Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography

This standard is issued under the fixed designation D 4815; 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.

NOTE—Paragraph 15.2 was corrected editorially and the designation date was changed effective July 25, 1994.

1. Scope

1.1 This test method is designed for the determination of ethers and alcohols in gasolines by gas chromatography. Specific compounds determined are: methyl tert-butylether (MTBE), ethyl tert-butylether (ETBE), tert-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, n-propanol, isobutanol, tert-butanol, sec-butanol, n-butanol, and tert-pentanol (tert-amylalcohol).

1.2 Individual ethers are determined from 0.1 to 20.0 mass percent. Individual alcohols are determined from 0.1 to 12.0 mass percent. Equations used to convert to mass percent oxygen and to volume % of individual compounds are provided.

1.3 Alcohol-based fuels such as M-85 and E-85, MTBE product, ethanol product and denatured alcohol are specifically excluded from this method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

1.4 Benzene, while detected, cannot be quantified using this test method and must be analyzed by alternate methodology (Test Method D 3606 or D 4420).

1.5 SI (metric) units are preferred and used throughout this standard. Alternate units, in common usage, are also provided to increase clarity and aid the users of this test method.

1.6 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:

D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D 1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent

D 3606 Test Method for Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D 4420 Test Method for Aromatics in Finished Gasoline by Gas Chromatography

3. Terminology

3.1 Descriptions of Terms Specific to This Standard:

3.1.1 low volume connector—a 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.

3.1.2 MTBE—methyl tertiary-butylether.

3.1.3 ETBE—ethyl tertiary-butylether.

3.1.4 TAME—tertiary-amyl methyl ether.

3.1.5 DIPE—diisopropylether.

3.1.6 tertiary-amyl alcohol—tertiary-pentanol.

3.1.7 oxygenate—any oxygen-containing organic compound which can be used as a fuel or fuel supplement, for example, various alcohols and ethers.

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

\[ \text{split ratio} = \frac{(S + C)}{C} \]  (1)

where:

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

3.1.9 TCEP—1,2,3-tris-2-cyanoethoxypropane—a gas chromatographic liquid phase.

3.1.10 WCOT—a type of capillary gas chromatographic column prepared by coating the inside of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 An appropriate internal standard such as 1,2-dimethoxyethane (ethylene glycol dimethyl ether) is added to
the sample which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar TCEP column which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

4.2 After methycyclopentane, but before DlPE and MTBE elute from the polar column, the valve is switched to backflush the oxygenates onto a WCOT non-polar column. The alcohols and ethers elute from the non-polar column in boiling point order, before elution of any major hydrocarbon constituents.

4.3 After benzene and TAME elute from the non-polar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons.

4.4 The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of each component is calculated with reference to the internal standard.

5. Significance and Use

5.1 Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust and evaporative emissions are some of the concerns associated with oxygenated fuels.

5.2 This test method is applicable to both quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination.

6. Apparatus

6.1 Chromatograph—While any gas chromatographic system, which is capable of adequately resolving the individual ethers and alcohols that are presented in Table 1, can be used for these analyses, a gas chromatographic instrument which can be operated at the conditions given in Table 2, and having a column switching and backflushing system equivalent to Fig. 1 has been found acceptable. Carrier gas flow controllers shall be capable of precise control where the required flow rates are low (Table 2). Pressure control devices and gages shall be capable of precise control for the typical pressures required.

6.1.2 Detector—A thermal conductivity detector or flame ionization detector, can be used. The system shall have sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5:1 for 0.005 volume % concentration of an oxygenate.

6.1.3 Switching and Backflushing Valve—A valve, to be located within the gas chromatographic column oven, capable of performing the functions described in Section 11 and illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.

6.1.3.1 Valco Model No. A 4CIOWP, 1.6 mm (1/16 in.) fittings. This particular valve was used in the majority of the analyses used for the development of Section 15.

