



Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels by Voltammetric Analysis¹

This standard is issued under the fixed designation D 6447; 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 The test method covers the determination of the hydroperoxide content of aviation turbine fuels. The test method may also be applicable to the determination of the hydroperoxide content of any water-insoluble, organic fluid, particularly diesel fuels, gasolines, and kerosines.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all 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 6.3-6.5, Annex A1, and Annex A2.

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

D 3703 Test Method for Peroxide Number of Aviation Turbine Fuels

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 A quantity of sample is contacted with aqueous potassium iodide solution in the presence of acid. The hydroperoxides present are reduced by the potassium iodide. An equivalent amount of iodine is liberated, which is quantified by voltammetric analysis. The results are calculated and reported as millimoles (mmole) of hydroperoxide per litre of sample.

4. Significance and Use

4.1 This test method is functionally equivalent to Test Method D 3703, which uses an ozone depleting substance,

(1,1,2-trichloro-1,2,2-trifluoroethane). The use of an ozone depleting substance precludes U. S. military bases from utilizing Test Method D 3703. This test method and Test Method D 3703 measure the same peroxide species (primarily hydroperoxides) in aviation fuels.

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

4.3 The determination of the hydroperoxide number of fuels is significant because of the adverse effect of hydroperoxides upon certain elastomers in the fuel systems.

5. Apparatus

5.1 *Voltammetric Analyzer*³—The instrument used to quantify the liberated iodine is a voltammetric analyzer equipped with a three electrode system and a digital or analog output. The combination electrode system (see Fig. 1) consists of a glassy carbon disc (3-mm diameter) working electrode, a platinum wire (0.5 mm diameter) auxiliary electrode, and a platinum wire (0.5 mm diameter) reference electrode. The voltammetric analyzer applies a linear voltage ramp (0 to -1 V range with respect to the reference electrode) at a rate of 0.1 V/s to the auxiliary electrode. The current output of the working electrode is converted to voltage by the voltammetric analyzer, using the gain ratio of 1V/20 μ A. The peak height or peak area of the voltammetric response to iodine is outputted to an analog or digital recording device (0 to 1 V full scale).

5.2 *Vortex Mixer*,⁴ with a 2800 to 3000 rpm motor and a pad suitable for mixing test tubes and vials.

5.3 *Pipette*, or equivalent, capable of delivering volumes required in the test method, such as 0.2, 1, and 2 mL.

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 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 Voltammetric analyzers specifically designed to perform hydroperoxide value determinations of aviation turbine fuels are commercially available from The University of Dayton Research Institute. Voltammographs, which can be set up to perform hydroperoxide value determinations of aviation turbine fuels, are available from BAS, West Lafayette, IN and EG&G Princeton Applied Research, Princeton, NJ.

⁴ Vortex mixers suitable for mixing the prepared standard and sample solution are available from Barnstead/ThermoLyne, Dubuque, IA and Fisher Scientific Co., Pittsburgh, PA.

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

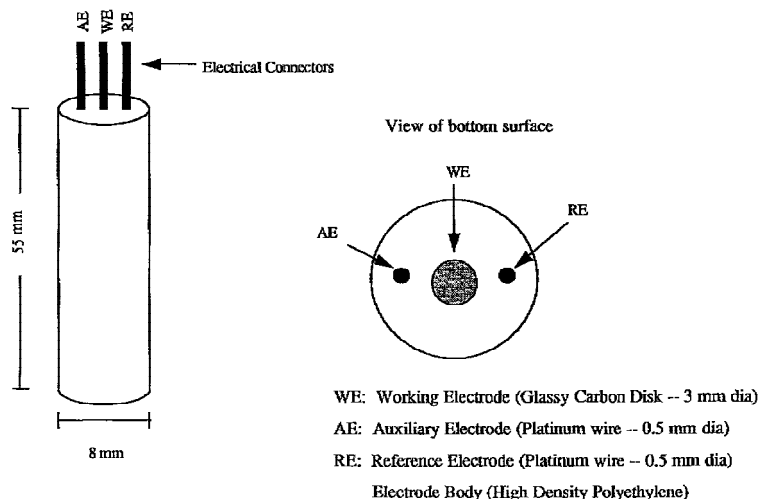


FIG. 1 Combination Electrode

5.4 *Volumetric Flasks (optional)*, 100 and 500 mL capacity.
 5.5 *Glass Vials*, 5 or 10 mL capacity.

6. Reagents and Materials

6.1 *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's purity suffices to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6.3 *Acetic Acid Solution*—Mix 0.5 g of concentrated hydrochloric acid (HCl) (**Warning**—Poison. Corrosive. Can be fatal if swallowed. Causes severe burns. Harmful if inhaled. See Annex A1.1), 0.5 g of water, and 24 g of glacial acetic acid (CH₃COOH) (**Warning**—Poison. Corrosive. Combustible. Can be fatal if swallowed. Causes severe burns. Harmful if inhaled. See Annex A1.2) in a suitable container. Store in a closed container. The acetic acid solution shall be prepared biweekly.

