



Standard Test Method for Measurement of Hindered Phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep Voltammetry¹

This standard is issued under the fixed designation D 6971; 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 This test method covers the voltammetric determination of hindered phenol and aromatic amine antioxidants in new or used type non-zinc turbine oils in concentrations from 0.0075 mass % up to concentrations found in new oils by measuring the amount of current flow at a specified voltage in the produced voltammogram.

1.2 *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:²

- D 1193 Specification for Reagent Water
- D 2272 Test Method for Oxidation Stability of Steam Turbine Engine Oils by Rotating Pressure Vessel
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D 4378 Practice for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines
- D 6224 Practice for In-Service Monitoring of Lubricating Oil for Auxiliary Power Plant Equipment
- D 6810 Test Method for Measurement of Hindered Phenolic Antioxidant Content In HL Turbine Oils by Linear Sweep Voltammetry

2.2 ISO Standards:³

- ISO 6743 Part 4, Lubricants, Industrial Oils, and Related Products

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.09.0C on Oxidation of Turbine Oils.

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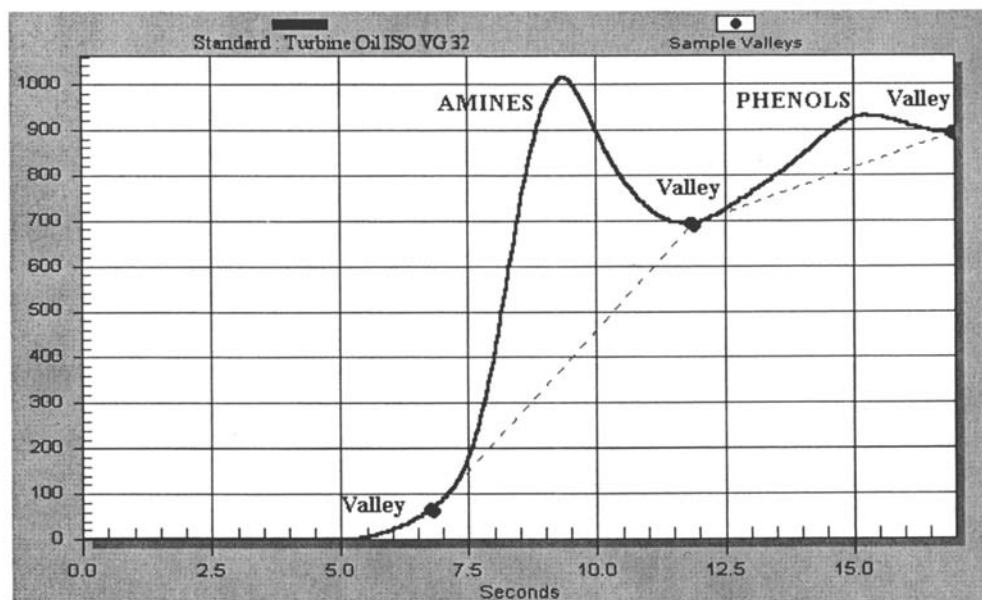
² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

3. Summary of Test Method

3.1 A measured quantity of sample is dispensed into a vial containing a measured quantity of acetone based electrolyte solution and a layer of sand. When the vial is shaken, the hindered phenol and aromatic amine antioxidants and other solution soluble oil components present in the sample are extracted into the solution and the remaining droplets suspended in the solution are agglomerated by the sand. The sand/droplet suspension is allowed to settle out and the hindered phenol and aromatic amine antioxidants dissolved in the solution are quantified by voltammetric analysis. The results are calculated and reported as mass % of antioxidant or as millimoles (mmol) of antioxidant per litre of sample for prepared and fresh oils and as a percent remaining antioxidant for used oils.

3.2 Voltammetric analysis is a technique that applies electro-analytic methods wherein a sample to be analyzed is mixed with an electrolyte and a solvent, and placed within an electrolytic cell. Data is obtained by measuring the current passing through the cell as a function of the potential applied, and test results are based upon current, voltage, and time relationships at the cell electrodes. The cell consists of a fluid container into which is mounted a small, easily polarized, working electrode, and a large, non-polarizable, reference electrode. The reference electrode should be massive relative to the working electrode so that its behavior remains essentially constant with the passage of small current; that is, it remains unpolarized during the analysis period. Additional electrodes, such as auxiliary electrodes, can be added to the electrode system to eliminate the effects of resistive drop for high resistance solutions. In performing a voltammetric analysis, the potential across the electrodes is varied linearly with time, and the resulting current is recorded as a function of the potential. As the increasing voltage is applied to the prepared sample within the cell, the various additive species under investigation within the oil are caused to electrochemically oxidize. The data recorded during this oxidation reaction can then be used to determine the remaining useful life of the oil type. A typical current-potential curve produced during the practice of the voltammetric test can be seen by reference to Fig. 1. Initially



NOTE—x-axis = time (seconds) and y-axis is current (arbitrary units). Top line in Fig. 1 is voltammogram of a fresh R&O turbine oil showing valley indicators before and after antioxidant valleys.

