Designation: D 5599 – ~~95~~00

An American National Standard

Standard Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection[1]

This standard is issued under the fixed designation D 5599; 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 a gas chromatographic procedure for the quantitative determination of organic oxygenated compounds in gasoline having a final boiling point not greater than 220°C and oxygenates having a boiling point limit of 130°C. It is applicable when oxygenates are present in the 0.1 to 20 % by mass range.

1.2 This test method is intended to determine the mass concentration of each *oxygenate compound* present in a gasoline. This requires knowledge of the identity of each oxygenate being determined (for calibration purposes). However, the oxygen-selective detector used in this test method exhibits a response that is proportional to the mass of *oxygen*. It is, therefore, possible to determine the mass concentration of *oxygen* contributed by any oxygenate compound in the sample, whether or not it is identified. Total oxygen content in a gasoline may be determined from the summation of the accurately determined individual oxygenated compounds. The summed area of other, uncalibrated or unknown oxygenated compounds present, may be converted to a mass concentration of oxygen and summed with the oxygen concentration of the known oxygenated compounds.

1.3 The values stated in SI units are to be regarded as the 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent[2]

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[1] This test method is under the jurisdiction of ASTM Committee ~~D-2~~ D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography.

Current edition approved ~~Sept.~~ Nov. 10, ~~1995.~~ 2000. Published November ~~1995.~~ 2000. Originally published as D 5599 – 94. Last previous edition D 5599 – 9~~4~~5.

D 4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants[3]
D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[3]
~~D 4626 Practice for Calculation of Gas Chromatographic Response Factors[3]~~
E 594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography[4]
E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration[5]
E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *independent reference standards*—calibration samples of the oxygenates which are purchased or prepared from materials independent of the quality control check standards and used for intralaboratory accuracy.

3.1.2 *oxygenate, n*—an oxygen-containing compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement. **D 4175**

3.1.3 *quality control check standards*—calibration samples of the oxygenates for intralaboratory repeatability.

4. Summary of Test Method

4.1 An internal standard of a noninterfering oxygenate, for example, 1,2-dimethoxyethane (ethylene glycol dimethyl ether) is added in quantitative proportion to the gasoline sample. A representative aliquot of the sample and internal standard is injected into a gas chromatograph equipped with a capillary column operated to ensure separation of the oxygenates. Hydrocarbons and oxygenates are eluted from the column, but only oxygenates are detected with the oxygen-selective flame ionization detector (OFID). A discussion of this detector is presented in Section 6.

4.2 Calibration mixtures are used for determining the retention times and relative mass response factors of the oxygenates of interest. Suggested calibrant materials are listed in 8.2.

4.3 The peak area of each oxygenate in the gasoline is measured relative to the peak area of the internal standard. A quadratic least-squares fit of the calibrated data of each oxygenate is applied and the concentration of each oxygenate calculated.

NOTE 1—While 1,2-dimethoxyethane has been found to be an appropriate internal standard, other oxygenates may be used provided they are not present in the sample and do not interfere with any compound of interest.

5. Significance and Use

5.1 In gasoline blending, the determination of organic oxygenated compounds is important. Alcohols, ethers, and other oxygenates are added to gasoline to increase the octane number and to reduce tailpipe emissions of carbon monoxide. They must be added in the proper concentration and ratios to meet regulatory limitations and to avoid phase separation and problems with engine performance or efficiency.

5.2 This test method provides sufficient oxygen-to-hydro-carbon selectivity and sensitivity to allow determination of oxygenates in gasoline samples without interference from the bulk hydrocarbon matrix.

6. Theory of OFID Operation

6.1 The detection system selective for organic oxygen consists of a cracking reactor, hydrogenating reactor (methanizer), and a flame ionization detector (FID). The cracking reactor, connected immediately after the gas chro-matographic capillary column, consists of a Pt/Rh capillary tube. Carbon monoxide (CO) is formed from compounds containing oxygen according to the following reaction:

$$C_xH_yO_z \rightarrow zCO + (y/2)H_2 + (x - z)C \quad (1)$$

6.2 An excess layer of carbon is created in the Pt/Rh tube of the cracking reactor from the introduction of hydrocarbons from the sample or, if so designed, from a hydrocarbon (for example, pentane or hexane) doping system, or both. This layer of carbon facilitates the cracking reaction and suppresses hydrocarbon response.

6.3 The carbon monoxide formed in the cracking reactor is converted to methane in the hydrogenating reactor according to the following reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

The CH_4 is subsequently detected with an FID.

6.4 The methanizer consists either of a short porous layer open tubular (PLOT) glass capillary tube internally coated with aluminum oxide with adsorbed nickel catalyst or stainless steel tubing containing a nickel-based catalyst. It is installed within or before the FID and is operated in the range from 350 to 450°C, depending on the instrument's manufacturer.

