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An American National Standard

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

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^{ε1} ~~Note—Editorial corrections were made throughout in November 2000.~~

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.001 on Absorption Spectroscopic Methods.

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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 SI units of measurement are preferred and used throughout 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:

D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method²

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter³

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards³

D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tert*-Amyl Alcohol, and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography³

D 5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection⁴

E 1655 Practice for Infrared; Multivariate; Quantitative Analysis⁵

2.2 Other Standard:

GC/OFID EPA Test Method—Oxygen and Oxygenate Content Analysis⁶ (by way of gas chromatography with oxygen-selective flame ionization detection)

3. Terminology

3.1 Definitions:

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

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

² Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vol 05.02.

⁴ Annual Book of ASTM Standards, Vol 05.03.

⁵ Annual Book of ASTM Standards, Vol 03.06.

⁶ 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.

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.

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.

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.⁶

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 *Standards/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 D 4057 (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 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 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 to 5°C.

9. Preparation, Calibration, and Validation of Calibration 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 E 1655. 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 validation of the calibration instrument. Note that bias and slope adjustments are specifically not recommended to improve calibration or prediction statistics for IR multivariate models.

9.3 Validation of Calibration Instrument—The calibration of the instrument must be qualified according to the procedure in order 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.

9.3.1 Preparation of Validation Standards—The minimum matrix of validation standards is presented in Table 1. Additional

TABLE 1 Minimum Recommended Concentrations for Validation of Calibration Instrument—All Concentrations are in mass %

Sample	Base Gas ^A		40	MTBE	ETBE	Ethanol	Concentration to At-Bu
	-42.0 mass % O	42.7 mass % O					
-2	A			5			
Methanol	4.00 mass %	5.41 mass %		5			
-3	A	16.5					
Ethanol	5.76 mass %	7.77 mass %	10.1 mass %				
-4	A	9			1.5	-2	
tert-Butanol	9.26 mass %	12.5 mass %			1.5	-2	
-5	A		18.5				
MTBE	11.0 mass %	14.9 mass %	18.5				
-6	A	4	12				-1.25
TAME	12.8 mass %	17.2 mass %	12				-1.25
-7	A			17			
DIPE	12.8 mass %	17.2 mass %		17			
-8	A			-9.5	4		
ETBE	12.8 mass %	17.2 mass %		-9.5	4		
-9	A				5.5		
10	A			3	3.5		
11	A					12	
12	A		-9			-6	
13	A						16.5
14	A			-7			10
15	A	-7	-3	-6			
16	A	-5	-5	-3		-3	-5
17	A		-1.5		2	2	
18	A	-2		7			
19	B			9			
20	B			6			
21	B	14					
22	B	10			2	-1.5	
23	B		16.5				
24	B	-4	11				-2
25	B			15.5			
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			

^ABase 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.

validation standards may be added. Prepare multicomponent validation standards of the oxygenates by mass according to Practice D 4307 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 D 4815, D 5599, 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 validation standards 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 and 20°C. None of the samples or base gasolines used in the validation or calibration may be used for the calibration (or recalibration) of an instrument.

9.3.2 *Analysis of Validation Standards*—The validation standards should be analyzed by the procedure specified in Section 11. If necessary, results should be converted from volume to mass % by the calculations described in Section 12.

9.3.3 *Criteria for Validation of Calibration*—The calibration is considered to be validated if the following specifications are all met:

9.3.3.1 *Accuracy of Each Oxygenate*—Analysis of **each** of the oxygenates in **each** of the validation standards must be within the criteria established in Table 2. If it is known that an analyte is not present in a particular validation sample, the value determined for that analyte must be less than the criteria also established in Table 2.

9.3.3.2 *Overall Accuracy*—The standard error of prediction (SEP) for each analyte summed over all samples in the validation set must be within the criteria established in Table 3.

9.3.3.3 *Overall Repeatability*—Each sample of the validation set must be run twice. Repeat determinations of any sample can differ by no more than 0.3 mass %.

9.3.4 *Frequency of Validation*—Once the calibration of the instrument has been validated, it need only be revalidated when either the instrument has been recalibrated due to repair or when the quality control check samples are outside of the test tolerance.

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 D 4307 and should be at the expected concentration level for that oxygenate. The recommended quality control standard concentrations are found in Table 4 1.

10.2 The individual oxygenate values obtained must agree within $\pm 5\%$ relative of the values in the prepared quality control standard (for example, MTBE 14.0 ± 0.7 mass %) or to within ± 0.3 mass % absolute, whichever is greater (for example, methanol 4.0 ± 0.3 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 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 calibration standards, qualification samples, or quality control standards.

