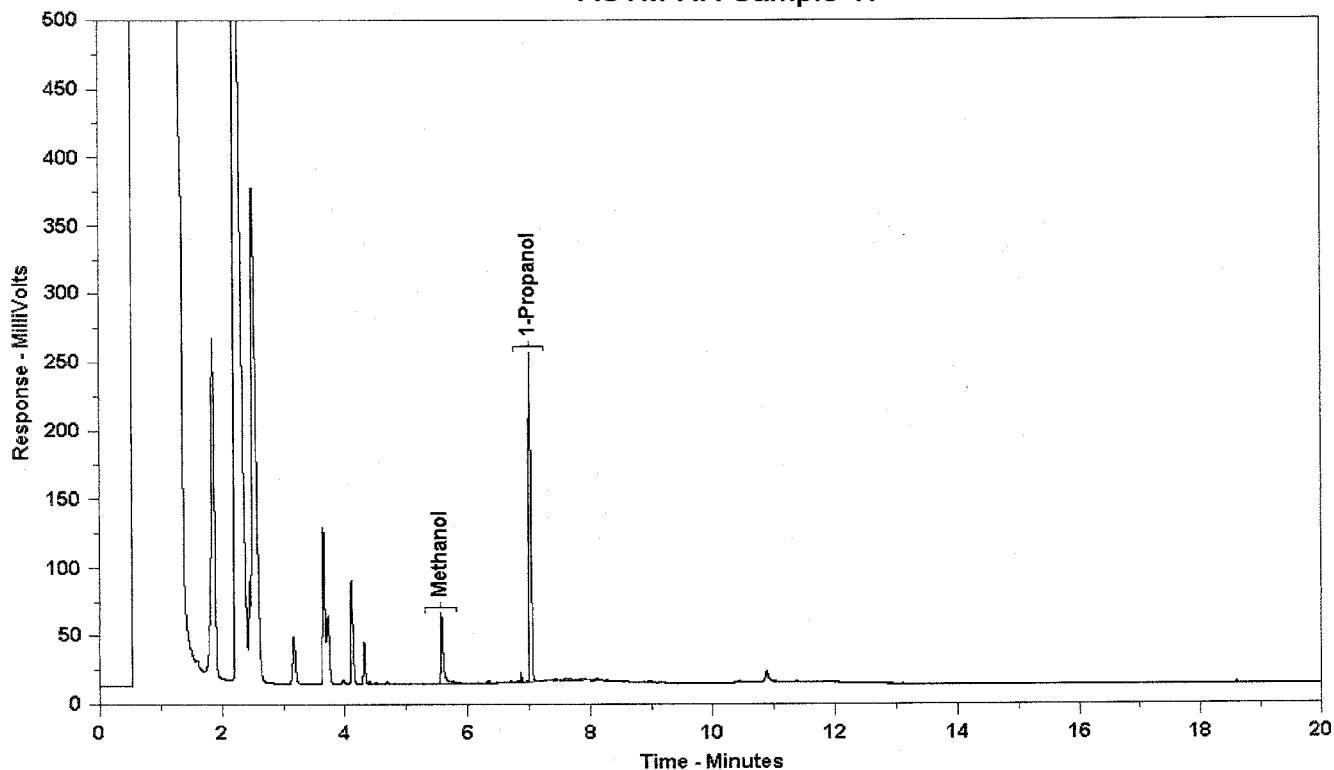


FIG. 8 Chromatogram Obtained with Configuration C

TABLE 4 Configuration D (Pressure Switching and Backflush of Pre-column) Approximate Operating Conditions (Pre-column and Polar WCOT in Same Oven)

Gas chromatography (GC): Pre-column/analytical WCOT's	CP SIL 5CB 10 m × 0.53 mm ID df = 5.0 μm and CP-Lowox 10 m × 0.53 mm ID
Injector type	PTV direct injection (packed columns equipped with adapter for installing 0.53 mm ID wide bore WCOT)
Injector split ratio	Direct injection: no split
Injection size	1.0 μL
Injector temperature	250°C isothermal
Oven temperature	100°C (2.5 min); 40°C/min to 290°C (25.0 min)
Carrier gas	Nitrogen
Carrier gas flow rates	Flow at the detector in forward flush 15 mL/min. Flow at the detector in backflush 8 mL/min

losses of the methanol, an aliquot for analysis may be transferred under slight pressure to a sealed vial by connecting a transfer tube from the sample container to the vial. The sealed vial is allowed to cool prior to the addition of the toluene solvent as described in Section 12.

