Designation: D6447 – 09

# StandardTest Method for Hydroperoxide Number of Aviation Turbine Fuels by Voltammetric Analysis[1]

This standard is issued under the fixed designation D6447; 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 standard. No other units of measurement are included in this 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]

D1193 Specification for Reagent Water

D3703 Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels

D4057 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 and Test Method D3703 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/20μA. 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 Lubricantsand 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

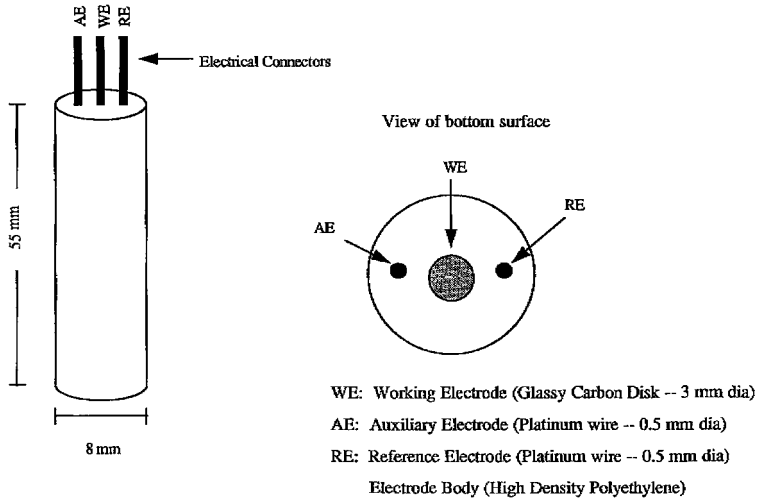


**FIG. 1 Combination Electrode**

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 D1193.

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 ($CH_3COOH$) (**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 ($K_2Cr_2O_7$) (**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 $K_2Cr_2O_7$ 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* $K_2Cr_2O_7$ 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 D4057.

## 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* $K_2Cr_2O_7$ 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,

[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.