Designation: D3703 – 13

Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels[1]

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.

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 Fuels[3]

4500-C1 B. Iodometric Method I—Standard Methods for the Examination of Water and Wastewater[4]

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 [$(CH_3)_3COOH$] and cumene hydroperoxide [$C_6H_5C(CH_3)_2OOH$]. 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

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[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 D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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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] 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.

*A Summary of Changes section appears at the end of this standard 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 carcinogenetic. 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 ($K_2Cr_2O_7$) in water and dilute to 500 mL in a volumetric flask. This solution is 0.1 *N*. As an alterative, 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* $K_2Cr_2O_7$ solution with water to 1000 mL in a volumetric flask.)

7.9 *Potassium Iodate Solution, Standard (0.1 N)*—optional, ACS reagent grade, for use in standardizing the 0.1 *N* sodium thiosulfate solution. Dissolve 3.567 g KIO_3 dried at 103 °C ± 2 °C for 1 h, in distilled water and dilute to 1000 mL in a volumetric flask to yield a 0.1 *N* solution. As an alternative, the lab may use a commercially prepared solution.

7.10 *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* $Na_2S_2O_3$ solution from a microburet until color just disappears. Add a sufficient quantity of $Na_2S_2O_3$ 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

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[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.

0.01 *N* $K_2Cr_2O_7$ solution plus two drops of HCl, the blue color should develop. Store this solution under nitrogen or carbon dioxide.

7.11 *Sodium Thiosulfate Solution, Standard (0.1 N),* Dissolve 12.5 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) plus 0.1 g of sodium carbonate (Na_2CO_3) in 500 mL of water (the Na_2CO_3 is added to stabilize the $Na_2S_2O_3$ solution). Let this solution stand a week or more before using. Standardize using any appropriate technique, such as the one indicated in 4500-C1 B involving either a 0.1 *N* $K_2Cr_2O_7$ solution or a 0.1 *N* KIO_3 solution. Standardize at intervals frequent enough to detect changes of 0.0005 in normality.

7.12 *Sodium Thiosulfate Solution, Standard (0.005 N),* Prepare a twenty-fold dilution of the 0.1 *N* $Na_2S_2O_3$ solution prepared in 7.11, using a volumetric flask. One way to accomplish this is to dilute 100 mL of 0.1 *N* $Na_2S_2O_3$ solutions with water to 2000 mL in a volumetric flask. Prepare this solution fresh with restandardized 0.1 *N* $Na_2S_2O_3$ solution when any change of 0.0005 or over in normality is detected.

7.13 *Starch Solution,* Make a paste of 6 g of arrowroot starch or soluble iodometric starch with cold water. Pour the paste into 1 L of boiling water. Add 20 g of potassium hydroxide (KOH), mix thoroughly, and allow to stand for approximately 2 h. Add 6 mL of glacial acetic acid. Mix thoroughly and then add sufficient HCl (sp gr 1.19) to adjust the pH value of the solution to 4.0. Store in a glass-stoppered bottle. Starch solution prepared in this manner can remain chemically stable for up to one year.

7.14 *t-Butyl Hydroperoxide, (CH3)3COOH, 90% minimum purity,* Make working standards with iso-octane to cover the range of the expected results.

8. Sampling

8.1 Samples shall be taken in accordance with the procedures described in Practice D4057.

8.2 If samples cannot be tested immediately, they should be stored in a refrigerator at a temperature between 1 and 4°C (35 and 40°F). Bring the sample to room temperature before testing.

9. Procedure

9.1 Select the appropriate weight of sample from the following table:

Estimated Peroxide Number, mg/kg	Sample Mass, g
0 to 10	50
11 to 30	35
31 to 50	25
51 to 80 (Note 2)	10
81 to 100	5

NOTE 2—The precision statement was based up to 50 mg/kg oxygen. The precision might not apply for samples greater than 50 mg/kg.

9.2 Weigh the sample, accurate to 1 mg, into a 250-mL iodine flask that has been flushed with nitrogen or carbon dioxide. With a measuring cylinder, add 25 mL of 2,2,4-trimethylpentane (**Warning—**See A1.1). Pass a vigorous flow of nitrogen or carbon dioxide through the solvent for at least 1 min; then, without stopping the gas flow, add 20 mL of acetic acid solution and reduce the flow of gas so that the rate is one bubble per second. Add 2 mL of KI solution and mix vigorously for 30 ± 1 s. Set the flask aside to stand for 5 min ± 3 s.

9.3 At the end of the reaction period, add 100 mL of water and stop the gas flow. Add 5 mL of starch solution. Titrate with 0.005N $Na_2S_2O_3$ solution to the disappearance of the blue color.

