Designation: D7423 – 17

Standard Test Method for Determination of Oxygenates in C2, C3, C4, and C5 Hydrocarbon Matrices by Gas Chromatography and Flame Ionization Detection[1]

This standard is issued under the fixed designation D7423; 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 gas chromatographic procedure for the quantitative determination of organic oxygenates in C2, C3, C4, and C5 matrices by multidimensional gas chromatography and flame ionization detection. This test method is applicable when the hydrocarbon matrices have a final boiling point not greater than 200 °C. Oxygenate compounds include, but are not limited to, those listed in Table 1. The linear working range for oxygenates is 0.50 mg⁄kg to 100 mg⁄kg.

1.2 This test method is intended to determine the mass concentration of each oxygenate in the hydrocarbon matrix. Oxygenate compound identification is determined by reference standards and column elution retention order.

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

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

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D1835 Specification for Liquefied Petroleum (LP) Gases

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D6849 Practice for Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 Additional terminology related to the practice of gas chromatography can be found in Practice E355.

3.2 *Definitions:*

3.2.1 *liquefied petroleum gas (LPG), n*—a mixture of normally gaseous hydrocarbons, predominantly propane or butane, or both, that has been liquefied by compression or cooling, or both, to facilitate storage, transport, and handling. **D4175**

3.2.2 *oxygenate, n*—an oxygen-containing ashless organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement. **D4175**

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *Dean's switching method*—representative aliquot of sample is injected on-column using a sample valve (or via a gas

[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.D0.04 on C4 and C5 Hydrocarbons.

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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

TABLE 1 Oxygenates and Typical Retention Times

Components	Retention Time (min)
Dimethyl ether	6.18
Diethyl ether	8.44
Acetaldehyde	8.89
Ethyl tert-butyl ether	10.66
Methyl tert-butyl ether (MTBE)	10.92
Diisopropyl ether	11.22
Propionaldehyde (Propanal)	12.00
Tertiary amyl methyl ether (TAME)	13.19
Propyl ether	14.00
Isobutylaldehyde	14.10
Butylaldehyde	14.50
Methanol	14.91
Acetone	15.39
Isovaleraldehyde	16.00
Valeraldehyde	16.10
2-Butanone (MEK)	17.14
Ethanol	17.51
N-propyl alcohol and isopropanol	19.20 (co-elution)
Allyl Alcohol	20.00
Isobutanol, Tert-butyl alcohol, Sec-Butanol	20.24 (co-elution)
N-butanol	20.84

chromatograph split inlet). The sample passes onto a nonpolar column, which elutes the lighter hydrocarbons in boiling point order to the analytical column and backflushes the heavier hydrocarbons to vent. The oxygenate compounds elute from the analytical column and are detected via a flame ionization detector.

3.3.2 *Dean's switching method direct inject*—gas chromatographic valve configuration equipped with a valve connected directly to the precolumn. This technique is commonly used for the determination of oxygenates in ethene and propene concentrates. This configuration provides the lowest detection limits such as those commonly required for ethene and propene concentrates.

3.3.3 *Dean's switching method equipped with a split inlet*—gas chromatographic valve configuration equipped with a gas chromatograph split inlet for sample introduction into the precolumn. This configuration is commonly used for the determination of oxygenates in C5 hydrocarbon mixtures. This technique using this configuration might not provide the detection limits noted in the scope of this test method. If lower detection limits are required, then the user should consider using the on-column valve direct injection technique.

3.3.4 *valve cut method*—commonly used for the determination of oxygenates in C4 hydrocarbon mixtures. This technique using a split inlet might not provide the detection limits noted in the scope of this test method. If lower detection limits are required, then the user should consider using the on-column valve direct injection technique.

3.3.5 *valve cut method equipped with a split inlet*—representative aliquot of sample is injected via a gas chromatograph split inlet for sample introduction into the precolumn. The sample passes onto a nonpolar column, which elutes the lighter hydrocarbons in boiling point order to the analytical column and the heavier hydrocarbons to vent. The oxygenate compounds elute from the analytical column and are detected via a flame ionization detector.

3.4 *Acronyms:*

3.4.1 *DIPE*—diisopropylether.

3.4.2 *ETBE*—ethyl *tert*-butylether.

3.4.3 *MEK*—2-butanone.

3.4.4 *MTBE*—methyl *tert*-butylether.

3.4.5 *TAME*—*tert*-amyl methylether.

3.4.6 *PLOT*—porous layer open tubular capillary column.

