



Designation: ~~D7754 – 11~~<sup>e1</sup> D7754 – 16

## Standard Test Method for Determination of Trace Oxygenates in Automotive Spark-Ignition Engine Fuel by Multidimensional Gas Chromatography<sup>1</sup>

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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

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<sup>e1</sup> NOTE—~~Research report information was added editorially to Section 14 in November 2015.~~

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### 1. Scope—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~~10 ~~mg/μg/Kg–kg~~ to ~~2000~~2000 ~~mg/μg/Kg–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~~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 ~~Alternate~~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:*<sup>2</sup>

[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<sub>1</sub> to C<sub>4</sub> 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:*

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<sup>1</sup> 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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<sup>2</sup> 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

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:

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

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~~ 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 *ppm*, *n*—parts per million, or micrograms per gram (mg/kg).

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%~~ 100 % polydimethyl siloxane or ~~5%~~ 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.

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

| 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       |
| 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       |
| 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       |
| 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       |
| 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       |
| 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       |
| 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       |
| 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       |
| tert-Pentanol | 25.1     | 88.1   | 102      | 2.148 | -0.04 | 0.998       |
| 1,2-DME       | 26.0     | 90.1   | 85       | ...   | ...   | ...         |

<sup>A</sup> For coeluting compounds the response is assigned to the first peak listed. Values may be different for different instruments.

