



Designation: D5845 – 21

Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol and *tert*-Butanol in Gasoline by Infrared Spectroscopy¹

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 1.7 % to 5.5 % by mass, ethanol from 1.5 % to 10 % by mass, *tert*-butanol from 1.6 % to 12 % by mass, DIPE from 1.2 % to 17 % by mass, MTBE from 2.0 % to 16.4 % by mass, ETBE from 2.0 % to 18.5 % by mass, and TAME from 1.5 % to 18.5 % by mass.

1.2 This test method is applicable to oxygenate(s) in gasoline singularly or in multiple mixtures hereof according to the oxygenates and mass percent ranges given in 1.1.

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.*

1.5 *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.*

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. 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 C₁ to C₄ Alcohols in Gasoline by Gas Chromatography
- D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection
- D8321 Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements

NOTE 1—D5845 was developed with reference to E1655. A significant enhancement has been made to E1655 and is designated as D8321. D8321 is the preferred standard Practice and describes the mathematics, that is, the regression algorithms to develop calibration equations that are also described in E1655. Replace E1655 with D8321.

NOTE 2—Surrogate methods such as D5845 may indicate that they make use of the creation of multivariate calibration equations described therein D8321, but they should not claim to follow the procedures described herein.

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)

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.

*A Summary of Changes section appears at the end of this standard

3. Terminology

3.1 Definitions:

3.1.1 *diluent, n*—a substance used to dilute something.

3.1.1.1 *Discussion*—In this standard, the diluents are termed base gasoline A, B, and C, which are the diluents consisting of gasoline blend stocks used to dissolve the oxygenates to create the calibration and instrument qualification matrix solutions. The base stocks must not contain measurable oxygenates. The known base socks are:

(1) Base gasoline A should be a gasoline with at least 60 % alkylate. A suggested recipe for base gasoline A is 60 % alkylate, 30 % full range reformat, and 10 % light straight run.

(2) Base gasoline B should be a gasoline with at least 60 % full range reformat. A suggested recipe for base gasoline B is 60 % full range reformat, 30 % FCC gasoline, and 10 % light straight run.

(3) Base gasoline C the composition is not known

3.1.2 *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.

3.1.3 *oxygenate, n*—a molecule composed solely of carbon, hydrogen, and oxygen.

3.1.3.1 *Discussion*—In this standard, the oxygenates of interest are: methanol, ethanol, *tert*-butanol, DIPE, MTBE, ETBE, and TAME.

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 uses the detector response for the selected regions in the spectrum to compute the concentration for each component in an unknown based on multivariate models for each component.

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 Diisopropyl 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 D8321. 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.

10. Quality Control Standards

10.1 Confirm the proper operation of the instrument each day it is used by analyzing at least one quality control standard

of known oxygenate content for each oxygenate to be determined. These standards should be made up by mass according to Practice D4307 and should be at the expected concentration level for that oxygenate. The recommended quality control standard concentrations are found in Table 1.

10.2 *The individual oxygenate values obtained must agree within ±5 % relative of the values in the prepared quality control standard* (for example, MTBE 14.0 % ± 0.7 % by mass) or to within ±0.3 % by mass absolute, whichever is greater (for example, methanol 4.0 % ± 0.3 % by mass). If the individual values are outside the specified range, recalibrate the instrument according to the procedures in 9.2. The quality control standards should not be used for the calibration or recalibration of the instrument. **Do not analyze samples without meeting the quality control specifications.**

11. Procedure

11.1 Equilibrate the samples to between 15 °C and 38 °C before analysis.

11.2 Follow the manufacturer’s instructions for establishing a baseline for the instrument, introducing a sample into the sample cell and operating the instrument. If the instructions call for a non-oxygenated gasoline to be used in establishing the baseline, use a non-oxygenated gasoline that is different from the non-oxygenated gasolines used in the preparation of either calibration standards, validation of qualification samples, or quality control standards.

11.3 Thoroughly clean the sample cell by introducing enough sample to the cell to ensure the cell is washed a minimum of three times with the test solution.

11.4 Establish that the equipment is running properly by running the quality control standards prior to the analysis of unknown test samples (see Section 10).

11.5 Introduce the sample in the manner established by the manufacturer. Obtain the concentration reading produced by the instrument.