FIG. 1 Aromatic Amine and Hindered Phenol Voltammetric Response in the Neutral Test Solution with Blank Response Zeroed

the applied potential produces an electrochemical reaction having a rate so slow that virtually no current flows through the cell. As the voltage is increased, as shown in Fig. 1, the electro-active species (for example, substituted phenols) begin to oxidize at the working electrode surface, producing an anodic rise in the current. As the potential is further increased, the decrease in the electro-active species concentration at the electrode surface and the exponential increase of the oxidation rate lead to a maximum in the current-potential curve shown in Fig. 1.

4. Significance and Use

4.1 The quantitative determination of hindered phenol and aromatic amine antioxidants in a new turbine oil measures the amount of these compounds that has been added to the oil as protection against oxidation. Beside phenols, turbine oils can be formulated with other antioxidants such as amines which can extend the oil life. In used oil, the determination measures the amount of original (hindered phenol and aromatic amine) antioxidants remaining after oxidation has reduced its initial concentration. This test method is not designed or intended to detect all of the antioxidant intermediates formed during the thermal and oxidative stressing of the oils, which are recognized as having some contribution to the remaining useful life of the used or in-service oil. Nor does it measure the overall stability of an oil, which is determined by the total contribution of all species present. Before making final judgment on the remaining useful life of the used oil, which might result in the replacement of the oil reservoir, it is advised to perform additional analytical techniques (as in accordance with Test Methods D 6224 and D 4378; see also Test Method D 2272), having the capability of measuring remaining oxidative life of the used oil.

4.1.1 This test method is applicable to non-zinc type of turbine oils as defined by ISO 6743 Part 4, Table 1. These are refined mineral oils containing rust and oxidation inhibitors, but not antiwear additives.

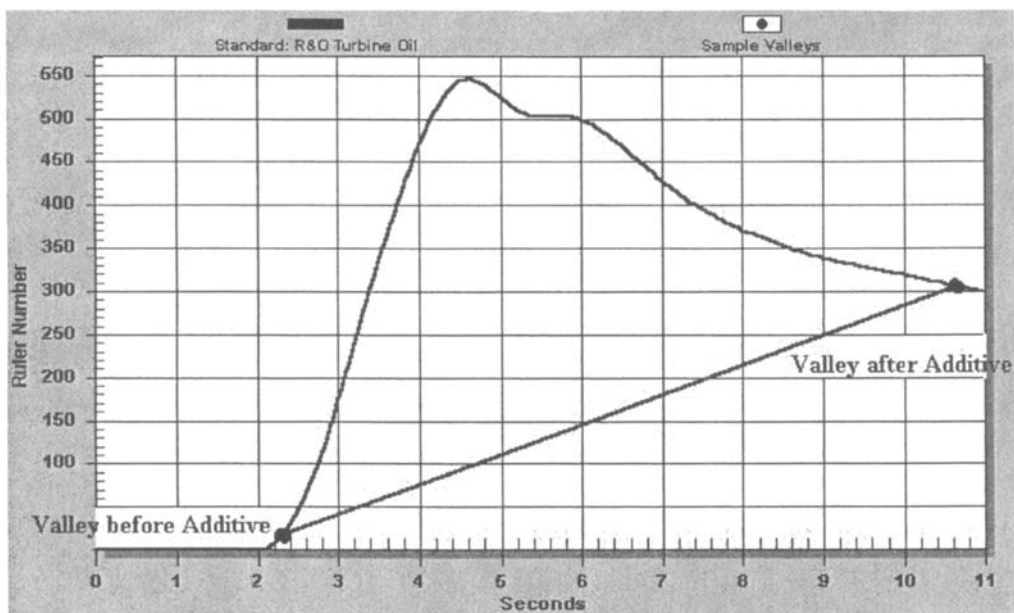
4.2 The test is also suitable for manufacturing control and specification acceptance.