6.1.3.2 Valco Model No. C1OW, 0.8 mm (1/32 in.) fittings. This valve is recommended for use with columns of 0.32 mm inside diameter and smaller.

6.1.3.3 Some gas chromatographs are equipped with an auxiliary oven which can be used to contain the valve and polar column. In such a configuration, the nonpolar column is located in the main oven and the temperature can be adjusted for optimum oxygenates resolution.

6.1.4 An automatic valve switching device must be used to ensure repeatable switching times. Such a device should be synchronized with injection and data collection times.

6.1.5 Injection System—The chromatograph should be equipped with a splitting-type inlet device if capillary columns or flame ionization detection are used. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

6.1.5.1 Some gas chromatographs are equipped with on-column injectors and autosamplers which can inject small samples sizes. Such injection systems can be used provided that sample size is within the limit of the column and detectors optimum efficiency and linearity.

6.1.5.2 Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully for introducing representative samples into the gas chromatographic inlet.

6.2 Data Presentation or Calculation, or Both:

6.2.1 Recorder—A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less can be used to

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention Time, Min.</th>
<th>Molecular Weight</th>
<th>Relative Density at 15.56°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2.90</td>
<td>0.58</td>
<td>0.43</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.15</td>
<td>0.63</td>
<td>0.46</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.46</td>
<td>0.69</td>
<td>0.51</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>3.63</td>
<td>0.76</td>
<td>0.56</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>4.15</td>
<td>0.82</td>
<td>0.61</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>4.55</td>
<td>0.90</td>
<td>0.67</td>
</tr>
<tr>
<td>MTBE</td>
<td>5.64</td>
<td>1.00</td>
<td>0.74</td>
</tr>
<tr>
<td>sec-Butanol</td>
<td>5.33</td>
<td>1.06</td>
<td>0.79</td>
</tr>
<tr>
<td>DlPE</td>
<td>5.76</td>
<td>1.14</td>
<td>0.86</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>6.00</td>
<td>1.19</td>
<td>0.87</td>
</tr>
<tr>
<td>ETBE</td>
<td>6.43</td>
<td>1.28</td>
<td>0.95</td>
</tr>
<tr>
<td>tert-Pentanol</td>
<td>6.43</td>
<td>1.28</td>
<td>0.95</td>
</tr>
<tr>
<td>1,2-Dimethoxyethane</td>
<td>6.80</td>
<td>1.35</td>
<td>1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>Flows, mL/min</th>
<th>Carrier Gas: Helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Oven</td>
<td>60</td>
<td>to injector 75</td>
</tr>
<tr>
<td>Injector, °C</td>
<td>200</td>
<td>Sample size, µL</td>
</tr>
<tr>
<td>Detector—TCD, °C</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>—FID, °C</td>
<td>250</td>
<td>3</td>
</tr>
<tr>
<td>Valve °C</td>
<td>80</td>
<td>Total Analysis time</td>
</tr>
</tbody>
</table>

A Sample size must be adjusted so that hydrocarbons in the range of 0.1 to 12.0 mass % and ethers in the range of 0.1 to 20.0 mass % are eluted from the column and measured linearly at the detector. A sample size of 1.0 µl has been introduced in most cases.
FIG. 1 Analysis of Oxygenates in Gasoline Schematic of Chromatographic System

Valve in RESET Position

monitor detector signal. Full-scale response time should be 1 s or less with sufficient sensitivity and stability to meet the requirements of 6.1.2.

6.2.2 Integrator or Computer—Means shall be provided for determining the detector response. Peak heights or areas can be measured by computer, electronic integration or manual techniques.

6.3 Columns, Two as follows:

6.3.1 Polar Column—This column performs a preseparation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed onto the non-polar column in 6.3.2. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.1.1 can be used. The column shall perform at the same temperature as required for the column in 6.3.2, except if located in a separate auxiliary oven as in 6.1.3.3.

