



Designation: D7590 – 22

Standard Guide for Measurement of Remaining Primary Antioxidant Content In In-Service Industrial Lubricating Oils by Linear Sweep Voltammetry¹

This standard is issued under the fixed designation D7590; 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.

INTRODUCTION

Under normal thermal and oxidative working conditions, which degrade the chemical composition of the oil's basestock and gradually deplete the oil's additive package, good oil condition monitoring procedures are necessary to determine and planning corrective actions before the oil properties changes have passed their warning limits. Antioxidant monitoring practices are a vital part of modern oil condition monitoring practices to achieve lubrication excellence. This guide addresses the correct guidelines for voltammetric data interpretation.

1. Scope*

1.1 This guide covers the voltammetric analysis for qualitative measurements of primary antioxidants in new or in-service type industrial lubricants detectable in concentrations as low as 0.0075 % by 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 guide can be used as a resource for a condition monitoring program to track the oxidative health of a range of industrial lubricants which contain primary antioxidants. In order to avoid excessive degradation of the base-oil, these primary antioxidants play a major role to protect the lubricants against thermal-oxidative degradation. This guide can help users with interpretation and troubleshooting results obtained using linear sweep voltammetry (LSV).

1.3 When used as part of oil condition monitoring practices, it is important to apply trend analysis to monitor the antioxidant depletion rate relative to a baseline sample rather than use voltammetry for an absolute measurement of the antioxidant concentration. The trending pattern provides a proactive means to identify the level of oil degradation or abnormal changes in the condition of the in-service lubricant.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

¹ This guide 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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1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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

D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration

D6810 Test Method for Measurement of Hindered Phenolic

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.

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

Antioxidant Content in Non-Zinc Turbine Oils by Linear Sweep Voltammetry

D6971 Test Method for Measurement of Hindered Phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep Voltammetry

D7214 Test Method for Determination of the Oxidation of Used Lubricants by FT-IR Using Peak Area Increase Calculation

2.2 *ISO Standards*:³

ISO 4406.2 Hydraulic fluid power—Fluids—Method for coding the level of contamination by solid particles

2.3 *Other Standards*:⁴

VGB Guideline VGB-M 416 M In-Service Monitoring of Turbine Oils

3. Terminology

3.1 *Definitions*:

3.1.1 See Terminology **D4175** for a more extensive list of terms used in this test method.

3.1.2 *electrolytic cell, n*—an electrochemical cell in which chemical reactions are caused by applying an external potential difference greater than, and opposite to, the galvanic electromotive force of the cell. **IUPAC**⁵

3.1.3 *linear sweep voltammetry, n*—a technique applied to the monitoring of antioxidant additive content in lubricants, where the current is detected as an applied potential is increased linearly over a period of time.

3.1.4 *voltammogram, n*—the plot of current versus voltage.

4. Oil Condition Monitoring Programs

4.1 Most industrial lubricants consist of mineral or synthetic oils compounded with oxidation and rust inhibitors. Depending upon their application and the performance level desired, specific required amounts of other additives such as metal deactivators, pour depressants, extreme pressure additives, and foam suppressants can also be present.

4.2 With modern formulations of industrial lubricants, the antioxidants play a major role in protecting the base-oil against excessive degradation. To prevent this base-oil degradation, resulting in the eventual build-up of deposits, varnish and sludge, the monitoring of the antioxidants represents a proactive information on the remaining oxidative health of the in-service lubricant. Oxidation is a chemical reaction between oxygen atoms with the base oil hydrocarbon molecules, which are converting the hydrocarbon molecules into oxidation products and subsequently weak organic acids. The rate of oxidation depends on the presence of antioxidant additives, which controls the speed of oxidation, but eventually the antioxidants are consumed. Consequently as part of modern proactive maintenance strategies, it is vital to know at any time during

the operating cycle of the lubricants, its condition by assessing the remaining activity of antioxidants, to prevent the oxidative degradation of the base oil.