## 9. Preparation of Apparatus and Establishment of Conditions

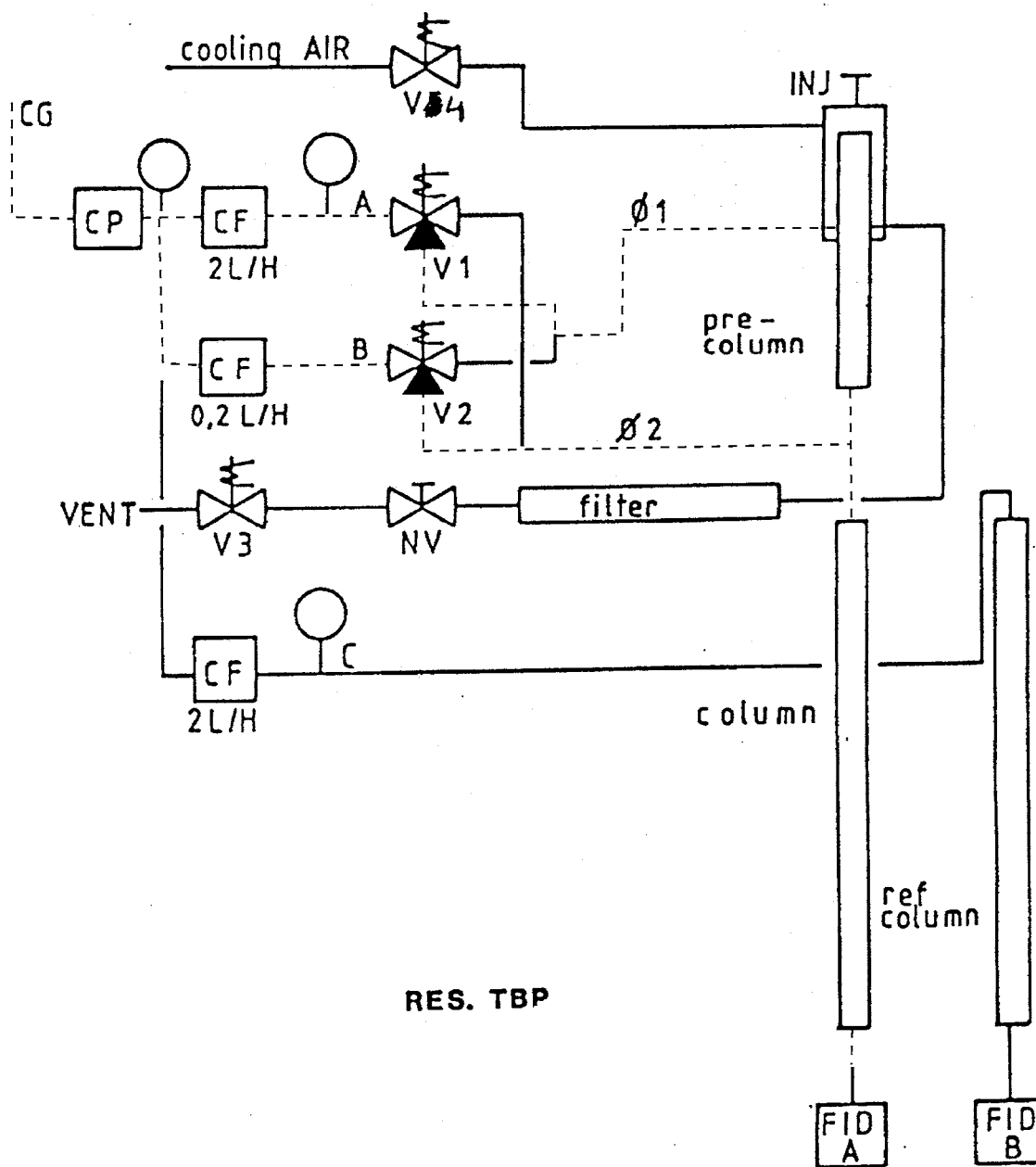
9.1 *Assembly*—Configure the GC system in a multidimensional configuration as described in 6.1. Configurations that were used successfully are described in 6.1 and may be used as a guideline. Connect the WCOT columns to the chromatographic system, including the multidimensional switching device, using low volume connectors and inert narrow bore tubing. It is important to minimize the volume of the chromatographic system that comes in contact with the sample; otherwise, peak broadening will occur.

9.2 This section gives details on how to set up two of the configurations described in 6.1. For other configurations, adjust cut times appropriately.

9.2.1 *Configuration A*—Adjust the operating conditions. Table 1 gives example conditions. Modifications to column lengths and so forth may require different operating conditions. Check the system for leaks before proceeding further.

