Designation: D7754 – 16

Standard Test Method for Determination of Trace Oxygenates in Automotive Spark-Ignition Engine Fuel by Multidimensional Gas Chromatography[1]

This standard is issued under the fixed designation D7754; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of trace oxygenates in automotive spark-ignition engine fuel. The method used is a multidimensional gas chromatographic method using 1,2-dimethoxy ethane as the internal standard. The oxygenates that are analyzed are: methyl-tertiary butyl ether (MTBE), ethyl-tertiary butyl ether (ETBE), diisopropyl ether (DIPE), methanol, tertiary-amyl methyl ether (TAME), n-propanol, i-propanol, n-butanol, i-butanol, tert-butyl alcohol, sec-butyl alcohol, and tert-pentanol. Ethanol is usually not measured as a trace oxygenate since ethanol can be used as the main oxygenate compound in finished automotive spark-ignition fuels such as reformulated automotive spark-ignition fuels. The concentration range of the oxygenates covered in the ILS study was from 10 mg/kg to 2000 mg/kg. In addition this method is also suitable for the measurement of the C5 isomeric alcohols (2-methyl-1-butanol, 2-methyl-2-butanol) present from the fermentation of ethanol.

1.2 The ethanol blending concentration for which this test method applies ranges from 1 % to 15% by volume. Higher concentrations of ethanol coelute with methanol in the analytical column. Lower levels of ethanol, similar to the other oxygenate, can be calibrated and analyzed also. If higher ethanol concentrations are expected, the window cutting technique can be used to avoid ethanol from entering the analytical column and interfere with the determination of the other oxygenates of interest. Refer to Appendix X1 for details.

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

1.3.1 Alternative units, in common usage, are also provided to increase clarity and aid the users of this test method.

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]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography

D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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

3.1.2 *flame ionization detector (FID), n*—detector used to analyze the components eluting from the column.

3.1.3 *fluidic switch, n*—device that reverses the directional flow in a union T altering the pressure at the midpoint. In its simplest design it is also known as a Dean Switch.

3.1.4 *inlet, n*—capillary split/splitless inlet system operated in the split mode is recommended. Operate the inlet within its linear range.

3.1.4.1 *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 is expressed by:

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

[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.

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

where:

S = flow rate at the splitter vent, and
C = flow rate at the column outlet.

3.1.5 *low volume connector, n*—special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Sometimes this is referred to as zero dead volume union.

3.1.6 *multidimensional gas chromatography, n*—gas chromatographic technique where using hardware (valves, pressure switches, etc.) in which selected components from one column (primary column) are transferred to a secondary column differing in characteristics (film thickness, polarity, capacity, etc.) from the first column.

3.1.7 *WCOT column, n*—wall-coated open tubular, a type of capillary gas chromatographic column prepared by coating the inside of the capillary wall with a specified thin film of stationary phase. The coatings used are either 100 % polydimethyl siloxane or 5 % phenyl-polydimethylsiloxane.

3.1.7.1 *apolar column, n*—polydimethylsiloxane nonpolar column used as a pre-column.

3.1.7.2 *PLOT column-oxygen selective, n*—porous-layer open tubular which is an oxygenate selective capillary gas-solid chromatographic column. It is used as an analytical column.

4. Summary of Test Method

4.1 An appropriate internal standard of a product that is not present in refinery streams, such as 1,2-dimethoxy ethane (1,2-DME), is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a 4-port switching valve. The sample first passes onto an apolar (non-polar) polydimethylsiloxane WCOT column that performs a pre-separation of the trace oxygenates and elutes unwanted high boiling hydrocarbons to vent. The oxygenates and the DME are transferred to the analytical oxygen selective column by the switching valve. While the oxygenates and the DME are eluting from the analytical column, the inlet's carrier gas is used to elute the hydrocarbons from the pre-column to yield a stable baseline for the next analysis. The auxiliary pressure controller is used to provide carrier gas to the analytical column during the analysis.

4.2 The eluted components Table 1 are detected by one or two flame ionization detectors. In the single detector Configuration A (Fig. 1), only the components eluting from the analytical column are analyzed. In the two detector Configuration B (Fig. 2), detector one is used to monitor the apolar elution and aid in setting "heart-cut" times for specific oxygenates while the second detector is used to monitor the analytical column elution and also for the quantitation of the oxygenates. The second detector response is proportional to the oxygenates and DME components concentration. The signal is recorded, the peak areas are measured, and the concentration of each oxygenate is calculated with reference to the internal standard.

4.3 Alternatively, a fluidic switching system, Configuration C (Figs. 3 and 4) may be used instead of valve switching. In this system, the two columns are joined by a zero dead volume (ZDV) tee purged by an auxiliary carrier source. At injection, the auxiliary flow is low, and the inlet flow is sufficient so that at the midpoint where the two columns join, the flow is the required flow to transfer the oxygenates to the PLOT column. Thus, there is forward flow through the pre-column and the analytical column. Once the oxygenates have passed through to the analytical column, the inlet flow is decreased and the auxiliary flow is increased, which results in backflushing the pre-column through the split vent of the front inlet while the analytical column continues the separation.

5. Significance and Use

5.1 The analysis of trace oxygenates in automotive spark-ignition engine fuel has become routine in certain areas to ensure compliance whenever oxygenated fuels are used. In addition, test methods to measure trace levels of oxygenates in automotive spark-ignition fuel are necessary to assess product quality.

6. Apparatus

6.1 *Chromatograph*—A multidimensional gas chromatographic system, which is able to adequately resolve oxygenates and an internal standard and to eliminate hydrocarbon, as well as other interferences, is used for these analyses. The instrument is to be configured to operate using the approximate conditions listed in Table 2. The system requires a column switching mechanism equivalent to Fig. 1 or Fig. 2 if using a

TABLE 1 Component List with Retention and Calibration Characteristics for WCOT/PLOT Column Set Using Conditions of Table 2[A]

Component	RT (min)	Mol Wt	BP (°C)	Slope	y-Int	Corr. Coef.
ETBE	12.7	102.2	70 to 72	1.919	–0.02	0.999
MTBE	12.8	88.2	55 to 56	1.689	0.01	0.999
DIPE	12.9	102.2	68 to 69	2.124	–0.06	0.999
TAME	13.6	102.2	85 to 86	2.023	–0.02	0.999
Methanol	15.6	32.0	65	0.779	–0.09	0.997
Ethanol	18.7	46.1	78	1.352	0.19	0.999
iso-Propanol	22.2	60.1	81 to 83	1.504	–0.06	0.999
n-Propanol	22.2	60.1	97	...	...	...
t-Butanol	23.8	74.1	82	1.951	–0.12	0.999
s-Butanol	23.8	74.1	98	...	...	...
iso-Butanol	23.8	74.1	117	...	...	...
n-Butanol	24.4	74.1	118	1.906	–0.05	0.999
tert-Pentanol	25.1	88.1	102	2.148	–0.04	0.998
1,2-DME	26.0	90.1	85	...	...	...

[A] For coeluting compounds the response is assigned to the first peak listed. Values may be different for different instruments.

