



Designation: **D5622—16 D5622 – 17**

Standard Test Methods for Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis¹

This standard is issued under the fixed designation D5622; 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 These test methods cover the quantitative determination of total oxygen in gasoline and methanol fuels by reductive pyrolysis.

1.2 Precision data are provided for 1.0 % to 5.0 % oxygen by mass in gasoline and for 40 % to 50 % oxygen by mass in methanol fuels.

1.3 Several types of instruments can be satisfactory for these test methods. Instruments can differ in the way that the oxygen-containing species is detected and quantitated. However, these test methods are similar in that the fuel is pyrolyzed in a carbon-rich environment.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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.*

1.6 *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](#)

[D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography](#)

2.2 *Other Standards:*

[Clean Air Act \(1992\)](#)³

3. Summary of Test Method

3.1 A fuel specimen of 1 μ L to 10 μ L is injected by syringe into a 950 °C to 1300 °C high-temperature tube furnace that contains metallized carbon. Oxygen-containing compounds are pyrolyzed, and the oxygen is quantitatively converted into carbon monoxide.

3.2 A carrier gas, such as nitrogen, helium, or a helium/hydrogen mixture, sweeps the pyrolysis gases into any of four downstream systems of reactors, scrubbers, separators, and detectors for the determination of the carbon monoxide content, hence of the oxygen in the original fuel sample. The result is reported as mass % oxygen in the fuel.

¹ These test methods are under the jurisdiction of Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and are the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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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 *Federal Register*, Vol 57, No. 24, Feb. 5, 1992, p. 4408.

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

4. Significance and Use

4.1 These test methods cover the determination of total oxygen in gasoline and methanol fuels, and they complement Test Method **D4815**, which covers the determination of several specific oxygen-containing compounds in gasoline.

4.2 The presence of oxygen-containing compounds in gasoline can promote more complete combustion, which reduces carbon monoxide emissions. The Clean Air Act (1992) requires that gasoline sold within ~~certain~~certain specified geographical areas contain a minimum percent of oxygen by mass (presently ~~2.7 mass~~2.7 mass %) during certain portions of the year. The requirement can be met by blending compounds such as methyl *tertiary* butyl ether, ethyl *tertiary* butyl ether, and ethanol into the gasoline. These test methods cover the quantitative determination of total oxygen which is the regulated parameter.

4.2.1 Only seven U.S. states have such wintertime requirements, and others with EPA approval have opted out of the program. The minimum oxygen limit now varies from 1.8 % to 3.5 % by mass. For methanol/heavier alcohol blend EPA waivers, the maximum oxygen content allowed is 3.5 % or 3.7 % by mass.

4.2.1.1 Only ethanol is used for such blending in the U.S. Ethers are banned by some states and are not used in all states because of water contamination issues.

5. Apparatus

5.1 *Oxygen Elemental Analyzer*^{4,5,6,7,8}—A variety of instrumentation can be satisfactory. However, the instrument must reductively pyrolyze the specimen and convert oxygen to carbon monoxide.

5.1.1 *Test Method A*^{4,8}—Helium carrier gas transports the pyrolysis products through a combination scrubber to remove acidic gases and water vapor. The products are then transported to a molecular sieve gas chromatographic column where the carbon monoxide is separated from the other pyrolysis products. A thermal conductivity detector generates a response that is proportional to the amount of carbon monoxide.

5.1.2 *Test Method B*^{5,8}—Nitrogen carrier gas transports the pyrolysis products through a scrubber to remove water vapor. The pyrolysis products then flow through tandem infrared detectors that measure carbon monoxide and carbon dioxide, respectively.

5.1.3 *Test Method C*^{6,8}—A mixture of helium and hydrogen (95:5 %), helium, or argon transports the pyrolysis products through two reactors in series. The first reactor contains heated copper which removes sulfur-containing products. The second reactor contains a scrubber which removes acidic gases and a reactant which oxidizes carbon monoxide to carbon dioxide (optional). The product gases are then homogenized in a mixing chamber, which maintains the reaction products at absolute conditions of temperature, pressure, and volume. The mixing chamber is subsequently depressurized through a column that separates carbon monoxide (or carbon dioxide, if operating in the oxidation mode) from interfering compounds. A thermal conductivity detector measures a response proportional to the amount of carbon monoxide or carbon dioxide.

5.1.4 *Test Method D*^{7,8}—Nitrogen carrier gas transports the pyrolysis products through scrubbers to remove acidic gases and water vapor. A reactor containing cupric oxide at 325 °C oxidizes the carbon monoxide to carbon dioxide, which in turn is transported into a coulometric carbon dioxide detector. Coulometrically generated base titrates the acid formed by reacting carbon dioxide with monoethanolamine.

5.2 A technique must be established to make a quantitative introduction of the test specimen into the analyzer. Specimen vials and transfer labware must be clean and dry.