9.2.1.1 *Setting Cut Times*—With the pre-column connected to the monitor FID, the transfer valve OFF, and the temperature and flow conditions as indicated in the method, inject the 1000 ppm calibration solution, and record the chromatogram. Identify the peak for methanol and the peak for 1-propanol. From this retention time data, set the methanol transfer valve time ON to 0.5 min before the methanol starts eluting, and the methanol transfer valve time OFF to 0.5 min after the methanol





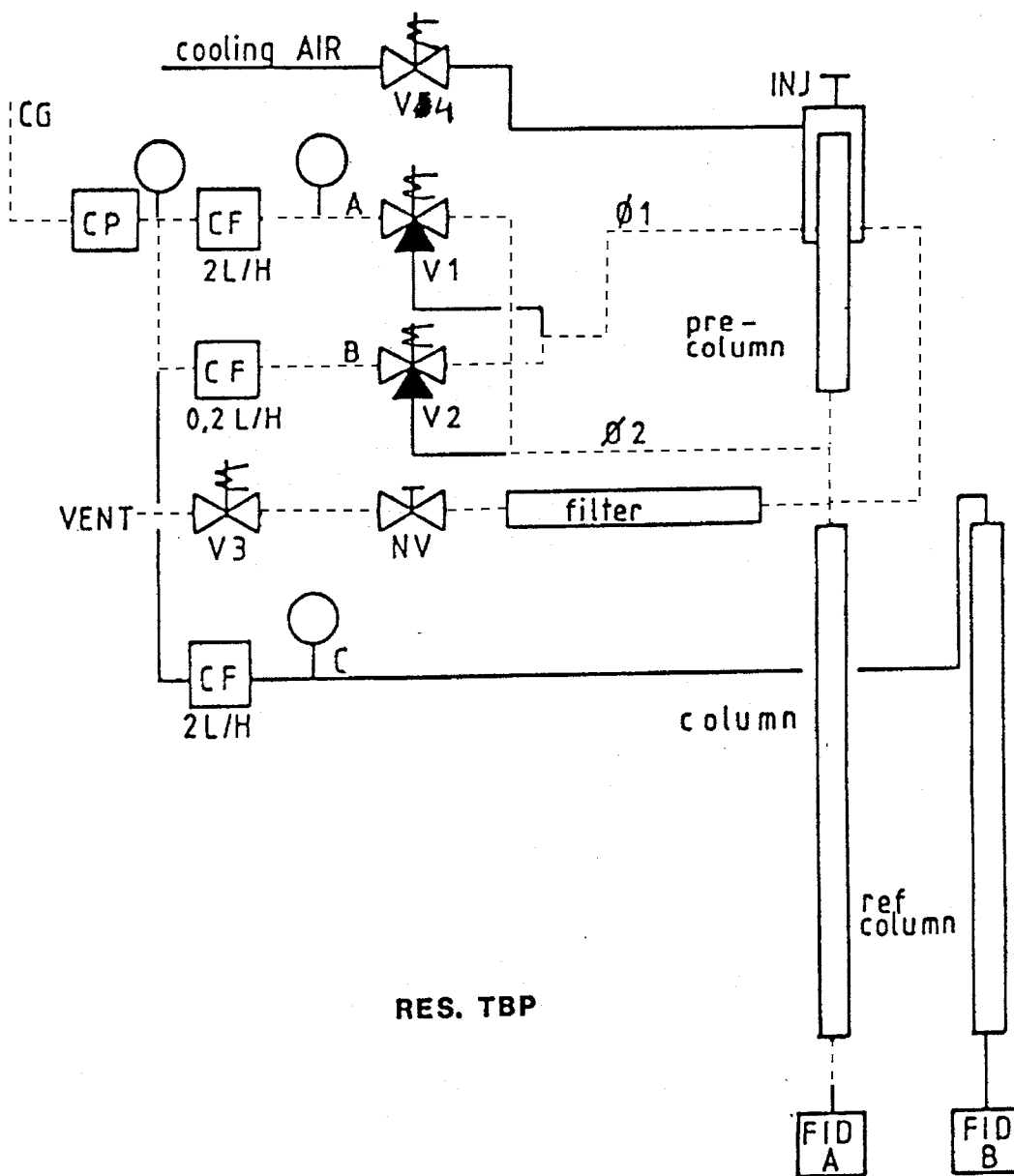
NOTE 1—Current position: forward flush for heartcutting from pre-column to PLOT column for oxygenates (FID B not used).  
 NOTE 2—CG = carrier gas. The dotted line indicates the carrier gas flow path for foreflush and backflush.