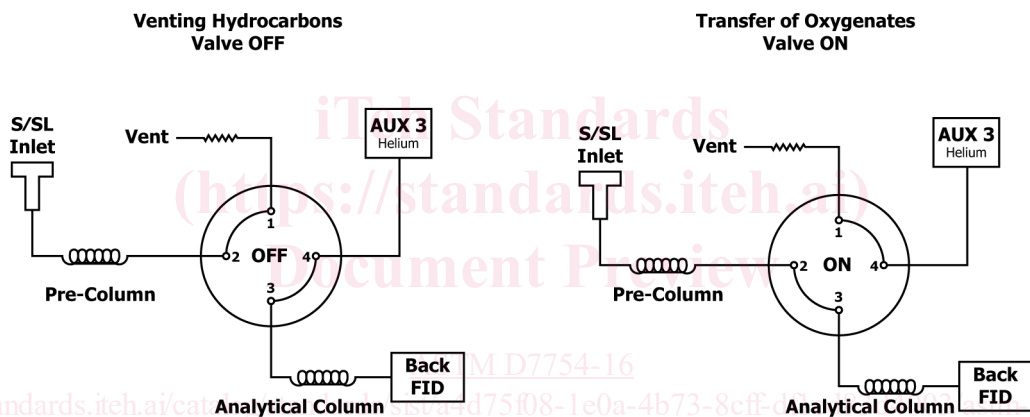


FIG. 1 Schematic of Chromatographic System—Configuration A

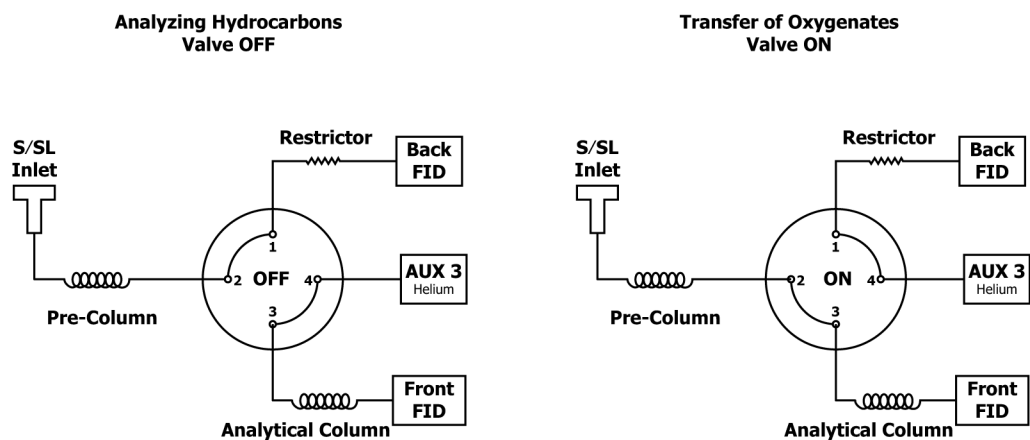


FIG. 2 Schematic of Chromatographic System—Configuration B

## 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

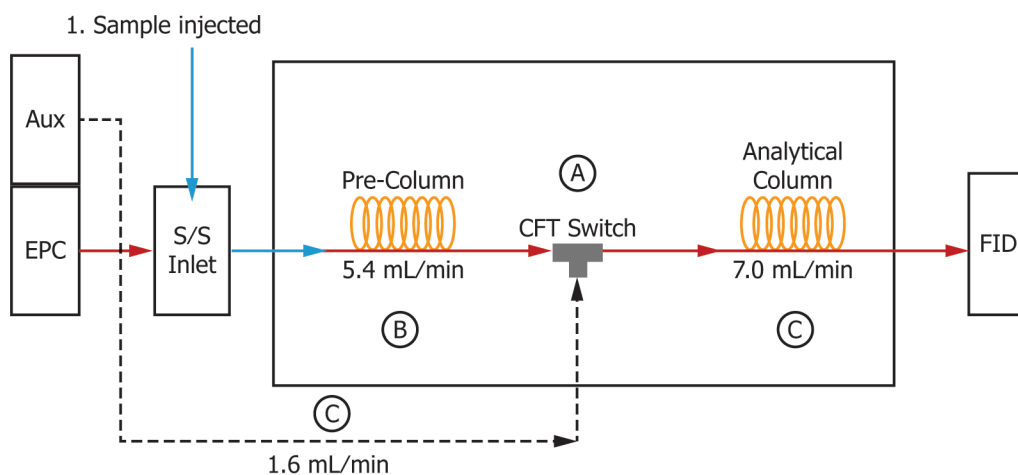


FIG. 3 Fluidic Switch Schematic—Oxygenate Transfer

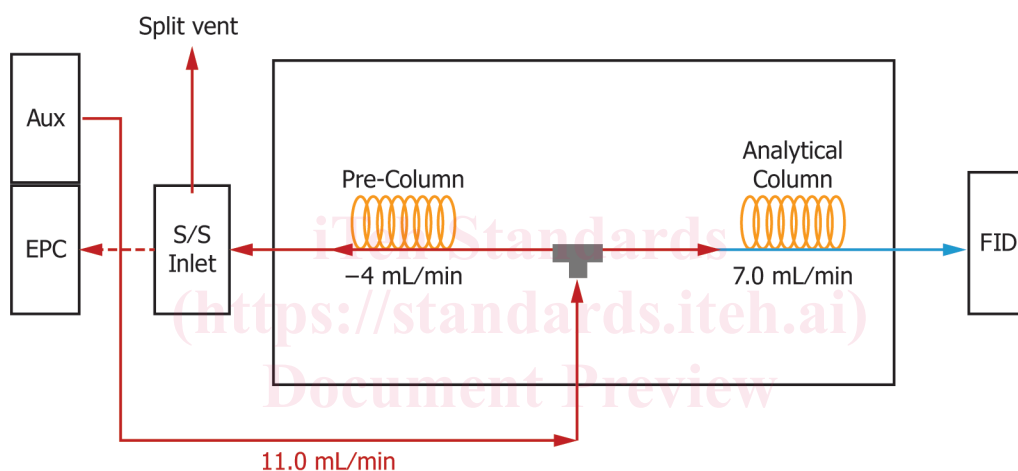


FIG. 4 Fluidic Switch Schematic—Pre-column Backflush

<https://standards.iteh.ai/catalog/standards/sist/a4d75f08-1e0a-4b73-8c1f-df1ed83d4003/astm-d7754-16>

equivalent to Fig. 1 or Fig. 2 if using a 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  $\pm 1 \text{ mg/ppm (m/m)-kg}$  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 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 Figs. 3 and 4 Fig. 3 and Fig. 4.