6.3.1.1 TCEP Micro-Packed Column,* 560 mm (22 in.) by 1.6 mm (1/16 in.) outside diameter by 0.38 mm (0.015 in.) inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20% (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW). This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

6.3.2 Non-Polar (Analytical) Column—Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.2.1 and illustrated in Fig. 2 can be used.

6.3.2.1 WCOT Methyl Silicone Column, 30 m (1181 in.) long by 0.53 mm (0.021 in.) inside diameter fused silica WCOT column with a 2.6 μm film thickness of cross-linked methyl siloxane. This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

7. Reagents and Materials

7.1 Carrier Gas—Carrier gas appropriate to the type of detector used. Helium has been used successfully. The minimum purity of the carrier gas used must be 99.95 mol %.

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

NOTE 2: Warning—These materials are flammable and can be harmful or fatal if ingested or inhaled.

7.3 Methylene Chloride—Used for column preparation. Reagent grade free of non-volatile residue.

* Available from Hewlett Packard Co., Avondale, PA.
8. Preparation of Column Packings

8.1 TCEP Column Packing:

8.1.1 Any satisfactory method, used in the practice of the art that will produce a column capable of retaining the C1 to C4 alcohols and MTBE, ETBE, DIPE and TAME from components of the same boiling point range in a gasoline sample. The following procedure has been used successfully.

8.1.2 Completely dissolve 10 g of TCEP in 100 mL of methylene chloride. Next add 40 g of 80/100 mesh Chromosorb P(AW) to the TCEP solution. Quickly transfer this mixture to a drying dish, in a fume hood, without scraping any of the residual packing from the sides of the container. Constantly, but gently, stir the packing until all of the solvent has evaporated. This column packing can be used immediately to prepare the TCEP column.

9. Sampling

9.1 Every effort should be made to ensure that the sample is representative of the fuel source from which it is taken. Follow the recommendations of Practice D 4057 or its equivalent when obtaining samples from bulk storage or pipelines.

9.2 Upon receipt in the laboratory, chill the sample in its original container to 0 to 5°C (32 to 40°F) before any subsampling is performed.

9.3 If necessary, transfer the chilled sample to a vapor tight container and store at 0 to 5°C (32 to 40°F) until needed for analysis.

10. Preparation of Micro-Packed TCEP Column

10.1 Wash a straight 560 mm length of 1.6 mm outside diameter (0.38 mm inside diameter) stainless steel tubing with methanol and dry with compressed nitrogen.

10.2 Insert 6 to 12 strands of silvered wire, a small mesh screen or stainless steel frit inside one end of the tube. Slowly add 0.14 to 0.15 g of packing material to the column and gently vibrate to settle the packing inside the column. When strands of wire are used to retain the packing material inside the column, leave 6.0 mm (0.25 in.) of space at the top of the column.

10.3 Column Conditioning—Both the TCEP and WCOT columns are to be briefly conditioned before use. Connect the columns to the valve (see 11.1) in the chromatographic oven. Adjust the carrier gas flows as in 11.3 and place the valve in the RESET position. After several minutes, increase the column oven temperature to 120°C and maintain these conditions for 5 to 10 min. Cool the columns below 60°C before shutting off the carrier flow.

11. Preparation of Apparatus and Establishment of Conditions

11.1 Assembly—Connect the WCOT column to the valve system using low volume connectors and 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.

11.2 Adjust the operating conditions to those listed in Table 2, but do not turn on the detector circuits. Check the system for leaks before proceeding further.

11.2.1 If different polar and nonpolar columns are used, or capillary columns of smaller ID are used, or both, it can be necessary to use different optimum flows and temperatures.

11.3 Flow Rate Adjustment:

11.3.1 Attach a flow measuring device to the column vent with the valve in the RESET position and adjust the pressure to the injection port to give 5.0 mL/min flow (14 psig). Soap bubble flow meters are suitable.

11.3.2 Attach a flow measuring device to the split injector vent and adjust the flow from the split vent using the A flow controller to give a flow of 70 mL/min. Recheck the column vent flow set in 11.3.1 and adjust if necessary.