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[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 14.02.
[5] *Annual Book of ASTM Standards*, Vol 15.05.

NOTE 2—Gasolines with high sulfur content may cause a loss in detector sensitivity thereby limiting the number of samples that can be analyzed before the catalyst needs replacement.

7. Apparatus

7.1 *Gas Chromatograph*—Any gas chromatograph can be used having the following performance characteristics:

7.1.1 *Column Temperature Programmer*— The chromatograph must be capable of reproducible linear temperature programming over a range sufficient for separation of the components of interest.

7.1.2 *Sample Introduction System*—Any system capable of introducing a representative 0.1 to 1.0-µL liquid sample into the split inlet device of the gas chromatograph. Microlitre syringes, autosamplers, and liquid sampling valves have been used successfully. The split injector should be capable of accurate split control in the range from 10:1 to 500:1.

7.1.3 *Carrier and Detector Gas Control*— Constant flow control of carrier and detector gases is critical to optimum and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictors. The gas flow rates are measured by any appropriate means. The supply pressure of the gas delivered to the gas chromatograph must be at least 70 kPa (10 psig) greater than the regulated gas at the instrument to compensate for the system back pressure. In general, a supply pressure of 550 kPa (80 psig) will be satisfactory.

7.2 *OFID Detector System*, consisting of a cracking reactor, methanizer, and FID. A schematic of a typical OFID system is shown in Fig. 1.

7.2.1 The detector must meet or exceed the typical specifications given in Table 1 of Practice E 594 while operating in the normal FID mode as specified by the manufacturer.

7.2.2 In the OFID mode, the detector shall meet or exceed the following specifications: (*a*) equal to or greater than 10^3 linearity, (*b*) less than 100-ppm mass oxygen (1-ng O/s) sensitivity, (*c*) greater than 10^6 selectivity for oxygen compounds over hydrocarbons, (*d*) no interference from coeluting compounds when 0.1 to 1.0-µL sample is injected, (*e*) equimolar response for oxygen.

7.3 *Column*—A 60-m by 0.25-mm inside diameter fused silica open tubular column containing a 1.0-µm film thickness of bonded methyl silicone liquid phase is used. Equivalent columns which provide separation of all oxygenates of interest may be used.

7.4 *Integrator*—Use of an electronic integrating device or computer is required. The device and software should have the following capabilities:

7.4.1 Graphic presentation of the chromatogram,

7.4.2 Digital display of chromatographic peak areas,

7.4.3 Identification of peaks by retention time,

7.4.4 Calculation and use of response factors, and

7.4.5 Internal standard calculation and data presentation.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagents grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

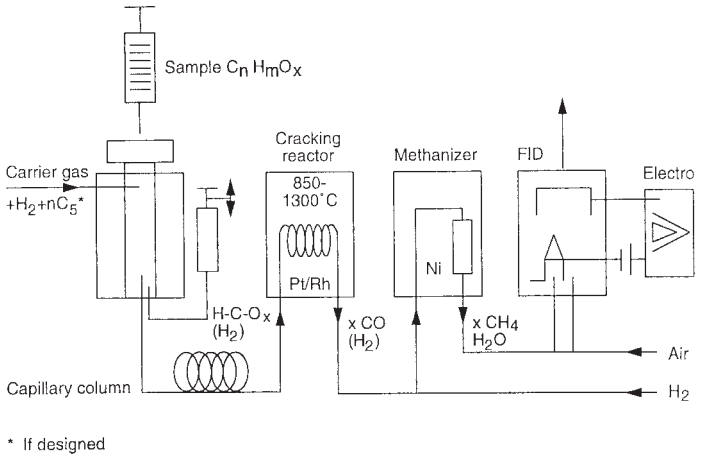


FIG. 1 Schematic of an OFID

such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Calibrant Materials*—The following compounds may be used for calibrating the detector: methanol, ethanol, *n*-propanol, iso-propanol, *n*-butanol, *tert*-butanol, *sec*-butanol, iso-butanol, *tert*-pentanol, methyl *tert*-butylether (MTBE), *tert*-amylmethylether (TAME), ethyl *tert*-butylether (ETBE), di-iso-propylether ~~(DIPE).~~

~~NOTE 3—~~**Warning:** ~~These~~ (DIPE). (**Warning**—These materials are very flammable and may be harmful or fatal when ingested, inhaled, or allowed to be absorbed through the skin.)

8.3 *Internal Standard*—Use one of the compounds listed in 8.2 that is not present in the sample. If all of the materials in 8.2 are likely to be present in the test sample, use another organic oxygenate of high-grade purity that is separated from all other oxygenates present (for example, 1,2-dimethoxyethane).

8.4 *Dopant*—If the OFID is so designed, reagent-grade pentane is used as a hydrocarbon dopant for the cracking ~~reactor.~~

~~NOTE 4—~~**Warning:** ~~Pentane~~ reactor. (**Warning**—Pentane is extremely flammable and harmful when inhaled.)