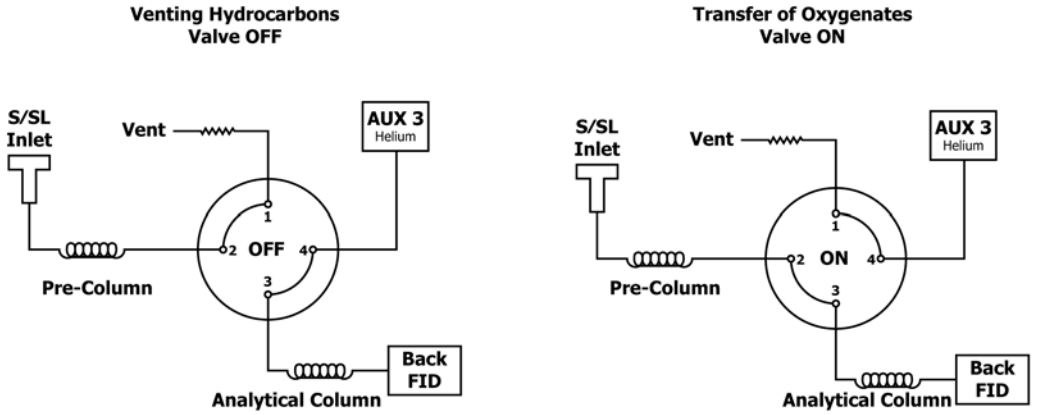


FIG. 1 Schematic of Chromatographic System—Configuration A

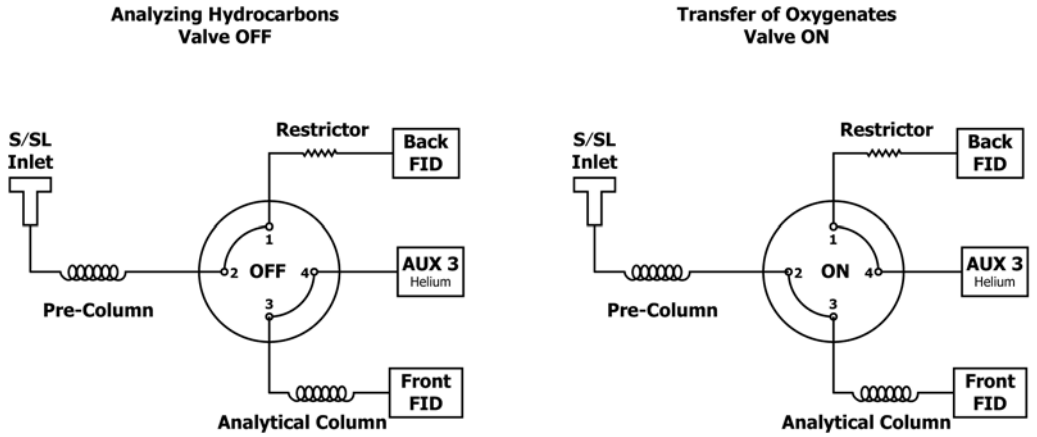


FIG. 2 Schematic of Chromatographic System—Configuration B

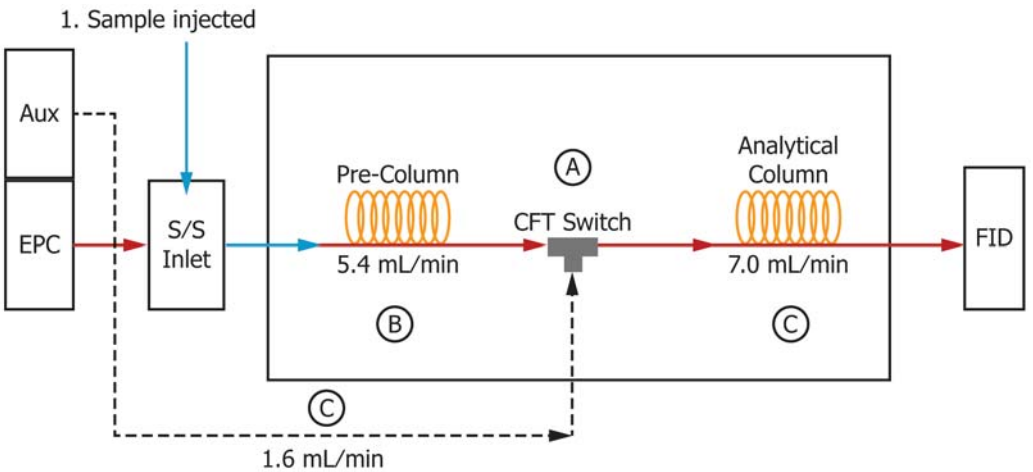


FIG. 3 Fluidic Switch Schematic—Oxygenate Transfer

valve system. If using a fluidic system then the fluidic switch and auxiliary flow control are required as shown in Fig. 3 and Fig. 4. Carrier gas flow controllers (EPC) shall be capable of precise control where the flow rates are low. Pressure control devices and gages shall be capable of precise control for the typical pressures required.

6.1.1 *Detector*—Two-flame ionization detectors are preferably used (Configuration B), although the analysis can be performed using only one detector (Configuration A and C). The system shall have sufficient sensitivity and stability to obtain a signal-to-noise ratio of at least 5 to 1 for a 1 mg/kg concentration of any oxygenate. In the fluidic system only one detector is used.

6.1.2 *Switching Valve*—A switching valve, to be located within the gas chromatographic column oven or separate oven, capable of performing the functions described in 9.2 and

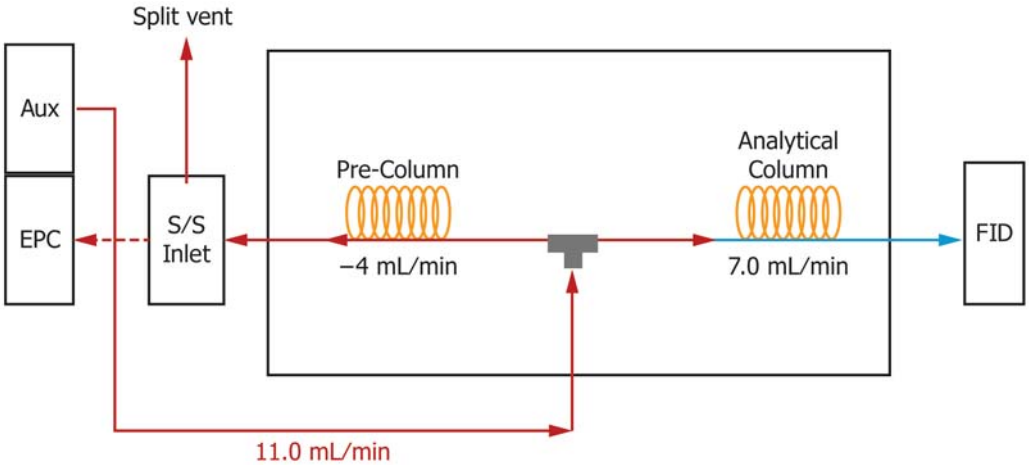


FIG. 4 Fluidic Switch Schematic—Pre-column Backflush

TABLE 2 Chromatographic Conditions

Configuration	Switching Valve	Fluidic Switch
Carrier Gas	Helium	Helium
Injection Volume	1.0 µL	1.0 µL
Inlet:	Split/Splitless (Split mode)	Split/Splitless (Split mode)
Temperature	250 °C	250 °C
Split Ratio	10:1	10:1
Pressure[A]	51.7 kPa, Constant Pressure	17.8 kPa, Flow Program Mode
Columns and Flows		
Pre-column	30 m by 0.53 mm by 5.0 µm PDMS 7.5 mL/min @ 60 °C	15 m by 0.53 mm by 1.5 µm 5 % phenyl PDMS Initial Flow: 5.4 mL/min @ 60 °C Hold for 1.5 min Ramp: 90 mL/min to -5 mL/min Hold until end of run
Analytical Column	10 m by 0.53 mm by 10 µm Oxygen Selective 7.5 mL/min@ 60 °C	10 m by 0.53 mm by 10 µm Oxygen Selective 7.0 mL/min constant flow
Oven:		
Initial Temperature	60 °C	60 °C
Initial Hold	6.0 min	6.0 min
Ramp 1	10 °C/min	10 °C/min
Final Temperature	150 °C	150 °C
Final Hold	5.0 min	5.0 min
Ramp 2	10 °C/min	10 °C/min
Final Temperature	220 °C	220 °C
Final Hold	3.0 min	3.0 min
Total Time	30 min	30 min
Detector:	FID	FID
Temperature	275 °C	275 °C
Hydrogen	40 mL/min	40 mL/min
Air	450 mL/min	450 mL/min
Make-up (N2)	10 mL/min	10 mL/min
Valve Temperature	150 °C	N/A
Auxiliary Pressure	73.1 kPa	10.3 kPa
Vent Restrictor	76 cm in length 0.16 cm (O.D.) and 0.25 mm (I.D.) SS	N/A
Default Valve Times (for complete analysis):		
Initial	OFF	N/A
0.50 min	ON	N/A
4.50 min	OFF	N/A

[A] For Configuration A valve timing determination, 9.2, set the inlet pressure to 34.5 kPa.

illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration. Alternatively a Deans switching arrangement can also be used as shown in Fig. 3 and Fig. 4.

6.1.2.1 A commercially available valve: 1.6 mm fittings, 0.75 mm ports was used in the method development. An equivalent valve may be used.

6.1.2.2 *Fluidic Switch,* as an option to the two-position switching valve. See 4.3, Table 2, and Figs. 3 and 4 for a description. Additional flow source is required as well as hardware, which is located in the oven for the column connection.

6.1.2.3 Some gas chromatographs are equipped with an auxiliary oven, which can be used to contain the valve at an

isothermal temperature. In such a configuration, the two capillary columns are located in the main oven and connected to the valve by using low dead volume and inert stainless steel tubing terminated in the GC oven.

6.1.2.4 An automatic valve switching device is used to ensure repeatable switching times. Such a device is synchronized with injection and data collection times. For the pressure switching approach, automatic precise and stable pressure control shall be used. Fluidic systems require both a fluidic switch and a programmable auxiliary pressure source to maintain and program flows.

6.1.3 *Injection System*—The chromatograph is to be equipped with a heated splitting-type inlet device containing a replaceable glass deactivated liner (single-taper style) with deactivated glass wool at the bottom to retain non-vaporized components). Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector efficiency and linearity.

6.1.3.1 A microliter automatic syringe injector is used for introducing representative samples into the gas chromatographic inlet and for adequate repeatability.

6.2 *Data Acquisition System:*

6.2.1 *Computer*—A data acquisition system containing a computer and data acquisition software is required.

6.2.2 *Integrator*—Alternatively, an integrator can be used to measure peak areas and to perform the analytical calculations.

6.3 *Column Class:*

6.3.1 *Apolar (Non-polar) Pre-Column*—This column performs a pre-separation of the oxygenates and internal standard from hydrocarbons in the same boiling point range. Unless a separate auxiliary oven is provided for it, the apolar column shall perform at the same temperature as the polar column does.

6.3.1.1 *WCOT Methyl Silicone Pre-Column*—30 m long by 0.53 mm inside diameter fused silica column with a 5 µm film thickness of cross-linked polydimethylsiloxane. With fluidic switch (Configuration C) a 30 m long by 0.53 mm with a 1.5 µm 5 % phenyl polydimethyl siloxane is recommended.

6.3.2 *Polar Analytical Column*—Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.1 and which separation efficiency is illustrated in Figs. 5 and 6 can be used.

6.3.2.1 *LowOx or GS OxyPLOT Polar Analytical Column*—10 m long by 0.53 mm inside diameter fused silica PLOT column with a 10 µm film thickness. These columns were used in the method development to provide the precision and bias data referred to in Section 14.

7. Reagents and Materials

7.1 *Gases:*

7.1.1 Helium, carrier gas, a minimum purity of 99.995 % is required. Oxygen scrubbers are recommended to safeguard the WCOT columns.

7.1.2 For the FID, hydrogen (99.9995 % with air as the remainder) and nitrogen (99.995 %, as make up) are used. (**Warning—**Observe high pressure precautions with all compressed gases. Observe flammable gas precautions with hydrogen.)