4.3 Antioxidant monitoring guidelines have been part of International Standards such as Practice **D4378**, Practice **D6224**, and VGB Guideline VGB-M 416 M, as well International OEM Maintenance Specifications. This guide presents guidelines for the lubricant professionals using voltammetric techniques as part of their regular maintenance strategies, such as data interpretation, oil analysis frequency, combination with other condition monitoring tests, etc.

5. Summary of Linear Sweep Voltammetric (LSV) Test Method

5.1 Linear Sweep Voltammetric (LSV) test can be performed on any type of industrial lubricant containing at least one type of antioxidant. The voltammetric test is a comparative test method. By establishing a comparison between its reference oil (fresh oil or standard) and its used oil, this guide can be used without the specific knowledge on the category to which the antioxidants belong.

5.2 ASTM International has two standards, Test Method **D6810** and **D6971**, that shall enable the measurement of the remaining phenolic and aminic type of antioxidants. No standard test method has been developed for the detection of other type of antioxidants by linear voltammetry, although LSV also has detection capabilities for these types of secondary antioxidants (such as zinc dialkyl dithiophosphates).⁶

5.3 A measured quantity of sample is dispensed into a vial containing a measured quantity of a selected test solution and containing a layer of sand. When the vial is shaken, the antioxidants and other solution soluble oil components present in the sample are extracted into the electrolytic 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 antioxidants dissolved in the test solution are quantified by voltammetric analysis. The results are calculated and reported as mass percent 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.

5.4 Voltammetric analysis is a technique that applies electroanalytic methods wherein a sample to be analyzed is mixed with an electrolyte and a solvent (acetone or ethanol based), 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

³ Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, <http://www.iso.org>.

⁴ Available from VGB PowerTech e.V., P. O. Box 10 39 32, D-45039 Essen, Klinkestraße 27 - 31, D-45136 Essen, <http://www.vgb.org>.

⁵ Inczedy, J., Lengyel, T., and Ure, A. M., *Orange Book: IUPAC Compendium on Analytical Nomenclature, Definitive Rules 1997*, 3rd Edition, Blackwell Science, 1998.

⁶ "Remaining Useful Life Measurements of Diesel Engine Oils, Automotive Engine Oils, Hydraulic Fluids, and Greases Using Cyclic Voltammetric Methods," STLE, *Lubrication Engineering*, Vol 51, 3, pp. 223–229.