8.5 *Instrument Gases*—The gases supplied to the gas chromatograph and detector are:

8.5.1 Air, zero ~~grade.~~

~~NOTE 5—~~**Warning:** ~~Compressed~~ grade. (**Warning**—Compressed air is a gas under high pressure and supports combustion.)

8.5.2 Hydrogen, pure grade, 99.9 mol ~~%.~~

~~NOTE 6—~~**Warning:** ~~Hydrogen~~ %. (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

8.5.3 Helium or nitrogen as column carrier gas, 99.995 mol % minimum purity, or a blend of 95 % helium/5 % hydrogen, depending on the instrument's ~~manufacturer.~~

~~NOTE 7—~~**Warning:** ~~Helium~~ manufacturer. (**Warning**—Helium and nitrogen are compressed gases under high pressure.)

8.5.4 Additional purification of the carrier, air, and hydrogen is recommended. Use molecular sieves, Drierite, charcoal, or other suitable agents to remove water, oxygen, and hydrocarbons from the gases.

8.6 *Sample Container*—Glass vials with crimp on or screwdown sealing caps with self-sealing polytetrafluoroethylene (PTFE)–faced rubber membranes are used to prepare calibration standards and samples for analyses.

9. Preparation of Apparatus

9.1 *Chromatograph and OFID*—Place instrument and detector into operation in accordance with the manufacturer's instructions. Install the capillary column according to Practice E 1510. Adjust the operating conditions to provide for separation of all oxygenates of interest. Typical conditions used with the column specified in 7.3 are listed in Table 1.

9.2 *System Performance*—At the beginning of each day of operation, inject an oxygenate-free gasoline sample into the chromatograph to ensure minimum hydrocarbon response. If hydrocarbon response is detected, the OFID is not operating effectively and must be optimized according to the manufacturer's instructions before the sample can be analyzed.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacop~~eutic~~eal Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Typical Operating Conditions

Temperatures, °C	
Injector	250
Column	50°C (hold 10 min), ramp 8°/min to 250°C
Detector Methanizer	350–450
Reactor	850–1300
Flows, mL/min	
Column carrier gas	1
Detector gases	Air: 300
	H_2:30
Auxiliary (for dopant, if available)	H_2: 0.6
Sample Size	0.1–1.0 µL[A]
Split Ratio	100–1

[A] Sample size and split ratio must be adjusted so that the oxygenates in the range from 0.1 to 20.0 mass % are eluted from the column and measured linearly at the detector. Each laboratory must establish and monitor the conditions that are needed to maintain linearity with their individual instruments. Nonlinearity is most commonly observed when using an OFID with samples containing high levels of individual oxygenates and can be compensated for by either decreasing the sample size, increasing the split ratio, or diluting the sample with an oxygenate-free gasoline. A sample size of 0.5 µL and a split ratio of 100:1 has been used successfully in most cases.

10. Calibration and Standardization

10.1 *Retention Time Identification*— Determine the retention time of each oxygenate component by injecting small amounts either separately or in known mixtures. Table 2 gives typical retention times for the oxygenates eluting from a 60-m methyl silicone column temperature programmed according to conditions given in Table 1. A chromatogram of a blend of oxygenates is given in Fig. 2.

10.2 *Preparation of Calibration Samples*— The calibration samples are prepared gravimetrically in accordance with Practice D 4307 by blending known weights of organic oxygenate compounds (such as listed in 8.2) with a known weight internal standard and diluting to a known weight with an oxygenate-free gasoline. The calibration samples should contain the same oxygenates (in similar concentrations) as are expected in the sample under test. Before preparing the standards, determine the purity of the oxygenate stocks and make corrections for the impurities found. Whenever possible, use stocks of at least 99.9 % purity. Correct for the purity of the components for water content determined by Test Method D 1744 or Test Method E 1064. Quality control check standards may be prepared from the same oxygenate stocks and by the same analyst. Quality control check standards must be prepared from separate batches of the final diluted standards.

10.2.1 Tare a glass sample container and its PTFE-faced rubber septum sealing cap. Transfer a quantity of an oxygenate to the sample container and record the mass of the oxygenate to the nearest 0.1 mg. Repeat this process for any additional oxygenates of interest except the internal standard. Add oxygenate-free gasoline to dilute the oxygenates to the desired concentration. Record the mass of gasoline added to the nearest 0.1 mg, and determine and label the standard according to the mass % quantities of each oxygenate added. These standards are not to exceed 20 mass % for any individual pure component due to potential hydrocarbon breakthrough or loss, or both, of calibration linearity. To minimize evaporation of light components, chill all chemicals and gasoline used to make standards.