7.2 *Standards for Calibration and Identification*—Standards of oxygenates and the internal standard are required for establishing identification by retention time as well as calibration for quantitative analysis. These materials shall be of known purity and free of the other components to be analyzed. (**Warning—**These materials are flammable and can be harmful or fatal if ingested or inhaled.). The following oxygenates: ethanol, methyl-tertiary butyl ether (MTBE), ethyl-tertiary

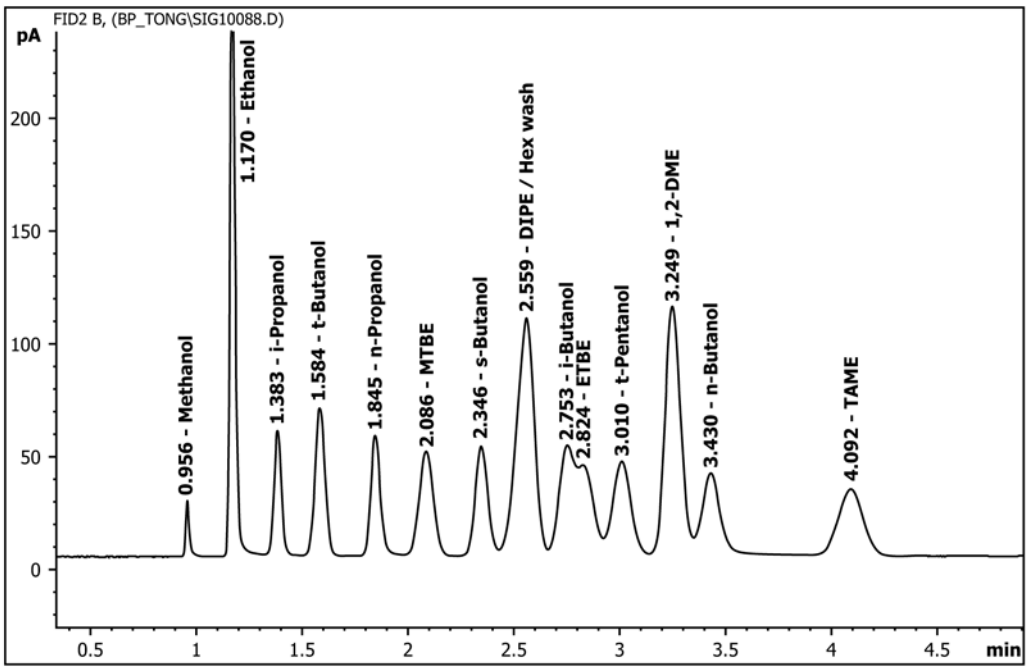
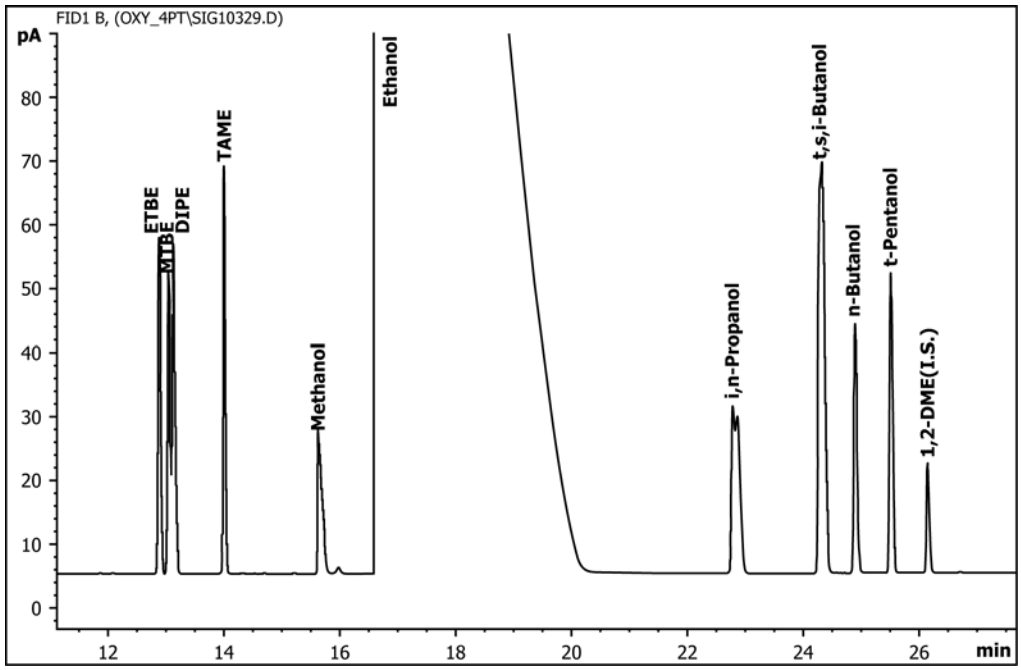


FIG. 5 Oxygenate Elution Pattern, from WCOT Pre-column Only



NOTE 1—Calibration Standard—250 mg/kg oxygenates, 7.5 % ethanol, and 200 mg/kg internal standard in *iso*octane.

FIG. 6 Oxygenate Elution Pattern from WCOT/PLOT Column Set Using Conditions in Table 2

butyl ether (ETBE), diisopropyl ether (DIPE), methanol, tertiary-amyl methyl ether (TAME), n-propanol, i-propanol, n-butanol, i-butanol, tert-butyl alcohol, sec-butyl alcohol, and tert-pentanol are to be used with the highest purity available (98 % to 99 %). Ethanol is usually not measured as a trace sample component.

7.3 iso*octane, or 2,2,4-Trimethylpentane*—Used for preparation of calibration standards and dilution of automotive spark-ignition fuel samples. In some cases, cyclohexane may be used provided it meets all of the requirements of the method. Using cyclohexane, since it elutes in the cut window of the oxygenates, may cause difficulty in finding individual cut times (see Appendix X1). (**Warning—***iso*octane and cyclohexane are flammable and may be harmful if inhaled. High concentrations may cause unconsciousness or death).

7.4 *1,2-Dimethoxyethane (1,2-DME or ethylene glycol dimethyl ether)*—Used as the internal standard. Use Reagent or Chromatography grade.

8. Sampling

8.1 Every effort should be made to ensure that the sample is representative of the finished automotive spark-ignition fuel from which it is taken. The use of multiple samples that are mixed or composite sampling is recommended. The use of epoxy-lined cans are recommended for storage or shipping of the sample, or both. Follow the recommendations of Practice D4057, when obtaining samples from bulk storage or pipelines. Samples that contain free layer of water will require special treatment. For the latter samples, it may be necessary to separate and analyze the water and hydrocarbon phases separately. The water phase may be determined from a separate method. For such analysis, it is necessary to know the amount of water and hydrocarbon phases to determine a total methanol content for the sample.

8.2 Prior to analysis, allow the sample container as received to equilibrate to ambient temperature.

9. Preparation of Apparatus and Establishment of Conditions

9.1 *Determine Configuration*—Refer to 4.2 to determine which configuration the chromatographic system is designed for the analysis. For a valve configuration the dual detector Configuration B (Fig. 2) is recommended due to the fact that the system can be assembled with no modifications to determine the cut times from the pre-column.

9.1.1 Figs. 1 and 2 are plumbing schematics for using a commercially available switching valve. This system is described primarily in the following sections–Configurations A and B.

9.1.2 Figs. 3 and 4 are the plumbing schematics for using a commercially available fluidic switching system.

9.2 *Configuration A (Single Detector Configuration):*

9.2.1 *Assembly*—Refer to Fig. 1. First connect the polydimethylsiloxane pre-column (6.3.1) to the detector directly to set the cut time (9.2.4) 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.

9.2.2 *Vent Restrictor*—The vent restrictor is intended to simulate the restriction caused by the PLOT column on the pre-column. This is needed to ensure accurate cut time determination while the valve is in the OFF position. A piece of stainless steel tubing, 70 cm in length, 0.16 cm O.D. and having 0.254 mm I.D., will approximate the column resistance.

9.2.3 *Conditions*—Establish the operating conditions listed in Table 2. This gives example conditions for the columns systems used in the development of this method. With the pre-column connected to the FID directly, the inlet pressure should be adjusted to ~31.0 kPa. This will set the column flow to approximately 6.8 mL/min at 60 °C. This is necessary since there is no simulation for the restriction caused by the PLOT column when the pre-column is installed directly to the FID. Modifications to column lengths etc. may require different operating conditions. Check the system for leaks before proceeding further. Condition the system overnight before proceeding.

9.2.4 *Setting Valve Times*—Once Configuration A is set up and the pre-column is connected to the detector, determine the retention time of the oxygenates through the pre-column.

9.2.5 Inject 1 µL of a ~300 mg/kg solution without ethanol or internal standard. To prepare this, add 20 µL of the solution made in 10.3 to 5 mL of *iso*octane. Record the chromatogram, and identify the peaks for each oxygenate using Fig. 5. From this retention time data, set the oxygenate transfer valve time ON to 0.5 min before the methanol starts eluting, and valve time OFF to 0.5 min after the TAME peak returns to baseline. The times should be incorporated into the analysis method before calibration is begun.

9.2.6 Reassemble the system by reinstalling the PLOT column to the diagram in Fig. 1 and Table 2 using low-volume connectors and inert narrow bore tubing. It is important to minimize the volume of the connections into and from the valve. Proceed to place the Valve in the ON position so that the apolar column and PLOT column are in series. Inject the sample as described in 9.2.5 and leave the valve in the ON position as determined in 9.2.5. Using the times determined in 9.2.5 transfer the oxygenates to the PLOT column.

9.3 *Configuration B (Dual Detector Configuration):*

9.3.1 *Assembly*—For Configuration B, connect the WCOT and PLOT columns to the valve system as shown in Fig. 2 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.

9.3.2 *Vent Restrictor*—The vent restrictor is intended to simulate the restriction caused by the PLOT column on the pre-column. This is needed to ensure accurate cut time determination while the valve is in the OFF position (see Fig. 2). A piece of stainless steel tubing, 70 cm in length, 0.16 cm O.D. and having 0.254 mm I.D., will approximate the column resistance.

9.3.3 *Conditions*—Establish the operating conditions listed in Table 2. This gives example conditions for the columns systems used in the development of this test method. Modifications to column lengths etc. may require different operating conditions. Check the system for leaks before proceeding further. Condition the system overnight before proceeding at an oven temperature of 200 °C.

9.3.4 *Setting Valve Times*—With the valve in the OFF position determine first the retention time of the oxygenates through the apolar. Subsequently the same is repeated but with the valve in the ON position.

9.3.5 Switch the valve to the OFF position to monitor the pre-column only. Inject 1 µL of a ~300 mg/kg solution without ethanol or internal standard. To prepare this, add 20 µL of the solution made in 10.3 to 5 mL of *iso*octane. Record the chromatogram. Identify the peaks for each oxygenate using Fig. 5. From this retention time data, set the oxygenate transfer valve time ON to 0.5 min before the methanol starts eluting, and valve time OFF to 0.5 min after the TAME peak returns to baseline. The times should be incorporated into the analysis method before calibration is begun.