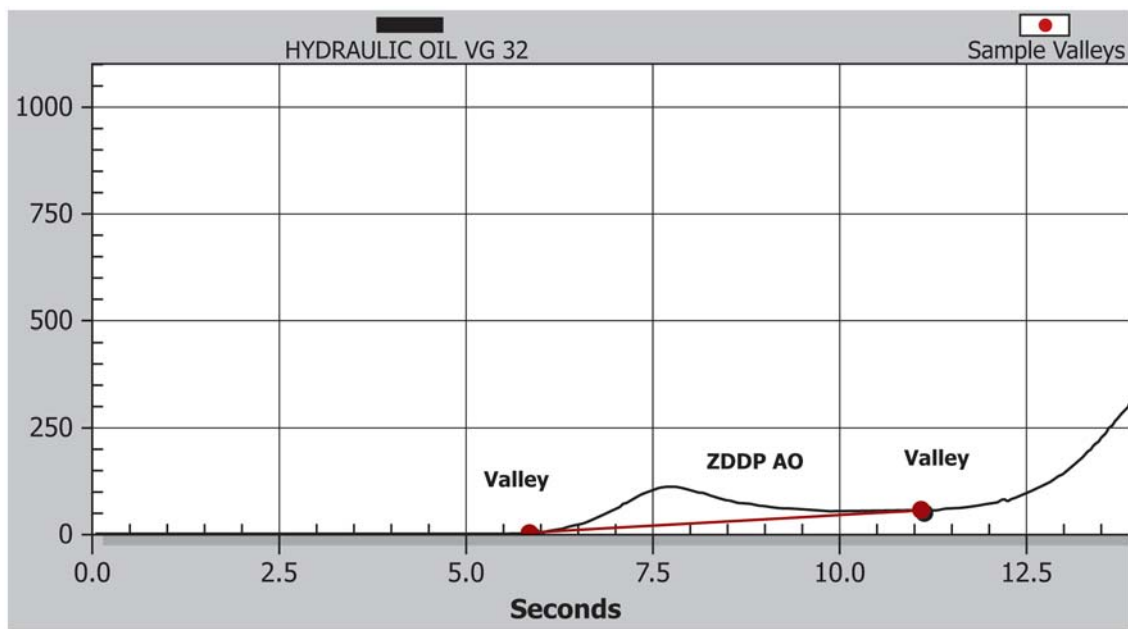


FIG. 1 Zinc Dialkyl Dithiophosphate (ZDDP) Voltammetric Response in the Neutral Test Solution with Blank Response Zeroed

remains unpolarized during the analysis period. Additional electrodes, 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 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 electroactive 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 electroactive 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.

6. Significance and Use

6.1 The quantitative determination of remaining antioxidants for in-service industrial oils by measuring the amount of these additives that have been added to the oil as protection against oxidation. Industrial lubricants, such as turbine oils, compressor oils, gear oils, hydraulic oils, bearing lubricants and greases can be formulated with a wide variety of antioxidants types such as phenols and amines (as primary antioxidants), which are working synergistically and therefore all important to be monitored individually. For in-service oils, the LSV determines and compares the amount of original

primary antioxidants remaining after oxidation have reduced its initial concentration.

6.2 This guide covers procedures for primary antioxidants such as amines and phenols, as described by Test Method D6971 and D6810.

6.3 LSV 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. In order to measure the overall stability of an oil (including contribution of intermediates present), and 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 (in accordance with Practice D4378 and Practice D6224).

6.4 This guide is applicable to a wide range of industrial oils, both mineral or synthetic based, which can contain rust and oxidation inhibitors, antiwear additives such as zinc dialkyl dithiophosphates on gear oils, circulating oils, transmission oils and other industrial lubricating oils.

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

6.6 When a voltammetric analysis is obtained for a industrial lubricant inhibited with at least one type of antioxidant, there is an increase in the current of the produced voltammogram between 5 s to 8 s (or 0.5 V to 0.8 V applied voltage) (see Note 1) for the zinc dialkyl dithiophosphate type of antioxidant (Fig. 1), an increase in the current of the produced voltammogram between 8 s to 12 s (or 0.8 V to 1.2 V applied voltage) (Fig. 2) (see Note 1) for the aromatic amines, and increase in the current of the produced voltammogram between 13 s and 16 s (or 1.3 V to 1.6 V applied voltage) (see Note 1) for the hindered phenols or carbamates in the neutral acetone solution