~~10.2.2 Add~~

10.2.2 Tare the glass sample container, a PTFE-faced rubber septum sealing cap, and contents prepared in 10.2.1. Add a quantity of an internal standard (such as 1,2-dimethoxyethane) and ~~reweigh the contents. Record the difference in masses as the~~ record its mass ~~of internal standard~~ to the nearest 0.1 mg. The mass of the internal standard should be between 2 and 6 % of the mass of the calibration sample.

10.2.3 Ensure that the prepared standard is thoroughly mixed, and transfer approximately 2 mL of the solution to a vial compatible with the autosampler if such equipment is used.

10.2.4 At least five concentrations of each of the expected oxygenates should be prepared. The standards should be as equally spaced as possible within the range and may contain more than one oxygenate. A blank for zero concentration ~~assessments must~~ assessment shall also be ~~included before each standard.~~ included. Additional standards should be prepared for other oxygenates of concern.

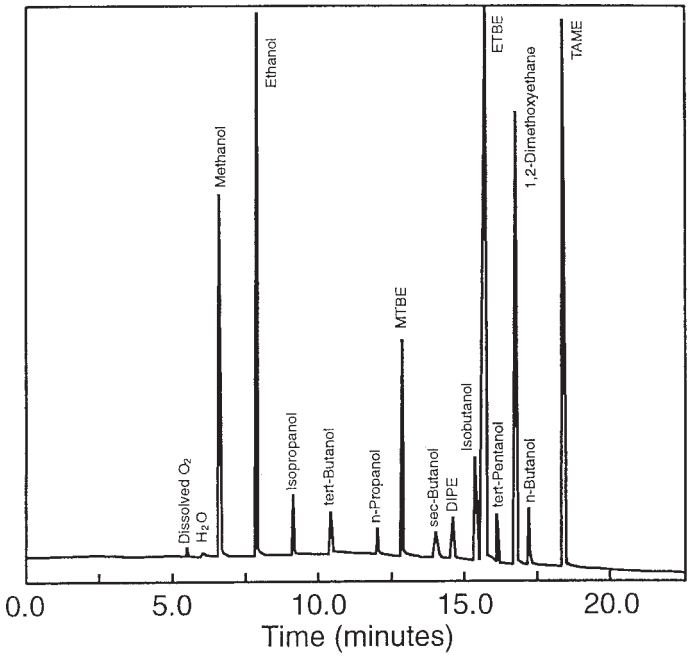
NOTE 3—If carryover is suspected to possibly occur, the blank should be run following a calibration sample containing high levels of oxygenates.

10.3 *Standardization*—Run the calibration samples and establish ~~the~~ a calibration curve ~~for each oxygenate. The area under each peak in the resulting chromatogram is considered~~ by performing a ~~quantitative measure~~ least-squares fit of the ~~corresponding compound. Using the peak area~~ response ratios of ~~each oxygenate and~~ the ~~internal standard, calculate the relative mass response factor for each~~ oxygenate ~~(relative~~ standards to their amount ratios, as follows.

TABLE 2 Oxygenates Retention Times, Relative Response Factors, and Molecular Masses (Conditions as in Table 1)

Compound	Retention Time min	Molecular Mass	Relative Response Factors[A,B]	Relative Response Factors[B,C,D]
Dissolved Oxygen	5.33	32.0	D	D
Water	5.89	18.0	D	D
Methanol	6.45	32.0	0.70	0.98
Ethanol	7.71	46.1	0.99	0.97
Isopropanol	8.97	60.1	1.28	0.96
tert-Butanol	10.19	74.1	1.63	0.99
n-Propanol	11.76	60.1	1.30	0.98
MTBE	12.73	88.2	1.90	0.97
sec-Butanol	13.92	74.1	1.59	0.97
DIPE	14.53	102.2	2.26	1.00
*Iso*butanol	15.32	74.1	1.64	0.99
ETBE	15.49	102.2	2.25	0.99
tert-Pentanol	15.97	88.1	2.03	1.04
1,2-dimethoxyethane	16.57	90.1	1.00	1.00
n-Butanol	17.07	74.1	1.69	1.03
TAME	18.23	102.2	2.26	1.00

[A] Based on mass percent oxygenate compound basis.
[B] Relative to 1,2-dimethoxyethane.
[C] Based on mass percent oxygen basis.
[D] Not determined.



NOTE 1—Operating conditions in accordance with Table 1.
FIG. 2 Chromatogram of an Oxygenates Blend

10.3.1 Calculate the ~~internal standard) in accordance with Practice D 4626 and Eq 3:~~ response ratio (rsp_s):

~~$$RF_s = (W_s/A_s)(A_i/W_i) \quad (3)$$~~

$$rsp_s = (A_s/A_i) \quad (3)$$

~~Wi~~

where:

~~RF_s = relative mass response factor of the test oxygen compound,~~
~~W_s = mass of the test oxygen compound in the calibration sample, g,~~
~~W_i = mass of the internal standard in the calibration sample, g,~~
A_s = peak area of the test oxygen compound in the calibration sample, and
A_i = peak area of the internal standard in the calibration sample~~.~~.

