



Designation: D3703 – 07(Reapproved 2012)

Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels¹

This standard is issued under the fixed designation D3703; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the determination of the hydroperoxide content expressed as hydroperoxide number of aviation turbine, gasoline and diesel fuels.

1.2 The range of hydroperoxide number included in the precision statement is 0 to 50 mg/kg active oxygen as hydroperoxide.

1.3 The interlaboratory study to establish the precision of this test method consisted of spark-ignition engine fuels (regular, premium and California Cleaner-Burning gasoline), aviation gasoline, jet fuel, ultra low sulfur diesel, and biodiesel. However, biodiesel was not included in the precision calculation because of the large differences in results within labs and between labs.

1.4 This test method detects hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide. It does not detect sterically-hindered hydroperoxides such as dicumyl and di-t-butyl hydroperoxides.

1.5 Di-alkyl hydroperoxides added commercially to diesel fuels are not detected by this test method.

1.6 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.7 *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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 7.3, 7.6, 9.2, and Annex A1.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D6447 Test Method for Hydroperoxide Number of Aviation Turbine Fuels by Voltammetric Analysis

2.2 *Other Standards:*

CRC Report No. 559 Determination of the Hydroperoxide Potential of Jet Fuels³

4500-C1 B. Iodometric Method I—Standard Methods for the Examination of Water and Wastewater⁴

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *hydroperoxide, n*—organic peroxide having the generalized formula ROOH.

3.1.1.1 *Discussion*—This test method detects hydroperoxides such as t-butyl hydroperoxide [(CH₃)₃COOH] and cumene hydroperoxide [C₆H₅C(CH₃)₂OOH]. It does not detect sterically-hindered hydroperoxides such as dicumyl and di-t-butyl hydroperoxides.

3.1.2 *hydroperoxide number, n*—an indication of the quantity of oxidizing constituents present in certain liquid fuels as determined by this test method.

3.1.2.1 *Discussion*—The higher the quantity of oxidizing constituents in the fuels, the higher the hydroperoxide number.

4. Summary of Test Method

4.1 A quantity of sample dissolved in 2,2,4-trimethylpentane is contacted with aqueous potassium iodide solution. The hydroperoxides present are reduced by the

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 Available from the Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA 30346.

⁴ Published by the American Health Assoc., the American Water Works Assoc. and Water Environment Federation. Available from American Public Health Publication Sales, P. O. Box 753, Waldorf, MD 20604–0753.

potassium iodide. An equivalent amount of iodine is liberated, which is titrated with an aqueous sodium thiosulfate solution. The results are calculated as milligrams of hydroperoxide per kilogram of sample expressed as hydroperoxide number. (See [Note 1.](#))

NOTE 1—The original standard D3703 was published in 1978 as Standard Test Method for Peroxide Number of Aviation Turbine Fuels. This test method originally used carbon tetrachloride (CCl_4), which was determined to be carcinogenic. CCl_4 was later replaced with 1,1,2-trichloro-1,2,2-trifluoroethane. 1,1,2-trichloro-1,2,2-trifluoroethane is an ozone depleting substance. The use of an ozone depleting substance precludes its use by many operators.

5. Significance and Use

5.1 The magnitude of the hydroperoxide number is an indication of the quantity of oxidizing constituents present. Deterioration of the fuels results in the formation of hydroperoxides and other oxygen-carrying compounds. The hydroperoxide number measures those compounds that will oxidize potassium iodide.

5.2 The determination of the hydroperoxide number of aviation turbine fuels, gasoline and diesel is significant because of the adverse effect of hydroperoxide upon certain elastomers in the fuel systems.

5.3 The determination of hydroperoxide number of gasoline is significant because hydroperoxides have been demonstrated to decrease both Research and Motor Octane Numbers. In addition, hydroperoxides have adverse effects on certain fuel system components.

5.4 The determination of hydroperoxide number of diesel fuel is significant because hydroperoxides have been demonstrated to increase the Cetane Number. In addition, hydroperoxides have adverse effects on certain fuel system components.

6. Apparatus

6.1 *Iodine Number Flask*, 250 mL, glass-stoppered.

6.2 *Burettes*, 10-mL, 25-mL, Class A with polytetrafluoroethylene (PTFE) stop cock.

6.3 *Volumetric Flasks*, 100-mL and 1000-mL, 2000 mL Class A with PTFE stoppers.

6.4 *Mixing Cylinders*, 100 mL and 500-mL, glass-stoppered.

6.5 *Microburet*, 10-mL, Class A.

6.6 *Analytical Balance*, capable of weighing to the nearest milligram.

6.7 *Brown Bottles*, 100-mL, 300-mL, 1000-mL with screw caps with inert inserts.

6.8 *Measuring Cylinders*, 25-mL and 100-mL.

7. Reagents

7.1 *Purity of Reagents*—Reagent 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.⁵ 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.

7.1.1 Commercially available solutions already prepared may be used in place of laboratory preparations, if they meet the method requirements.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the requirement of Type I, II, or III of Specification [D1193](#).

7.3 *Acetic Acid Solution*—Mix 4 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) with 996 mL of glacial acetic acid (CH_3COOH). (**Warning**—Poison. Corrosive. Combustible. Can be fatal if swallowed. Causes severe burns. Harmful if inhaled. See [A1.2](#)).

7.4 *Nitrogen Gas*, 99.9995% Minimum purity

7.5 *Carbon Dioxide*, 99.9995% Minimum purity

7.6 *2,2,4-trimethylpentane (iso-octane)*, (**Warning**—Flammable, dangerous fire risk. Toxic by injection and inhalation. See [A1.1](#)).

7.7 *Potassium Dichromate Solution, Standard (0.1 N)*, ACS reagent grade. Dissolve 2.452 g of the dried potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in water and dilute to 500 mL in a volumetric flask. This solution is 0.1 N. As an alternative, the lab may use commercially prepared solution.

7.8 *Potassium Dichromate Solution, Standard (0.01 N)*, (**Warning**—Avoid contact with eyes and skin and avoid breathing of dust)—Dilute 100 mL of 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution with water to 1000 mL in a volumetric flask.)

7.9 *Potassium Iodide Solution*, Dissolve 120 g of potassium iodide (KI) in 100 mL of water. Larger quantities of solution may be prepared, provided the concentration of KI in water is equivalent. Protect the solution from sunlight by storing in brown bottles and blanketed with nitrogen or carbon dioxide. Discharge any color from this solution by placing 1 mL of KI solution, 50 mL of water, and 5 mL of starch solution in a 300-mL flask and blanketing with nitrogen or carbon dioxide. If a blue color develops, add 0.005 N $\text{Na}_2\text{S}_2\text{O}_3$ solution from a microburet until color just disappears. Add a sufficient quantity of $\text{Na}_2\text{S}_2\text{O}_3$ solution, thus determined, to the main KI solution to convert all free iodine to iodide. When properly prepared, 1 mL of KI solution should not turn blue when starch solution is added, but with starch plus one drop of 0.01 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution plus two drops of HCl, the blue color should develop. Store this solution under nitrogen or carbon dioxide.

7.10 *Sodium Thiosulfate Solution, Standard (0.1 N)*, Dissolve 12.5 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) plus 0.1 g of sodium carbonate (Na_2CO_3) in 500 mL of water (the Na_2CO_3 is added to stabilize the $\text{Na}_2\text{S}_2\text{O}_3$ solution). Let this

⁵ *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.