6.1.2.1 A commercially available valve:  $1.6 \text{ mm}$  fittings,  $0.75 \text{ mm}$  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-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.

**TABLE 2 Chromatographic Conditions**

| Configuration                                | Switching Valve   | Fluidic Switch  |
|--|---|---|
| Carrier Gas                                  | Helium  | Helium  |
| Injection Volume                             | 1.0 $\mu$ L   | 1.0 $\mu$ L   |
| Inlet:                                       | Split/Splitless (Split mode)  | Split/Splitless (Split mode)  |
| —Temperature                                 | 250°C   | 250°C   |
| Temperature                                  | 250 °C  | 250 °C  |
| Split Ratio                                  | 10:1  | 10:1  |
| Pressure <sup>A</sup>                        | 7.5 psi, Constant Pressure  | 2.58 psi, Flow Program Mode   |
| Pressure <sup>A</sup>                        | 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 $\mu$ m PDMS<br>7.5 mL/min @ 60°C            | 15 m by 0.53 mm by 1.5 $\mu$ m 5% phenyl PDMS<br>Initial Flow: 5.4 mL/min @ 60°C<br>Hold for 1.5 min<br>Ramp: 90 mL/min to -5 mL/min<br>Hold until end of run |
| Pre-column                                   | 30 m by 0.53 mm by 5.0 $\mu$ m PDMS<br>7.5 mL/min @ 60°C            | 15 m by 0.53 mm by 1.5 $\mu$ m 5% phenyl PDMS<br>Initial Flow: 5.4 mL/min @ 60°C<br>Hold for 1.5 min<br>Ramp: 90 mL/min to -5 mL/min<br>Hold until end of run |
| Analytical Column                            | 10 m by 0.53 mm by 10 $\mu$ m Oxygen Selective<br>7.5 mL/min @ 60°C | 10 m by 0.53 mm by 10 $\mu$ m Oxygen Selective<br>7.0 mL/min constant flow  |
| Analytical Column                            | 10 m by 0.53 mm by 10 $\mu$ m Oxygen Selective<br>7.5 mL/min @ 60°C | 10 m by 0.53 mm by 10 $\mu$ m Oxygen Selective<br>7.0 mL/min constant flow  |
| Oven:  |   |   |
| —Initial Temperature                         | 60°C  | 60°C  |
| Initial Temperature                          | 60 °C   | 60 °C   |
| —Initial Hold                                | 6.0 min   | 6.0 min   |
| Initial Hold                                 | 6.0 min   | 6.0 min   |
| —Ramp 1                                      | 10°C/min  | 10°C/min  |
| Ramp 1                                       | 10 °C/min   | 10 °C/min   |
| —Final Temperature                           | 150°C   | 150°C   |
| Final Temperature                            | 150 °C  | 150 °C  |
| Final Hold                                   | 5.0 min   | 5.0 min   |
| —Ramp 2                                      | 10°C/min  | 10°C/min  |
| Ramp 2                                       | 10 °C/min   | 10 °C/min   |
| —Final Temperature                           | 220°C   | 220°C   |
| 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   |
| Temperature                                  | 275 °C  | 275 °C  |
| Hydrogen                                     | 40 mL/min   | 40 mL/min   |
| Air  | 450 mL/min  | 450 mL/min  |
| Make-up (N <sub>2</sub> )                    | 10 mL/min   | 10 mL/min   |
| Valve Temperature                            | 150°C   | N/A   |
| Valve Temperature                            | 150 °C  | N/A   |
| Auxiliary Pressure                           | 10.6 psi  | 1.50 psi  |
| Auxiliary Pressure                           | 73.1 kPa  | 10.3 kPa  |
| Vent Restrictor                              | 30 by 1/16 by<br>0.010 in. SS†                                      | N/A   |
| Vent Restrictor                              | 76 cm in length<br>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   |

<sup>A</sup> For Configuration A valve timing determination, 9.2, set the inlet pressure to  $-5$  psi/34.5 kPa.