6.4 *Potassium Dichromate Solution, Standard (0.1 N)*—Recrystallize twice from an aqueous solution of potassium dichromate (K₂Cr₂O₇) (**Warning**—Poison. Can be fatal if swallowed. Avoid contact with eyes and skin, and avoid breathing of dust, possible cancer hazard, strong oxidizer. See Annex A1.2). Dry at 120°C to constant mass. Dissolve 2.452 g of the purified K₂Cr₂O₇ in water and dilute to 500 mL in a volumetric flask. This solution is 0.1 N. Commercially available solutions certified to this standard can also be used.

6.5 *Potassium Dichromate Solution, Standard (0.002 N)* (**Warning**—Avoid contact with eyes and skin.)—Dilute 2.0 mL of 0.1 N K₂Cr₂O₇ solution with water to 100 mL in a volumetric flask. Store in a closed container.

6.6 *Potassium Iodide Solution*—Dissolve 6 g of potassium iodide (KI) in 5 g of water. Store in a closed container. Do not use if the solution shows any color or is cloudy.

6.7 *Potassium Chloride Solution*—Dissolve 4 g of potassium chloride (KCl) in 20 g of water. Store in a closed container.

7. Sampling

7.1 Samples shall be taken in accordance with the procedures described in Practice D 4057.

8. Procedure

8.1 *Electrode Cleaning Solution Preparation*—Transfer equal amounts of the acetic acid solution and distilled water into a 5 mL glass vial. One way to do this is to use separate pipettes for each material that can deliver a 2 mL volume.

8.2 *Blank Preparation (0 mmole)*—Into a 5 mL glass vial, in succession, pipette 1 mL of KCl solution, 1 mL of acetic acid solution, and 0.2 mL of KI solution. Reversal of mixing order will result in high blank readings of the voltammetric analyzer calibration. Cap the vial and shake for 5 s using a vortex mixer (see 5.2).

8.3 *Standard Preparation (1 mmole)*—Into a 5 mL glass vial, in succession, pipette 1 mL of 0.002 N K₂Cr₂O₇ solution, 1 mL of acetic solution, and 0.2 mL of KI solution. Cap the vial and shake for 5 s using a vortex mixer (see 5.2).

8.4 Calibration:

8.4.1 The voltammetric analyzer used in this test method gives linear results between 0.2 and 2 mmole. Below 0.1 mmole, the signal to noise ratio becomes large. Although the voltammetric analyzer is linear between 0.1 and 2 mmole, calibration is conducted with a blank (0 mmole) and 1 mmole standard for convenience. Values obtained between 1 and 2 mmole are still considered valid even though they lie outside the range in which the instrument is calibrated.

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.

8.4.1.1 *Blank Reading (0 mmole)*—Insert the combination electrode of the voltammetric analyzer into the cleaning solution, remove, and rub dry the bottom electrode surface with a nonabrasive cloth or paper towel. Insert the combination electrode into the prepared blank solution (with minimal delay after preparation) and perform the voltammetric analysis (see 5.1) for liberated iodine. Record the reading. Remove the combination electrode from the blank solution, and rub dry the bottom surface of the electrode. Run at least three tests of the prepared blank to ensure the blank value has leveled off. Complete the blank determinations within 3 min of mixing the reagents.

8.4.1.2 *Standard Reading (1 mmole)*—Insert the combination electrode of the voltammetric analyzer into the cleaning solution, remove, and rub dry the bottom electrode surface with a nonabrasive cloth or paper towel. Insert the combination electrode into the prepared standard solution (with minimal delay after preparation) and perform the voltammetric analysis (see 5.1) for liberated iodine. Record the reading. Remove the combination electrode from the standard solution, and rub dry the bottom surface of the electrode. Run at least three tests of the standard to ensure the value is stable and repeatable. Complete the standard determinations within 3 min of mixing reagents.

8.4.2 *Calibration Frequency*—Recalibration with freshly prepared blank and standard solutions should be performed after a set of samples has been tested at one time, with a ten sample maximum within that set.

8.5 *Sample Analysis:*

8.5.1 *Volume Selection*—Select the appropriate volume of sample from the following table. If the hydroperoxide value is unknown, use 1 mL of sample. If the determined hydroperoxide value is below 0.1 or above 2 mmole, repeat the analysis after selecting the appropriate volume of sample from the following table.