~~Since five concentrations of each expected oxygenate are used, calculate the response factors for all five concentration levels and take~~and the ~~averaged value as the relative mass response factor of the test oxygen compound.~~

~~10.3.1 Plot the response ratio (rsp_s):~~

~~$$rsp_s = (A_s/A_i) \quad (4)$$~~

~~as the *y*-axis versus~~ amount ratio (amt_s)~~:~~
):

$$amt_s = (W_s/W_i) \quad (4)$$

~~as the~~
~~*x*-axis calibration curves for each oxygenate. Check the correlation *r*~~

where: [2]
W^s = mass of the test oxygen compound in the calibration sample, g, and
~~*value*~~
~~*for*~~
~~*each*~~
~~*oxygenate*~~
~~*calibration.*~~
~~*The*~~
~~r^2~~

w_i = mass of the internal standard in the calibration sample, g,

~~value should be at least 0.99 or bet-ter.~~

~~For~~ for each level of each oxygenate, *s*.

10.3.2 For each oxygenate, *s*, calibration ~~data~~ set, obtain the quadratic least-squares fit equation in the following ~~form:~~ form (forced through the origin):

~~$$rsp_s = (b_o)(amt_s) + b_1 (amt_s)^2 \quad (5)$$~~

$$rsp_s = (b_o)(amt_s) + b_l (amt_s)^2 \quad (5)$$

~~b1~~ bl

where:

rsp_s = response ratio for oxygenate *s* (*y*-axis),
b_o = linear regression coefficient for oxygenate *s*,
amt_s = amount ratio for oxygenate *s* (*x*-axis), and
~~$b1_l$~~ = quadratic regression coefficient.

10.3.3 Fig. 3 gives an example of a quadratic least-squares fit for MTBE and the resulting equation in the form of Eq ~~6:~~

~~10.3.2 As a quality assurance check, calculate~~ 5. Check the ~~relative response factors on a mass % oxygen basis~~ correlation r^2 value for each ~~oxygen compound according to the following equation:~~

~~$$RF_{ox} = (RF_s)(MW_i/MW_s)(N_s/N_i) \quad (7)$$~~

~~MWi~~

~~where: r~~

~~RF_{ox}^2~~ = ~~relative response factor based on mass of oxygen,~~
~~RF_s~~ = ~~relative mass response factor of the test oxygen compound, as calculated in 10.3 (Eq 3),~~
~~MW_i~~ = ~~molecular mass of the internal standard in the calibration sample, g/mol,~~
~~MW_s~~ = ~~molecular mass of the test oxygen compound in the calibration sample as given in Table 2, g/mol,~~
~~N_s~~ = ~~number of oxygen atoms per molecule of test oxygen compound, and~~
~~N_i~~ = ~~number of oxygen atoms per molecule of internal standard.~~

~~The relative response factor (mass of oxygen basis)~~ value should ~~not deviate from unity by more than ±5 %. Table 2 gives typical relative response factors (on both mass of oxygenates and mass of oxygen basis) for the oxygenates in Fig. 2.~~ be at least 0.99 or better.

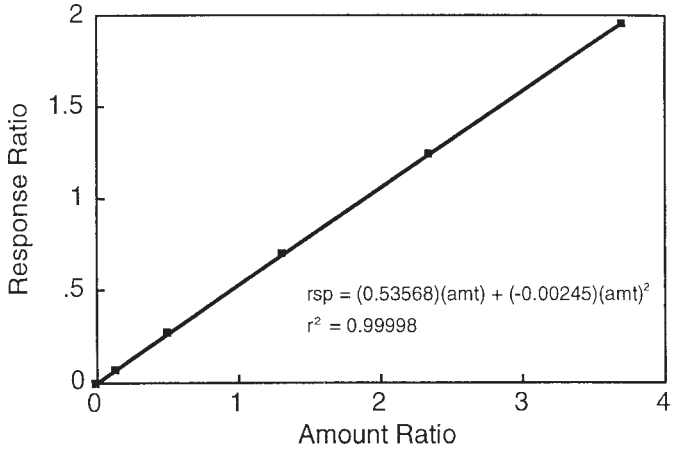


FIG. 3 An Example of a Quadratic Least-Squares Fit for MTBE

11. Procedure

11.1 Keep samples refrigerated until ready for analysis. Bring samples to room temperature prior to analysis.

11.2 Tare the sample container and its rubber-faced PTFE-faced sealing cap. Transfer 1 to 10 g of the sample to the container and seal immediately. Weigh the sample container and contents to the nearest 0.1 mg and record the mass of test sample.