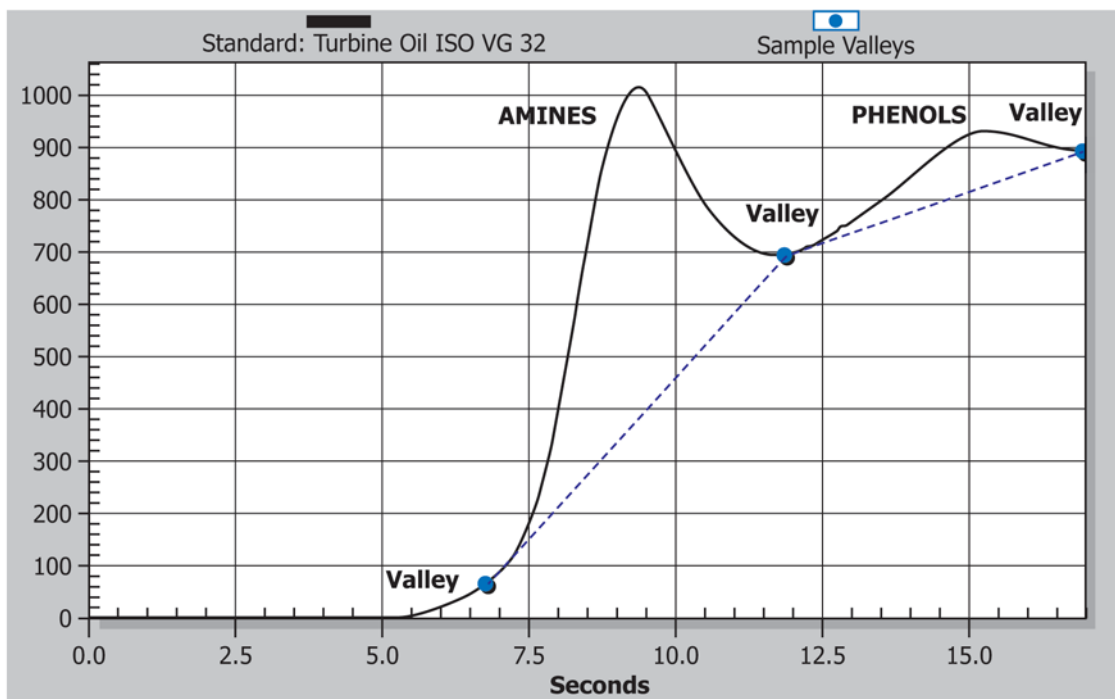


FIG. 2 Aromatic Amine and Hindered Phenol Voltammetric Response in the Neutral Test Solution with Blank Response Zeroed

(Fig. 2: x-axis 1 s = 0.1 V), or both. 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. 1-6 were obtained with a platinum reference electrode and a voltage scan rate of 0.1 V/s.

6.7 For industrial lubricants containing zinc dialkyl dithiophosphate type of antioxidants, there is an increase in the current of the produced voltammogram between 5 s to 8 s (or 0.5 V to 0.8 V applied voltage) (see Note 1) by using the neutral acetone test solution (see Fig. 1). There is no corresponding ASTM International standard describing the test method procedures for measuring zinc dialkyl dithiophosphates type of antioxidants in industrial lubricants.

6.8 For industrial lubricants containing only aromatic amines as antioxidants, there is an increase in the current of the produced voltammogram between 8 s to 12 s (or 0.8 V to 1.2 V applied voltage) (see Note 1) for the aromatic amines, by using the neutral acetone test solution (first peak in Fig. 2) as described in Test Method D6971.

6.9 For industrial lubricants containing only hindered phenolic antioxidants, it is preferable to use a basic alcohol solution rather than the neutral acetone solutions, to achieve an increase in the current of the produced voltammogram between 3 s to 6 s (or 0.3 V to 0.6 V applied voltage) (see Note 1) in basic alcohol solution (Fig. 3: x-axis 1 s = 0.1 V) as described in Test Method D6810.

7. Voltammetric Test Apparatus

7.1 *Voltammetric Analyzer*⁷—Specifically designed to perform antioxidant determinations of industrial oils. The instrument used to quantify the hindered phenol and aromatic amine antioxidants is a voltammograph equipped with a three-electrode system (referred further to as the probe) 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 and D6971. The voltammetric analyzer applies a linear voltage ramp (0 V to -1.7 V range with respect to the reference electrode) at a rate of 0.01 V/s 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 V to 1 V full scale) as shown in Figs. 1 and 2.

7.2 *Vortex Mixer*—A vortex mixer with a 2800 r/min to 3000 r/min motor and a pad suitable for mixing test tubes and vials. Ultrasonic shakers may also be used to achieve a quick and efficient shaking of the prepared test solution.

7.3 *Pipet*—or equivalent, capable of delivering sample volumes required in this guide from 0.10 mL to 0.50 mL.

7.4 *Solvent Dispenser*—or equivalent, capable of delivering volumes of analytical test solution (see 7.3) required in this guide, such as 3.0 mL and 5.0 mL.