3.4.7 *WCOT*—wall coated open tubular capillary column.

4. Summary of Test Method

4.1 This test method shall be configured using either the Dean's switching method or the valve cut method. Each method shall be configured using an on-column valve direct inject technique or a gas chromatograph split inlet. The on-column valve direct inject technique is configured by connecting the head of the precolumn directly to the injection valve.

4.2 The detector response and retention times for each oxygenate peak in a calibration standard is measured and used to externally calibrate the flame ionization detector response. The concentration of each oxygenate is calculated by the external standard technique. Calibration materials are listed in Table 1.

5. Significance and Use

5.1 The determination of oxygenates is important in the manufacture of ethene, propene, 1-3 butadiene, C4 hydrocarbons, and C5 hydrocarbons. Alcohols, ethers, aldehydes, and ketones are trace impurities in these hydrocarbons. Oxygenates decrease catalyst activity in downstream polymerization processes.

6. Apparatus

6.1 *Gas Chromatograph*—Any gas chromatograph equipped with a flame ionization detector (FID) and having sensitivity of 0.01 mg⁄kg. The gas chromatograph must be capable of linear temperature control from 50 °C to 320 °C for

the capillary column oven. The gas chromatograph must be capable of controlling multiple valve events. Carrier gas flow controllers and or electronic pressure control modules shall be capable of precise control where the required flow rates are low (see Table 2). Pressure control devices and gages shall be capable of precise control for the typical pressures required. The temperature program rate must repeat to within 0.1 °C and provide retention time repeatability of 0.05 min throughout the temperature program.

6.2 *Carrier Gas Preparation:*

6.2.1 Moisture present in the carrier gas causes chromatographic problems. The oxygenates column has very high retention. Due to this characteristic, moisture and trace impurities in the carrier gas are trapped at the beginning of this column. Therefore carrier gas filters or the use of any device which can be used to eliminate trace levels of oxygen and water are strongly recommended. Additionally, frequent reconditioning and longer than usual column condition times may be necessary to maintain the performance of this column for the most accurate results from this test method.

6.2.2 *Carrier Gas Filters*—Oxygen and molecular sieve type moisture filters.

6.3 *Columns:*

6.3.1 *Nonpolar (Precolumn) Column*—This column performs a pre-separation of the light hydrocarbon fraction up to and including TAME. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.2 can be used.

6.3.2 *WCOT Methyl Silicone Column,* 25 m long by 0.53 mm inside diameter fused silica WCOT column with a 1.0 µm film thickness of crosslinked methyl siloxane. A column of this description was used in the repeatability study referred to in Section 16.

6.4 *Polar (Analytical) Column*—This column performs a separation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed to vent through the nonpolar column. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.4.1 can be used.

6.4.1 *Oxygenates PLOT column,* 10 m long by 0.53 mm inside diameter, with a stationary phase composed of a barium sulfate adsorbent mixture, coated onto a fused silica column. At a minimum the column should have sufficient retention for methanol that it elute after n-tridecane (RI > 1300) and must have sufficient efficiency and capacity to resolve the oxygenates listed in Table 1 to provide accurate quantitative results equivalent to those shown in Section 16. A column of this description was used in the repeatability study referred to in Section 16.

6.5 *Sample Introduction:*

6.5.1 *Switching Valve*—A valve with an operating temperature of 225 °C and operating pressure of 27.57 bar, to be located within a heated enclosure or in the main oven. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.

6.5.2 *Liquid Sampling Valve*—A valve with an operating temperature of 75 °C and operating pressure of 68.94 bar, to be located outside of the oven and used in sampling propane concentrates, butane samples or other LPG samples. The repeatability of this test is dependent upon a consistent cylinder pressure. It is strongly suggested that the use of a floating piston cylinder be used and that the sample be pressurized to 13.78 bar above the vapor pressure of the sample prior to sampling.

6.5.3 *Low Pressure Liquid Sampling*—A valve syringe adapter may be used to sample low vapor pressure liquids such as C5 concentrates.

