Designation: D 5599 – 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]

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]

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

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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.

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:

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

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.

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.

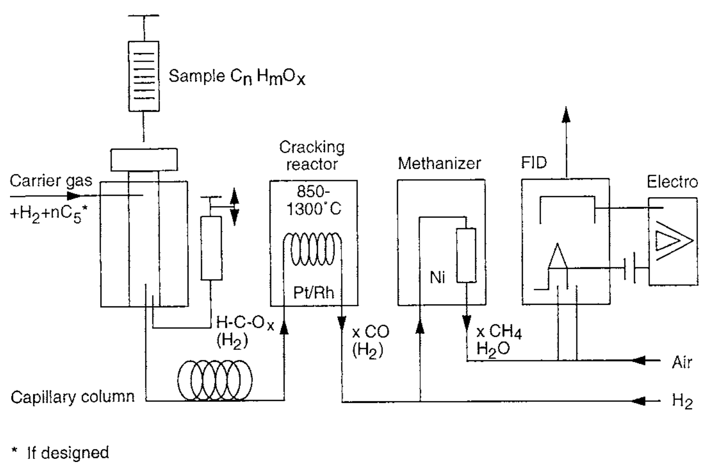

FIG. 1 Schematic of an OFID

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 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). (**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 %. (**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 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.

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.

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.

[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.