11.3.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same column vent flow set in 11.3.1. This is necessary to minimize flow changes when the valve is switched.

11.3.4 Switch the valve to the inject position RESET and adjust the B flow controller to give a flow of 3.0 to 3.2 mL/min at the detector exit. When required for the particular instrumentation used, add makeup flow or TCD switching flow to give a total of 21 mL/min at the detector exit.

11.4 When a thermal conductivity detector is used, turn on the filament current and allow the detector to equilibrate. When a flame ionization detector is used, set the hydrogen and air flows and ignite the flame.

11.5 Determine the Time to Backflush—The time to backflush will vary slightly for each column system and must be determined experimentally as follows. The start time of the integrator and valve timer must be synchronized with the injection to accurately reproduce the backflush time.

11.5.1 Initially assume a valve BACKFLUSH time of 0.23 min. With the valve RESET, inject 1 to 3 µL of a blend containing at least 0.5% or greater oxygenates (7.3), and simultaneously begin timing the analysis. At 0.23 min, rotate the valve to the BACKFLUSH position and leave it there until the complete elution of TAME is realized. Record this time as the RESET time, which is the time at which the valve is returned to the RESET position. When all of the remaining hydrocarbons are backflushed the signal will return to a stable baseline and the system is ready for another analysis. The chromatogram should appear similar to the one illustrated in Fig. 2.

11.5.1.1 Ensure that the BACKFLUSH time is sufficient to quantitatively transfer the higher concentrations of the ethers, specifically MTBE, into the nonpolar column.

11.5.2 It is necessary to optimize the valve BACKFLUSH time by analyzing a standard blend containing oxygenates. The correct BACKFLUSH time is determined experimentally by using valve switching times between 0.20 and 0.35 min. When the valve is switched too soon, C5 and lighter hydrocarbons are backflushed and are co-eluted in the C4 alcohol section of the chromatogram. When the valve BACKFLUSH is switched too late, part or all of the ether component (MTBE, ETBE or TAME) is vented resulting in an incorrect ether measurement.

11.5.2.1 DIPE may require a BACKFLUSH time slightly shorter than the other ethers. The system may require reoptimization if the analysis of DIPE is required.

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11.5.3 To facilitate setting BACKFLUSH time, the column vent in Figure 1 can be connected to a second detector (TCD or FID) as described in Test Method D 4420 and used to set BACKFLUSH TIME based on the oxygenates standard containing the ethers of interest.

12. Calibration and Standardization

12.1 Identification—Determine the retention time of each component by injecting small amounts either separately, or in known mixtures or by comparing the relative retention times with those in Table 1.

12.1.1 In order to ensure minimum interference from hydrocarbons, it is strongly recommended that a fuel devoid of oxygenates be chromatographed to determine the level of any hydrocarbon interference.

12.2 Preparation of Calibration Samples—Prepare multi-component calibration standards of the oxygenates and concentration ranges of interest by mass according to Test Method D 4307. For each oxygenate, prepare a minimum of five calibration standards spanning the range of the oxygenate in the samples. As an example, for full range calibration, 0.1, 0.5, 2, 5, 10, 15, and 20 mass percent of each oxygenate may be used. Before preparing the standards, determine the purity of the oxygenate stocks and make corrections for the impurities found. Whenever possible, use stocks of at least 99.9 % purity. Correct the purity of the components for water content determined by Test Method D 1744. To minimize evaporation of light components, chill all chemicals and gasoline used to prepare standards. Prepare standards by transferring a fixed volume of oxygenates using pipettes or eye droppers (for volumes below one volume percent) to 100 mL volumetric flasks or septum capped vials as follows. Cap and record the tare weight of the volumetric flask or vial. Do not contaminate with free gasoline or a mixture of hydrocarbons such as isooctane/mixed xylenes (63.35 volume percent). Do not exceed 30 °C (86°F) when not in use.