6.5.4 *Low Pressure Gas Sampling Valve*—A valve with an operating temperature of 225 °C and operating pressure of 27.57 bar to be placed in a heated enclosure maintained at approximately 150 °C and used to sample ethene vapor. An external sample loop is installed on this valve. A 1000 µL sample loop has been used successfully. The sample loop

TABLE 2 Chromatographic Operating Conditions

Parameter	Dean's Switch (Fig. 1)	Dean's Switch (Fig. 2)	Valve Cut (Fig. 3)
Valve 1°C	Ambient	Ambient	Ambient
Valve 1 Sample Size, µL	2	2	2
Valve 2°C	150	150	150
Valve 2 Sample Size, µL - mL	500 – 2	500 – 2	500 – 2
Injector, °C	Not Applicable	250	250
Split Ratio	Not Applicable	1:1 - x[A]	1:1 - x[A]
Backflush, min	2.0 – 4.0	2.0 – 4.0	2.0 – 4.0
Column Oven Standby, °C	200	200	200
Initial Column Oven, °C	50	50	50
Initial Hold, min	5	5	5
Rate, °C/min	10	10	10
Final Column Oven, °C	240	240	220
Final Hold, min	5	5	5
Precolumn Flow, mL/min	5	5	5
Analytical Column Flow, mL/min	7	7	7
Needle Valve 1 Flow, mL/min	15	15	Not Applicable
Needle Valve 2 Flow, mL/min	6	6	Not Applicable
Detector, °C	300	300	300
Detector Range	[B]	[B]	[B]

[A] Split ratio shall be experimentally determined using appropriate gravimetric standards to obtain the desired minimum detection requirements.
[B] Detector Range—Adjust the detector range to a setting which shall provide sufficient voltage to assure the detection of small concentrations of each oxygenate but as to avoid detector signal saturation.

sample size shall be sized experimentally to provide desired detection limits. This valve must reproduce to within 5 percent relative standard deviation on each component.

6.5.5 *Heated Valve Enclosure*—Any enclosure capable of maintaining the valve and sample loop at 150 °C.

6.5.6 *Connecting Tees*—Any tees that can provide an inert connection.

6.5.7 *Tubing*—Any tubing capable of providing an inert connection.

6.5.8 *Needle Valve*—Micrometering valve capable of low flow control 2 mL⁄min to 90 mL⁄min.

6.6 *Data Acquisition*—Any computerized data acquisition system shall be used for peak area integration and graphic presentation of the chromatogram. Alternatively any integrator system can also be used for chromatographic peak area integration.

7. Reagents and Materials

7.1 *Purity of Reagents*—Before preparing the calibration standards, determine the purity of the oxygenate stocks and make corrections for the impurities found. Whenever possible, use stocks of 98 % purity or better. The calibration materials are listed in Table 1.

7.2 *Calibration Standard Mixture*—A standard mixture containing known concentrations of each oxygenate listed in Table 1 should be prepared gravimetrically. This mixture shall be used as an external calibration standard.

7.3 *Compressed Hydrogen*—Less than 1 mg⁄kg hydrocarbon impurities for FID fuel gas.

7.4 *Compressed Helium*—Gas purity 99.999 %. Note that helium supplies often contain low level amounts of water. Water can dramatically deteriorate the performance of the analytical column (oxygenates column). It is strongly recommended that the use of a molecular sieve or other suitable water removal system be implemented to eliminate the possibility of contaminating the analytical column with oxygen or water.

7.5 *Compressed Air*—Zero grade (gas purity 99.999 %).

7.6 *Instrument Air*—Compressed air for pneumatic actuation of valves.

8. Sampling

8.1 Every effort should be made to ensure that the sample is representative of the source from which it is taken. Follow the recommendations of Practice D1265, D1835, D6849 or their equivalent, when obtaining and storing samples from bulk storage or pipelines.

9. Installation of Carrier Gas Filters

9.1 The carrier gas shall require pretreatment with an oxygen and water removal system.

9.2 On the gas chromatograph carrier gas supply line, install the oxygen and water removal filters. Any filters, traps or getter type device can be used to assure removal of both oxygen and water from the carrier gas used for this gas chromatograph.

10. Preparation of Apparatus and Establishment of Conditions

10.1 Install the gas chromatograph according to the manufacturer's instructions. Set the gas chromatograph parameters according to those noted in Table 2.

10.2 *Column Installation:*

10.2.1 Install the column, tubing and valve configuration as shown in Figs. 1-3, as desired. Apply carrier gas flows by slowly pressurizing the column. (**Warning—**Avoid pressure shocks, especially in combination with electronic pressure controlled flow. When setting flows add approximately 10 kPa per second while checking flows.)

10.2.2 Condition the column for at least 16 h under carrier gas flow, with a multi-cycle ramped temperature program technique starting at 50 °C and increasing to 100 °C hold for 1 h then increase and ramp the temperature by 10 °C⁄min up to 320 °C.

