Designation: D5622 – 17

Standard Test Methods for Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis[1]

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 C_1 to C_4 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 µL to 10 µL 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.

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 specified geographical areas contain a minimum percent of oxygen by mass (presently 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

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[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**

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 pyrolize 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.

6. Reagents

6.1 *Purity of Reagents*[9]—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 Anhydrous methanol, 99.8 % minimum assay, can be used to calibrate the instrument for the analysis of methanol fuels.

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

6.3 The instrument manufacturers require additional reagents.

6.3.1 *Test Method A:*[4,8]

6.3.1.1 Anhydrone (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.

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[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 CO_2 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.

[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.

6.3.2 *Test Method B:*[5,8]

6.3.2.1 Anhydrone (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 Anhydrone (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 Anhydrone (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. Calibration and Standardization

9.1 *Calibration for Test Methods A, B, and C, Oxygenates in Gasoline:*

9.1.1 Use a syringe to introduce 1 µL to 10 µL, or 1 mg to 10 mg, of the blank. The amount of specimen must be precisely known. Measure the response. Repeat the introduction and measurement until stable readings are observed.

9.1.2 In a similar fashion, introduce an appropriate quantity of calibration standard and measure the response. Repeat two times with the same quantity of the calibration standard. If the blank corrected responses do not agree within 2 % relative, take corrective action and repeat the calibration.

9.1.3 Calculate the *K*-factor as follows:

$$K = \frac{C_{std} \times M_{std}}{R_{avg}} \tag{1}$$

where:

C_{std} = mass % oxygen in the calibration standard,
M_{std} = mass of the calibration standard, mg,
= volume of the calibration standard (µL) × density of the calibration standard (g/mL), and
R_{avg} = average of the blank corrected responses.

NOTE 1—Density can be determined by Test Method D1298 or Test Method D4052.

9.2 *Calibration for Test Methods A, B, and C, Methanol Fuels*—Repeat procedure 9.1; however, substitute anhydrous methanol for the calibration standard used. For methanol fuels, a unique *K*-factor can be necessary.

9.3 *Calibration for Test Method D*—This test method does not require calibration; however, a quality control standard must be analyzed to ensure proper operation of the instrument. A blank must also be analyzed periodically to ensure consistent responses.

9.4 *Quality Control (QC):*

9.4.1 Introduce the QC standard in the same manner as the calibration standards. Calculate the percent oxygen (m/m) as described in Section 10.

9.4.2 When results obtained on the QC standard do not agree with the certified values within 2 % relative, take corrective action and repeat the calibration and quality control.

9.4.3 For Test Method D, when the recovery of oxygen from the QC sample is less than 0.85 (that is, 85 %), take corrective action and repeat the quality control. Recoveries that are greater than 0.85 but less than unity can be used to correct the calculated result (refer to the *r* parameter in Section 10).

9.5 *Procedure:*

9.5.1 Introduce the samples, and record the instrument response. Calculate the results as described in Section 10. Use the appropriate *K*-factor for oxygenates in gasoline and methanol fuels.

9.5.2 Recalibrate the instrument with the appropriate calibration standard after each set of ten samples.

10. Calculation and Report

10.1 Calculate the mass % oxygen for the QC standard and samples as follows:

$$\text{Mass \% Oxygen} = \frac{R \times K}{M \times r} \tag{2}$$

where:

R = blank corrected instrument response,
K = K-factor, refer to Eq 1, assume unity for Test Method D,
M = mass of sample, mg,
= volume (µL) × density (g/mL), and
r = recovery, refer to 9.4.3, assume unity for Test Methods A, B, and C.

10.2 For instruments with computer data systems, the calculation of the *K*-factor (Eq 1) and the calculation of mass % oxygen (Eq 2) can be automatic with a digital readout provided.

10.3 Report mass % oxygen to the nearest 0.01 %.

11. Precision and Bias[10]

11.1 *Precision*—The precision of these test methods was determined by statistical analysis of interlaboratory test results. Twelve laboratories analyzed in duplicate eight different samples, providing a total of 13 data sets. One laboratory used two different test methods. The breakdown on data sets by test method is: Test Method A, three; Test Method B, two; Test Method C, three; Test Method D, five. The statistical analysis was performed on the set of 13 data sets because the reductive pyrolysis technique is common to all four test methods. Separate statistics were not determined for individual test methods. The sample set included anhydrous methanol and gasoline stocks that were spiked with one or more of the following: *iso*butanol, *n*-butanol, *sec*-butanol, *tert*-butanol, di-*iso*propyl ether, ethanol, ethyl *tert*-butyl ether, methanol, methyl *tert*-butyl ether, *n*-propanol, *iso*propanol, *tert* -amyl methyl ether.

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

Mass % Oxygen Range	*Repeatability*, Mass % Oxygen
1.0 % to 5.0 %	0.06 %
40 % to 50 %	0.81 %

11.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials, would in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty.

Mass % Oxygen Range	*Reproducibility*, Mass % Oxygen
1.0 % to 5.0 %	0.26 %
40 % to 50 %	0.81 %

11.2 *Bias*—Bias was determined from interlaboratory results obtained on NIST SRM 1838, which contains ethanol. The null hypothesis that was tested was that the true difference between the grand average result and the NIST certified value is zero. The result of the hypothesis testing was that if the true difference was zero, the determined difference would occur by chance approximately 50 % of the time. Hence, the null hypothesis of *no difference* or *no bias* is accepted.

12. Keywords

12.1 carbon dioxide; carbon monoxide; di-*iso*propyl ether; ethanol; ethyl *tert*-butyl ether; *iso*butanol; *iso*propanol; methanol; methyl *tert*-butyl ether; *n*-butanol; *n*-propanol; oxygen; reductive pyrolysis; *sec*-butanol; *tert*-amyl methyl ether; *tert*-butanol

APPENDIX

(Nonmandatory Information)

X1. EFFECT OF WATER IN GASOLINE-CONTAINING OXYGENATES

X1.1 The Clean Air Act (1992) requirement for oxygenates in gasoline implicitly excludes waterborne oxygen from the specification for total oxygen. Experimental evidence indicates that for typical oxygenated gasolines, the maximum amount of soluble water is approximately 0.1 mass %. This corresponds to 0.09 mass % oxygen, which is very close to the repeatability of these test methods. When oxygen from dissolved water must be excluded from the analysis, the gasoline can be pretreated with potassium carbonate or Molecular Sieve 3A prior to analysis by these test methods.

X1.2 According to the patent literature,[11] gasoline can be treated with potassium carbonate to remove dissolved water. Test Method B was used to analyze five different gasolines that were spiked with 0.1 mass % water. These gasolines contained one or more of the following oxygenates at concentrations typical of gasolines: *tert*-amyl methyl ether, ethanol, ethyl *tert*-butyl ether, *sec*-butanol, *n*-butanol, methanol, di-*iso*propyl ether, *n*-propanol. A few millilitres of each water-spiked gasoline were treated with 200 mg of potassium carbonate prior to analysis. The results obtained on the treated, spiked samples did not differ from the results obtained on the neat gasolines by more than 0.02 mass % oxygen, which is within the repeatability of these test methods.

X1.3 The literature[12] describes an alternative technique for removing water from gasoline, namely, treatment of the gasoline with Molecular Sieve 3A. In an experiment similar to that described in X1.2, water-spiked, oxygenated gasolines were pretreated with Sieve 3A prior to analysis by Test Method B. The results obtained on the sieve-treated, spiked samples did not differ from the results obtained on the neat gasolines by more than the repeatability of these test methods.

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[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1338. Contact ASTM Customer Service at service@astm.org.

[11] U.S. Patent No. 4 539 013, Sept. 3, 1985.

[12] Burfield, D. R., and Smithers, R. H., "Desiccant Efficiency in Solvent and Reagent Drying," *Journal of Organic Chemistry*, Vol 48, No. 14, 1983, pp. 2420–2422.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D5622 – 16) that may impact the use of this standard. (Approved May 1, 2017.)

(1) Mentions of specific NIST SRMs have been deleted from the following subsections: 6.2, 6.3, 9.1.2, 9.1.3, 9.2, 9.4.1, 9.4.3, and Footnote 10.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D5622 – 95 (2011)) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Added Practice D4177 to Referenced Documents.
(2) Updated information in 4.2.1 on current EPA rules regarding oxygenates in gasoline.
(3) Added reference to an additional sampling procedure in 7.1.

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