FIG. 9 Flow Scheme of Configuration D

peak returns to baseline. Set the 1-propanol transfer valve time ON to 0.5 min before the 1-propanol starts eluting, and the 1-propanol transfer valve time OFF to 0.5 min after the 1-propanol peak returns to baseline. The transfer valve should turn on and off twice during the analysis. The times should be incorporated into the analysis method before calibration is begun. After setting the initial heart-cut times, reevaluate them, using the automated operating conditions that will be used for calibration and sample analysis, to ensure that no retention time shifts have occurred due to pressure or flow imbalances when the two columns are connected in series. If necessary, readjust the flows or pressures, and repeat the reevaluation.

9.2.1.2 To safeguard the PLOT column for oxygenates, avoid injecting crude oil samples until the valve times are properly optimized using calibration standards.

9.2.1.3 It is recommended that when all of the analyses are completed, the GC oven temperature be maintained at 250°C and the pre-column carrier head pressure be maintained at 60 psi using the electronic pressure controller for at least several hours. This procedure conditions the PLOT column for oxygenates, which may trap carrier gas contaminants at the normal 40°C starting temperature, and also elutes residual heavy hydrocarbons from the pre-column. Periodically, 25 cm can be cut off the front of the polydimethylsiloxane column to remove



NOTE 1—Current position: Backflush (FID B not used).

NOTE 2—CG = carrier gas. The dotted line indicates the carrier gas flow path for foreflush and backflush.

FIG. 10 Flow Scheme for Configuration D

heavy nonvolatiles. The frequency can be determined from the analysis of quality control samples, by evaluating the SQC results and also from chromatographic performance, such as peak tailing and so forth. After cutting the polydimethylsiloxane column, reevaluate the heart-cut times and adjust, as necessary, to meet the specification in 9.2.1.1.

9.2.2 Configuration C—Adjust the operating conditions to those listed in Table 3, or equivalent. Check the system for leaks before proceeding further.

9.2.2.1 Setting the Backflush Time—It is essential that the appropriate backflush time be determined to prevent heavy contaminants from reaching the analytical column and potentially interfering with the determination of methanol. This test

method restricts the carbon number range allowed to pass through to the analytical column to  $\sim C_{10}$ -minus. The procedure used is as follows:

- (1) Prepare a timing standard containing approximately 1000 ppm (m/m) of normal paraffins  $C_9$ ,  $C_{10}$ , and  $C_{11}$  in toluene.
- (2) Inject the timing standard into the GC in the foreflush position with no backflush.
- (3) Analyze the resulting chromatogram and determine the position of each of the normal paraffin peaks.
- (4) Starting at an arbitrary backflush time (30 s is a good starting point) reinject the sample and analyze the chromatogram for the presence of the normal paraffin peaks.

**TABLE 5 Configuration E (Pressure Switching and Backflush of Pre-column Through Injection Port) Approximate Operating Conditions (Pre-column and Polar WCOT in Same Oven)**

Gas chromatography (GC): Column 1/Column 2  Injector type  Injector split ratio Injection size Injector temperature Oven temperature Carrier gas Backflush pressure switching  Carrier gas linear velocity	Column 1: polydimethylsiloxane, 5 μm, 10 m × 0.53 mm Column 2: CP-Lowox, 10 m × 0.53 mm Split/splitless used in split mode; the inlet liner is a 4 mm liner with a taper at the bottom and glass wool in the center of the liner 7:1 1 μL 325°C 150°C (3 min); 20°C/min to 300°C (5 min) Helium After the alcohols elute from the CP-Lowox column, the injection port pressure is reduced to 0.5 psi and simultaneously the PCM (Fig. 11) pressure is increased to 99 psi at 35 psi/min. Column 1: 31 cm/s Column 2: 50 cm/s
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(5) If a significant amount of C<sub>10</sub> and C<sub>11</sub> are visible, reduce the backflush time in 2-s increments and repeat 9.2.2.1(4) until little or no C<sub>10</sub> is visible. There should not be any significant decrease in the C<sub>9</sub> peak area. Record this time as the backflush time. Conversely, if none of the peaks are visible, increase the backflush time in 2-s increments and repeat 9.2.2.1(4) until C<sub>10</sub> is small or not visible.

NOTE 3—Backflush time is dependent upon specific instrument operating conditions, such as flow rate and temperature.