11.3 ~~I~~Tare the sample container and contents, then inject through the rubber membrane a volume of the same internal standard used in generating the ~~standards and reweigh the sample container and contents.~~ standards. Record the ~~difference as the~~ mass of internal standard added to the nearest 0.1 mg. The mass of internal standard should be 2 to 6 % of the test sample but not less than 50 mg.

11.4 Ensure that the sample (gasoline plus internal standard) is thoroughly mixed. Transfer an aliquot of the solution to a vial compatible with the autosampler if such equipment is used. Seal the vial with a ~~TFE-fluorocarbon-lined~~ PTFE-lined septum cap.

11.5 Inject a suitable quantity (0.1 to 1.0 µL) of the sample containing internal standard into the chromatograph using the same technique and sample size as used for the calibration standards. The test portion size should be such as not to exceed the capacity of the column or linearity of the detector.

11.6 Acquire peak area and retention time data by way of electronic integrator or computer and, if desired, also by chart recorder.

12. Calculation and Report

12.1 Calculate the mass % of each calibrated oxygenate as follows:

12.1.1 After identifying the various oxygenates by retention times, obtain the areas of all calibrated oxygenate peaks and that of the internal standard. Calculate the area response ratio (rsp_s) for each of the oxygenates using Eq ~~4~~ 3 (10.3.1).

12.1.2 Calculate the amount ratio (amt_s) for each calibrated oxygenate in the gasoline sample, by substituting that oxygenate's response ratio (rsp_s) and the coefficient of its quadratic calibration curve into Eq ~~6~~ 5 (10.3.1) and solving.

12.1.3 Apply Eq ~~8~~ 6 to determine the mass % of each calibrated oxygenate.

$$w_s = \frac{(amt_s)(W_i)(100\ \%)}{W_g} \tag{6}$$

where:

w_s = mass % of oxygenate in gasoline sample,
amt_s = amount ratio of oxygenate as determined in 12.1.2,
W_i = mass of internal standard added to gasoline sample, g, and
W_g = mass of gasoline sample, g.

12.1.4 If the mass % of any oxygenate exceeds its calibrated range, gravimetrically dilute a portion of the original sample with oxygenate-free gasoline to a concentration within the calibrated range and analyze the diluted sample in accordance with Section 11 and 12.1. Correct all mass % oxygenate values by multiplying by the dilution factor.

12.2 Calculate the total *MTBE-equivalent* mass % of uncalibrated oxygenates as follows:

12.2.1 Sum the peak areas of the uncalibrated oxygenates that are present. Do not include the peak areas due to dissolved oxygen, water, and the internal standard. Calculate the response ratio (rsp_s) for the summed areas of the uncalibrated oxygenates using Eq ~~4~~ 3 (10.3.1).

12.2.2 Calculate the amount ratio (amt_s) for the uncalibrated oxygenates in the gasoline sample by substituting the response ratio (determined in 12.2.1) and the coefficients of the MTBE calibration curve into Eq ~~6~~ 5 (10.3.1) and solving.

12.2.3 Apply Eq ~~8~~ 6 (12.1.3) to determine the total MTBE-equivalent mass % of the uncalibrated oxygenates.

12.3 Calculate the total mass % oxygen in the gasoline sample as follows:

12.3.1 Convert the mass % oxygenate of each individual, calibrated oxygenate to mass % oxygen and sum according to the following equation:

~~$$O_{cal} = \Sigma \frac{[(w_s)(16.0)(N_s)]}{M_s}$$~~ (7)

$$O_{cal} = \Sigma \frac{[(w_s)(16.0)(N_s)]}{M_s} \tag{7}$$

or

$$O_{cal} = \frac{[w_1][16.0][N_1]}{M_1} + \frac{[w_{2][16.0][N_2]}}{M_2} + \ldots \tag{8}$$

where:

O_{cal} = total mass percent oxygen from the calibrated oxygenates,
w_s = mass % of each oxygenate as determined using Eq ~~8,~~ 6,
N_s = number of oxygen atoms in the oxygenate molecule,
M_s = molecular mass of the oxygenate as given in Table 2, and
16.0 = atomic mass of oxygen.

TABLE 3 Precision Interval as Determined from Cooperative Study Data Repeatability

