



Designation: D5599 – 22

# Standard Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection<sup>1</sup>

This standard is issued under the fixed designation D5599; 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 ( $\epsilon$ ) 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 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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D1744 Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent (Withdrawn 2016)<sup>3</sup>
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- E355 Practice for Gas Chromatography Terms and Relationships
- E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
- E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration
- E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

## 3. Terminology

### 3.1 Definitions:

3.1.1 This test method makes reference to common gas chromatographic procedures, terms, and relationships. Detailed

<sup>1</sup> 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 D02.04.0L on Gas Chromatography Methods.

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

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

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

definitions of these can be found in Practices E355 and E594 and Terminology D4175.

3.1.2 *check standard, n—in QC testing*, material having an accepted reference value (ARV) used to determine the accuracy of the measurement system.

3.1.2.1 *Discussion*—In the context of this test method, check standard refers to a spark ignition fuel.

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

#### 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.

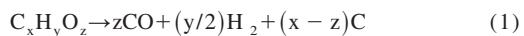
#### 5. Significance and Use

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-hydrocarbon 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 chromatographic capillary column, consists of a Pt/Rh capillary tube. Carbon monoxide (CO) is formed from compounds containing oxygen according to the following reaction:



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:



The CH<sub>4</sub> 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 °C to 450 °C, depending on the instrument's manufacturer.

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 µL 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 E594 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<sup>3</sup> linearity, (b) less than 100 ppm mass oxygen (1 ng O/s) sensitivity, (c) greater than 10<sup>6</sup> selectivity for oxygen compounds over hydrocarbons, (d) no interference from coeluting compounds when 0.1 µL to 1.0 µL sample is injected, (e) equimolar response for oxygen.

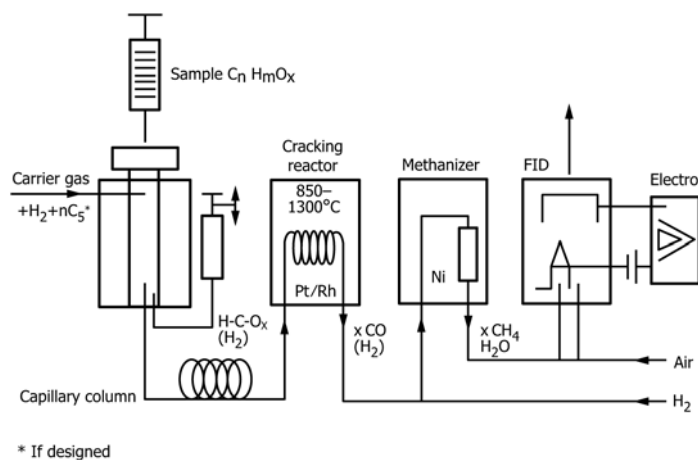


FIG. 1 Schematic of an OFID

7.3 *Column*—A 60 m by 0.25 mm inside diameter fused silica open tubular column containing a 1.0  $\mu\text{m}$  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 such specifications are available.<sup>4</sup> 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). (**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. (**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. (**Warning**—Compressed air is a gas under high pressure and supports combustion.)

8.5.2 Hydrogen, pure grade, 99.9 % mol minimum purity. (**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. (**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 screw-down sealing caps with self-sealing polytetrafluoroethylene (PTFE)-faced rubber membranes are used to prepare calibration standards and samples for analysis.

## 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 E1510. 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.

<sup>4</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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. Pharmacopeial 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 °C – 450 °C
Reactor	850 °C – 1300 °C
Flows, mL/min	
Column carrier gas	1
Detector gases	Air: 300 mL/min H <sub>2</sub> : 30 mL/min
Auxiliary (for dopant, if available)	H <sub>2</sub> : 0.6 mL/min
Sample Size	0.1 µL – 1.0 µL <sup>A</sup>
Split Ratio	100 – 1

<sup>A</sup> Sample size and split ratio must be adjusted so that the oxygenates in the range from 0.1 % mass 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 D4307 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