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~~ 30 m long by ~~0.53 mm~~ 0.53 mm inside diameter fused silica column with a ~~5 μm~~ 5 μm film thickness of cross-linked polydimethylsiloxane. With fluidic switch (Configuration C) a ~~30 m~~ 30 m long by ~~0.53 mm~~ 0.53 mm with a ~~1.5 μm~~ 5%–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~~ 10 m long by ~~0.53 mm~~ 0.53 mm inside diameter fused silica PLOT column with a ~~10 μm~~ 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%~~ 99.995 % is required. Oxygen scrubbers are recommended to safeguard the WCOT columns.

7.1.2 For the FID, hydrogen (~~99.9995%~~ 99.9995 % with air as the remainder) and nitrogen (~~99.995%~~ 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 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 (~~98–99%~~ 98 % to 99 %). Ethanol is usually not measured as a trace sample component.

7.3 ~~Iso-octane~~ isooctane, 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~~ isooctane 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.

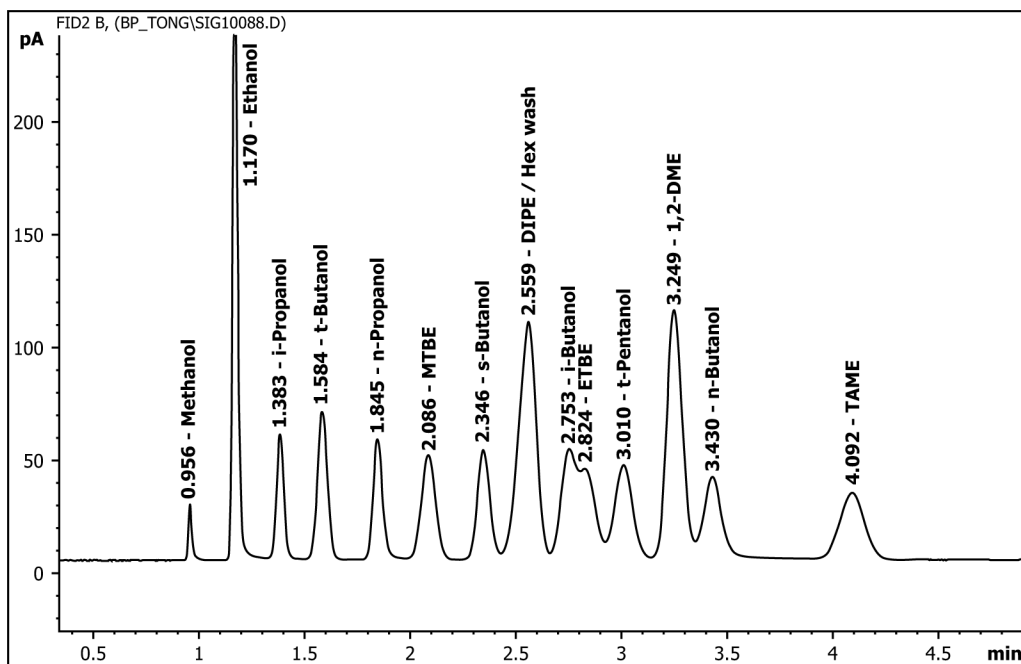
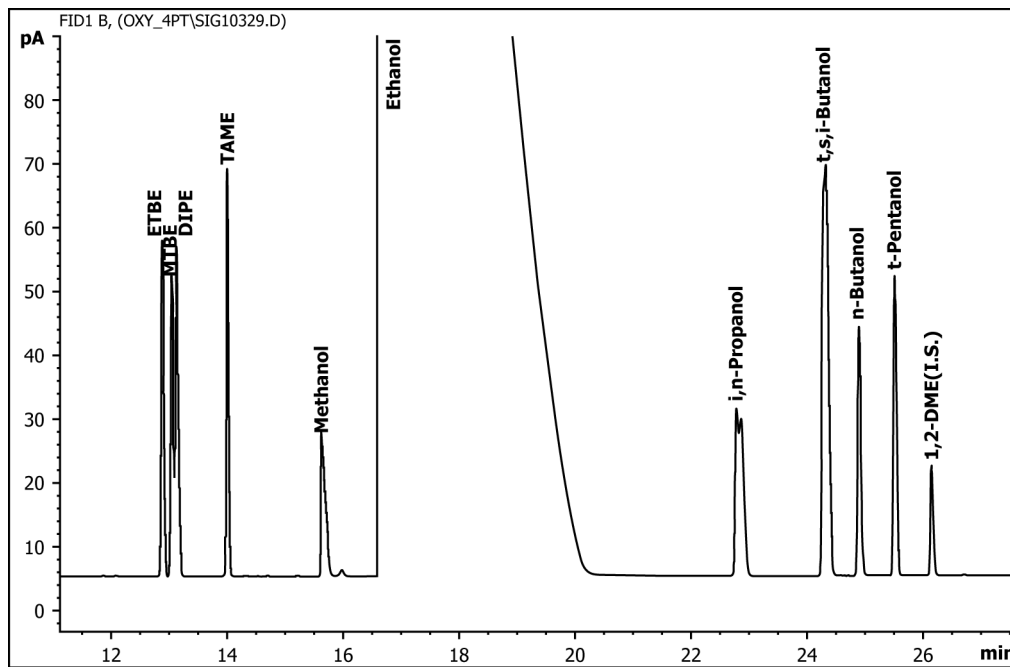