Component Wt %	Repeatability													
	MeOH	EtOH	iPA	tBA	nPA	MTBE	sBA	DIPE	iBA	ETBE	tAA	nBA	TAME	Total Oxygen
0.20	0.03	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.03	0.03	0.02	...
0.50	0.05	0.02	0.03	0.03	0.03	0.03	0.02	0.03	0.02	0.01	0.04	0.04	0.03	...
1.00	0.07	0.03	0.04	0.05	0.04	0.05	0.03	0.05	0.03	0.04	0.05	0.06	0.04	0.03
2.00	0.10	0.06	0.06	0.08	0.05	0.07	0.04	0.08	0.05	0.07	0.07	0.08	0.06	0.06
3.00	0.12	0.08	0.07	0.10	0.06	0.09	0.05	0.10	0.07	0.10	0.08	0.10	0.08	0.08
4.00	0.13	0.11	0.08	0.12	0.06	0.11	0.06	0.12	0.09	0.13	0.09	0.11	0.09	0.11
5.00	0.15	0.13	0.09	0.14	0.07	0.13	0.07	0.14	0.11	0.16	0.10	0.13	0.10	0.13
6.00	0.17	0.16	0.10	0.16	0.07	0.14	0.08	0.16	0.12	0.19	0.10	0.14	0.11	...
10.00	0.22	0.25	0.14	0.22	0.09	0.19	0.10	0.22	0.18	0.29	0.13	0.17	0.15	...
12.00	0.24	0.29	0.15	0.25	0.09	0.21	0.11	0.25	0.21	0.34	0.14	0.19	0.17	...
14.00	...	...	...	...	...	0.23	...	0.28	...	0.39	...	...	0.18	...
16.00	...	...	...	...	...	0.25	...	0.30	...	0.43	...	...	0.20	...
20.00	...	...	...	...	...	0.28	...	0.35	...	0.53	...	...	0.23	...
Component Wt %	Reproducibility													
	MeOH	EtOH	iPA	tBA	nPA	MTBE	sBA	DIPE	iBA	ETBE	tAA	nBA	TAME	Total Oxygen
0.20	0.06	0.07	0.06	0.05	0.04	0.02	0.05	0.05	0.05	0.07	0.07	0.14	0.08	...
0.50	0.14	0.16	0.13	0.11	0.09	0.05	0.10	0.10	0.11	0.14	0.12	0.18	0.15	...
1.00	0.25	0.27	0.21	0.20	0.17	0.10	0.17	0.16	0.19	0.25	0.18	0.22	0.24	0.13
2.00	0.45	0.47	0.35	0.28	0.31	0.19	0.28	0.26	0.34	0.43	0.26	0.27	0.39	0.23
3.00	0.64	0.65	0.47	0.48	0.45	0.28	0.38	0.35	0.47	0.60	0.33	0.31	0.51	0.32
4.00	0.82	0.82	0.59	0.61	0.58	0.37	0.47	0.43	0.60	0.75	0.39	0.33	0.62	0.41
5.00	1.00	0.98	0.69	0.72	0.70	0.46	0.55	0.50	0.72	0.89	0.44	0.36	0.73	0.49
6.00	1.17	1.13	0.79	0.84	0.82	0.55	0.63	0.57	0.84	1.03	0.48	0.38	0.83	...
10.00	1.81	1.70	1.15	1.26	1.29	0.89	0.91	0.82	1.28	1.54	0.64	0.44	1.17	...
12.00	2.12	1.97	1.32	1.46	1.51	1.06	1.04	0.93	1.49	1.78	0.71	0.46	1.33	...
14.00	...	...	...	...	...	1.23	...	1.04	...	2.01	...	...	1.48	...
16.00	...	...	...	...	...	1.39	...	1.15	...	2.23	...	...	1.63	...
20.00	...	...	...	...	...	1.72	...	1.34	...	2.66	...	...	1.90	...

12.3.2 Convert the total MTBE-equivalent mass % of uncalibrated oxygenates to mass % oxygen accordings to the following equation:

$$O_{uncal} = \frac{(w_{su})(16.0)(N_s)}{M_s} \quad (9)$$

where:

O_{uncal} = total mass % oxygen from the uncalibrated oxygenates,
W_{su} = MTBE-equivalent mass % of uncalibrated oxygenates,
N_s = number or oxygen atoms in MTBE molecule,
M_s = molecular mass of MTBE as given in Table 2, and
16.0 = atomic mass of oxygen.

12.3.3 Calculate the total mass % oxygen in the gasoline sample by summing the contributions from the calibrated components and the uncalibrated components.

$$O_{tot} = O_{cal} + O_{uncal} \quad (10)$$

12.4 Report the mass % oxygenate of each calibrated oxygenate to the nearest 0.01 %. Also report the total mass % oxygen in the gasoline sample to the nearest 0.1 %.

13. Quality Control Checks

13.1 Routinely monitor the intralaboratory repeatability and accuracy of the analysis as follows:

13.1.1 *Intralaboratory Repeatability*:

13.1.1.1 Quality control check standards may be prepared from the same oxygenate stocks prepared in 10.2 and covering the range given in 13.1.1.4.

13.1.1.2 Prepare and analyze duplicates of the quality control check standards at a rate of one per analysis batch or at least one per ten samples, whichever is more frequent.