9.2.3 Replacement of the inlet septum should be performed at least every 30 to 50 injections to reduce the possibility of leaks. Liner replacement should be performed regularly if system performance degrades (see Section 11). When using a split injector, contamination of the split vent line may occur with high boiling hydrocarbons. The injection port and split vent line should be inspected and cleaned as necessary after 150 to 200 injections or when performance deteriorates when quality control samples are analyzed.

9.3 *Verification of Detectability*—Inject a 2 ppm (m/m) solution of methanol in toluene and ensure that a signal/noise ratio of at least five is observed.

## 10. Calibration and Standardization

10.1 *Identification*—After the system’s cut times are established, determine the retention time of the methanol and of the 1-propanol internal standard using a calibration solution.

10.1.1 To ensure minimum interference from hydrocarbons, it is strongly recommended that a crude oil devoid of methanol be chromatographed to determine the level of any hydrocarbon interference.

10.2 *Preparation of Calibration Standards*—Prepare multiple calibration standards of methanol in the concentration range of interest, by mass, in accordance with Practice D4307.

10.2.1 Prepare a minimum of seven calibration standards spanning the range of approximately 5 to 1000 ppm (m/m) of methanol, and each containing 500 ppm (m/m) of the 1-propanol internal standard, in toluene. Standard concentrations should bracket the expected range of methanol concentrations. The standards may be prepared from a more concentrated stock solution of methanol in toluene (for example, 5000 μg/g, prepared by adding 0.5 g of methanol to 99.5 g of toluene). The 1-propanol internal standard stock solution may be prepared by adding 0.5 g of 1-propanol to 99.5 g of toluene.

Larger batches of standards may also be prepared proportionally. The calibration standard solutions should be stored in tightly sealed bottles in a dark place below 5°C. Table 6 gives an example of the masses for preparation of working standards derived from the stock solution for a set of calibration standards 5, 25, 75, 125, 250, 500, and 1000 ppm (m/m).  $W_i$  and  $W_{is}$  in Table 6 represent the actual micrograms in each of the final calibration standards. Recalculate  $W_i$  and  $W_{is}$  to reflect the actual weights used:

$$W_i = \tag{2}$$

actual μg in calibration standard of methanol =  
 concentration of methanol stock solution (μg/g) ×  
 actual mass of methanol stock solution added to  
 calibration standard (g)

$$W_{is} = \tag{3}$$

actual μg in calibration standard of 1-propanol internal standard =  
 concentration of 1-propanol stock solution (μg/g) ×  
 actual mass of 1-propanol stock solution added to  
 calibration standard (g)

10.2.1.1 Before preparing the standards, determine the purity of the methanol and make corrections for the impurities found. Ensure that the toluene and 1-propanol internal standard meet the methanol specification in 7.3 and 7.4.

NOTE 4—The toluene and 1-propanol internal standard meet the methanol impurity specification if a solution of 500 ppm of the 1-propanol internal standard prepared in toluene is analyzed, and the area of the methanol detected, if any, corresponds to less than the area observed for a 2 ppm methanol calibration standard solution containing an equivalent amount (500 ppm) of 1-propanol (see 10.2.1).

### 10.3 Standardization:

10.3.1 Analyze the calibration standards and establish the calibration curve for methanol. Plot the response ratio,  $rsp_i$  as the y-axis versus the amount ratio  $amt_i$ , as the x-axis to generate the calibration curve (see Fig. 5 for an example plot):

$$rsp_i = (A_i/A_{is}) \tag{4}$$

where:

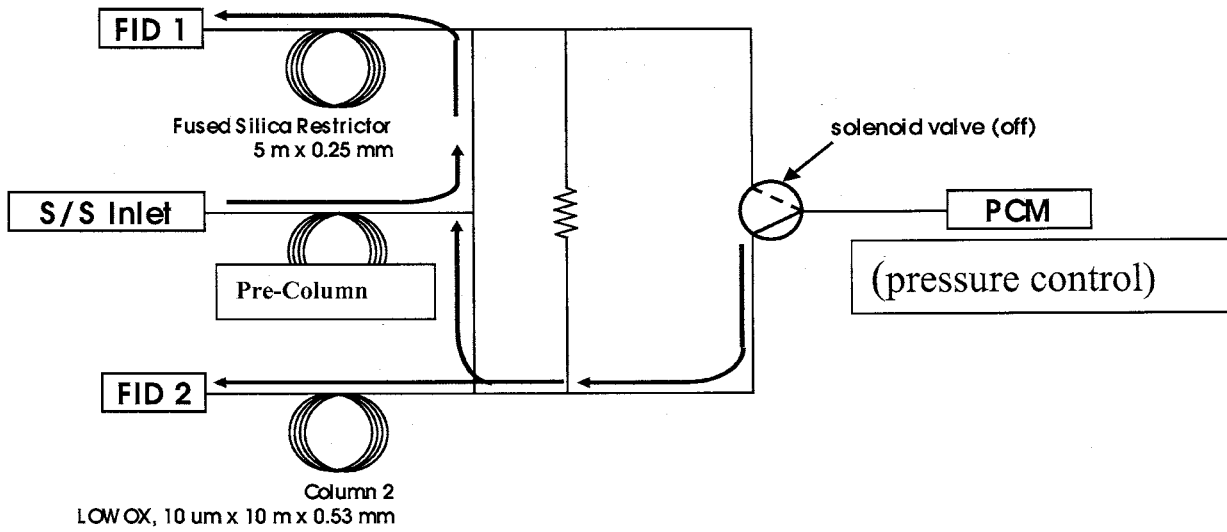
$A_i$  = area of methanol, and

$A_{is}$  = area of 1-propanol internal standard.

$$amt_i = W_i/W_{is} \tag{5}$$

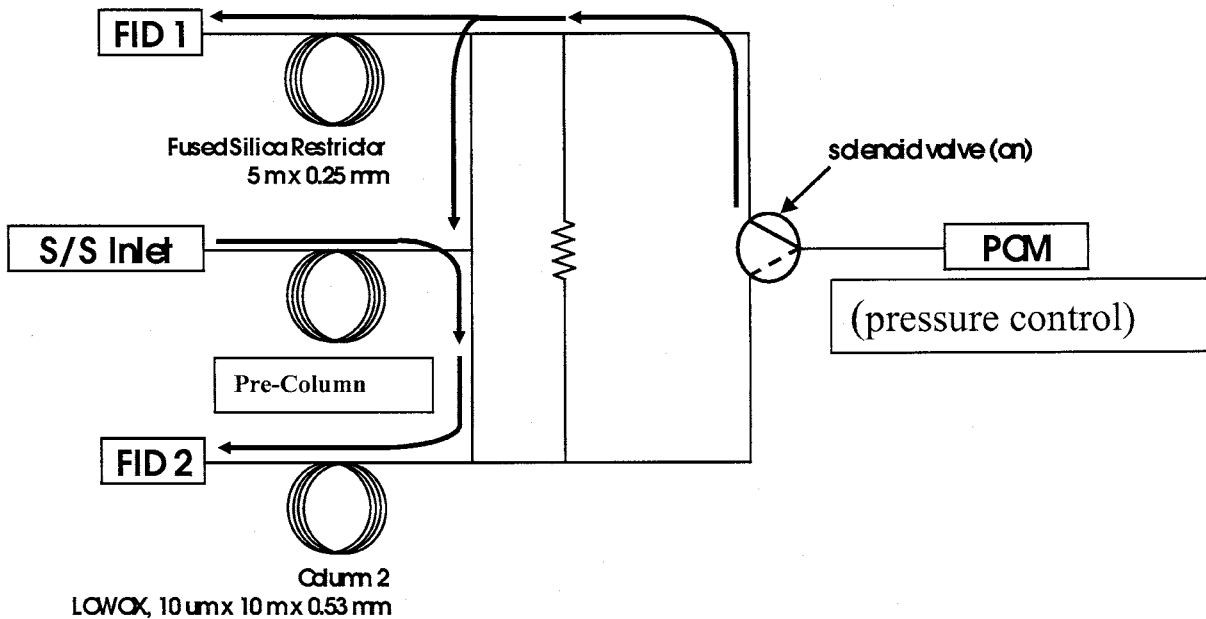
**Deans Switch**

Switch off, column 1 effluent goes to monitor FID (no heart cut)



**Deans Switch**

Switch on, column 1 effluent is cut to LOWOX column



NOTE—Backflush (not indicated) of Col 1 through S/S Inlet by Reducing Inlet Pressure and Increasing Pressure at PCM Pressure Control.  
**FIG. 11 Flow Scheme for Configuration E**

**TABLE 6 Recommended Preparation of Calibration Standards**

Desired Methanol Concentration	Amount of 5000 µg/g Methanol Stock Solution (g)	Amount of 5000 µg/g of 1-propanol Internal Standard Solution (g)	Amount of Toluene (Diluent) (g)	$W_i$ (µg)	$W_{is}$ (µg)
1000	20.0	10.0	70.0	100 000	50 000
500	10.0	10.0	80.0	50 000	50 000
250	5.0	10.0	85.0	25 000	50 000
125	2.5	10.0	87.5	12 500	50 000
75	1.5	10.0	88.5	7500	50 000
25	0.5	10.0	89.5	2500	50 000
5	0.1	10.0	89.9	500	50 000

where:

$W_i$  = mass of methanol in the calibration standard, and  
 $W_{is}$  = mass of 1-propanol internal standard in the calibration standard.