⁷ Trademark of Fluitec International, 1997 Newborn Rd. Rutledge, GA 30663 (USA), Nieuwbrugstraat 73 B-1830, Machelen, Belgium (Europe), www.fluitec.com.

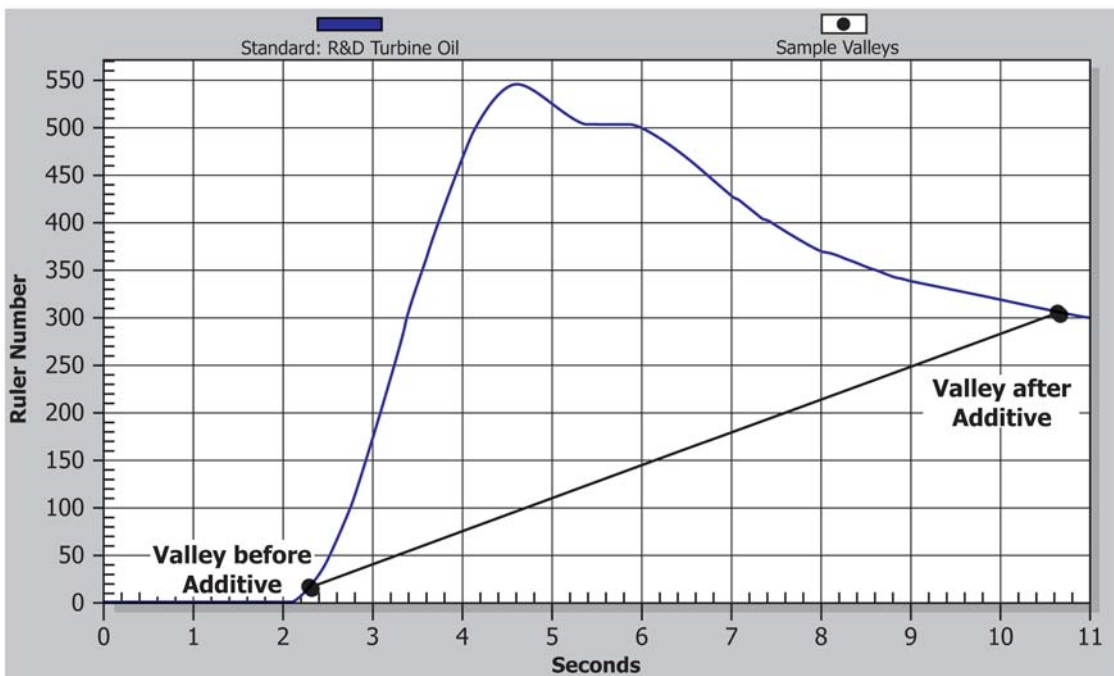


FIG. 3 Hindered Phenol Voltammetric Response in Basic Test Solution with Blank Response Zeroed