FIG. 5 Oxygenate Elution Pattern, from WCOT Pre-column Only





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

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

iteh Standards  
(<https://standards.iteh.ai>)

## 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, 30 by 70 cm in  $\frac{1}{4}$  by 0.010 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  $\sim 4.5$  psi,  $\sim 31.0$  kPa. This will set the column flow to approximately 6.86 mL/min at  $60^\circ\text{C}$ . 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  $\mu$ L~~ 1  $\mu$ L of a ~~~300~300 mg/-ppm-kg~~ solution without ethanol or internal standard. To prepare this, add ~~20  $\mu$ L~~ 20  $\mu$ L of the solution made in 10.3 to 5 mL ~~5 mL~~ of iso-octane:isooctane. 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~~ 0.5 min before the methanol starts eluting, and valve time OFF to ~~0.5 min~~ 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, ~~30 by 70 cm in~~ 1/4 by 0.010 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~~ 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  $\mu$ L~~ 1  $\mu$ L of a ~~~300~300 mg/-ppm-kg~~ solution without ethanol or internal standard. To prepare this, add ~~20  $\mu$ L~~ 20  $\mu$ L of the solution made in 10.3 to 5 mL ~~5 mL~~ of iso-octane:isooctane. 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~~ 0.5 min before the methanol starts eluting, and valve time OFF to ~~0.5 min~~ 0.5 min after the TAME peak returns to baseline. The times should be incorporated into the analysis method before calibration is begun.

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### 9.4 Configuration C (Single Detector Configuration Using a Fluidic Switch System: [dfled83d4003/astm-d7754-16](https://doi.org/10.1117/1.4834003))

9.4.1 The pre-column and the analytical column are linked by fluidic switch (CFT) purged union (see Fig. 3). The ~~Inlet~~ Inlet EPC delivers ~~5.45.4 mL/-mL/min-min~~ to both columns. The ~~Aux~~ AUX EPC delivers ~~1.61.6 mL/-mL/min-min~~ to the ~~Capillary Flow Technology~~ capillary flow technology (CFT) union. This increases the flow to the analytical column to ~~7.07.0 mL/-mL/min-min~~. Under these conditions the oxygenates are transferred in about ~~1.5 min~~ 1.5 min.