Sample Volume, mL	Estimated Hydroperoxide Number, mmole/L
5	below 0.02
3	0.03 to 0.10
1	0.11 to 2.0
0.5	2.1 to 4.0
0.2	4.1 to 10

8.5.2 *Sample Preparation*—Transfer the sample into a 5-mL glass vial. (Use a 10-mL glass vial if sample volume is above 3 mL.) In succession, transfer 1 mL of acetic acid solution and 0.2 mL of KI solution into the vial, cap the vial, and shake for 20 s, using a vortex mixer. Pipette 1 mL of KCl solution into the vial, cap the vial, and shake gently by hand for 2 s. Let the vial stand undisturbed for 10 s, allowing two layers to form. Use an appropriate size pipette to transfer a volume of test specimen from the lower (aqueous) layer into a second, clean vial. Perform each sample analysis (see 8.5.3) within 3 min of mixing reagents. (The transfers can be accommodated using pipettes or other suitable means).

8.5.3 *Sample Analysis*—Insert the combination electrode of the voltammetric analyzer into the cleaning solution, remove, and rub dry the bottom electrode surface with a nonabrasive cloth or paper towel. Insert the combination electrode into the prepared sample solution (the aqueous layer pipetted into a

second vial) and perform the voltammetric analysis (see 5.1) for liberated iodine. Record the reading. Remove the electrode from the sample solution, wipe off the sides and bottom surface of the electrode, insert the electrode into the cleaning solution, and rub dry the bottom surface of the electrode with a nonabrasive cloth or paper towel.

9. Calculation

9.1 *Hydroperoxide Number Calculation*—Calculate the hydroperoxide number as follows:

$$\text{Hydroperoxide Number, mmole/L of fuel} \quad (1)$$

$$= \frac{\text{Sample Reading} - \text{Blank Reading}}{(\text{Standard Reading} - \text{Blank Reading}) \times \text{Sample Volume (mL)}}$$

9.2 *Hydroperoxide Number Conversion to Parts Per Million (ppm)*—If required, the hydroperoxide number in mmole/L can be converted to ppm as follows:

$$\text{ppm} = \frac{(16) \times [\text{mmole/L}]}{(d)} \quad (2)$$

where:

ppm = hydroperoxide number in ppm,
d = density of fuel in kg/L at test temperature (when density information is not available, an approximation of *d* = 0.8 may be used), and
 = hydroperoxide number in mmole/L.

10. Precision and Bias ⁶

10.1 The following criteria should be used for judging the acceptability of results (95 % of confidence). The interlaboratory study (ILS) was performed with nine laboratories performing hydroperoxide analyses on a total of seven different samples involving aviation turbine and diesel fuels.

10.1.1 *Repeatability*—The difference between concurrent test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials, would, in the long run, and in the normal and correct operation of this test method, exceed the following values in only 1 case in 20:

$$\text{Repeatability } (r) = 0.2153 \times (x + 0.0004)^{0.3997} \text{ mmole/L} \quad (3)$$

where:

x = mean value.

10.1.2 *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, and in the normal and correct operation of this test method, exceed the following values in only 1 case in 20:

$$\text{Reproducibility } (R) = 0.8036 \times (x + 0.0004)^{0.3997} \text{ mmole/L} \quad (4)$$

where:

x = mean value.

10.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for this test method of measuring the hydroperoxide number of aviation turbine engine fuels, no bias statement is made.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1537.

11. Keywords

11.1 aviation fuels—turbine; hydroperoxide number; peroxide

ANNEXES

(Mandatory Information)

A1. MATERIAL WARNING STATEMENTS

A1.1 *Hydrochloric Acid (concentrated)*—(Warning—Poison. Corrosive. Can be fatal if swallowed. Causes severe burns. Harmful if inhaled.)

A1.2 *Acetic Acid (glacial)*—(Warning—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)

A1.3 *Potassium Dichromate*—(Warning—Poison. Can be fatal if swallowed. Avoid contact with eyes and skin, and avoid breathing of dust. Strong oxidizer. Possible cancer hazard.)

A2. PRECAUTIONARY HANDLING STATEMENTS

A2.1 The following safety precautions should be followed in handling the materials listed in Annex A1.

A2.1.1 Do not get in eyes, on skin, or on clothing.

A2.1.2 Do not breathe vapor, spray, or mist.

A2.1.3 Dilute by addition of acid to water.

A2.1.4 Keep away from heat and open flame.

A2.1.5 Keep in tightly closed container in approved storage cabinet.

A2.1.6 Keep cool.

A2.1.7 Loosen closure carefully when opening.

A2.1.8 Use with adequate ventilation.

A2.1.9 Keep container closed when not in use.

A2.1.10 Use protective clothing and goggles when handling.

A2.1.11 Wash thoroughly after handling.

SUMMARY OF CHANGES

Subcommittee D02.05 has identified the location of selected changes to this standard since the last issue (D 6447–99) that may impact the use of this standard.

(1) Updated 1.1.

(2) Updated repeatability and reproducibility statements to

reflect the results determined as part of an interlaboratory study that was conducted.

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