Designation: D6971 – 09 (Reapproved 2014)

Standard Test Method for Measurement of Hindered Phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep Voltammetry[1]

This standard is issued under the fixed designation D6971; 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 in-service 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]

D1193 Specification for Reagent Water

D2272 Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4378 Practice for In-Service Monitoring of Mineral Turbine Oils for Steam, Gas, and Combined Cycle Turbines

D6224 Practice for In-Service Monitoring of Lubricating Oil for Auxiliary Power Plant Equipment

D6810 Test Method for Measurement of Hindered Phenolic Antioxidant Content in Non-Zinc Turbine Oils by Linear Sweep Voltammetry

2.2 *ISO Standards:*[3]

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

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 test solution and a layer of sand. When the vial is shaken, the hindered phenol and aromatic amine antioxidants and other test solution soluble oil components present in the sample are extracted into the test solution and the remaining droplets suspended in the test 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 test 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 in-service 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 test solution, 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 test 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

[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 D02.09.0C on Oxidation of Turbine Oils.

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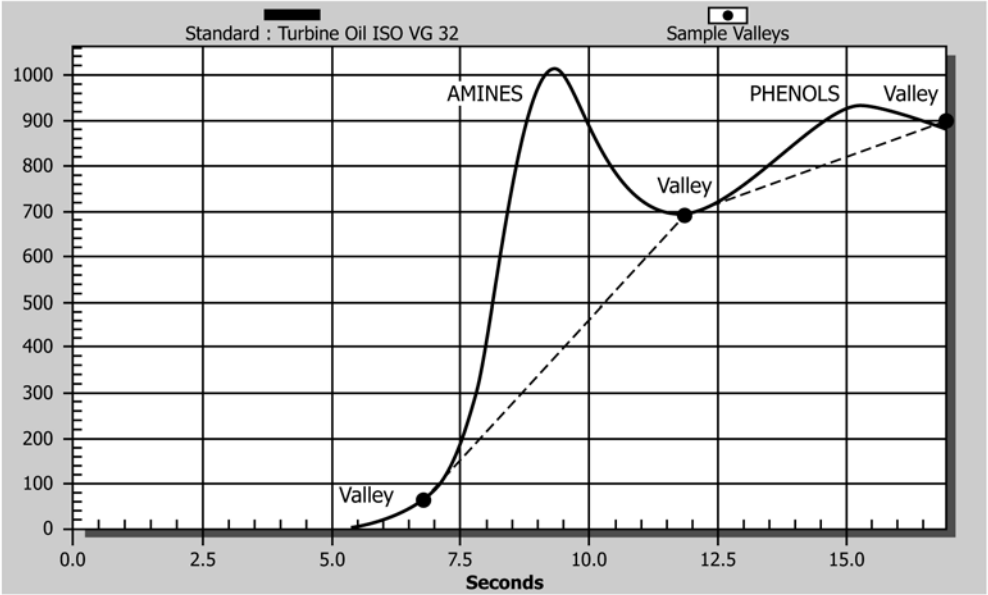
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.



NOTE 1—*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

Fig. 1. Initially 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 in-service 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 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 in-service 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 D6224 and D4378; see also Test Method D2272), having the capability of measuring remaining oxidative life of the in-service 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.

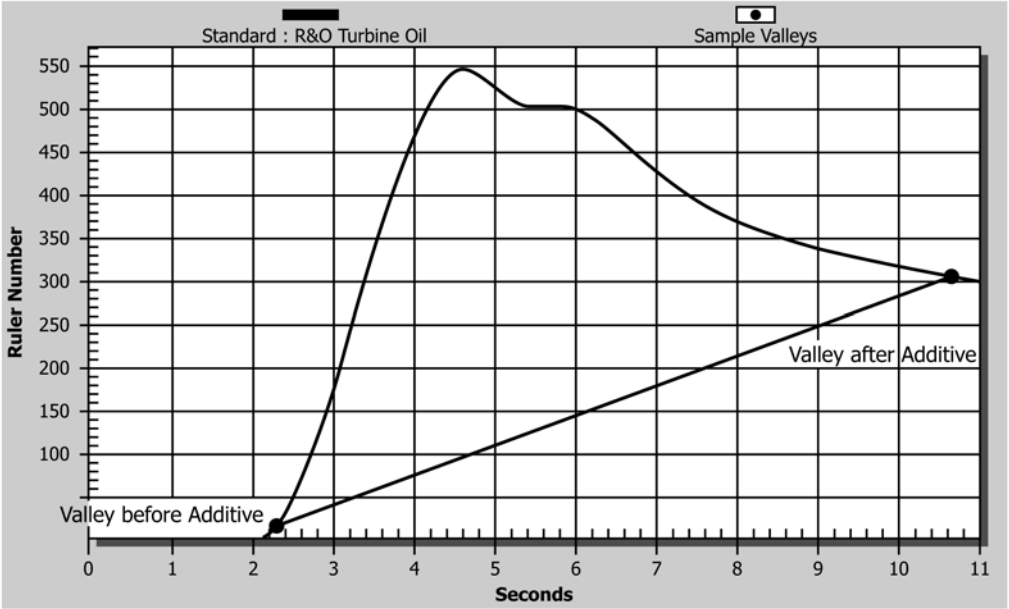
4.2 The test is also suitable for manufacturing control and specification acceptance.