10.3 *Dean's Switching Method Direct Inject or Split Inlet—Flow Setting:*

10.3.1 Dean's switching system flow tuning using column configuration shown in Fig. 1. Equilibrate the column oven to 50 °C. Place the two-way valve in the normally off position preventing the system from backflushing out through needle valve #1. Place the three-way solenoid valve in the on position thereby allowing flow to pass from the secondary carrier flow out through needle valve #2. Set the needle valve #2 vent flow to 7 mL⁄min. Measure flows at the flame ionization detector vent. Adjust the primary mass flow controller (EPC A) flow to approximately 5 mL⁄min ± 0.5 mL⁄min. Place the three-way solenoid in the off position and adjust secondary carrier flow controller (Aux 3) to yield a combined total flow of 12 mL⁄min through the flame ionization detector vent. Place the two-way solenoid valve in the on position and set backflush needle valve #1 vent flow at 15 mL⁄min. Place the two-way solenoid valve back to the off position. Turn detector flows on and light the flame ionization detector.

10.4 *Dean's Switching Method Direct Inject or Split Inlet—Determine the Time to Backflush:*

10.4.1 Initially set the two-way valve backflush time to 4.0 min. With the two-way valve off, inject an aliquot of a mixture containing at least 50 mg⁄kg of TAME. Verify the retention time of the TAME peak at approximately 13 min. Experimentally determine the time required for the complete elution of TAME, by decreasing the backflush time in 0.2 min increments prior to each successive injection. Set the two-way valve backflush time such that the time allows for the complete elution of TAME. The chromatogram should appear similar to the one illustrated in Fig. 4.

10.5 *Valve Cut Method—Flow Setting:*

10.5.1 Valve cut method system flow tuning using column configuration shown in Fig. 3. Equilibrate the column oven to 50 °C. Place valve #3 in the normally off position thereby placing the system in the foreflush position The precolumn outlet flow shall vent through valve #3. Measure flows at the flame ionization detector vent. Adjust the secondary mass flow controller (Aux B) flow to 8 mL⁄min. Place valve #3 in the on position. Adjust the primary mass flow controller (Aux A) flow