9.4 *Configuration C (Single Detector Configuration Using a Fluidic Switch System:*

9.4.1 The pre-column and the analytical column are linked by fluidic switch (CFT) purged union (see Fig. 3). The iInlet EPC delivers 5.4 mL/min to both columns. The AUX EPC delivers 1.6 mL/min to the capillary flow technology (CFT) union. This increases the flow to the analytical column to 7.0 mL/min. Under these conditions the oxygenates are transferred in about 1.5 min.

9.4.2 High boiling point compounds are retained in the pre-column. Oxygenates and low boiling point hydrocarbons elute into analytical column. Oxygenates are trapped at the front of the analytical column. After TAME has eluted to the analytical column, the pre-column flow is reversed.

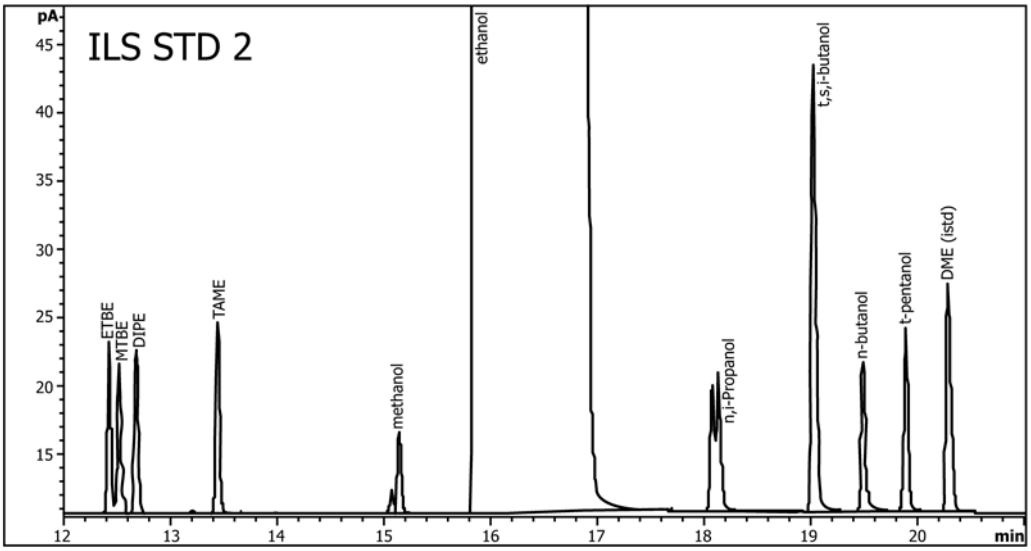
9.4.3 Inlet EPC flow is reduced to 4 mL/min (Fig. 4) and AUX EPC flow is increased to 11 mL/min. Gas flow through the fluidic switch backflushes the pre-column in order to send high boiling compounds out the front inlet split vent. Oven temperature program begins and oxygenates are separated on the analytical column. A typical chromatogram using this system is shown in Fig. 7.

9.5 *Verification of Detectability*—Inject a 5 mg/kg calibration solution and ensure that a signal/noise level of at least 5 is observed. Adjustment of the split ratio may be needed depending on the detector. See Fig. 8. The peaks for this level (5 mg/kg) have a height of about 2 pA.

9.6 *Conditioning*—To protect the PLOT column, avoid injecting samples until the valve times are properly optimized using calibration standards. It is recommended that when all of the analyses are completed, the GC oven temperature be maintained at 220 °C, with the pre-column carrier head pressure maintained at 138 kPa using the electronic pressure controller for at least several hours. This procedure conditions the PLOT column, which may trap carrier gas contaminants at the normal 60 °C starting temperature, and also elute residual heavy hydrocarbons from the pre-column. Periodically 25 cm can be cut off from the front of the polydimethylsiloxane column to remove heavy non-volatiles. The frequency can be determined from the analysis of quality control samples, by evaluating the QC results (see Section 13) and also from chromatographic performance, such as peak tailing etc.

10. Calibration and Standardization

10.1 *Preparation of Calibration Standards*—Prepare multicomponent oxygenate calibration standards by mass in accordance with Test Method D4307. Prepare a minimum of five calibration standards spanning the range of approximately



NOTE 1—Conditions in Table 2. Calibration Standard – mg/kg internal standard in *iso*octane.

FIG. 7 Oxygenate Elution Pattern from WCOT/PLOT Column Set Using the Fluidic Switch System

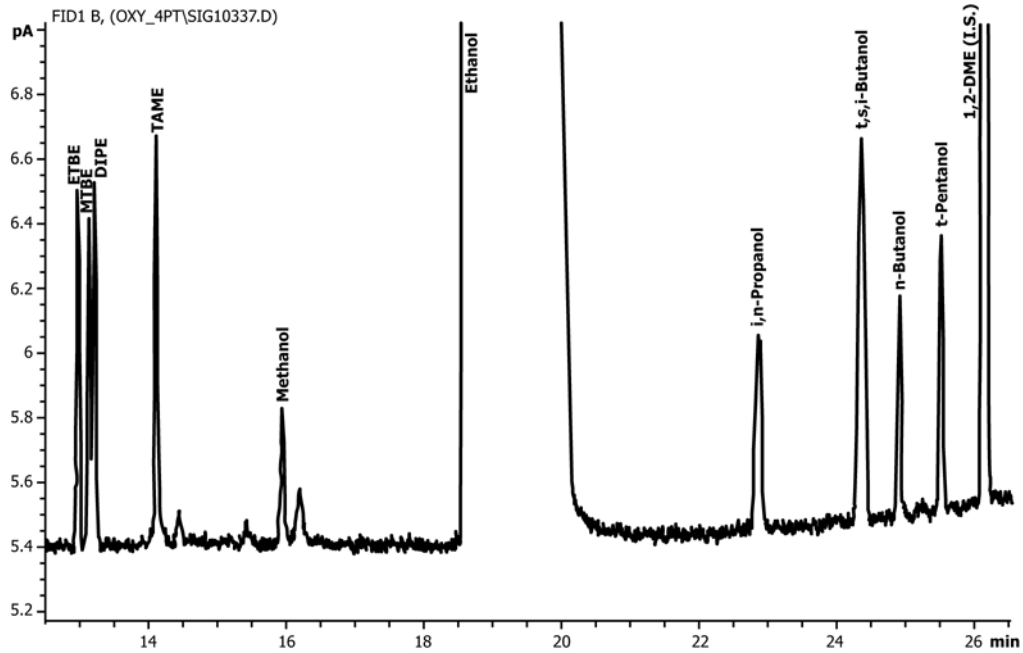


FIG. 8 Signal to Noise Verification—5 mg/kg Oxygenate/1.0 % Ethanol Calibration Standard with Conditions of Table 2.

10 mg/kg to 1000 mg/kg of each oxygenate and a constant 250 mg/kg of internal standard in *iso*octane. Standard concentrations should bracket the range of oxygenate concentrations expected. Four stock solutions are prepared to use in the preparation of the final calibration solutions: an 8.3 % (A), a 10000 mg/kg (B) and a 1000 mg/kg oxygenate solution (C) as well as a 2500 mg/kg internal standard solution (D). Ethanol is not included here but can be added to the analyte list if the stream to be analyzed does not contain the component and trace amounts are to be determined.

10.2 Before preparing the standards, determine the purity of *iso*octane reagent and each oxygenate to make corrections for the impurities found. Whenever possible, use stocks of at least of 99.9 % purity. Correct the purity of the components for water content, determined by Test Method D6304.

10.3 *Oxygenate Stock Solution A*—Add 3 mL of each of the 12 oxygenates listed in 7.2 in a capped 50 mL bottle or equivalent container. Record the weight to the nearest 0.1 mg. Do not include the internal standard, 1,2-DME, or the ethanol at this point. This solution will have each oxygenate at ~8.3 wt%. Calculate the mass percent using Eq 2.

$$\text{Mass percent} = \text{mass of component } i\ (g)/\text{total mass of solution } (g) \times 100 \quad (2)$$

10.4 *Oxygenate Stock Solution B*—For levels 1000 mg/kg, 500 mg/kg, and 250 mg/kg. In a tared 100 mL volumetric

flask, add 12 mL of the Oxygenate Stock Solution A prepared in 10.3 and record the weight to the nearest 0.1 mg. Fill to the mark with *iso*octane and record the weight. Calculate the concentration of each oxygenate using Eq 3 (~10 000 mg/kg).

$$\text{Concentration of component } I,\ mg/kg = W\%i \times (Mi/Mt) \times 10^4 \quad (3)$$

where:

$W\%i$ = percent mass of component i in 10.3 (%),
Mi = mass of solution prepared in 10.4 (g), and
Mt = total mass of solution in 10.4 (g)

10.5 *Oxygenate Stock Solution C*—For levels 100 mg/kg, 50 mg/kg, and 10 mg/kg. In a tared 100 mL volumetric flask, add 1.2 mL of the Oxygenate Stock Solution A prepared in 10.3 and record the weight to the nearest 0.1 mg. Fill to the mark with *iso*octane and record the weight. Calculate the concentration of each using Eq 3 (~1000 mg/kg).

10.6 *Internal Standard Working Solution D*—First prepare a ~5 % solution by adding 5 mL 1,2-DME to a tared 100 mL volumetric flask. Record the weight to the nearest 0.1 mg. Fill the flask to the mark with *iso*octane and record the weight. Calculate the concentration of DME using Eq 4. Then, in another 100 mL flask, add 4 mL of this solution, record the weight, and dilute to the mark with *iso*octane and record the weight again. Calculate the concentration of this solution D using Eq 5 (~2500 mg/kg).

$$\text{Mass percent of } DME\ (M\%_{DME}) = mass\ of\ DME\ (g)/Mt\ (g) \times 100 \quad (4)$$

where:

$M\%_{DME}$ = mass percent of first DME 5 % solution prepared in 10.5,
Mass of DME = mass in grams of DME, and
Mt = total mass of solution.

$$\text{mg/kg of DME Stock solution D, } = M\%_{DME} \times (M_{DME}/M_{DMET}) \times 10^4 \quad (5)$$

where:

$M\%_{DME}$ = mass percent of first DME 5 % solution,
M_{DME} = mass of first DME 5 % solution (g), and
M_{DMET} = total mass of solution (g).