5.3 For instruments that measure carbon monoxide only, pyrolysis conditions must be established to quantitatively convert oxygen to carbon monoxide.

5.4 A system of scrubbers and separators must be established to effectively remove pyrolysis products that interfere with the detection of carbon monoxide or carbon dioxide, or both.

5.5 The detector responses must be linear with respect to concentration, or nonlinear responses must be detectable and accurately related to concentration.

5.6 Selected items are available from the instrument manufacturer.

5.6.1 Pyrolysis tubes,

5.6.2 Scrubber tubes, and

5.6.3 Absorber ~~Tubes:~~tubes.

⁴ The sole source of supply of the apparatus (Thermo Scientific formerly known as Carlo Erba Models 1108, 1110, now FLASH 1112 and FLASH 2000) known to the committee at this time is CE Elantech, Inc., 170 Oberlin Ave. N., Ste 5, Lakewood, NJ 08701.

⁵ The sole source of supply of the apparatus (Leco Model RO-478) known to the committee at this time is Leco Corp., 3000 Lakeview Ave., St. Joseph, MI 49085.

⁶ The sole source of supply of the apparatus (Perkin-Elmer Series 2400) known to the committee at this time is Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859.

⁷ The sole source of supply of the apparatus (UIC, Inc./Coulometrics Model 5012 CO₂ coulometer and Model 5220 autosampler-furnace) known to the committee at this time is UIC Inc., Box 863, Joliet, IL 60434.

⁸ If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

6. Reagents

6.1 *Purity of Reagents*⁹—~~Reagent grade~~ ~~Reagent-grade~~ chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. 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.

6.2 *Calibration Standards:*

~~6.2.1 NIST SRM 1837,¹⁰ which contains certified concentrations of methanol and *t*-butanol in reference fuel, can be used to calibrate the instrument for the analysis of oxygenates in gasoline.~~

6.2.1 Anhydrous methanol, 99.8 % minimum assay, can be used to calibrate the instrument for the analysis of methanol fuels.

6.2.2 *Isooctane*, or other hydrocarbons, can be used as the blank provided the purity is satisfactory.

~~6.3 *Quality Control Standard*—NIST SRM 1838¹⁰ can be used to check the accuracy of the calibration.~~

6.3 The instrument manufacturers require additional reagents.

6.3.1 *Test Method A:*^{4,8,8}

6.3.1.1 Anhydron (anhydrous magnesium perchlorate),

6.3.1.2 Ascarite II (sodium hydroxide on silica),

6.3.1.3 Helium carrier gas, 99.995 % pure,

6.3.1.4 Molecular sieve, 5Å, 60 to 80 mesh,

6.3.1.5 Nickel wool,

6.3.1.6 Nickelized carbon, 20 % loading,

6.3.1.7 Quartz chips, and

6.3.1.8 Quartz wool.

6.3.2 *Test Method B:*^{5,8}

6.3.2.1 Anhydron (anhydrous magnesium perchlorate),

6.3.2.2 Carbon pyrolysis pellets, and

6.3.2.3 Nitrogen carrier gas, 99.99 % pure.

6.3.3 *Test Method C:*^{6,8}

6.3.3.1 Anhydron (anhydrous magnesium perchlorate),

6.3.3.2 Ascarite II (sodium hydroxide on silica),

6.3.3.3 Carrier gas, either helium (95 %)/hydrogen (5 %), mixture, 99.99 % pure; helium, 99.995 % pure; or argon, 99.98 % pure,

6.3.3.4 Copper plus, wire form, and

6.3.3.5 Platinized carbon.

6.3.4 *Test Method D:*^{7,8}

6.3.4.1 Anhydron (anhydrous magnesium perchlorate),

6.3.4.2 Ascarite II (sodium hydroxide on silica),

6.3.4.3 Copper (II) oxide,

6.3.4.4 Coulometric cell solutions, including a cathode solution of monoethanolamine in dimethyl sulfoxide and an anode solution of water and potassium iodide in dimethyl sulfoxide,

6.3.4.5 Nickelized carbon, 20 % loading, and

6.3.4.6 Nitrogen carrier gas, 99.99 % pure.

7. Sampling

7.1 Take samples in accordance with the instructions in Practices **D4057** or **D4177**.

7.2 Visually inspect the samples, and when there is evidence of nonuniformity, take fresh samples.

7.3 Store the samples in a cold room or a laboratory refrigerator designed for storage of chemicals.

8. Preparation of Apparatus

8.1 Prepare the instrument in accordance with the manufacturer's recommendations. These test methods require that correct operating procedures are followed for the model used. Instrument design differences make it impractical to specify all of the required operating conditions.

8.2 The carrier gas can be scrubbed to remove traces of oxygen and oxygen-containing compounds.

⁹ *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 *Annual 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.