10.3.2 *Linear Least Squares Fit*—For the calibration data set, obtain the linear least squares fit equation in the form:

$$rsp_i = (m_i)(amt_i) + b_i \quad (6)$$

where:

$rsp_i$  = response ratio for methanol/1-propanol internal standard (y-axis),  
 $m_i$  = slope of linear equation for calibration curve,  
 $amt_i$  = amount ratio for methanol/1-propanol internal standard (x-axis), and  
 $b_i$  = y-axis intercept.

10.3.3 Calculate the correlation  $r^2$  value for the calibration curve. The value  $r^2$  should be at least 0.99 or better. The correlation  $r^2$  may be calculated directly by the data system or can be obtained by using plotting software.

10.4 To test the value of the y-intercept, prepare a sample using only toluene instead of the crude oil sample as described in Section 12. The calculated result from this analysis must yield a methanol content of no greater than  $\pm 3$  ppm methanol.

NOTE 5—A single calibration curve approach has worked well in the inter-laboratory cooperative study. However, if the specifications in 10.3.3 and 10.4 cannot be attained using the described single curve calibration procedure, then it may be necessary to develop two calibration curves by using at least five calibration standards for each curve. For example, one curve may be used for concentrations <100 ppm and another for concentrations >100 ppm to attain the specifications in 10.3.3 and 10.4. In addition, if this dual calibration curve approach is used, then the requirements in Section 11 must also be attained for the check standard(s) corresponding to the respective calibration curve ranges. At least one participant in the cooperative study successfully reported results using the dual calibration approach.

## 11. Quality Control Standards

11.1 After the calibration has been completed, analyze two quality control check standards of methanol in crude oil(s). The check standards may be prepared in-house, obtained from crosscheck programs, or prepared by a commercial vendor in sealed ampoules, or a combination thereof. If sealed ampoules of commercial check standards are used, then the ampulization of the vials must include continuous stirring of the crude oil mixture containing the methanol during the vial filling process and follow Practice D6596. In cases where such commercial check standards are not available, prepare the check standards in-house using crude oils as described in 11.3. In-house and

commercially prepared check standards using the above procedure were successfully prepared and tested using this test method.

11.2 The concentrations of methanol for the two check standards must be in the lower concentration range in one, for example, 20 to 30 ppm, and in the upper concentration range in the other, for example, 600 to 700 ppm. Analyze the quality control check samples as described in the sample preparation procedure (Section 12). The methanol concentration value obtained must agree within  $\pm 25$  % (for example, methanol  $20 \pm 5$  ppm) for the 20 to 30 ppm sample and  $\pm 7$  % (for example, methanol  $650 \pm 46$  ppm) relative for the 600 to 700 ppm sample. If the individual values are outside the specified range, verify calibration and instrument parameters, accuracy of the preparation of quality control reference material, sample handling, and so forth. Do not analyze samples without meeting the check standard quality control specifications.

11.2.1 The upper level quality control check sample may be prepared by weighing approximately 70 mg of methanol into a 100 mL volumetric flask and diluting to the mark with a light crude oil containing <2 ppm methanol. The mass of the crude oil added is obtained and recorded. After shaking well, more dilute solutions may be prepared by gravimetrically diluting aliquots of the stock with crude oil containing <2 ppm methanol.

11.3 Bracket the samples with the quality control check standards. Analyze the check standards at least after every 5 samples analyzed. If the check samples do not meet the specifications in 11.2, results obtained for the samples analyzed immediately preceding the check samples are considered suspect and the samples must be rerun.

## 12. Procedure

12.1 *Preparation of Sample*—Sample the crude oil as described in Section 8. Weigh out 5.0 g of sample. Add 5.0 mL of a toluene solution containing 1000 micrograms/gram of the 1-propanol internal standard in toluene. Avoid having a large headspace volume above the mixed sample liquid. A headspace volume of less than or equal to the liquid volume of the diluted sample is recommended. Obtain the exact mass of the 1-propanol internal standard added ( $W_{is}$ ):

$$W_{is} =$$

[concentration of 1-propanol solution (for example, 1000 µg/g)] ×  
 [mass (in g) of the 5.0 mL of 1-propanol internal standard solution added to the sample]

12.1.1 Record all masses to nearest 0.1 mg. Thoroughly mix the resulting solution for at least 1 min on a vortex or equivalent mixer. Transfer an aliquot of the solution into a glass GC vial. Seal the GC vial with a TFE-fluorocarbon-lined septum. If the sample is not to be immediately analyzed, store below 5°C (40°F).