10.7 *Preparation of Calibration Standards:*

10.7.1 *Stock Calibration Solutions*—Table 3 gives an example of volumes for preparation of working standards derived from the stock solutions for a set of oxygenate calibration standards consisting of 10 mg/kg, 50 mg/kg, 100 mg/kg, 250 mg/kg, 500 mg/kg, and 1000 mg/kg. The standards assume ethanol is present in the streams to be analyzed in percent levels so the calibration for ethanol consists of 1.0 %, 2.5 %, 5.0 %, 7.5 %, 10 %, and 15 % by mass. Levels of ethanol at milligrams per kilogram (mg/kg), similar to the other oxygenates, can be calibrated and analyzed for.

10.7.2 *Concentration Determination*—Use Eq 6 to calculate the concentration in milligrams per kilogram (mg/kg) for each component, including the internal standard, in each solution. The concentration of ethanol can be determined from the percent levels calculated in Table 3

$$\text{Concentration of component } i = Ci \times (MI/Mt) \quad (6)$$

where:

Ci = concentration, mg/kg, of i in stock solution,
MI = mass of stock solution added (g), and
Mt = total mass of solution (g).

10.7.3 *Working Calibration Solutions*—In a 10 mL volumetric flask, add 1 mL of the Internal Standard Working Solution D prepared in 10.6 and record the weight. Fill to the mark with one of the calibration solutions prepared in 10.7.1 and record the weight. This solution is injected using the conditions described in Table 2.

10.7.4 Reapply Eq 6 to account for the dilution with internal standard. These concentrations will be used in the calibration tables created.

10.8 Store capped stock solutions and calibrations solutions below 5 °C when not in use.

10.9 *Standardization:*

10.9.1 *Cut Time Determination and Identification*—In order to insure that the intended oxygenates enter the PLOT column it is necessary to determine the retention time through the apolar pre-column. This easily accomplished by using the solution of the oxygenates prepared in *iso*octane as described in 10.4. If the system has two detectors as described as Configuration B, inject the *iso*octane solution in the apolar column only. Verify that all the oxygenates have eluted prior to the *iso*octane. Note the time for the complete elution of TAME. This will be your cut time. For Configuration A, remove the PLOT column and install the restrictor to the FID. Inject the sample as described in 9.2.5 and 9.3.5. After the system cut times are established, determine the retention times of the oxygenates and internal standard using a calibration solution. After the determination of the cut time restore the system so that the columns are initially in series. Fig. 5 shows the elution order in the apolar column while Fig. 6 shows the complete oxygenate mixture separated in the combined apolar and PLOT column.

10.9.1.1 Optimize chromatographic conditions to obtain complete separation of the first three eluting peaks, that is, ETBE, MTBE, and DIPE. Maximum resolution of these peaks is critical for accurate quantification of each individual component. Difficulties were noted during the Iinterlaboratory

TABLE 3 Preparation of Stock Calibration Solutions

Oxy / EtOH Concentration	Oxy Stock B (mL)	Oxy Stock C (mL)	EtOH, neat (mL)	Diluent, I-C8 (mL)	Total Vol (mL)
1000 mg/kg / 15 %	11.00	...	15.00	74.00	100
500 mg/kg / 10 %	5.50	...	10.00	84.50	100
250 mg/kg / 7.5 %	2.75	...	7.50	89.75	100
100 mg/kg / 5 %	...	11.00	5.00	84.00	100
50 mg/kg / 2.5 %	...	5.50	2.50	92.00	100
10 mg/kg / 1.0 %	...	1.10	1.00	97.90	100

study of the separation of these three peaks. Suggestions for the proper resolution of these three peaks are given in Appendix X2.

10.9.1.2 *Retention Time Shifts*—Due to the peak shape and elution characteristics associated with a PLOT column, the retention time of ethanol will vary from approximately 16 min to 18 min depending on the concentration. It should also be noted that the peaks eluting before ethanol could also shift slightly depending on the concentration of ethanol. For accurate identification of these early eluting peaks, compare the sample with a calibration standard with similar ethanol concentration. See Fig. 9.

10.9.1.3 *Coelutions*—Two sets of coeluting peaks are observed with the PLOT column. The first is normal and iso-propanol. This has been seen to be partially resolved in some cases but calibration is difficult and so it is recommended the peaks be integrated together and summing their concentrations for calibration. The other set is the tertiary, secondary, and iso-butanols. Treat these as one peak for integration and sum their concentrations for calibration as C4 alcohols. Refer to Table 4 for relative response factors to aid in determining the error associated with this technique.

10.9.1.4 *Possible Interferences*—Certain aldehydes and ketones will elute near the components of interest. Also other polar low-boiling compounds, such as dienes, can also be present in the analysis range. The oxygenates: acetone, 2-butanone, methyl ethyl ketone and acetaldehyde have very close retention times to the oxygenates of interest in this method. The user should be aware that changes in temperature and flow may cause these oxygenates to coelute with the oxygenates of interest. On the other hand, the presence of the oxygenates mentioned above has not been detected in finished gasoline.

10.9.2 Analyze the calibration standards and establish a calibration curve for each oxygenate. Plot the response ratio *rspi* as the *y* axis versus the amount ratio *amti* as the *x* axis, See Fig. 10 for an example plot.

$$rspi = Ai/As \tag{7}$$

where:

Ai = area of component i
As = area of internal standard

$$amti = Wi/Ws \tag{8}$$

where:

Wi = mass of component *i* in the calibration standard.
Ws = mass of internal standard in the calibration standard.

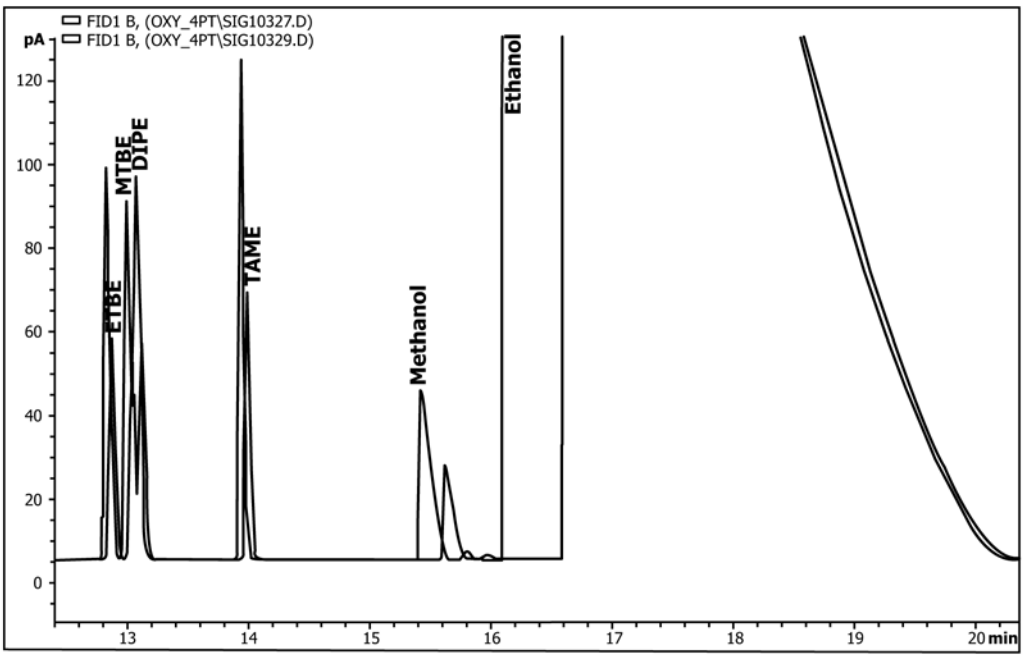
10.9.3 *Linear Least Squares Fit*—For the calibration data set, obtain the linear least squares fit equation in the form:

$$rspi = (mi)(amti) + bi \tag{9}$$

where:

rspi = response ratio for oxygenate/internal standard (*y*-axis)
mi = slope of linear equation for calibration curve
amti = amount ratio for methanol/internal standard (*x* -axis)
bi = *y*-axis intercept

10.9.3.1 An optimum calibration requires that the *y*-intercept (*bi*) be kept at a minimum. A value greater than 1 % of the slope should be cause for concern. If the value is positive, the calibration solutions may need to be recalculated or prepared again. A negative value could also be explained by poor calibration standards but also could be due to oxygenate adsorption in the system.



NOTE 1—500 mg/kg Oxy/10 % EtOH standard and 250 mg/kg Oxy/7.5 % EtOH standard overlaid.

FIG. 9 Retention Time Shift—Dependent on Ethanol Concentration

TABLE 4 Coelutions and Estimation of Error Determination

Component	RRF[A]	Slope[B]	% Difference
Iso-Propanol	1.2433	1.4952	16.8
n-Propanol	1.6044	...	7.3
iso-Butanol	1.9050	1.9512	2.4
tert-Butanol	1.8976	...	2.7
sec-Butanol	1.6678	...	14.5

[A] Relative Response Factor relative to DME calculated from Test Method D4815 data.
[B] From the Linear Least Squares Fit Eq 9 calibration curve data.