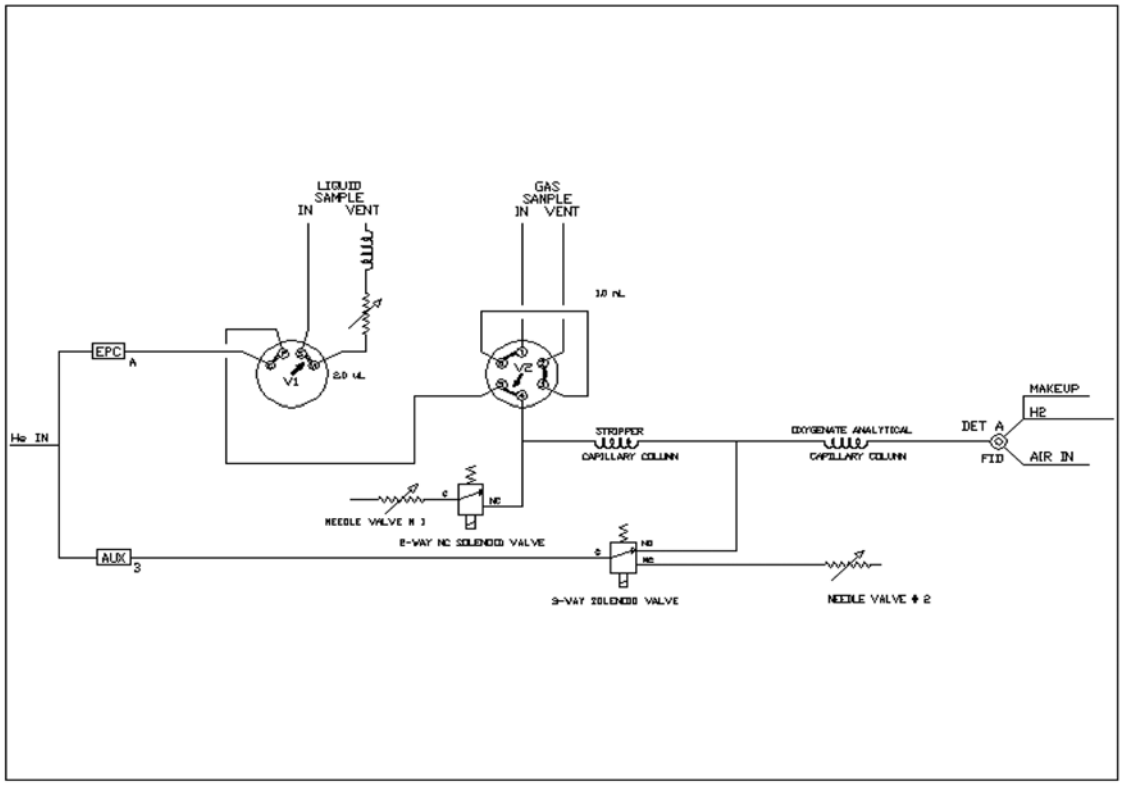

FIG. 1 Schematic of a Low Level Oxygenates Multidimensional Column Configuration (Dean's Switching Method Direct Inject Technique)

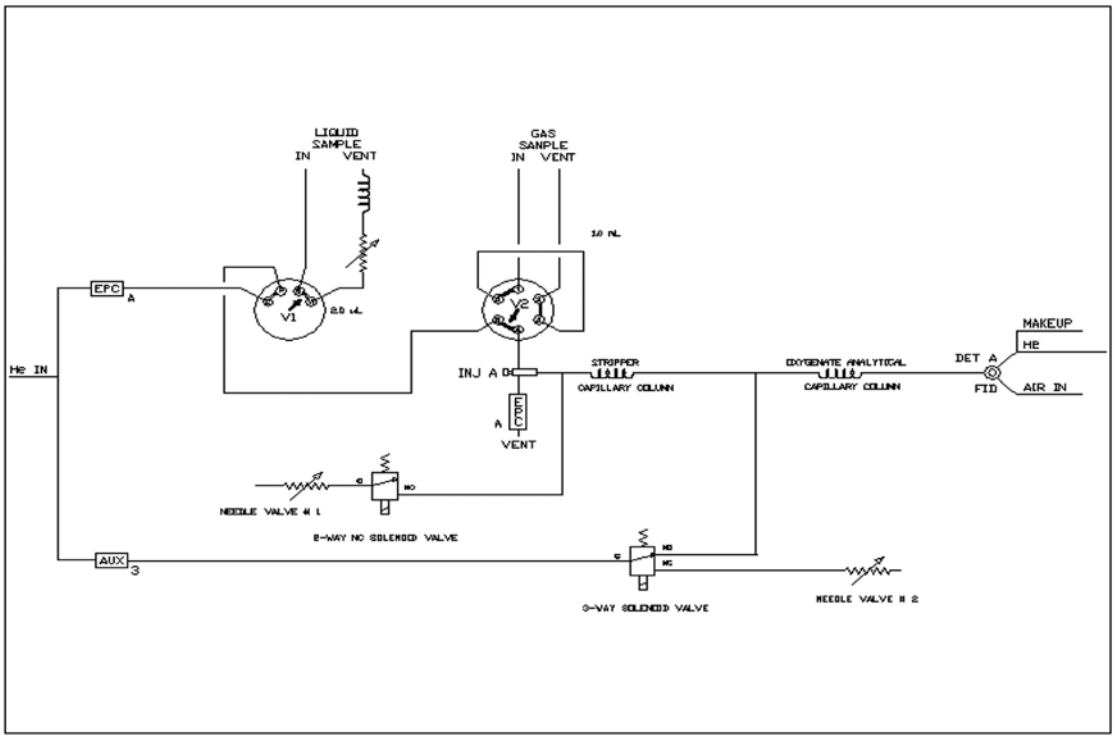

FIG. 2 Schematic of a Low Level Oxygenates Multidimensional Column Configuration (Dean's Switching Method Split Inlet)

to yield a total flow of 12 mL/min. Place valve #3 back to the off position. Turn detector flows on and light the flame ionization detector.

10.6 *Valve Cut Method—Determine the Time to Backflush:*

10.6.1 Valve cut method using column configuration shown in Fig. 3. Initially set the valve #3 backflush time to 4.0 min.