12.3 Standardization:

12.3.1 Run the calibration standards and establish the calibration curve for each oxygenate. Plot the response ratio (rsp):

\[ rsp_i = \frac{Ai}{As} \] (2)

where:

\( Ai \) = area of oxygenate, and

\( As \) = area of internal standard.

as the y-axis versus the amount ratio (amt):

\[ amt_i = \frac{Wi}{Ws} \] (3)

where:

\( Wi \) = mass of oxygenate, and

\( Ws \) = mass of internal standard.

as the x-axis calibration curves for each oxygenate. Check the correlation \( r^2 \) value for each oxygenate calibration. The \( r^2 \) value should be at least 0.99 or better. \( r^2 \) is calculated as follows:

\[ r^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)(\Sigma y^2)} \] (4)

where:

\[ x = \frac{X_i - \overline{X}}{\overline{X}} \] (5)

\[ y = \frac{Y_i - \overline{Y}}{\overline{Y}} \] (6)

and:

\[ X_i = \text{amt}_i \text{ ratio data point}, \]

\[ X = \text{average values for all (amt) data points}, \]

\[ Y_i = \text{corresponding rsp} \text{ ratio data point}, \]

\[ Y = \text{average values for all (rsp) data points}. \]

12.3.2 Table 3 gives an example on the calculation of \( r^2 \) for an ideal data set \( X_i \) and \( Y_i \):

12.3.3 For each oxygenate i calibration data set, obtain the linear least-squares fit equation in the form:

\[ (rsp_i) = (m_i)(amt_i) + b_i \] (7)

where:

\( (rsp_i) = \text{response ratio for oxygenate i (y-axis)}, \]

\( m_i = \text{slope of linear equation for oxygenate i}, \]

\( amt_i = \text{amount ratio for oxygenate i (x-axis)}, \]

\( b_i = y-\text{axis intercept}. \]

12.3.4 The values \( m_i \) and \( b_i \) are calculated as follows:

\[ m_i = \frac{\Sigma xy}{\Sigma x^2} \] (8)

and

\[ b_i = \frac{Y_i}{m_i} \] (9)

12.3.5 For the example in Table 3:

\[ m_i = \text{average values for all oxygenates, including the internal standard added. Store the capped calibration standards below 5°C (40°F) when not in use.} \]

12.3.6 For an optimum calibration, the absolute value of the y-intercept \( b_i \) must be at a minimum. In this case, \( A_i \) approaches zero when \( w_i \) is less than 0.1 mass percent. The equation to determine the mass percent oxygenate i or \( w_i \), reduces to Eq 13. The y-intercept can be tested using Eq 13 below:

<table>
<thead>
<tr>
<th>TABLE 3</th>
<th>Example Calculation of Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_i )</td>
<td>( y_i )</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>( x = 3.0 )</td>
<td>( y = 1.5 )</td>
</tr>
</tbody>
</table>

\[ \overline{x} = \frac{\Sigma x}{n} \]

\[ \overline{y} = \frac{\Sigma y}{n} \]

\[ r^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)(\Sigma y^2)} \] (10)

\[ r = \frac{\overline{x}\overline{y}}{\sqrt{(\overline{x}^2)(\overline{y}^2)}} \]

\[ t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}} \] (11)

\[ b = \frac{\overline{y} - m\overline{x}}{n} \] (12)

\[ \text{where:} \]

\( n = \text{number of data points}. \]

\[ \overline{x} = \frac{\Sigma x}{n} \] (13)

\[ \overline{y} = \frac{\Sigma y}{n} \] (14)

\[ r = \text{correlation coefficient for an ideal data set}. \]

\[ x \] and \( y \) are the average values for all oxygenates, including the internal standard added. Store the capped calibration standards below 5°C (40°F) when not in use.

Note 5—Normally the \( b_i \) value is not zero and may be either positive or negative. Figure 3 gives an example of a linear least-squares fit for MTBE and the resulting equation in the form of Eq 7 above.