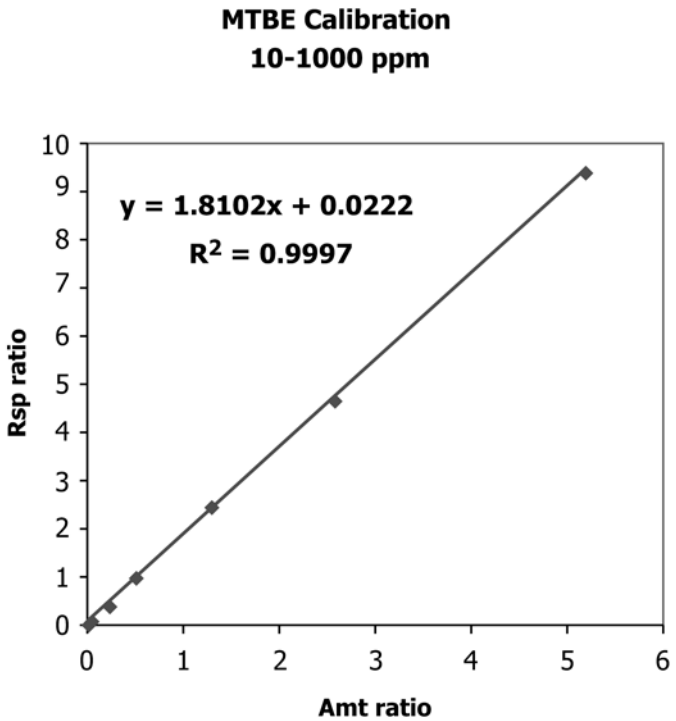


FIG. 10 Example of Least Squares Fit Calibration for MTBE

10.9.4 Calculate the correlation coefficient r^2 value for 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.

11. Procedure

11.1 *Preparation of Sample*—Add 1 mL of the 1,2-DME internal standard stock solution to 9.0000 g of sample. The concentration of internal standard is then 200 mg/kg. Record all masses to nearest 0.1 mg. Mix well the resulting solution for at least 1 min on a vortex or equivalent mixer. Transfer an aliquot of the solution into a glass gas chromatographic (GC) vial. Seal the GC vial with a TFE-fluorocarbon-lined septum. If the sample is not immediately analyzed, store below 5 °C. Do not store for more than 24 h.

11.2 *Chromatographic Analysis*—Introduce a representative aliquot of the sample, containing internal standard, into the gas chromatograph, using the same technique and sample size as used for the calibration analysis. Tables 1 and 2 contain approximate suggested conditions. Synchronize sample introduction with the start of recording and integrating devices. Obtain a chromatogram or integrated peak report, or both, which displays the retention times and integrated area of each detected component.

11.3 *Interpretation of Chromatogram*—Compare the retention times of sample to those of the calibration analysis to determine the identities of each oxygenate.

12. Calculations and Reporting

12.1 *Calculation of Oxygenate Concentration in Sample, mg/kg*—After identifying an oxygenate, measure the areas of the peak and of the internal standard. From the least squares fit calibrations, Eq 9, calculate the absolute mass of the oxygenate (Wi) in micrograms in the automotive spark-ignition fuel samples using the response ratio (*rspi*) of the areas for the oxygenate to that of the internal standard as follows in Eq 10.

$$Wi = [(Ai/As - bi)/mi] \times Ws \quad (10)$$

where:

Wi = µg of oxygenate in the sample,
Ai = area of oxygenate peak in sample,
As = area of internal standard added to sample,

bi = *y*-intercept of I from Eq 9,
mi = slope of I from Eq 9, and
Ws = µg of internal standard added {grams IS stock × conc. of stock (µg/g)}.

Then to determine the mg/kg levels of each oxygenate, apply the following equation:

$$Ci = Wi/Mt \quad (11)$$

where:

Ci = concentration of oxygenate, mg/kg,
Wi = µg of oxygenate in the sample, and
Mt = total mass of solution, g.

12.2 *Error Determination*—For the coelution referred to in 10.9.1.3, some error will be associated with identification of a single oxygenate while calibrating with an average RRF of a mixture of two or three oxygenates with different RRFs. Refer to Table 4 for RRF values for each of the coeluting peaks and the magnitude of the approximation when detecting a single component of the coelution.

13. Quality Control Reference Material

13.1 After the calibration has been completed, prepare two quality control check standard reference materials of selected oxygenates in automotive spark-ignition fuels or (preferred) use any reference automotive spark-ignition fuel samples which have been used in round robins or cross check programs for which mean values of selected oxygenate concentrations have been determined. One concentration should be in the lower concentration range, for example, 10 mg/kg to 30 mg/kg, and another in the upper concentration range, for example, 600 mg/kg to 1000 mg/kg. Analyze the reference material as described in the sample preparation procedure. The oxygenate concentration values obtained shall agree within ±15 % for the 10 mg/kg to 30 mg/kg reference material and ±5 % relative for the 600 mg/kg to 1000 mg/kg reference material. If the individual values are outside the specified range, verify calibration and instrument parameters, the accuracy of the preparation of quality control reference material, etc. Do not analyze samples without meeting the quality control specifications.

13.2 The check standards may be prepared by weighing 0.60 g of the oxygenate stock solution prepared in 10.3 and 5.00 g neat ethanol in 94.4 g of an oxygenate-free automotive spark-ignition fuel sample to prepare the upper end check standard. This corresponds to a 500 mg/kg oxygenate and 5 % ethanol spiked sample. After shaking well, more dilute solutions may be prepared by diluting gravimetrically aliquots of the stock with additional oxygenate-free automotive spark-ignition fuel. Treat this sample like any other and add the appropriate amount of internal standard before injection.

13.3 Analyze the quality control reference materials before every batch of samples. Bracket the samples with the reference material. If the reference materials do not meet the specifications in Section 13.1, the samples analyzed immediately preceding the reference material are considered suspect and should be reanalyzed.

14. Precision and Bias

14.1 *Precision*—The precision of this test method was determined by statistical examination of a round robin study.[3] This study involved five (5) laboratories and six (6) gravimetrically spiked automotive spark-ignition fuel samples at varied concentration levels within the range of the method. All samples were analyzed by duplicate analysis. The Precision is shown in Table 5 and Example calculations are shown in Table 6. It is to be noted that the precision showed in Table 5 covers only for the ranges indicated in Table 5. Precision should not be used outside of the ranges specified in Table 5.

14.2 *Repeatability (r)*—The difference between successive 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 correct operation of the test method, exceed the values in Table 5 only in one case in twenty.

14.3 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials would in the long run, exceed the values in Table 5 only in one case in twenty. When only a single test result is available, the reproducibility limit can be used to calculate a range (test result ± reproducibility limit) outside of which a second test result would expect to fall about one time in twenty. Reproducibility results are shown in Table 5.

14.4 *Bias*—No information can be presented on the bias of this procedure because an accepted reference material is not available.

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1809. Contact ASTM Customer Service at service@astm.org.

TABLE 5 Repeatability and Reproducibility[A]

Component	Repeatability	Reproducibility	As per ILS
	r (mg/kg)	R (mg/kg)	Range (mg/kg)
ETBE	$0.1503X^{0.8876}$	$0.3221X^{0.8876}$	13 to 1759
MTBE	$0.2548X^{0.8476}$	$0.5809X^{0.8476}$	18 to 1717
DIPE	$0.2678X^{0.7085}$	$2.3323X^{0.4916}$	13 to 1703
TAME	$0.2545X^{0.7467}$	$0.3736X^{0.7467}$	13 to 1842
Methanol	$0.1272X^{0.9217}$	$0.2045X^{0.9217}$	12 to 1881
n,i-Propanol	$0.1173X^{0.9183}$	$0.1720X^{0.9183}$	19 to 1904 ea
t,s,i-Butanol	$0.003845X^{1.3463}$	$0.008489X^{1.3463}$	19 to 1891 ea
n- Butanol	$1.4747X^{0.4455}$	$3.4596X^{0.4455}$	12 to 1952
t-Pentanol	$0.4487X^{0.6306}$	$0.9752X^{0.6306}$	13 to 1958

[A] X = value obtained from analysis in mg/kg. Do not extrapolate outside the ranges noted.

TABLE 6 Example Calculation of Precision for 100 mg/kg, 250 mg/kg, and 600 mg/kg Oxygenates

	100 mg/kg		250 mg/kg		600 mg/kg	
	r	R	r	R	r	R
ETBE	9	19	20	43	44	94
MTBE	13	29	27	63	58	131
DIPE	7	22	13	35	25	54
TAME	8	12	16	23	30	44
Methanol	9	14	21	33	46	74
n,i-Propanol	8	12	19	27	42	61
t,s,i-Butanol	2	4	7	14	21	47
n- Butanol	11	27	17	40	25	60
t-Pentanol	8	18	15	32	25	55

15. Keywords

15.1 alcohols; automotive spark-ignition fuel; ethers; gas chromatography; oxygenates

APPENDIXES

(Nonmandatory Information)

X1. INDIVIDUAL OXYGENATE ANALYSIS

X1.1 This appendix details the procedure for analyzing individual oxygenates by using multiple cut times; one time for the oxygenate of interest and one for the internal standard. This is based on the switching valve configuration. Alternative cut times will have to be determined for instruments configured with a fluidic switch.

X1.2 This procedure allows for positive identification of coeluting peaks. Due to the boiling point elution characteristics of the apolar pre-column, the normal and iso-propanol as well as the tert-, sec-, and iso-butanol peaks elute at very different times. Therefore specific cut time windows can be selected to elute the suspected oxygenate. These specific windows can be determined using the chromatogram of the calibration standard run through the pre-column only.

X1.2.1 An amount of ethanol will be seen in most analyses depending on its concentration. This is due to the tailing effect from the pre-column. Part of this tail will be seen with most cut time windows. If ethanol is to be determined in the percent range, use the complete cut time established in Section 9.

X1.3 If ethanol is present at concentration ranges higher than 15 %, its elution into the PLOT column can be prevented by opening a time window so that the ethanol is vented by introducing a cut time window that will exclude the ethanol from entering the analytical column. This window can be set at an approximate time of 1.1 min to 1.4 min. This will significantly reduce interferences with minor components present in the sample.

X1.3.1 Due to the lower amount of ethanol introduced into the PLOT column using this procedure, the retention times of the ethers and methanol will elute ~0.2 min later than expected than if the calibration was done using the complete cut time window of 0.5 min to 5.0 min. Refer to 10.9.1.