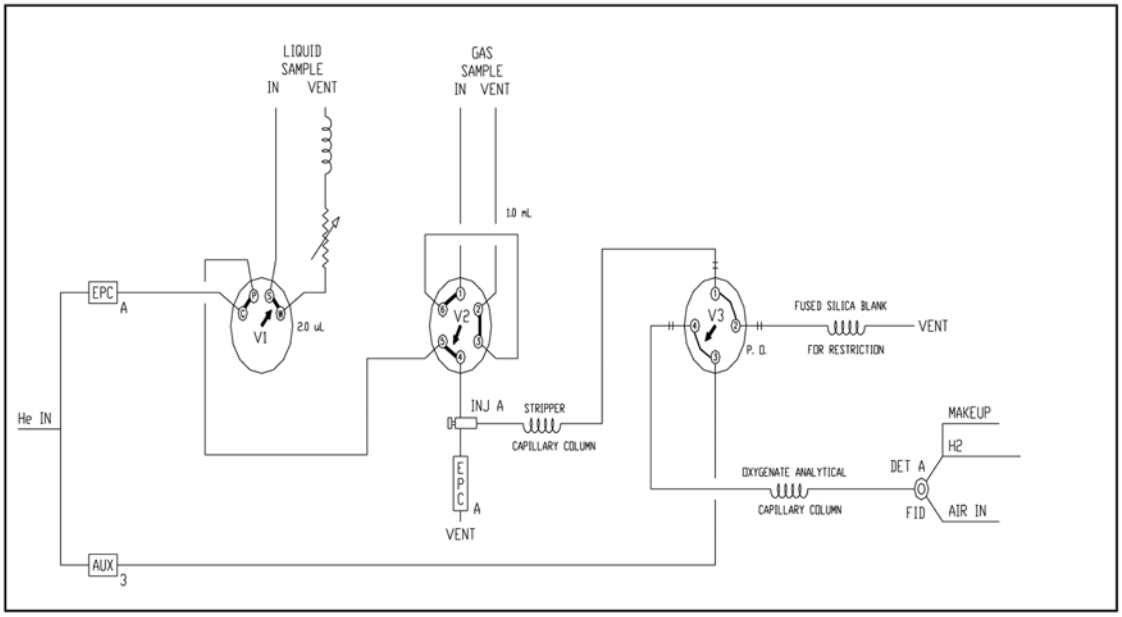

FIG. 3 Schematic of a Low Level Oxygenates Multidimensional Column Configuration (Valve Cut Method)

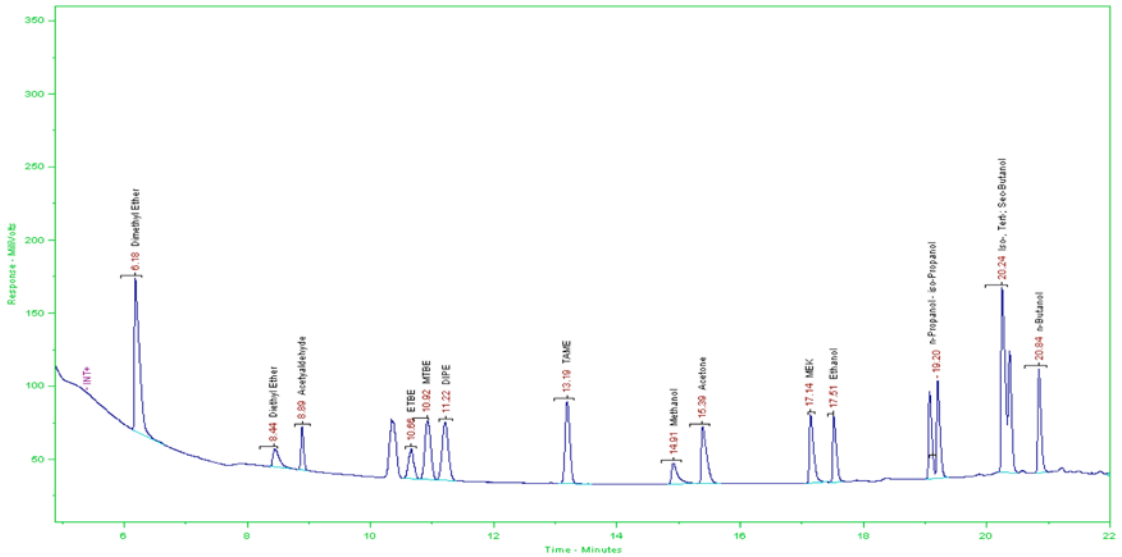

FIG. 4 Typical Oxygenates Chromatogram (refer to Appendix X2, Table X2.1 for oxygenate concentrations)

Inject an aliquot of a blend containing at least 50 mg/kg of TAME and verify the existence of the TAME peak at approximately 13 min ± 1.0 min. Experimentally determine the time required for the complete elution of TAME by decreasing the backflush time in 0.2 min increments prior to each successive injection. Set the backflush valve #3 time such that the time allows for the complete elution of TAME. A blend containing all of the desired oxygenates (Table 1) shall be analyzed to verify the system conditions. The chromatogram should appear similar to the one illustrated in Fig. 4.