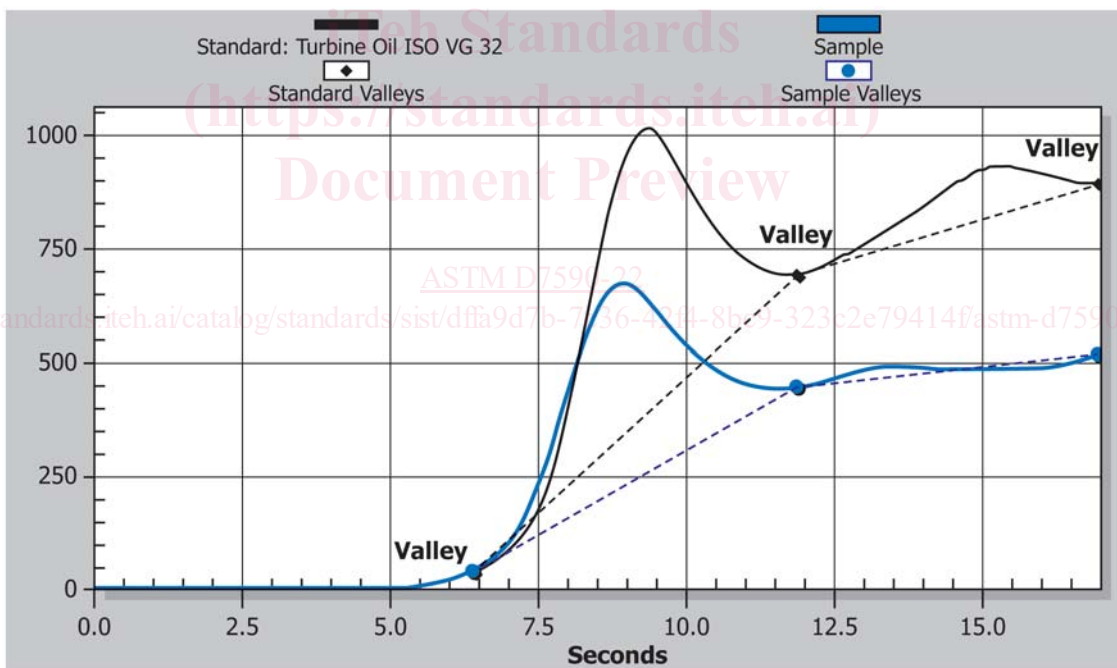


FIG. 4 Voltammetric Reading for an In-service Oil Sample Comparing Aromatic Amines (additive #1) and Hindered Phenols (additive #2) Peaks (in the Neutral Test Solution)—Standard (top line) and Sample In-Service Oil (lower line)

7.5 *Glass Vials with Caps*—4 mL or 7 mL capacity, and containing 1 g of sand.

7.6 *Sand*—Required to be white quartz suitable for chromatography within the size range of 200 μm to 300 μm \pm 100 μm .

