Designation: D7590 – 22

Standard Guide for Measurement of Remaining Primary Antioxidant Content In In-Service Industrial Lubricating Oils by Linear Sweep Voltammetry[1]

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.

1.5 *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

[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.

Current edition approved Nov. 15, 2022. Published December 2022. Originally approved in 2009. Last previous edition approved in 2014 as D7590 – 09 (2014). DOI: 10.1520/D7590-22.

[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.