11. Calibration and Standardization

11.1 *Identification*—Determine the retention time of each oxygenate component by injecting known calibration mixtures and recording the retention time of each oxygenate accordingly. The typical retention times are noted in Table 1.

11.2 *Chromatographic Analysis*—Introduce a representative aliquot of the calibration mixture or sample into the gas chromatograph. 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 oxygenate component.

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

11.4 Calibration is performed by sampling an appropriate calibration mixture containing the desired oxygenates of known concentrations into the gas chromatograph and measuring the flame ionization detector response.

11.5 Flame ionization detector response factors shall be calculated using either peak area or peak height. Each oxygenate response factor is calculated based on multiple analysis. It is suggested that the average of three injections be used in the calculation of the response factor. The calculation is as follows:

$$\text{Response factor Oxygenate X} = \text{Concentration for Oxygenate X}/\text{Area for Oxygenate X} \quad (1)$$

12. Procedure

12.1 *Sampling LPG Type Samples Using a Valco Liquid Sampling Valve:*

12.1.1 If it is necessary to test a sample in a non-piston type cylinder, then it should be purged prior to connecting the cylinder to the gas chromatograph sampling system. In a hood, invert the cylinder and purge a small aliquot of the sample through the cylinder valve to remove any moisture or particulate matter which might be present. This cylinder shall be pressurized with either helium or nitrogen prior to connecting the cylinder to the gas chromatograph sampling system.

12.1.2 Connect the sample cylinder to the valve sample inlet port tubing. Close the sample waste outlet valve. Open the sample cylinder valve and allow the liquid sample to fill the line. Slowly open and close the sample waste outlet valve and allow the sample to thoroughly purge the sample tubing. Allow the pressure to equilibrate then actuate the gas chromatograph sample valve to inject the sample into the precolumn.

12.2 *Sampling Low Pressure Gas Samples Using a Valco Gas Sampling Valve:*

12.2.1 A pre-vaporized sample is purged into the gas sample valve sample loop and out to a constant and controlled atmospheric pressure vent. The gas sample valve sample loop and supply tubing pressure is allowed to equilibrate to atmospheric pressure. After the pressure equilibrates to atmospheric pressure, actuate the gas chromatograph sample valve to inject the sample into the precolumn.

13. Calculation

13.1 The concentration for each oxygenate is calculated as follows:

$$\text{Concentration for Oxygenate X} = (\text{Response Factor Oxygenate X})\,(\text{Area for Oxygenate X}) \quad (2)$$

14. Report

14.1 Report individual oxygenate concentrations of the test sample using units of mg/kg, rounded to the nearest 0.1 mg/kg.

15. Quality Control

15.1 Confirm the satisfactory performance of the instrument and the test procedure by analyzing a quality control sample at least once each day the analyzer is used.

15.2 When quality control/quality assurance (QC/QA) protocols are already established in the testing facility, they can be used, provided they include procedures to monitor the reliability of the test results. Refer to Appendix X1 for additional information.

16. Precision and Bias

16.1 The precision of this test method is based on an interlaboratory study of D7423 conducted in 2015. As part of this study, three properties were measured, each by as many as six laboratories. Every "test result" represents an individual determination, and all laboratories were asked to report results in duplicate. Practice D6300 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. RR:D02-1827.[3]

16.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

16.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

16.1.1.2 Repeatability limits are listed in Table 3.

16.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

16.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

16.1.2.2 Reproducibility limits are listed in Table 3.

16.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

16.1.4 Any judgment in accordance with statements 16.1.1 and 16.1.2 would have an approximate 95 % probability of being correct.

16.2 *Bias*—No certified reference material was included in the test specimens distributed as part of this ILS, therefore no statement on bias is being made.

16.3 The precision statement was determined through statistical examination of all usable data, from six laboratories, on six different hydrocarbon matrices.

17. Keywords

17.1 gas chromatograph; oxygenates

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1827. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Repeatability and Reproducibility for Oxygenates (mg/kg)

NOTE 1—Where: X = the average individual oxygenate concentration of two results in mg/kg.