9.4 Titrate a reagent blank just prior to each set of unknown determinations, following the same procedure as described in 9.1 – 9.3. (See Note 3.)

NOTE 3—This end point is of the returning type. The end point intended in this method is the disappearance of the blue color for 30 s or longer. If there is no blue color upon the addition of the starch solution, there is no detectable hydroperoxide and therefore there is no need to titrate the solution with $Na_2S_2O_3$ solution.

10. Quality Control

10.1 Confirm the performance of the test procedure by analyzing a known hydroperoxide such as t-butylhydroperoxide or cumyl hydroperoxide.

11. Calculation

11.1 Calculate the peroxide number as follows:

$$\text{Hydroperoxide number, mg/kg} = \left[(A - B)N \times 1000 \times 8\right]/S \quad (1)$$

where:

X = measured hydroperoxide number,
A = millilitres of $Na_2S_2O_3$ solution required for titration of the sample,
B = millilitres of $Na_2S_2O_3$ solution required for titration of the blank,
N = normality of the $Na_2S_2O_3$ solution,
8 = milliequivalent of hydroperoxide number, and
S = grams of sample used, accurate to 0.001 g.

12. Report

12.1 Report the result calculated in 11.1 to three (3) significant figures.

12.2 If there is no detectable hydroperoxide (see Note 3), report "None Detected."

13. Precision and Bias[6]

13.1 *Precision*—The precision of this method was determined from an interlaboratory study (ILS). The study contained thirteen (13) fuel samples which were tested in nine (9) laboratories in duplicate. The fuel types in the study were: regular and premium gasoline, ultra low sulfur diesel, Jet A, and isooctane blank. A biodiesel fuel was also included in the study but was not used in calculating the precision statement because of the variabilities between laboratories.

13.1.1 *Repeatability*—The difference between two successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1630.

operation of the test method, exceed the following values only in one case in twenty:

$$Repeatability = 0.2829*X + 0.0001 \wedge 0.6596 \text{ mg/kg} \quad (2)$$

where:

X = measured hydroperoxide number in Eq 1.

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

$$Reproducibility = 2.3046*X + 0.0001 \wedge 0.6596 \text{ mg/kg} \quad (3)$$

where:

X = measured hydroperoxide number in Eq 1.

13.2 *Bias*—The bias was obtained from standards made from t-butylhydroperoxide in iso-octane to give 5 and 50 mg/kg (ppm) hydroperoxide number. The measured values were 4.97 + 0.97 mg/kg (ppm) and 45.2 + 7.82 mg/kg (ppm).

13.3 *Relative Bias*—The measured hydroperoxide number results obtained by Test Method D6447 from the same standards identified in 13.2 were 8.51 mg/kg (ppm) and 84.9 mg/kg (ppm) respectively. Test Method D6447 has a range about 2-40 mg/kg hydroperoxide number. The results from the ILS indicate that Test Method D6447 is biased high in respect to D3703 and expected results.

14. Keywords

14.1 aviation fuels; diesel fuel; gasoline; hydroperoxide; hydroperoxide number; turbine fuel

ANNEX

(Mandatory Information)

A1. WARNING STATEMENTS

A1.1 2,2,4-Trimethylpentane (Isooctane)

A1.1.1 (**Warning—**Flammable, dangerous fire risk, explosive limits in the air 1-6%.)

A1.1.1.1 Use with adequate ventilation.

A1.1.1.2 Keep container closed.

A1.1.1.3 Avoid prolonged breathing of vapor or spray mist.

A1.1.1.4 Avoid prolonged or repeated contact with skin.

A1.1.1.5 Toxic by ingestion and inhalation.

A1.2 Acetic Acid (Glacial)

A1.2.1 **Warning**—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

A1.2.1.1 Do not get in eyes, on skin, or on clothing.

A1.2.1.2 Do not breathe vapor, spray, or mist.

A1.2.1.3 Dilute by addition of acid to water.

A1.2.1.4 Keep away from heat and open flame.

A1.2.1.5 Keep in tightly closed container in approved acid storage cabinet.

A1.2.1.6 Keep cool.

A1.2.1.7 Loosen closure carefully when opening.

A1.2.1.8 Use with adequate ventilation.

A1.2.1.9 Keep container closed when not in use.

A1.2.1.10 Use protective clothing and goggles when handling.

A1.2.1.11 Wash thoroughly after handling.

A1.3 Potassium Dichromate

A1.3.1 (**Warning—**Avoid contact with eyes and skin and avoid breathing of dust.)

SUMMARY OF CHANGES

Subcommittee D02.05 has identified the location of selected changes to this standard since the last issue (D3703 – 07 (2012)) that may impact the use of this standard. (Approved Oct. 1, 2013.)

(1) Added a new 7.9.

(2) Revised 7.11.

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