8. Sampling

8.1 Obtain the sample in accordance with Practice D4057.

9. Test Solutions – Reagents and Selection

9.1 *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. Other grades may be

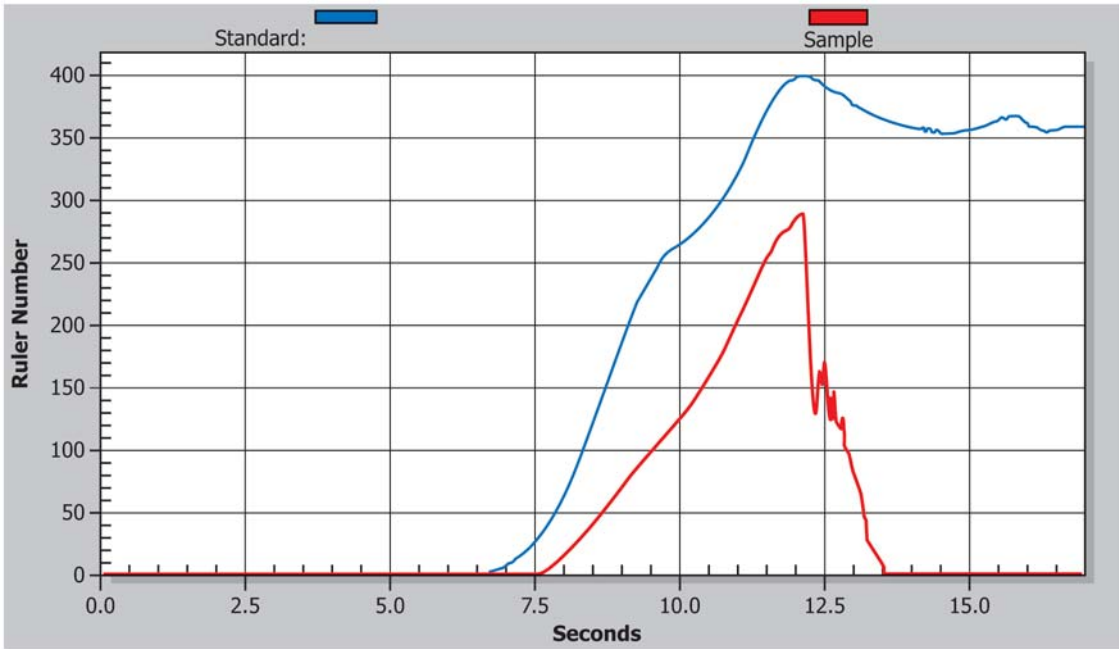


FIG. 5 a Filming Problems Due to Oil Solubility

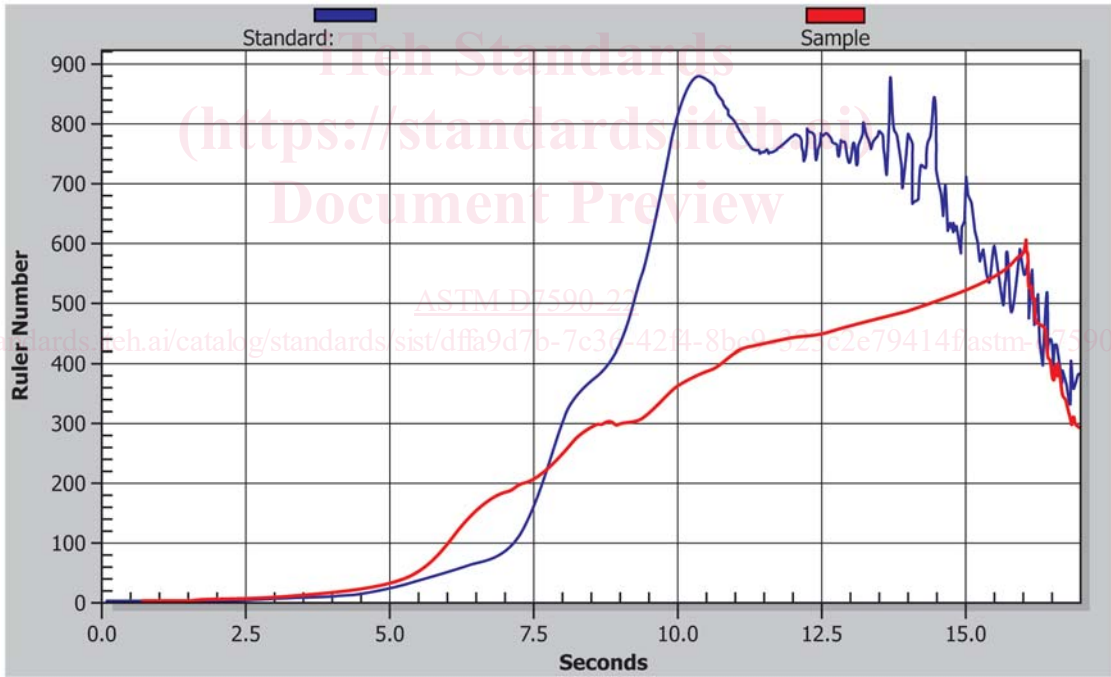


FIG. 5 b Filming Due to Additive Concentration (continued)