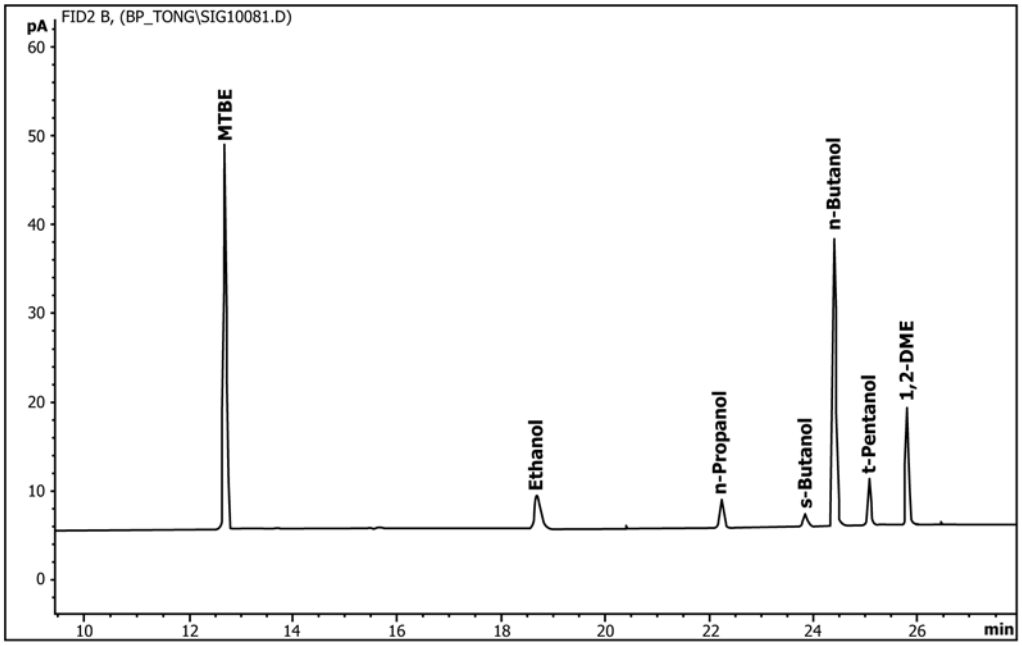
X1.4 Table X1.1 details the specific cut time windows for each oxygenate. Some of the windows do overlap due to partial resolution of the peaks from the pre-column using the conditions set in Table 2. Figs. 5 and 6 shows the elution time of the oxygenates from the pre-column for the cut time determination.

X1.4.1 Fig. X1.1 shows a chromatogram of the analysis of MTBE and 1,2-DME. The cut time windows used are from Table X1.1 for the specific components in a sample containing 15 % ethanol. Notice the small residual of the ethanol peak.

TABLE X1.1 Cut Time Windows for Each Oxygenate

NOTE 1—The first time is the Valve-ON position, and the second is the Valve-OFF position. These windows are approximate and may need adjustment depending on the instrument. If using a fluidic switch, times may be different.

Component	Window (min)
ETBE	2.7 to 3.0
MTBE	1.9 to 2.2
DIPE	2.4 to 2.7
TAME	3.8 to 4.4
Methanol	0.8 to 1.1
Ethanol	1.1 to 1.4
i-Propanol	1.2 to 1.5
n-Propanol	1.7 to 2.0
i-Butanol	2.6 to 2.9
s-Butanol	2.2 to 2.5
t-Butanol	1.4 to 1.7
n-Butanol	3.3 to 3.6
t-Pentanol	2.8 to 3.2
1,2-DME	3.1 to 3.4



NOTE 1—Traces of other oxygenates due to overlapping windows.

FIG. X1.1 MTBE and Internal Standard Analysis Using Cut Time Windows from Table X1.1

X2. IDENTIFICATION OF OXYGENATE ANALYSIS

X2.1 During the ILS study it was noticed the difficulty in the separation and identification of the oxygenates eluting prior to ethanol. Figs. X2.1-X2.4 represent cases, which clearly lead to incorrect concentrations of these oxygenates.

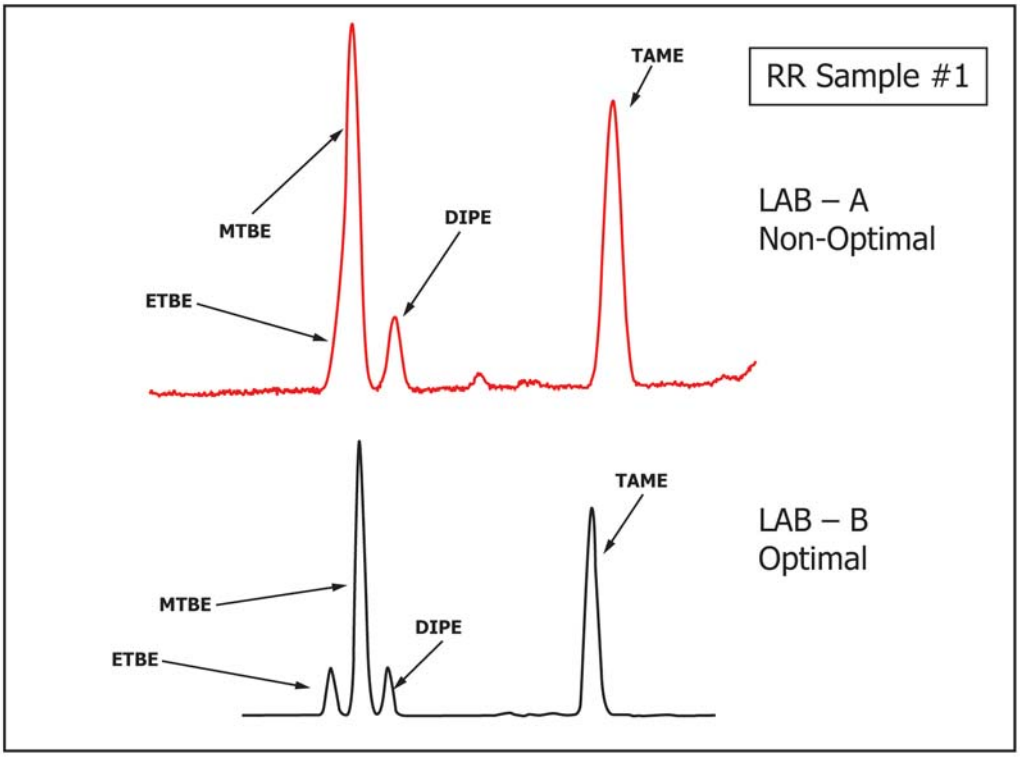


FIG. X2.1 Comparison of a Non-optimal and Optimal Resolution for a Sample Showing Incomplete Resolution between ETBE and MTBE

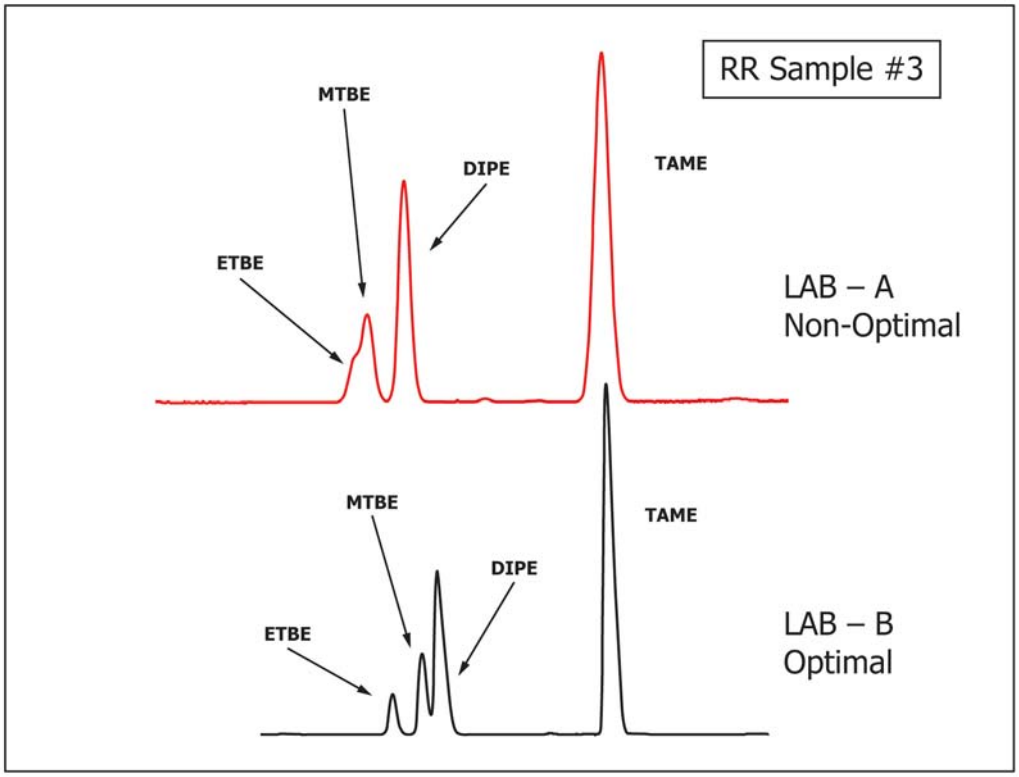


FIG. X2.2 Comparison of a Non-optimal and Optimal Resolution for a Sample Showing Incomplete Resolution between ETBE and MTBE, Having a Larger Concentration of DIPE