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) (see Note 1) 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) (see Note 1) for the hindered phenols in the neutral acetone test 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.

NOTE 1—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.

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) (see Note 1) 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 test solution rather than the neutral acetone test solutions, as there is an



NOTE 1—*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

increase in the current of the produced voltammogram between 3 to 6 seconds (or 0.3 to 0.6 V applied voltage) (see Note 1) in basic alcohol test solution (Fig. 2: *x*-axis 1 second = 0.1 V) in accordance with Test Method D6810.

5. Apparatus

5.1 *Voltammetric Analyzer*—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 D6810. 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 µA, 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,* 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.

5.4 *Test Solution Dispenser,* or equivalent, capable of delivering volumes of analysis test 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 µm ± 100 µm.

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.[4] 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 D1193, Type II.

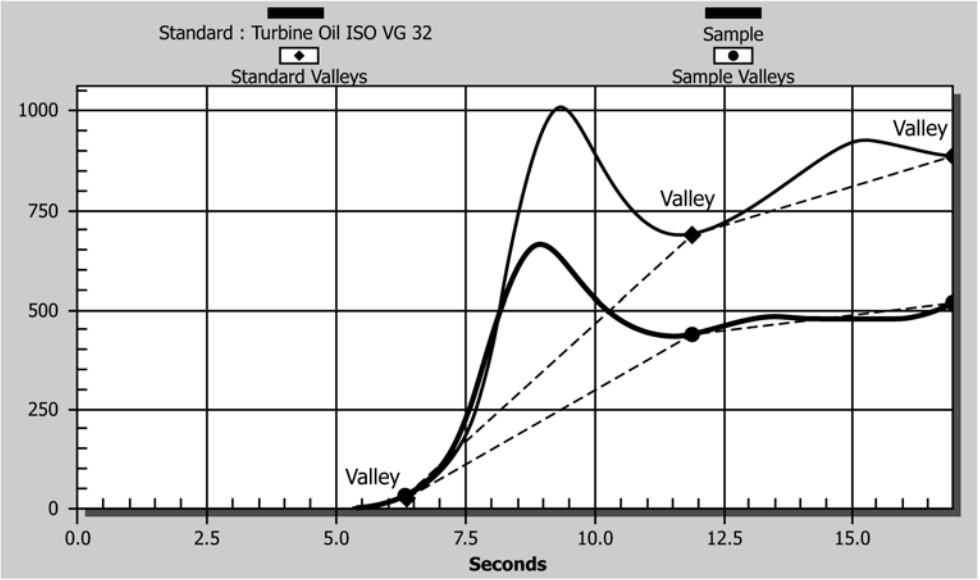
6.3 *Analysis Materials:*

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

6.3.2 *Alcohol Test Solution (Basic)*—Proprietary Yellow Test Solution, Ethanol test solution (1:10 distilled water/ethanol test solution) containing a dissolved base electrolyte. (**Warning**—Corrosive, poisonous, flammable, and a skin irritant. Harmful if inhaled.)

6.3.3 *Alcohol Cleansing Pads*—70 % isopropyl alcohol saturated cleansing pads (alcohol prepared skin cleansing pads, for the preparation of the skin prior to injection (antiseptic)).

[4] *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.



NOTE 1—Standard (top line) and sample in-service oil (lower line).

FIG. 3 Voltammetric Reading for a In-service Oil Sample Comparing Hindered Phenols and Aromatic Amines Peaks (in the Neutral Test Solution)

7. Sampling

7.1 Obtain the sample in accordance with Practice D4057.

8. Procedure

8.1 The voltammetric analyzer used in this test method gives linear results between 2 to 50 mmol for hindered phenols and aromatic amines using an oil sample size of 0.40 mL and 5.0 mL of the analysis test solution. The corresponding range of mass % depends on the molecular weight of the hindered phenol and aromatic amine, and the density of the base oil. For instance, the mass % range of 0.044 to 1.1 is equal to 2 to 50 mmol/L for a hindered phenol containing one hydroxyl group and with a molecular weight of 220 g/mol (2,6-di-*tert*-butyl-4-methylphenol) and an oil density of 1 g/mL. Below 2 mmol, the noise to signal ratio becomes large, decreasing the accuracy of the measurements. For measurements below 2 mmol or for fresh oils with high noise to signal ratios, the sample size should be increased to 0.60 mL and the volume of analysis test solution decreased to 3.0 mL.