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

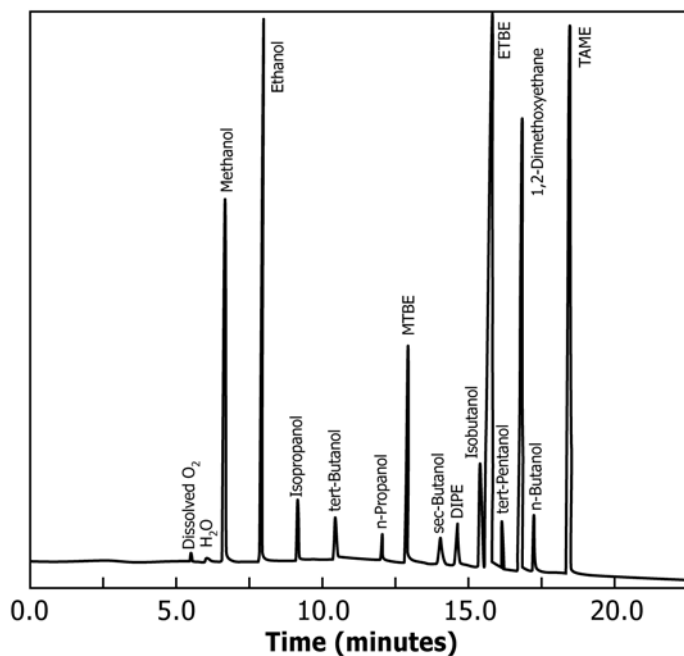
Compound	Retention Time min	Molecular Mass	Relative Response Factors <sup>A,B</sup>	Relative Response Factors <sup>B,C,D</sup>
Dissolved Oxygen	5.33	32.0	ND <sup>D</sup>	ND <sup>D</sup>
Water	5.89	18.0	ND <sup>D</sup>	ND <sup>D</sup>
Methanol	6.45	32.0	0.70	0.98
Ethanol	7.71	46.1	0.99	0.97
Isopropanol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

<sup>A</sup> Based on mass percent oxygenate compound basis.

<sup>B</sup> Relative to 1,2-dimethoxyethane.

<sup>C</sup> Based on mass percent oxygen basis.

<sup>D</sup> Not determined.



NOTE 1—Operating conditions in accordance with Table 1.

FIG. 2 Chromatogram of an Oxygenates Blend

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 D1744 or Test Method E1064. 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 percent 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 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 record its mass 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 assessment shall also be 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 a calibration curve by performing a least-squares fit of the response ratios of the oxygenate standards to their amount ratios, as follows.

10.3.1 Calculate the response ratio ( $rsp_s$ ):

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

where:

$A_s$  = peak area of the test oxygen compound in the calibration sample, and

$A_i$  = peak area of the internal standard in the calibration sample,

and the amount ratio ( $amt_s$ ):

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

where:

$W_s$  = mass of the test oxygen compound in the calibration sample, g, and

$W_i$  = mass of the internal standard in the calibration sample, g,

for each level of each oxygenate,  $s$ .

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

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

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

$b_l$  = 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 5. Check the correlation  $r^2$  value for each oxygenate calibration. The  $r^2$  value should be at least 0.99 or better.

## 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 g 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 Tare the sample container and contents, then inject through the rubber membrane a volume of the same internal standard used in generating the standards. Record the mass of

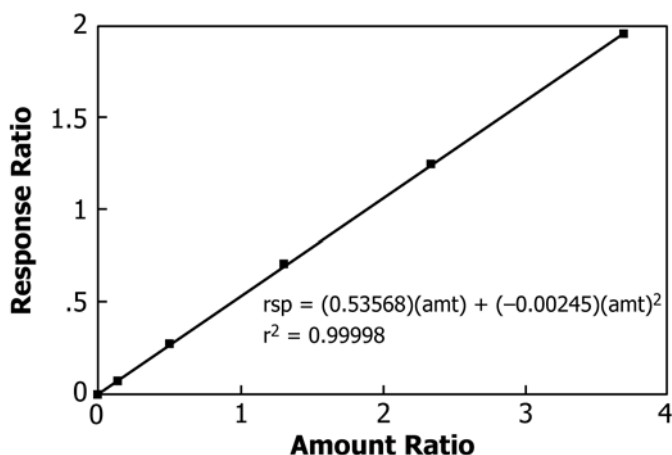


FIG. 3 Example of Quadratic Least-Squares Fit for MTBE

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 PTFE-lined septum cap.

11.5 Inject a suitable quantity (0.1  $\mu$ L to 1.0  $\mu$ L) 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 percent 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 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 5 (10.3.1) and solving.

12.1.3 Apply Eq 6 to determine the mass percent of each calibrated oxygenate.

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

where:

$w_s$  = mass percent 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.