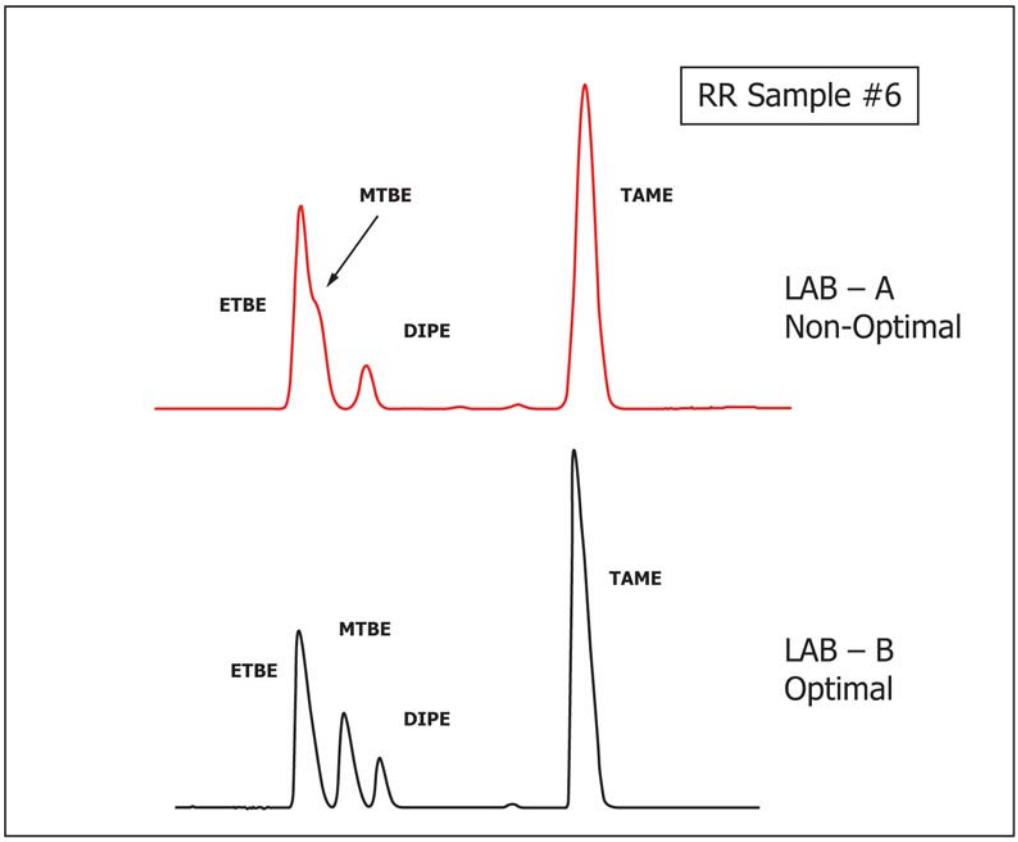
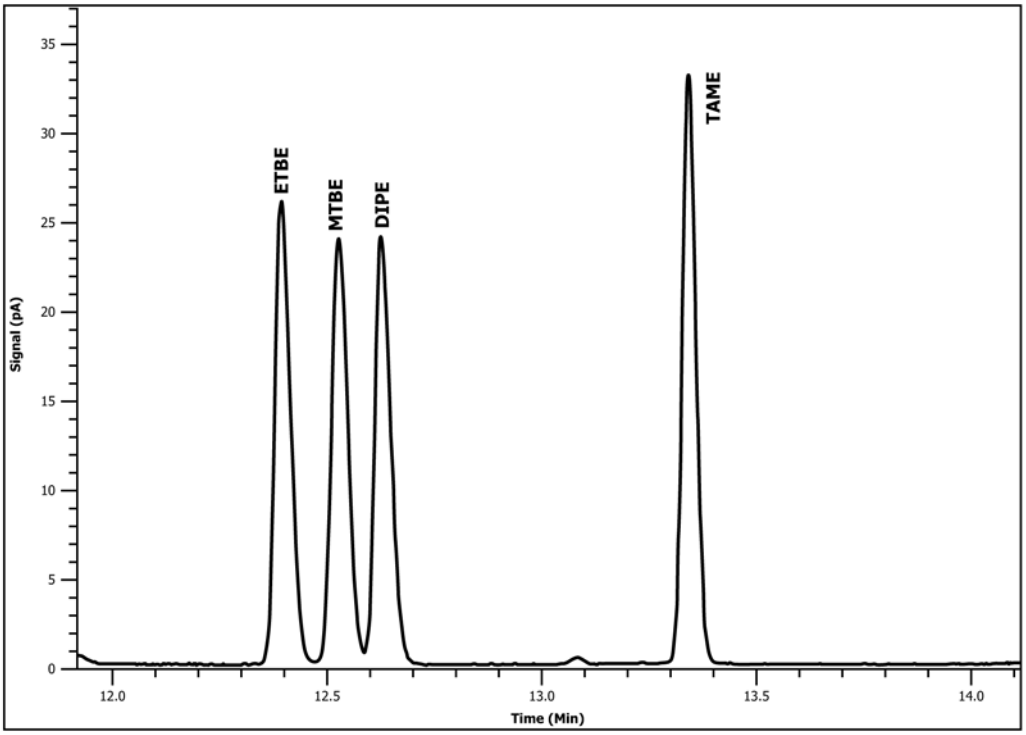


FIG. X2.3 Comparison of a Non-optimal and Optimal Resolution for a Sample Showing Incomplete Resolution between ETBE and MTBE, Having a Larger Concentration of ETBE



NOTE 1—Calibration Standard circa 90 mg/kg each component.

FIG. X2.4 Elution pattern from WCOT /PLOT Columns for ETBE, MTBE, DIPE and TAME Using Conditions in Table 2

X2.2 These coelutions occur due to relative amount of these three components ETBE, MTBE and DIPE occur a different relative quantities. This requires the observation that the peaks are not symmetrical indicating a coelution. This is best by having a standard of these threepeaks at the level of 20 mg/kg to 90 mg/kg.

X2.3 The following factors should be considered when optimizing the separation of these three components:

(1) Column flow

(2) Column Temperature (increase or decrease by 2 °C to 3 °C)

(3) Recondition the column at 200 °C for several hours.

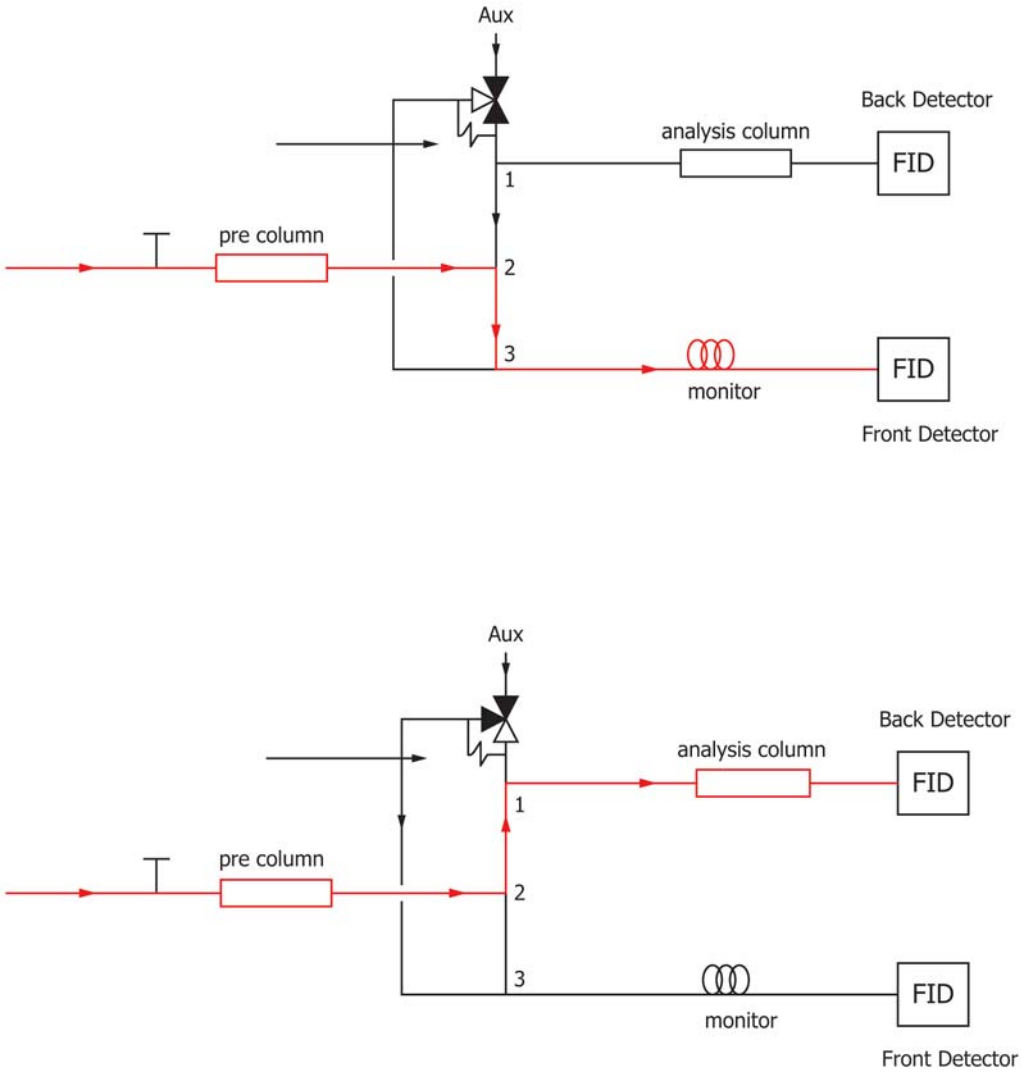
(4) Verify that all lines that are used in the chromatography are heated.

(5) Check that there is a smooth transition in flows when the valve is switched from in series to the PLOT column alone.

(6) Condition the apolar column.

X3. ADDITIONAL METHODOLOGY

X3.1 The "classic" Deans configuration also has been suggested for this method as an additional technique. A pre-column with a fluidic switch that can send sample to either a monitor column or an a analytical column, in single and dual detector configuration, which is similar to configuration C, is shown in Fig. X3.1. It allows for easy tuning of the cut-times. The entire separation principle is the same, but allows for flexibility in the use of the configurations. It is to be noted that this configuration was not used in determining the precision shown in Table 5.



NOTE 1—Upper figure shows the bypass mode to the monitor detector. Lower figure shows the transfer mode of the oxygenates to the analytical column and detector.

FIG. X3.1 Use of the Dean's Switch Technique for the Analysis of Trace Oxygenates

SUMMARY OF CHANGES

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D7754 – 11$^{\varepsilon 1}$) that may impact the use of this standard. (Approved Jan. 1, 2016.)

(1) Changed "ppm" to "mg/kg" throughout; otherwise updated SI unit formatting.