NOTE 6—Use the specified 5.0 g of sample. Sample sizes of less than 5.0 g may result in inaccurate determination of methanol.

12.2 Prepare the check standards similarly to 12.1. If the samples are not to be analyzed immediately, store the check standards along with the samples.

12.3 *Chromatographic Analysis*—Introduce a representative aliquot of the sample and check standards, containing 1-propanol internal standard, into the gas chromatograph, using the same technique and sample size as used for the calibration analysis. Start recording and integrating devices in synchronization with sample introduction. Obtain a chromatogram or integrated peak report, or both, which displays the retention time and integrated area of each detected component.

12.4 *Interpretation of the Chromatogram*—Compare the retention times of methanol and the 1-propanol internal standard in the sample with those obtained during the analysis of the calibration standards to determine the identities of the methanol and the 1-propanol.

### 13. Calculations and Reporting

13.1 *Calculation of Methanol Concentration in Sample*—After identifying the methanol and 1-propanol, measure the areas of the methanol and of the 1-propanol internal standard peaks. From the least squares fit calibrations, Eq 6, calculate the absolute mass of the methanol ( $W_i$ ) in micrograms in the crude oil sample using the response ratio ( $rsp_i$ ) of the area for the methanol peak to that of the 1-propanol internal standard as follows:

$$W_i = [(A_i/A_{is}) - b_i]/m_i \times W_{is} \quad (7)$$

where:

- $A_i$  = area of the methanol peak in the sample,
- $A_{is}$  = area of the 1-propanol internal standard peak,
- $W_{is}$  = micrograms of 1-propanol internal standard added to the sample, and
- $W_i$  = calculated micrograms of methanol in the sample.

13.2 To obtain ( $W_o$ ) ppm (m/m) methanol in the sample results:

$$W_o = \{W_i/W_g\} \quad (8)$$

where:

- $W_g$  = mass of crude oil sample, g, and
- $W_i$  = micrograms of methanol in the prepared sample from Eq 7.

13.3 Report results to the nearest ppm (m/m).

13.4 For samples containing less than 5 ppm (m/m) methanol, report results as less than 5 ppm (m/m).

### 14. Precision and Bias <sup>3</sup>

14.1 *Precision*—The precision of this test method as determined by a statistical examination of interlaboratory test results is as follows:

14.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and the correct operation of the test method, exceed the values in Tables 7 and 8 only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and the correct operation of the test method, exceed the values in Tables 7 and 8 only in one case in twenty.

NOTE 7—The precision stated in Table 7 is applicable to a concentration range of 15–900 ppm (m/m) methanol. The concentration range of the samples in the cooperative study indicated that the range of at least 5–900 ppm (m/m) methanol was detectable with the instrument configurations described in 6.1.

14.2 *Bias*—Bias cannot be determined for the procedure in this test method because no material having an accepted reference value is currently available.

### 15. Limit of Quantification

15.1 The PLOQ is 15 ppm (m/m).

### 16. Keywords

16.1 alcohols; crude oils; gas chromatography; methanol; multidimensional gas chromatography

<sup>3</sup> The ILS-based precision of this test method was obtained with a CP-Lowox oxygenates PLOT column from Varian Inc., Palo Alto, CA.

**TABLE 7 Repeatability and Reproducibility**

NOTE—X = ppm (m/m) methanol.

Repeatability ( <i>r</i> ) (ppm m/m)	Reproducibility ( <i>R</i> ) (ppm m/m)	Applicable Range (ppm m/m)
0.063(X + 60)	0.107(X + 60)	15 to 900

**TABLE 8 Calculation of Repeatability and Reproducibility at Selected Methanol Concentrations**

Methanol ppm (m/m)	Repeatability (ppm m/m)	Reproducibility (ppm m/m)
15	5	8
20	5	9
25	5	9
30	6	10
40	6	11
50	7	12
60	8	13
70	8	14
80	9	15
90	9	16
100	10	17
200	16	28
300	23	39
400	29	49
500	35	60
600	42	71
700	48	81
800	54	92
900	60	103

## SUMMARY OF CHANGES

Subcommittee D02.04.0L has identified the location of selected changes to this standard since the last issue (D7059-04<sup>e1</sup>) that may impact the use of this standard.

(I) Revised throughout (except Section 14 on Precision and Bias, and tables) to replace trade name CP-Lowox with generic “PLOT column for oxygenates.”

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