12. Calculation

12.1 *Conversion to Mass Concentration of Oxygenates*—If the instrument readings are in volume % for each component, convert the results to mass % according to Eq 1:

$$m_i = V_i (D_i/D_f) \tag{1}$$

TABLE 1 Recommended Concentrations for Individual Quality Control Standards

Oxygenate	Concentration to Attain		
	2.0 % mass O	2.7 % mass O	3.5 % mass O
Methanol	4.00 % mass	5.41 % mass	
Ethanol	5.76 % mass	7.77 % mass	10.1 % mass
tert-Butanol	9.26 % mass	12.5 % mass	
MTBE	11.0 % mass	14.9 % mass	
TAME	12.8 % mass	17.2 % mass	
DIPE	12.8 % mass	17.2 % mass	
ETBE	12.8 % mass	17.2 % mass	

TABLE 2 Pertinent Physical Constants

Component	CAS Number	Molecular Mass	Relative Density, 15.56 °C
Methanol	67-56-1	32.04	0.7963
Ethanol	64-17-5	46.07	0.7939
tert-Butanol	75-65-0	74.12	0.7922
MTBE	1634-04-4	88.15	0.7460
DIPE	108-20-3	102.18	0.7300
ETBE	637-92-3	102.18	0.7452
TAME	994-05-8	102.18	0.7758

where:

- m_i = mass % for each oxygenate to be determined,
- V_i = volume % of each oxygenate,
- D_i = relative density at 15.56 °C of the individual oxygenate as found in [Table 2](#),
- D_f = relative density of the fuel at 15.56 °C under study as determined by Practice [D1298](#) or Test Method [D4052](#).
If the density has not been measured, an assumed density of 0.742 should be used.

12.2 *Total Mass % Oxygen*—To determine the total oxygen content of the fuel, sum the mass % oxygen contents of all oxygenate components determined above according to [Eq 2](#):

$$W_{tot} = \sum [(m_i \times 16.0 \times N_i) / M_i] \quad (2)$$

where:

- W_{tot} = total mass % oxygen in the fuel,
- m_i = mass % for each oxygenate,
- 16.0 = atomic mass of oxygen,
- N_i = number of oxygen atoms in the oxygenate molecule, and
- M_i = molecular mass of the oxygenate molecule as given in [Table 2](#).

13. Report

13.1 Report results of each oxygenate and the total oxygen to the nearest 0.1 % by mass.

14. Precision and Bias⁴

14.1 A summary of the data used in the ILS to derive the Precision Statement is listed in [Table 3](#).

NOTE 3— For a complete listing of the gravimetric values of oxygenates

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1374. Contact ASTM Customer Service at service@astm.org.

and mixtures thereof in the ILS, see [Appendix X1](#).

14.2 The precision of the method as obtained by statistical examination of interlaboratory results is as follows:

14.3 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions 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 twenty:

Oxygenate	Repeatability (mass %)
MTBE	0.13
TAME	0.13
ETBE	0.15
Ethanol	0.13
Methanol	0.07
t-Butanol	0.10
DIPE	0.14
Total Oxygen Content	0.05

14.4 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials would, in the long run, exceed the following values only in one case in twenty:

Oxygenate	Reproducibility (mass %)
MTBE	0.98
TAME	1.36
ETBE	0.77
Ethanol	0.59
Methanol	0.37
t-Butanol	0.59
DIPE	0.79
Total Oxygen Content	0.30

14.5 *Bias*—No consistent bias was observed with the samples tested in the round robin and since a wide range of base gasolines was not tested, it is not possible to offer a definitive statement of bias except to note that biases were observed in the round robin.

