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.

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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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4.1 *The user is advised to obtain LPG safety training for the safe operation of this test method procedure and related activities. The eLearning training course "Liquefied Petroleum Gases Sampling Safety" is available on the ASTM.org website.*

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, Liquid Fuels, 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, n*—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**

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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, n*—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, n*—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, n*—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, n*—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