



Designation: D5599 – 22

Standard Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection¹

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 (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 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:²

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)³

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

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on 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.

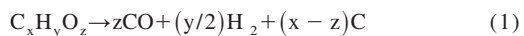
5. Significance and Use

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 CH₄ 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 10³ linearity, (b) less than 100 ppm mass oxygen (1 ng O/s) sensitivity, (c) greater than 10⁶ 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.