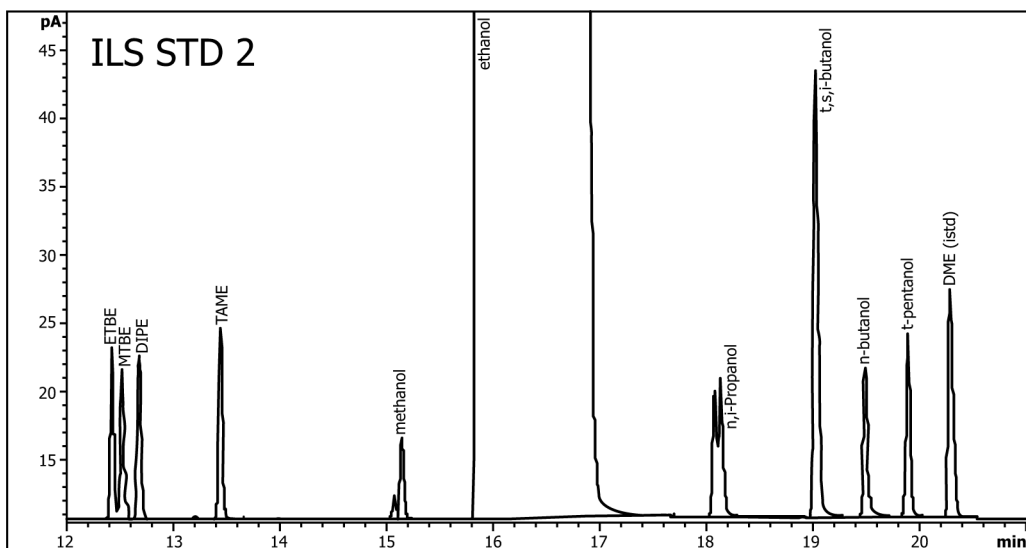
9.4.2 High boiling point compounds are retained in the pre-column. Oxygenates and low boiling point hydrocarbons elute into analytical column. Oxygenates are trapped at the front of the analytical column. After TAME has eluted to the analytical column, the pre-column flow is reversed.

9.4.3 Inlet EPC flow is reduced to ~~44 mL/-mL/min-min~~ (Fig. 4) and AUX EPC flow is increased to ~~111 mL/-mL/min-min~~. Gas flow through the ~~Fluidic Switch~~ 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.

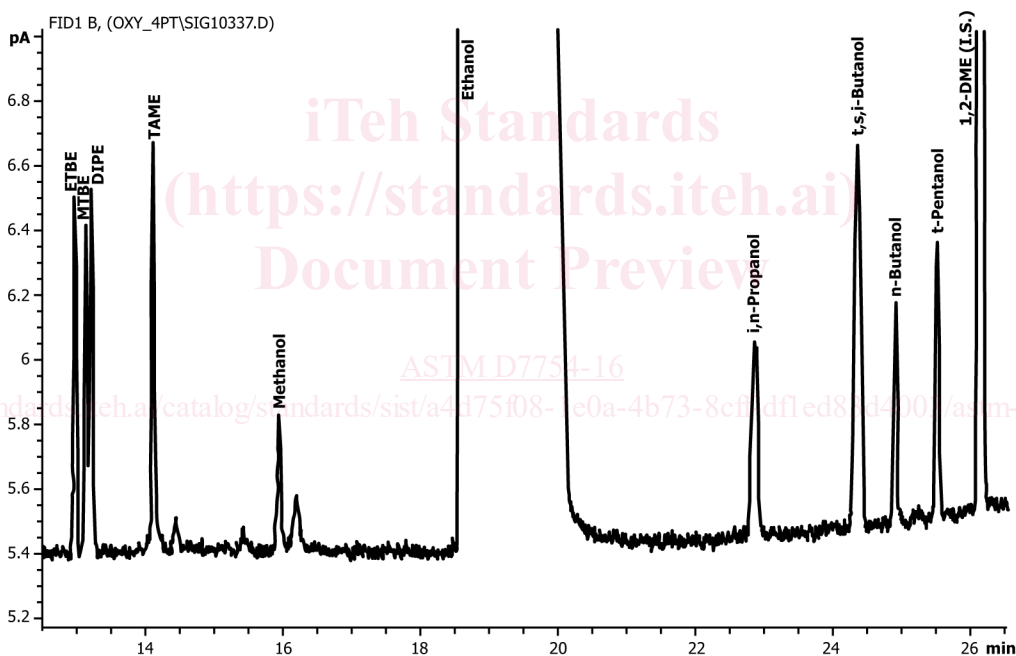
9.5 *Verification of Detectability*—Inject a ~~55 mg/-ppm (wt/wt)-kg~~ calibration solution and ensure that a signal/noise level of at least 5 is observed. Adjustment of the split ratio may be needed depending on the detector. See Fig. 8. The peaks for this level (~~5 (5 mg/-ppm m/m)-kg~~) have a height of about ~~2 pA~~ 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~~ 220 °C, with the pre-column carrier head pressure maintained at ~~20 psi~~ 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~~ 60 °C starting temperature, and also elute residual heavy hydrocarbons from the pre-column. Periodically ~~25 cm~~ 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.