TABLE 3 Summary of Interlaboratory Study

Oxygenate	No. of Participants: 11			Total Levels ^D	2 Replicates per sample	
	Base Gas A ^A Diluent % Mass	Base Gas B ^B Diluent % Mass	Base Gas C ^C Diluent % Mass		Average Mass % ^E	Ranges as Oxygen Mass % ^F
MTBE	14.00	2.06, 3.99, 5.06, 7.00, 8.97, 16.4	1.95, 4.13, 5.99, 7.85, 9.56, 13.9	13	7.76	0.35–3.00
TAME	16.46	1.50, 3.01, 5.00, 9.28, 12.01, 18.41	1.52, 3.99, 5.99, 7.73, 10.87, 16.45	13	8.48	0.23–2.88
ETBE	18.44	2.97, 5.99, 7.29, 9.51, 16.94	15.69, 7.94, 5.96, 3.91, 1.96	11	8.78	0.31–2.89
ETHANOL	9.50	2.06, 3.25, 3.99, 4.99, 7.04, 9.96	1.52, 2.93, 4.07, 5.00, 5.96, 9.01	13	5.33	0.67–4.42
METHANOL	5.75	1.67, 1.99, 3.49, 5.51	1.66, 2.03, 3.46, 5.15	9	3.41	0.8–2.88
t-BUTANOL	11.04	2.05, 3.03, 5.98, 12.04	1.57, 3.98, 8.15, 11.95	9	6.64	0.34–2.60
DIPE	16.98	1.24, 5.01, 10.11, 16.58	1.97, 6.83, 8.90, 16.42	9	9.23	0.19–2.60

^A Base gasoline A should be a gasoline with at least 60 % alkylate. A suggested recipe for base gasoline A is 60 % alkylate, 30 % full range reformat, and 10 % light straight run.

^B Base gasoline B should be a gasoline with at least 60 % full range reformat. A suggested recipe for base gasoline B is 60 % full range reformat, 30 % FCC gasoline, and 10 % light straight run.

^C Base gasoline C the composition is not known.

^D Total Levels is the sum total count of the number of mass% concentrations tested for each oxygenate in the ILS.

^E Average Mass is the sum of all mass % values for within each oxygenate divided by their total levels.

^F Ranges as Oxygen Mass % for each oxygenate is determined from the fraction of oxygen in the molecule multiplied by the lowest % mass and the highest mass %.

15. Keywords

15.1 alcohols; diisopropyl ether; ethanol; ethers; ethyl *tert*-butyl ether; infrared spectroscopy; methanol; methyl *tert*-butyl ether; motor gasoline; multivariate calibration; oxygenate; *tert*-amyl methyl ether; *tert*-butanol

ANNEX

(Mandatory Information)

A1. QUALIFICATION OF INSTRUMENT

A1.1 *Preparation of Qualification Samples*—The minimum matrix of qualification standards is presented in **Table A1.1**. Additional qualification standards may be added. Prepare multicomponent qualification standards of the oxygenates by mass according to Practice **D4307** or appropriately scaled for larger blends. To ensure that there is minimum interference from any oxygenate present in the base gasolines, a gas chromatographic analysis of the base gasolines must be performed to ensure the absence of oxygenates (use Test Methods

D4815, **D5599**, or GC-OFID). To ensure the insensitivity of the calibration to the hydrocarbon matrix of the base gasolines, the base gasolines used for preparation of the qualification samples should be different from the base gasoline(s) used for preparation of the calibration standards. To minimize the evaporation of light components, adjust the temperature of all chemicals and gasolines used to prepare standards to between 5 °C and 20 °C. None of the samples or base gasolines used in the qualification of calibration may be used for the calibration (or

TABLE A1.1 Minimum Matrix for Qualification Samples

NOTE 1—All concentrations are mass %.

Sample	Base Gas ⁴	MTBE	TAME	ETBE	Ethanol	Methanol	t-Butanol	DIPE
1	A				10			
2	A				5			
3	A	16.5						
4	A	9				1.5	2	
5	A		18.5					
6	A	4	12					1.25
7	A							
8	A			17				
9	A			9.5	4			
10	A				3	5.5		
11	A					3.5		
12	A		9				12	
13	A						6	
14	A			7				16.5
15	A	7	3	6				10
16	A	5	5	3				
17	A		1.5				3	5
18	A	2			2	2		
19	B				7			
20	B				9			
21	B	14			6			
22	B	10						
23	B		16.5			2	1.5	
24	B	4	11					
25	B			15.5				2
26	B			8	5			
27	B					5		
28	B				3	3.5		
29	B						12	
30	B		5				8	
31	B							16.5
32	B			6				9
33	B	6	3	4				
34	B	2	8	2			4	
35	B		1.5		1.5	1.5		7
36	B	8			4			

⁴Base gasoline A should be a gasoline with at least 60 % alkylate. A suggested recipe for base gasoline A is 60 % alkylate, 30 % full range reformat, and 10 % light straight run. Base gasoline B should be a gasoline with at least 60 % full range reformat. A suggested recipe for base gasoline B is 60 % full range reformat, 30 % FCC gasoline, and 10 % light straight run.