12.3.6 For an optimum calibration, the absolute value of the y-intercept \( b_i \) must be at a minimum. In this case, \( A_i \) approaches zero when \( w_i \) is less than 0.1 mass percent. The equation to determine the mass percent oxygenate i or \( w_i \), reduces to Eq 13. The y-intercept can be tested using Eq 13 below:
\[ w_i = \left( \frac{b_i}{m_i} \right) \left( \frac{W_s}{W_g} \right) \times 100 \% \]  

(13)

where:

- \( w_i \) = mass % oxygenate \( i \), where \( w_i \) is <0.1 mass %,
- \( W_s \) = mass of internal standard added to the gasoline samples, g, and
- \( W_g \) = mass of gasoline samples, g.

Note 6—Since in practice \( W_s \) and \( W_g \) vary slightly from sample to sample, use average values.

12.3.7 The following gives an example of the calculation for the y-intercept \( b_i \) test using Fig. 3 for oxygenate \( i \) (MTBE) for which \( b_i = 0.015 \) and \( m_i = 1.83 \). From 13.1, a typical sample preparation may contain approximately \( W_s = 0.4 \text{ g} \) (0.5 mL) of internal standard and approximately \( W_g = 7 \text{ g} \) (9.5 mL) of a gasoline sample. Substituting these values into Eq 13 yields:

\[ w_i = \left( \frac{0.015}{1.83} \right) \left( \frac{0.4 \text{ grams}}{7 \text{ grams}} \right) \times 100 \% \]

= 0.05 mass %

(14)

12.3.8 Since \( w_i \) is less than 0.1 mass percent, the y-intercept \( b_i \) has an acceptable value for MTBE. Similarly, determine \( w_i \) for all other oxygenates. For all oxygenates, \( w_i \) must be less than 0.1 mass percent. If any of the \( w_i \) values are greater than 0.1 mass percent, rerun the calibration procedure for oxygenate \( i \) or check instrument parameters and hardware or check for hydrocarbon interferences.

13. Procedure

13.1 Preparation of Sample—Transfer 0.5 mL of internal standard \( (W_s) \) by a volumetric pipette into a tared and capped 10 mL volumetric flask. Record weight to nearest 0.1 mg. Record the net mass of the internal standard added. Retare the capped flask. Fill the 10 mL volumetric flask to volume with sample, cap and record the net mass \( (W_g) \) to the nearest 0.1 mg of the sample added. Mix thoroughly and inject into the gas chromatograph. If using an automatic sampler then transfer an aliquot of the solution into a glass gas chromatographic (GC) vial. Seal the GC vial with a Teflon-lined septum. If the sample is not immediately analyzed, store below 5°C (40°F).

13.2 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. An injection volume of 1.0 to 3.0 \( \mu \text{L} \) with a 15:1 split ratio has been used successfully. Start recording and integrating devices in synchronization with sample introduction. Obtain a chromatogram or integrated peak report or both which displays the retention times and integrated area of each detected component.

13.3 Interpretation of Chromatogram—Compare the retention times of sample components to those of the calibration analysis to determine the identities of oxygenates present.

14. Calculations and Reporting

14.1 Mass Concentration of Oxygenates—After identifying the various oxygenates measure the area of each oxygenate peak and that of the internal standard. From the least-squares fit calibrations, as depicted in the MTBE example in Fig. 3, calculate the mass of each oxygenate \( (W_i) \) in the gasoline samples using the response ratio \( (\text{rsp}_i) \) of the areas of the oxygenate to that of the internal standard as follows:

\[ \text{rsp}_i = (m_i)(\text{amt}_i) + b_i \]  

(7)

where:

- \( m_i \) = slope of the linear fit,
- \( b_i \) = y-intercept, and
- \( \text{amt}_i \) = amount ratio as defined by Eq 3.

or

\[ \text{amt}_i = \frac{W_i}{W_s} = \frac{(\text{rsp}_i - b_i)}{m_i} \]  

(15)

or

\[ W_i = \left[ \frac{(\text{rsp}_i - b_i)}{m_i} \right] W_s \]  

(16)

or

\[ W_i = \left[ \frac{(AI/A_s - b_i/m_i)}{m_i} \right] W_s \]  

(17)

To obtain mass percent \( (w_i) \) results for each oxygenate:

\[ w_i = \frac{W_i(100 \%)}{W_g} \]  

(18)

where:

- \( W_g \) = weight of gasoline sample.