NOTE 1—Conditions in Table 2. Calibration Standard – ppm/mg/kg internal standard in *iso-octane-isooctane*.  
**FIG. 7 Oxygenate Elution Pattern from WCOT/PLOT Column Set Using the Fluidic Switch System**



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

## 10. Calibration and Standardization

10.1 *Preparation of Calibration Standards*—Prepare multi-component oxygenate calibration standards by mass in accordance with Test Method D4307. Prepare a minimum of five calibration standards spanning the range of approximately 10 mg/kg to 1000 mg/kg of each oxygenate and a constant 250 mg/kg of internal standard in *iso-octane-isooctane*. 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 1000 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-isooctane* 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~~ 3 mL of each of the 12 oxygenates listed in 7.2 in a capped ~~50 mL~~ 50 mL bottle or equivalent container. Record the weight to the nearest ~~0.1 mg~~ 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%~~ ~8.3 wt%. Calculate the ~~weight %~~ mass percent using Eq 2.

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

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

10.4 *Oxygenate Stock Solution B*—For levels ~~1000~~ 1000 mg / ~~500~~ kg, 500 mg / kg, and ~~250~~ 250 mg / ppm. kg. In a ~~tarred~~ 100 mL tared 100 mL volumetric flask, add ~~12 mL~~ 12 mL of the Oxygenate Stock Solution A prepared in 10.3 and record the weight to the nearest ~~0.1 mg~~ 0.1 mg. Fill to the mark with ~~iso-octane~~ isooctane and record the weight. Calculate the concentration of each oxygenate using Eq 3 (~~~10 000~~ (~10 000 mg ppm) / kg).

$$\text{ppm of component } i = W\%i \times (Mi/Mt) \times 10000 \quad (3)$$

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

where:

$W\%i$  = weight% of component  $i$  in 10.3 (%),

$W\%i$  = 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~~ 100 mg / ~~50~~ kg, 50 mg / kg, and ~~10~~ 10 mg / ppm. kg. In a ~~tarred~~ 100 mL tared 100 mL volumetric flask, add ~~1.2 mL~~ 1.2 mL of the Oxygenate Stock Solution A prepared in 10.3 and record the weight to the nearest ~~0.1 mg~~ 0.1 mg. Fill to the mark with ~~iso-octane~~ isooctane and record the weight. Calculate the concentration of each using Eq 3 (~~~1000~~ (~1000 mg ppm) / kg).

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

$$\text{Weight\% of DME (} W\%_{DME} \text{)} = \text{mass of DME (g)} / M_t \text{ (g)} \times 100 \quad (4)$$

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

where:

$M\%_{DME}$  = mass percent of first DME 5 % solution prepared in 10.5,

$\text{Mass of DME}$  = mass in grams of DME, and

$M_t$  = total mass of solution.

$$\text{ppm of DME Stock} = W\%_{DME} \times (M_{DME} / M_{DMET}) \times 10000 \quad (5)$$

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

where:

$W\%_{DME}$  = weight % of first DME 5% solution (%),

$M_{DME}$  = mass of first DME 5% solution (g), and

$M_{DMET}$  = total mass of solution (g).

$M_{DMET}$

$M\%_{DME}$  = 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~~ 10 mg / ~~50~~ kg, 50 mg / ~~100~~ kg, 100 mg / ~~250~~ kg, 250 mg / ~~500~~ kg, 500 mg / kg, and ~~1000~~ 1000 mg / ppm. (m/m). 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% (m/m). PPM levels of ethanol, 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 ppm-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: