Designation: D 5622 – 95 (Reapproved 2000)

An American National Standard

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 D 5622; 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 mass % oxygen in gasoline and for 40 to 50 mass % oxygen 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 the standard. The values given in parentheses are for information only.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[3]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tertiary*-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography[3]

2.2 *Other Standard:*

Clean Air Act (1992) [4]

3. Summary of Test Method

3.1 A fuel specimen of 1 to 10 µL is injected by syringe into a 950 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 D 4815, 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 the gasoline. These test methods cover the quantitative determination of total oxygen which is the regulated parameter.

5. Apparatus

5.1 *Oxygen Elemental Analyzer*[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.

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

Current edition approved Aug. 15, 1995. Published October 1995. Originally published as D 5622 – 94. Last previous edition D 5622 – 94.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] Federal Register, Vol 57, No. 24, Feb. 5, 1992, p. 4408.

[5] Carlo Erba Models 1106 and 1108 have been found satisfactory for these analyses. They are available from CE Elantech, Inc., 170 Oberlin Ave. N., Ste 5, Lakewood, NJ 08701.

[6] Leco Model RO-478 has been found satisfactory for this analysis. It is available from Leco Corp., 3000 Lakeview Ave., St. Joseph, MI 49085.

[7] Perkin-Elmer Series 2400 has been found satisfactory for this analysis. It is available from Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859.

[8] UIC, Inc./Coulometrics Model 5012 CO_2 coulometer and Model 5220 autosampler-furnace have been found satisfactory for this analysis. They are available from UIC Inc., Box 863, Joliet, IL 60434.

5.1.1 *Test Method A*[5]—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*[6]—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*[7]—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*[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 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.

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

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

6.3 *Quality Control Standard*—NIST SRM 1838[10] can be used to check the accuracy of the calibration.

6.4 The instrument manufacturers require additional reagents.

6.4.1 *Test Method A:* [5]

6.4.1.1 Anhydrone (anhydrous magnesium perchlorate),

6.4.1.2 Ascarite II (sodium hydroxide on silica),

6.4.1.3 Helium carrier gas, 99.995 % pure,

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

6.4.1.5 Nickel wool,

6.4.1.6 Nickelized carbon, 20 % loading,

6.4.1.7 Quartz chips, and

6.4.1.8 Quartz wool.

6.4.2 *Test Method B:*[6]

6.4.2.1 Anhydrone (anhydrous magnesium perchlorate),

6.4.2.2 Carbon pyrolysis pellets, and

6.4.2.3 Nitrogen carrier gas, 99.99 % pure.

6.4.3 *Test Method C:*[7]

6.4.3.1 Anhydrone (anhydrous magnesium perchlorate),

6.4.3.2 Ascarite II (sodium hydroxide on silica),

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

6.4.3.4 Copper plus, wire form, and

6.4.3.5 Platinized carbon.

6.4.4 *Test Method D:*[8]:

---

[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 *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.

[10] Available from the National Institute of Standards and Technology, Gaithersburg, MD 20899.