Analyte	Repeatability Limit (r)	Reproducibility Limit (R)
Acetone†	$(0.1821)(X^{0.5985})$	$(0.4424)(X^{0.5985})$
Acetyaldehyde	$0.2595(X + 0.0001)^{0.595}$	$1.0439(X + 0.0001)^{0.595}$
Diethyl Ether	$0.1869(X + 0.0001)^{0.5981}$	$0.5966(X + 0.0001)^{0.5981}$
Dimethyl Ether	$0.05321(X + 0.0001)^{0.9273}$	$0.2784(X + 0.0001)^{0.9273}$
DIPE	$0.1188(X-0.6566)^{0.5889}$	$0.5219(X-0.6566)^{0.5889}$
ETBE	$(0.06778)(X^{0.8512})$	$(0.3613)(X^{0.8512})$
Ethanol	$0.1626(X + 0.0001)^{0.7649}$	$0.6808(X + 0.0001)^{0.7649}$
Iso-Propanol	$(0.2458)(X^{0.5108})$	$(1.1222)(X^{0.5108})$
MEK	$(0.2009)(X^{0.5094})$	$(0.7171)(X^{0.5094})$
Methanol	$(0.2870)(X^{0.4887})$	$(1.9695)(X^{0.4887})$
MTBE	$(0.1261)(X^{0.6368})$	$(0.2861)(X^{0.9442})$
n-Butanol	$(0.1179)(X^{0.9278})$	$(0.3890)(X^{0.9278})$
Sec-Butanol	$(0.1063)(X^{0.8057})$	$(0.5578)(X^{0.8057})$
TAME	$0.2812(X + 0.0001)^{0.4011}$	$0.9946(X + 0.0001)^{0.4011}$

†Editorially corrected.

APPENDIXES

(Nonmandatory Information)

X1. QUALITY CONTROL PROTOCOL

X1.1 Monitor and control the stability and precision of the instrument by regularly analyzing a quality control (QC) sample.

X1.1.1 The type of QC sample used should be similar to the samples routinely analyzed by the instrument. An ample supply of QC material should be available for the intended period of quality control, and must be homogeneous and stable under the anticipated storage conditions.

X1.1.2 The frequency of QC testing is dependent on the criticality of the analysis, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each day of testing. The QC testing frequency should be increased if a large number of samples are routinely analyzed. However, when the testing process is demonstrated to be in statistical control, the QC testing frequency may be reduced.

X1.2 Record the QC sample results and analyze by control charts or other statistically equivalent techniques to immediately ascertain the statistical control status of the measurement process. See Practice D6299 and MNL 7A[4] for further guidance on QC and control charting techniques.

X1.2.1 Prior to using a QC sample control chart for assessing whether the measurement process is in statistical control, the user of the test method must have accumulated at least 15 suitable measurements and calculated an average value and control limits for the QC sample.

X1.2.2 Any QC sample result outside of control limits should trigger an investigation for root cause(s). The result of this investigation may indicate the need for instrument recalibration and other remedial action.

X1.2.3 Compare the site repeatability estimated from the QC sample with the published precision of this test method.

[4] MNL 7A, *Manual on Presentation of Data and Control Chart Analysis*, 7th edition, ASTM International, 2002.

X2. REFERENCE SAMPLE INFORMATION

X2.1 See Table X2.1.

TABLE X2.1 LPG Mixture Oxygenate Content (Chromatogram—Fig. 2) Conditions—Table 1: Dean's Switch 1a

Components	Concentration (mg/kg)
Dimethyl ether	25.2
Diethyl ether	1.4
Acetaldehyde	2.0
Ethyl tert-butyl ether	5.9
Methyl tert-butyl ether (MTBE)	6.4
Diisopropyl ether	2.3
Tertiary amyl methyl ether (TAME)	6.1
Methanol	4.5
Acetone	3.9
2-Butanone (MEK)	3.6
Ethanol	4.9
N-propyl alcohol, and isopropanol (co-elution)	4.7; 4.7
Isobutanol, Tert-butyl alcohol, Sec-Butanol (co-elution)	5.0; 5.0; 5.0
N-butanol	5.5

SUMMARY OF CHANGES

Subcommittee D02.D0 has identified the location of selected changes to this standard since the last issue (D7423 – 16a) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised caption of Fig. 4.

Subcommittee D02.D0 has identified the location of selected changes to this standard since the last issue (D7423 – $16^{\varepsilon 1}$) that may impact the use of this standard. (Approved Dec. 1, 2016.)

(1) Added new Appendix X2.

Subcommittee D02.D0 has identified the location of selected changes to this standard since the last issue (D7423 – 09 (2014)) that may impact the use of this standard. (Approved Feb. 15, 2016.)

(1) Revised Section 16.