TABLE 2 Maximum Error Allowed for Validation of Calibrant Physical Constants

Oxygenate Component	Error With CAS Number Oxygenate Is Known To Be Present, mass %, max	Error Molecular Weight Mass	Relative Density, mass %, max 15.56°C
MTBE	4.5	0.4	0.9
Methanol	67-56-1	32.04	0.7963
TAME	2-0	100.7	0.7939
Ethanol	64-17-5	46.07	0.7939
ETBE	4-2	42	0.9
tert-Butanol	75-65-0	74.12	0.7922
Ethanol	0-9	46.07	0.6
MTBE	1634-04-4	88.15	0.7460
Methanol	0-6	32.04	0.73
DIPE	108-20-3	102.18	0.7300
t-Butanol	0-9	74.12	0.7452
ETBE	637-92-3	102.18	0.7452
DIPE	4-2	102.18	0.7758
TAME	994-05-8	102.18	0.7758

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:

$$m_i = V_i (D_i/D_f) \quad (1)$$

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-5, 2,

D_f = relative density of the fuel at 15.56°C under study as determined by Practice D 1298 or Test Method D 4052. 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:

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

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-5, 2.

13. Report

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

14. Precision and Bias ⁷

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

14.2 *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

14.3 *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:

⁷ Supporting data available from ASTM International Headquarters. Request D02-1374.

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

14.4 *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.

15. Keywords

15.1 alcohols; diisopropyl ether; ethanol; ethers; ethyl *tert*-butyl ether; methanol; methyl *tert*-butyl ether; motor gasoline; 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 D 4307 or appropriately scaled for larger blends. To ensure that there is minimum interference from any

TABLE A1.1 Minimum Matrix for Qualification Samples

NOTE 1—All concentrations are mass %.

Sample	Base Gas ^A	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			17				
8	A			9.5	4			
9	A					5.5		
10	A				3	3.5		
11	A						12	
12	A		9				6	
13	A							16.5
14	A			7				10
15	A	7	3	6				
16	A	5	5	3			3	5
17	A		1.5		2	2		
18	A	2			7			
19	B				9			
20	B				6			
21	B	14						
22	B	10				2	1.5	
23	B		16.5					
24	B	4	11					2
25	B			15.5				
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			

^ABase 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.

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 D 4815, D 5599, 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 and 20°C. None of the samples or base gasolines used in the qualification of calibration may be used for the calibration (or recalibration) of an instrument.

A1.1.1 Analysis of Qualification Samples—The qualification samples should be analyzed by the procedure specified in Section 11. If necessary, results should be converted from volume to mass % by the calculations described in Section 12.

A1.1.2 Criteria for Qualification of Instrument—The instrument is considered to be qualified if the following specifications are all met:

A1.1.2.1 Accuracy of Each Oxygenate—Analysis of **each** of the oxygenates in **each** of the qualification standards must be within the criteria established in Table A1.2. If it is known that an analyte is not present in a particular qualification sample, the value determined for that analyte must be less than the criteria also established in Table A1.2.

A1.1.2.2 Overall Accuracy—The standard error of qualification (SEQ) for each analyte summed over all samples in the qualification set must be within the criteria established in Table A1.3.

A1.1.2.3 Overall Repeatability—Each sample of the qualification set must be run twice. Repeat determinations of any sample can differ by no more than 0.3 mass %.

A1.1.3 Frequency of Qualification—Once the calibration of the instrument has been qualified, it need only be requalified when either the instrument has been recalibrated due to repair or when the quality control check samples are outside of the test tolerance.

TABLE A1.2 Maximum Error Allowed for Qualification of Instrument

Oxygenate	Error When Oxygenate Is Known To Be Present, mass %, max	Error When Oxygenate Is Not Present, mass %, max
	MTBE	1.5
TAME	2.0	1.8
ETBE	1.2	1.9
Ethanol	0.9	0.6
Methanol	0.6	0.3
t-Butanol	0.9	0.9
DIPE	1.2	0.9

TABLE A1.3 Maximum Standard Error of Prediction Allowed for Qualification of Instrument

<u>Oxygenate</u>	<u>SEQ Summed Over Samples Containing The Oxygenate, max</u>	<u>SEQ Summed Over All Samples In The Qualification Set, max</u>
<u>MTBE</u>	<u>0.9</u>	<u>0.5</u>
<u>TAME</u>	<u>1.2</u>	<u>0.9</u>
<u>ETBE</u>	<u>0.75</u>	<u>0.6</u>
<u>Ethanol</u>	<u>0.4</u>	<u>0.25</u>
<u>Methanol</u>	<u>0.25</u>	<u>0.15</u>
<u>t-Butanol</u>	<u>0.55</u>	<u>0.45</u>
<u>DIPE</u>	<u>0.6</u>	<u>0.35</u>

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