4.3 When a voltammetric analysis is obtained for a turbine oil inhibited with a typical synergistic mixture of hindered phenol and aromatic amine antioxidants, there is an increase in the current of the produced voltammogram between 8 to 12 s (or 0.8 to 1.2 V applied voltage)⁴ for the aromatic amines, and an increase in the current of the produced voltammogram between 13 and 16 s (or 1.3 to 1.6 V applied voltage)⁴ for the hindered phenols in the neutral acetone solution (Fig. 1: x-axis 1 s = 0.1 V). Hindered phenol antioxidants detected by voltammetric analysis include, but are not limited to, 2,6-di-*tert*-butyl-4-methylphenol; 2,6-di-*tert*-butylphenol; and 4,4'-Methylenebis (2,6-di-*tert*-butylphenol). Aromatic amine antioxidants detected by voltammetric analysis include, but are not limited to, phenyl alpha naphthylamines, and alkylated diphenylamines.

4.4 For turbine oil containing only aromatic amines as antioxidants, there will only be an increase in the current of the produced voltammogram between 8 to 12 seconds (or 0.8 to 1.2 V applied voltage)⁴ for the aromatic amines, by using the neutral acetone test solution (first peak in Fig. 1).

4.5 For turbine oils containing only hindered phenolic antioxidants, it is preferable to use a basic alcohol solution

⁴ Voltages listed with respect to reference electrode. The voltammograms shown in Figs. 1 and 2 were obtained with a platinum reference electrode and a voltage scan rate of 0.1 V/s.



NOTE—x-axis = time (seconds) and y-axis is current (arbitrary units) with top line in Fig. 2 showing the fresh oil.

FIG. 2 Hindered Phenol Voltammetric Response in Basic Test Solution with Blank Response Zeroed

rather than the neutral acetone solutions, as there is an increase in the current of the produced voltammogram between 3 to 5 seconds (or 0.3 to 0.6 V applied voltage)⁴ in basic alcohol solution (Fig. 2: x-axis 1 second = 0.1 V) in accordance with Test Method D 6810.

5. Apparatus

5.1 *Voltammetric Analyzer*⁵—The instrument used to quantify the hindered phenol and aromatic amine antioxidants is a voltammograph equipped with a three-electrode system and a digital or analog output. The combination electrode system 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, as described in Test Method D 6810. The voltammetric analyzer applies a linear voltage ramp (0 to -1.8 V range with respect to the reference electrode) at a rate of 0.01 to 0.5 V/s (0.1 optimum) to the auxiliary electrode. The current output of the working electrode is converted to voltage by the voltammetric analyzer, using the gain ratio of 1 V/20 μ A, and is outputted to an analog or digital recording device (0 to 1 V full scale) as shown in Figs. 1 and 2.

5.2 *Vortex Mixer*,⁶ 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 sample volumes required in the test method, from 0.10 to 0.50 mL.

⁵ Voltammetric Analyzers specifically designed to perform antioxidant determinations of turbine oils are commercially available from Fluitec International, Dayton, OH and Koehler Instrument Company, Bohemia, NY.

⁶ Vortex mixers suitable for mixing the prepared standard and sample solution are available from Barnstead/Thermolyne (Dubuque, IA), Fisher Scientific Co. (Pittsburgh, PA).

5.4 *Solvent Dispenser*, or equivalent, capable of delivering volumes of analysis solution (see 6.3) required in the test method, such as 3.0 and 5.0 mL.

5.5 *Glass Vials*, with caps, 4 or 7 mL capacity and containing 1 g of sand. White quartz suitable for chromatography, within the size range of 200 to 300 μ m \pm 100 μ m.

6. Reagents

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.⁷ 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 specified, references to water that conforms to Specification D 1193, Type II.

6.3 Analysis Materials:

6.3.1 *Acetone Solution (Neutral)*—Proprietary Green Solution,⁸ Acetone solvent (1:10 distilled water/acetone solution) containing a dissolved neutral electrolyte. (**Warning**—Corrosive, poisonous, flammable, and a skin irritant. Harmful if inhaled.)

6.3.2 *Alcohol Solution (Basic)*—Proprietary Yellow Solution,⁸ Ethanol solvent (1:10 distilled water/ethanol solution)

⁷ *Reagent Chemical, American Chemical Society Specifications*, Am Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards*, by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the *United States Pharmacopeia*.

⁸ Voltammetric solutions are available from Fluitec International, Dayton OH, and Koehler Instrument Company, Bohemia, NY.