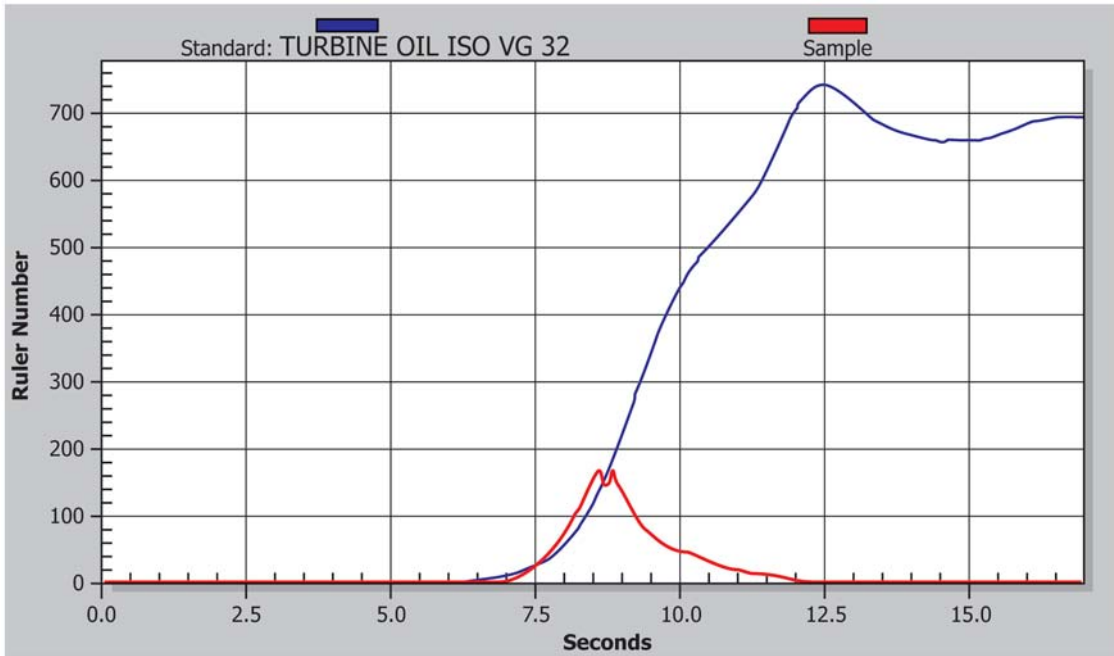


FIG. 5 c Filming Problems Due to Oil Solubility (continued)

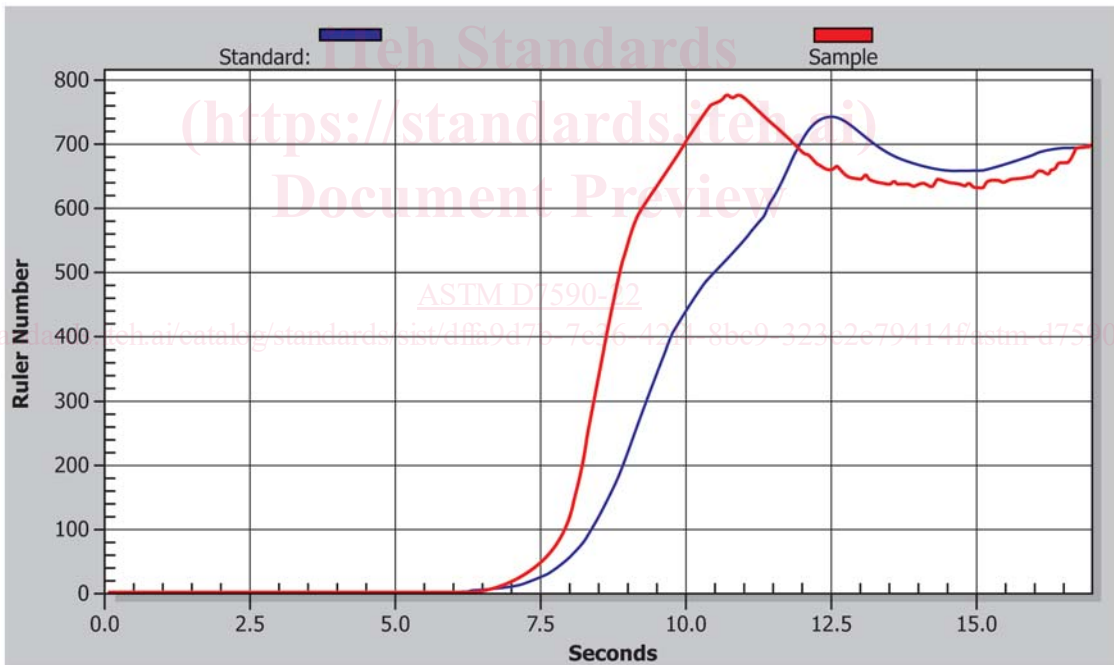


FIG. 6 Shifting of Antioxidant Peaks Due to Oil Solubility