Designation: D5845 – 01 (Reapproved 2016)

Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol and *tert*-Butanol in Gasoline by Infrared Spectroscopy[1]

This standard is issued under the fixed designation D5845; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of methanol, ethanol, *tert*-butanol, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE) in gasoline by infrared spectroscopy. The test method is suitable for determining methanol from 0.1 to 6 mass %, ethanol from 0.1 to 11 mass %, *tert*-butanol from 0.1 to 14 mass %, and DIPE, MTBE, ETBE and TAME from 0.1 to 20 mass %.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

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

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

E1655 Practices for Infrared Multivariate Quantitative Analysis

2.2 *Other Standard:*[3]

GC/OFID EPA Test Method—Oxygen and Oxygenate Content Analysis (by way of gas chromatography with oxygen-selective flame ionization detection)

3. Terminology

3.1 *Definitions:*

3.1.1 *multivariate calibration, n*—a process for creating a calibration model in which multivariate mathematics is applied to correlate the absorbances measured for a set of calibration samples to reference component concentrations or property values for the set of samples. The resultant multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the component concentration or property values for the unknown sample.

3.1.2 *oxygenate, n*—an oxygen-containing organic compound, which may be used as a fuel or fuel supplement, for example, various alcohols or ethers.

4. Summary of Test Method

4.1 A sample of gasoline is introduced into a liquid sample cell. A beam of infrared light is imaged through the sample onto a detector, and the detector response is determined. Regions of the infrared spectrum are selected for use in the analysis by either placing highly selective bandpass filters before or after the sample or mathematically selecting the regions after the whole spectrum is obtained. A multivariate mathematical analysis is carried out which converts the detector response for the selected regions in the spectrum of an unknown to a concentration for each component.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0F on Absorption Spectroscopic Methods.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Code of Federal Regulations, Part 80 of Title 40, Section 80.46(g); also published in the Federal Register, Volume 59, No. 32, February 16, 1994, p 7828.

5. Significance and Use

5.1 Alcohols and ethers are added to gasoline to produce a reformulated lower emissions gasoline. Alcohols and ethers may also be added to gasoline to increase the octane number. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Driveability, vapor pressure, phase separation, and evaporative emissions are some of the concerns associated with oxygenated fuels.

5.2 This test method is faster, simpler, less expensive and more portable than current methods.

5.3 This test method may be applicable for quality control in the production of gasoline.

5.4 This test method is not suitable for testing for compliance with federal regulations.[3]

5.5 False positive readings for some of the samples tested in the round robin were sometimes observed. As only extreme base gasolines were tested in the round robin, no definitive statement can be made as to the expected frequency or magnitude of false positives expected in a wider range of base gasolines.

6. Apparatus

6.1 *Mid-IR Spectrometric Analyzer,* of one of the following types:

6.1.1 *Filter-based Mid-IR Test Apparatus*—The type of apparatus suitable for use in this test method minimally employs an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, wavelength discriminating filters, a chopper wheel, a detector, an A-D converter, a microprocessor, and a sample introduction system.

6.1.2 *Fourier Transform Mid-IR Test Apparatus*—The type of apparatus suitable for use in this test method employs an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, a scanning interferometer, a detector, an A-D converter, a microprocessor and a sample introduction system.

6.1.3 *Dispersive Mid-IR Test Apparatus*—The type of apparatus suitable for use in this test method minimally employs an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, a wavelength dispersive element such as a grating or prism, a chopper wheel, a detector, an A-D converter, a microprocessor and a sample introduction system.

7. Reagents and Materials

7.1 *Samples for Calibration and Quality Control Check Solutions*—Use of chemicals of at least 99 % purity is highly recommended when preparing calibration and quality control check samples. If reagents of high purity are not available, an accurate assay of the reagent must be performed using a properly calibrated GC or other techniques (for example, water determination).

7.1.1 Base gasolines containing no oxygenates,
7.1.2 Methanol,
7.1.3 Ethanol,
7.1.4 *tert*-Butanol,
7.1.5 Methyl *tert*-butyl ether, MTBE,
7.1.6 Ethyl *tert*-butyl ether, ETBE,
7.1.7 *tert*-Amyl methyl ether, TAME, and
7.1.8 Di*iso*propyl ether, DIPE.

7.2 **Warning—**These materials are flammable and may be harmful if ingested or inhaled.

8. Sampling and Sample Handling

8.1 *General Requirements:*

8.1.1 Gasoline samples must be handled with meticulous care to prevent evaporative loss and composition changes.

8.1.2 Gasoline samples to be analyzed by the test method shall be obtained using method(s) specified by governmental regulatory agencies or by the procedures outlined in Practice D4057 (or equivalent). Do not use the "Sampling by Water Displacement" method as some alcohols or ethers might be extracted into the water phase.

8.1.3 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage in an appropriate ice bath or refrigerator at 0 °C to 5 °C.

8.1.4 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.

8.1.5 Perform the oxygenate determination on fresh samples from containers that are at least 80 % full. If sample containers are less than 80 % full or have been opened and sampled multiple times, a new sample shall be obtained.

8.2 *Sample Handling During Analysis:*

8.2.1 Prior to the analysis of samples by infrared spectroscopy, the samples should be allowed to equilibrate to the temperature at which they should be analyzed (15 °C to 38 °C).

8.2.2 After withdrawing the sample, reseal the container, and store the sample in an ice bath or a refrigerator at 0 °C to 5 °C.

9. Preparation, Calibration, and Qualification of the Infrared Test Apparatus

9.1 *Preparation*—Prepare the instrument for operation in accordance with the manufacturer's instructions.

9.2 *Calibration*—Each instrument must be calibrated by the manufacturer or user in accordance with Practice E1655. This practice serves as a guide for the multivariate calibration of infrared spectrometers used in determining the physical characteristics of petroleum and petrochemical products. The procedures describe treatment of the data, development of the calibration, and qualification of the instrument. Note that bias and slope adjustments are specifically not recommended to improve calibration or prediction statistics for IR multivariate models.

9.3 *Qualification of Instrument*—The instrument must be qualified according to the procedure in Annex A1 to ensure that the instrument accurately and precisely measures each oxygenate in the presence of typical gasoline compounds or other oxygenates that, in typical concentrations, present spectral interferences. General classes of compounds that will cause interferences include aromatics, branched aliphatic hydrocarbons, and other oxygenates.