14.2 Report the mass percent of each oxygenate to the nearest 0.01 mass percent.

14.3 Volumetric Concentration of Oxygenates—If the volumetric concentration of each oxygenate is desired, calculate the volumetric concentration according to Eq 14:

\[ V_i = w_i \left( \frac{D_i}{D_o} \right) \]  

(19)

where:

- \( w_i \) = mass percent of each oxygenate as determined using Eq 13,
- \( V_i \) = volume percent of each oxygenate to be determined,
TABLE 4  Precision Interval as Determined from Cooperative Study Data

<table>
<thead>
<tr>
<th>Component</th>
<th>Repeatability</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. %</td>
<td>Wt. %</td>
</tr>
<tr>
<td></td>
<td>MEOH</td>
<td>EtOH</td>
</tr>
<tr>
<td>0.20</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>0.50</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>1.00</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>2.00</td>
<td>0.14</td>
<td>0.09</td>
</tr>
<tr>
<td>3.00</td>
<td>0.17</td>
<td>0.12</td>
</tr>
<tr>
<td>4.00</td>
<td>0.20</td>
<td>0.14</td>
</tr>
<tr>
<td>5.00</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td>6.00</td>
<td>0.26</td>
<td>0.18</td>
</tr>
<tr>
<td>10.00</td>
<td>0.35</td>
<td>0.24</td>
</tr>
<tr>
<td>14.00</td>
<td>0.40</td>
<td>0.28</td>
</tr>
<tr>
<td>16.00</td>
<td>0.45</td>
<td>0.32</td>
</tr>
<tr>
<td>20.00</td>
<td>0.50</td>
<td>0.37</td>
</tr>
</tbody>
</table>

15. Precision and Bias

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

15.1.1 Reproducibility—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and the correct operation of the test method exceed the following values in Table 4 only in one case in twenty.

<table>
<thead>
<tr>
<th>Component</th>
<th>Repeatability</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. %</td>
<td>Wt. %</td>
</tr>
<tr>
<td></td>
<td>MEOH</td>
<td>EtOH</td>
</tr>
<tr>
<td>0.20</td>
<td>0.14</td>
<td>0.09</td>
</tr>
<tr>
<td>0.50</td>
<td>0.24</td>
<td>0.16</td>
</tr>
<tr>
<td>1.00</td>
<td>0.37</td>
<td>0.23</td>
</tr>
<tr>
<td>2.00</td>
<td>0.57</td>
<td>0.34</td>
</tr>
<tr>
<td>3.00</td>
<td>0.72</td>
<td>0.43</td>
</tr>
<tr>
<td>4.00</td>
<td>0.86</td>
<td>0.51</td>
</tr>
<tr>
<td>5.00</td>
<td>0.99</td>
<td>0.58</td>
</tr>
<tr>
<td>6.00</td>
<td>1.10</td>
<td>0.64</td>
</tr>
<tr>
<td>10.00</td>
<td>1.51</td>
<td>0.86</td>
</tr>
<tr>
<td>12.00</td>
<td>1.68</td>
<td>0.95</td>
</tr>
<tr>
<td>14.00</td>
<td>0.70</td>
<td>2.46</td>
</tr>
<tr>
<td>16.00</td>
<td>0.77</td>
<td>2.69</td>
</tr>
<tr>
<td>20.00</td>
<td>0.89</td>
<td>3.19</td>
</tr>
</tbody>
</table>

where: $D_i =$ relative density at 15.56°C (60°F) of the individual oxygenate as found in Table 2, and $D_f =$ relative density of the fuel under study as determined by Test Method D 1298 or D 4052.