13.1.1.3 Duplicates should be carried through all sample preparation steps independently.

13.1.1.4 The range (R) for duplicate samples should be less than the following limits:

Oxygenate	Concentration, mass %	Upper Limit for Range, mass %
Methanol	0.20 to 1.00	0.010 + 0.043C

Methanol	1.00 to 12.00	0.053C
Ethanol	1.00 to 12.00	0.053C
MTBE	0.20 to 20.00	0.069 + 0.029C
DIPE	1.00 to 20.00	0.048C
ETBE	1.00 to 20.00	0.074C
TAME	1.00 to 20.00	0.060C

where:
$C = (C_o + C_d)/2$
$R = |C_o - C_d|$
C_o = concentration of the original sample, and
C_d = concentration of the duplicate sample.

13.1.2 If these limits are exceeded, the sources of error in the analysis should be determined, corrected, and all analyses subsequent to and including the last duplicate analysis confirmed to be within the compliance specifications should be repeated.

13.2 *Intralaboratory Accuracy*:

13.2.1 If the measured concentration of a quality control check standard is outside the range of 100.0 ± 6.0 % of the theoretical concentration for a selected oxygenate of 1.0 mass % or above, the sources of error in the analysis should be determined, corrected, and all analyses subsequent to and including the last standard analysis confirmed to be within the compliance specifications should be repeated.

13.2.2 Independent reference standards may be purchased or prepared from materials that are independent of the quality control standards and should not be prepared by the same analyst. For the specification limits listed in 13.2.2.2, the concentration of the reference standards should be in the range given in 13.1.1.4.

13.2.2.1 Independent reference standards should be analyzed at a rate of one per analysis batch or at least one per 100 samples, whichever is more frequent.

13.2.2.2 If the measured concentration of an independent reference standard is outside the range of 100.0 ± 10.0 % of the theoretical concentration for a selected oxygenate of 1.0 mass % or above, the sources of error in the analysis should be determined, corrected, and all analyses subsequent to and including the last independent reference standard analysis confirmed to be within the compliance specifications in that batch should be repeated.

13.3 Control charts may be utilized to monitor the variability of measurements from the quality control check standards and independent reference standards in order to optimally detect abnormal situations and ensure a stable measurement process.

14. Precision and Bias [7]

14.1 Data obtained from a 10-laboratory round robin on the measurement of 13 oxygenates and total oxygen in 12 gasoline samples were examined. The precision of this test method as determined by a statistical examination of the interlaboratory test results based on 1,2-dimethoxyethane as the internal standard is as follows:

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run and in the normal and correct operation of the test method, exceed the following values only one case in twenty (see Table 3).

Repeatability for Oxygenates in Gasoline

Component	Repeatability
Methanol (MeOH)	0.07 ($X^{0.49}$)[A]
Ethanol (EtOH)	0.03 ($X^{0.92}$)
Iso-propanol (iPA)	0.04 ($X^{0.54}$)
tert-Butanol (tBA)	0.05 ($X^{0.65}$)
n-Propanol (nPA)	0.04 ($X^{0.35}$)
MTBE	0.05 ($X^{0.58}$)
sec-Butanol (sBA)	0.03 ($X^{0.54}$)
DIPE	0.05 ($X^{0.65}$)
Iso-butanol (iBA)	0.03 ($X^{0.79}$)
ETBE	0.04 ($X^{0.86}$)
tert-Pentanol (tAA)	0.05 ($X^{0.41}$)
n-Butanol (nBA)	0.06 ($X^{0.46}$)
TAME	0.04 ($X^{0.58}$)
Total Oxygen	0.03 ($X^{0.93}$)

[A] X is the mean mass % of the component.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following values in only one case in twenty (see Table 3).

Reproducibility in Oxygenates in Gasolines

Component	Reproducibility
Methanol (MeOH)	0.25 ($X^{0.86}$)
Ethanol (EtOH)	0.27 ($X^{0.80}$)

[7] Supporting data are available from ASTM Headquarters. Request RR:D02-1359.

Iso-propanol (iPA)	0.21 ($X^{0.71}$)
tert-Butanol (tBA)	0.20 ($X^{0.80}$)
n-Propanol (nPA)	0.17 ($X^{0.88}$)
MTBE	0.10 ($X^{0.95}$)
sec-Butanol (sBA)	0.17 ($X^{0.73}$)
DIPE	0.16 ($X^{0.71}$)
Iso-butanol (iBA)	0.19 ($X^{0.83}$)
ETBE	0.25 ($X^{0.79}$)
tert-Pentanol (tAA)	0.18 ($X^{0.55}$)
n-Butanol (nBA)	0.22 ($X^{0.30}$)
TAME	0.24 ($X^{0.69}$)
Total Oxygen	0.13 ($X^{0.83}$)

14.2 *Bias*—A statement of bias is currently being developed by the responsible study group.

15. Keywords

15.1 alcohols; DIPE (Di-iso-propylether); ETBE (ethyl *tert*-butylether); ethanol; gas chromatography; gasoline; methanol; MTBE (methyl *tert*-butylether); oxygenates; oxygen-selective detection; TAME (*tert*-amylmethylether)