8.2 *General Voltammetric Test Procedure*—The test procedure for voltammetric analysis will consist of the blank reading (calibration), followed by a standard reading, and finally the sample (in-service oil) reading.

8.2.1 *Blank Reading*—(0 mmol/L = 0 mass %).

8.2.1.1 The blank reading (voltammetric number) is a measurement of the analysis test solution by itself. The blank measurement gives a reference number with no antioxidant present (the zero baseline).

8.2.2 *Standard Reading*—(30 to 150 mmol/L—mass % dependent on density of fresh oil and molecular weight of antioxidant).

8.2.2.1 The standard reading is a measurement of a fresh, unused oil (containing hindered phenol and amines antioxidants) mixed with an appropriate analysis test solution. This measurement gives you a voltammetric reading (standard reading) that indicates the voltammetric response for the concentration hindered phenol and aromatic amines antioxidants being analyzed for the oil being tested.

8.2.3 *Sample (In-service Oil) Reading.*

8.2.3.1 The sample reading is a measurement of a fresh or in-service oil mixed with the same type of analysis test solution as the standard. This measurement will provide voltammetric readings that normally range between the blank and standard measurements, and reflect the concentration of hindered phenol and aromatic amine antioxidant present (fresh oil) or remaining (in-service oil) in the oil sample. Voltammetric readings for in-service oils will decrease as hindered phenol and aromatic amine antioxidants are depleted.

8.3 *Voltammetric Reading*—After the operator has selected the valleys before and after the antioxidant peaks (as shown in Fig. 1), the software (R-DMS[5]) will automatically identify and calculate the area above the baseline between the two valley indicators. This calculated area is then used for the sample reading (in-service oil), which will be established by comparing the in-service oil area to its standard (see Fig. 3) and make remaining antioxidant calculations (see Section 9).

8.3.1 If peak shifting is occurring, it is advised to repeat the voltammetric test after performing the cleaning of the electrode. If after this second test the peak shifting is occurring again, it is advised to drag the valley indicators manually to their shifted locations.

8.4 *Calibration (Blank Reading) Procedure*—Pipette 5.0 mL of analysis test solution into a 7 mL vial or other suitable container containing 1 g of sand. Insert the electrode of

[5] R-DMS is a software package trademarked by and available from Fluitec International, 1997 Newborn Rd., Rutledge, GA 30663, USA and Nieuwbrugstraat 73, B-1830, Machele, Belgium.

the voltammetric analyzer into the analysis test solution to wet the bottom surface of the electrode, remove, and rub dry the bottom electrode surface with a lint free paper towel. Insert the electrode into the vial so that the bottom of the electrode is submerged in the analysis test solution without resting on the sand layer on the bottom of the vial. Place the vial/probe upright into rack or foam block for testing. Perform the voltammetric analysis (see 5.1). Record the voltammetric reading in the voltage range of aromatic amines, 0.8 to 1.2 V (see Note 1) and the phenols, 1.3 to 1.6 V (see Note 1) in neutral test solution (Fig. 1). Remove the combination electrode from the blank test solution and rub dry the bottom surface of the electrode with a lint free paper towel. Run at least two tests of the analysis test solution to ensure the electrode is clean and the minimal blank value has been obtained.

8.4.1 *Calibration Frequency*—Recalibration with freshly prepared blank test solution shall be performed before each testing session.

8.5 *Standard and In-service Oil Sample Preparation Procedures*

8.5.1 *Steps:*

8.5.1.1 *Preparing Test Solution Step*—Remove seal and cap of the test solution vial. Pipette 5.0 mL of analysis test solution into a 7 mL vial or other suitable container containing 1 g of sand. Pipette 0.40 mL of the selected oil sample also into the 7 mL vial.

8.5.1.2 For measurements below 2 mmol or fresh oils with high noise-to-signal ratios, the sample size should be increased to 0.60 mL.

8.5.1.3 *Shaking Test Solution Step*—Cap the vial and shake vigorously using a vortex mixer for 20 s or by hand (between 50 and 60 shaking cycles/min.), until sand is thoroughly mixed. Place the prepared oil test solution upright in a rack or perforated foam block for a minimum time of 30 s to allow the sand to settle on the bottom of the vial with the oil.

8.5.1.4 *Cleaning Electrode Step*—Prepare the electrode for analysis by cleaning it. Use an alcohol-cleansing pad to wet the bottom surface of the electrode. The bottom of the electrode must be dried immediately with a clean lens tissue (lint free paper towel). The glassy carbon surface should always have a polished look before running a test. A glazed or cloudy look indicates the presence of a chemical film. If the probe tip is not cleaned properly, voltammetric readings can be distorted.