14.4 Report the volume percent of each oxygenate to the nearest 0.01 volume percent.

14.5 Mass Percent Oxygen—To determine the oxygen content of the fuel, convert and sum the oxygen contents of all oxygenated components determined above according to the following equation:

$$W_{tot} = \sum \frac{w_i \times 16.0 \times N_i}{M_i} \tag{20}$$

or

$$W_{tot} = \frac{w_1 \times 16.0 \times N_1 + w_2 \times 16.0 \times N_2}{M_1} + \ldots \tag{21}$$

where:

- $w_i =$ mass percent of each oxygenate as determined using Eq 13,
- $W_{tot} =$ total mass percent oxygen in the fuel,
- $M_i =$ molecular mass of the oxygenate as given in Table 2,
- $16.0 =$ atomic mass of oxygen, and
- $N_i =$ number of oxygen atoms in the oxygenate molecule.

14.6 Report the total mass percent of oxygen in the fuel to the nearest 0.01 mass percent.

15.1.2 Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following values in Table 4 only in one case in twenty.

Reproducibility Estimates in Oxygenates in Gasolines

<table>
<thead>
<tr>
<th>Component</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (MeOH)</td>
<td>0.37 (X₀.₆₁)</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>0.23 (X₀.₅₇)</td>
</tr>
<tr>
<td>Isopropanol (iPA)</td>
<td>0.42 (X₀.₆₇)</td>
</tr>
<tr>
<td>tert-Butanol (tBA)</td>
<td>0.19 (X₀.₆₇)</td>
</tr>
<tr>
<td>n-Propanol (nPA)</td>
<td>0.11 (X₀.₅₇)</td>
</tr>
<tr>
<td>MTBE</td>
<td>0.12 (X₀.₆₇)</td>
</tr>
<tr>
<td>sec-Butanol (sBA)</td>
<td>0.44 (X₀.₆₇)</td>
</tr>
<tr>
<td>DIPE</td>
<td>0.42 (X₀.₆₇)</td>
</tr>
<tr>
<td>Isobutanol (iBA)</td>
<td>0.42 (X₀.₆₇)</td>
</tr>
<tr>
<td>ETBE</td>
<td>0.36 (X₀.₆₇)</td>
</tr>
<tr>
<td>tert-Pentanol (tAA)</td>
<td>0.15 (X₀.₅₇)</td>
</tr>
<tr>
<td>n-Butanol (nBA)</td>
<td>0.22 (X₀.₅₇)</td>
</tr>
<tr>
<td>TAME</td>
<td>0.31 (X₀.₅₁)</td>
</tr>
<tr>
<td>Total Oxygen</td>
<td>0.09 (X₁.₀₇)</td>
</tr>
</tbody>
</table>

where $X$ is the mean mass percent of the component.

15.2 Bias—The National Institutes of Standards and Technology (NIST) provides selected alcohols in reference fuels. As an example the following standard reference materials (SRM) in reference fuels are available as described in the NIST Standard Reference Catalog.⁶

<table>
<thead>
<tr>
<th>SRM</th>
<th>Type</th>
<th>Nominal Concentration, Mass % of</th>
</tr>
</thead>
<tbody>
<tr>
<td>1829</td>
<td>Alcohols in Reference Fuel</td>
<td>MeOH</td>
</tr>
<tr>
<td>1837</td>
<td>Methanol and tert-butanol</td>
<td>0.335</td>
</tr>
<tr>
<td>1838</td>
<td>Ethanol</td>
<td>0.335</td>
</tr>
<tr>
<td>1839</td>
<td>Methanol</td>
<td>0.335</td>
</tr>
</tbody>
</table>

16. Keywords

16.1 alcohols; ethers; oxygenates; gasoline; gas chromatography; MTBE (Methyl tert-butylether); ETBE (Ethyl tert-butylether); TAME (Tert-amylmethylether); DIPE (Disopropylether)

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