8.5.1.5 *Running Test Step*—Insert the electrode into the vial so that the bottom of the electrode is submerged in the analysis test solution without resting on the sand layer on the bottom of the vial. Place the vial/probe upright into a rack or foam block for testing. Perform the voltammetric analysis (see 5.1) for hindered phenolic and aminic antioxidants. Record the valley to valley antioxidant readings in the voltage range of the amines, 0.8 to 1.2 V (see Note 1) and the phenols, 1.3 to 1.6 V (see Note 1) in the neutral test solution (Fig. 1). Remove the combination electrode from the oil test solution and repeat the cleaning procedure of the electrode. Run at least two tests (cleaning the electrode and shaking the standard for 10 s between tests) of the standard or in-service oil sample to ensure the value is stable and repeatable.

8.5.1.6 Make all measurements within 5 min after the initial mixing of the analysis test solution, selected sample, and sand.

8.5.2 When the manufacturer of the oil is known, and the uninhibited base oil is available, use it to prepare the standards (mmole or mass % antioxidant calculations). Prepare a standard containing in the range of 30 to 150 mmol/L of oil (0.5 to 3.0 mass %) of the selected phenolic and aminic antioxidant dissolved in an uninhibited base oil. The concentration should be selected to span the expected concentrations of the new and in-service oils.

8.5.3 Standard readings should be updated whenever new batches of lubricants are stocked, and checked periodically to monitor the amount of natural oxidation occurring in the stock during storage.

8.5.4 For fresh or in-service oils of unknown origin, use a typical fresh turbine oil as the standard (100 % remaining antioxidant calculations).

8.5.5 The analysis test solution and scan time should be the same for the blank, standard, and in-service oil sample.

9. Calculations

9.1 *Percent Hindered Phenol and Aromatic Amine Antioxidant Calculation*—If the hindered phenol and aromatic amine, antioxidant present in the oil sample is known, then the percent hindered phenol and aromatic amine antioxidant in the sample can be calculated as follows:

$$\%\ \text{of antioxidant} = \frac{\text{sample reading} - \text{blank reading}}{\text{standard reading} - \text{blank reading}} \times \%\ \text{antioxidant of standard}\ (\%) \quad (1)$$

where:

reading = valley to valley area (see 8.3) for antioxidants peaks between 0.8 to 1.6 V (see Note 1)

9.2 *Molar Concentration of Hindered Phenol and Aromatic Amine Antioxidant Calculation*—If the hindered phenol and aromatic amine antioxidant in the oil sample is unknown, then the millimoles of hindered phenol and aromatic amine antioxidant in the sample can be calculated as follows:

$$\text{concentration of antioxidant, mmole/L of oil} = \frac{\text{sample reading} - \text{blank reading}}{\text{standard reading} - \text{blank reading}} \times \text{antioxidant concentration of standard}\ (\text{mmol/L of oil}) \quad (2)$$

where:

reading = valley to valley area (see 8.3) for antioxidants peaks between 0.8 to 1.6 V (see Note 1)

9.3 *Percent Remaining Hindered Phenol and Aromatic Amine Antioxidant Calculation*—Calculate the percent remaining antioxidant in an in-service oil using the fresh oil as the 100 % standard with the following calculation:

$$\%\ \text{remaining antioxidant} = \frac{\text{sample reading} - \text{blank reading}}{\text{standard reading} - \text{blank reading}} \times 100\,\% \quad (3)$$

where:

reading = valley to valley area (see 8.3) for antioxidants peaks between 0.8 to 1.6 V (see Note 1)

10. Precision and Bias

10.1 *Statement of Precision*—The precision of this test method as obtained by statistical analysis of interlaboratory test results should be used for judging the acceptability of results (95 % of confidence).[6]

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 the test method, exceed the following values only in 1 case in 20: The repeatability standard deviation has been determined to be = $1.5094 \cdot (x + 8.6662)^{0.46390}$ %, where x denotes 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 the test method, exceed the following values only in 1 case in 20: The reproducibility standard deviation has been determined to be = $3.0067 \cdot (x + 8.6662)^{0.46390}$ %, where x denotes mean value.

10.2 *Statement of Bias*—No information can be presented on the bias procedure in Test Method D6971 since the result of this test is defined only in the terms of this test method.

11. Keywords

11.1 2,6-di-*tert*-butyl-4methylphenol; 2,6-di-*tert*-butylphenol; alkylated diphenylamine; aromatic amine antioxidant; hindered phenol antioxidant; in-service oils; linear sweep voltammetry; non-zinc turbine oils; phenyl alpha naphthylamine; turbine oil

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1548.