Designation: D3339 – 21

Standard Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration[1]

This standard is issued under the fixed designation D3339; 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 determination of acidic constituents in new or used petroleum products and lubricants soluble or nearly soluble in mixtures of toluene, and isopropyl alcohol. The test method is especially intended for cases in which the amount of sample available to be analyzed is too small to allow accurate analysis by Test Methods D974 or D664. It is applicable for the determination of acids having dissociation constants in water larger than 10^{-9}. Extremely weak acids having dissociation constants smaller than 10^{-9} do not interfere. Salts titrate if their hydrolysis constants are larger than 10^{-9}.

1.2 This test method can be used to indicate relative changes in acid number that occur in an oil during use under oxidizing conditions. Although the titration is made under definite equilibrium conditions, the method does not measure an absolute acidic property that can be used to predict performance of an oil under service conditions. No general relationship between bearing corrosion and acid number is known.

1.3 Since this test method requires substantially less sample than Test Methods D974 or D664, it provides an advantageous means of monitoring an oxidation test by changes in acid number by (*1*) minimizing test sample depletion for acid number analyses and thus minimizing the disturbance of the test or (*2*) allowing additional acid number analyses to be made while maintaining the same test sample depletion and thus providing additional data.

NOTE 1—Some oils, such as many cutting oils, rust-proofing oils, and similar compounded oils, or excessively dark-colored oils, may be more difficult to analyze by this test method due to obscurity of the color-indicator end point. These oils can be analyzed by Test Method D664 provided sufficient sample is available. However, this situation is much less likely using Test Method D3339 than using Test Method D974 due to the use of a more highly dilute sample during the titration and due to the greater stability of the end point color change. The acid numbers obtained by Test Method D3339 may or may not be numerically the same as those obtained by Test Method D664 but they should be of the same order of magnitude.

NOTE 2—The results obtained using this method have been found to be numerically the same as those obtained using Test Method D974, within the precision of the two methods, for new or oxidized lubricants of the type primarily intended for hydraulic or steam turbine type service. The oxidized lubricants were obtained using the Test Method D943 oxidation test. This correlation is shown by the correlation coefficient $r = 0.989$ with slope $s = +1.017$ and intercept $y = +0.029$, calculated using the acid numbers obtained using both titration methods for the samples used for the precision statement (12.2).[2]

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.* For specific warning statements, see Sections 7 and 9, A1.1.4, A2.3.1, and A2.10.1.

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:*[3]

D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration

D943 Test Method for Oxidation Characteristics of Inhibited Mineral Oils

D974 Test Method for Acid and Base Number by Color-Indicator Titration

D1193 Specification for Reagent Water

[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 D02.06 on Analysis of Liquid Fuels and Lubricants.

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[2] Use of the correlation coefficient is given in Mack, C., *Essentials of Statistics for Scientists and Technologists*, Plenum Press, New York, NY, 1967, or other publications on statistics.

[3] 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**

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions:*

3.1.1 *acid number, n*—the quantity of a specified base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified endpoint using a specified detection system.

3.1.1.1 *Discussion*—In this test method, acids or salts with dissociation constants greater than 10^{-9}, are titrated to a green end point with *p*-naphtholbenzein indicator.

3.1.2 *used oil, n*—any oil that has been in a piece of equipment (for example, an engine, gearbox, transformer or turbine) whether operated or not.

3.1.2.1 *Discussion*—Typically, in this test method, the acidity of oxidized hydraulic or steam turbine oils is measured.

4. Summary of Test Method

4.1 To determine the acid number a sample of the oil is dissolved in a solvent consisting of toluene, isopropyl alcohol, and a small amount of water. The resulting single-phase solution is titrated at room temperature under a nitrogen atmosphere with standardized 0.01 *M* potassium hydroxide (KOH) in isopropyl alcohol to the stable green color of the added *p*-naphtholbenzein indicator.

5. Significance and Use

5.1 This test method measures the acid number of oils obtained from laboratory oxidation tests using smaller amounts of sample than Test Methods D974 or D664. It has specific application in Test Method D943 in which small aliquots of oil are periodically removed for testing by Test Method D3339. This test method, therefore, provides a means of monitoring the relative oxidation of oils, by measuring changes in acid number, at different time intervals and under the various oxidizing test conditions.

6. Apparatus (Refer to Fig. 1)

6.1 *Titration Buret*—A micro scale, automatic buret with 0.01 mL subdivisions and at least a 2 mL buret capacity.

6.2 *Titrant Reservoir*—The preferred reservoir is one that is integral with the automatic buret, such as shown in Fig. 1. A titrant reservoir separate from the automatic buret may be used if the line connecting the reservoir with the buret is all glass. Exposure of the titrant to light should be minimized by use of amber glass for the reservoir, by wrapping the reservoir with foil such as aluminum foil, or by other suitable means. Also, the tube in the reservoir for titrant withdrawal is adjusted so that the end of the tube is about 20 mm from the bottom of the reservoir so that any precipitate that may collect on the bottom of the reservoir will not be disturbed. To further avoid disturbing any precipitate in the reservoir, movement of the reservoir must be minimized.

6.2.1 With either type of reservoir all entrances and exits to the buret and reservoir must be connected to absorption tubes to remove atmospheric carbon dioxide and water, for example, tubes containing 10 mesh to 20 mesh anhydrous calcium sulfate as desiccant and soda-lime as carbon dioxide absorbent. Precautions must be taken to prevent introduction of any soda-lime into the titrant reservoir or buret.

6.3 *Titration Beaker*—100 mL capacity tall-form Berzelius beaker without pouring spout. Approximate dimensions are 47 mm in inside diameter and 79 mm in height.

6.4 *Titration Beaker Purging Stopper*—A stopper to enclose the titration beaker. The stopper must be composed of an elastomeric material, such as neoprene, that is essentially unaffected by the titration solvent. Approximate stopper dimensions are 53 mm top diameter, 45 mm bottom diameter, and 25 mm height. The stopper is fitted with a 8 mm outside diameter glass inlet tube extending 15 mm ± 2 mm beyond the bottom of the stopper and with a 7 mm ± 1 mm inside diameter hole. The inlet tube and hole are placed on opposite sides of the stopper with a center-to-center separation distance of 30 mm ± 1 mm.

6.5 *Purge Gas Rotameter,* capable of indicating a flow rate of 10 L/h.

6.6 *Stirrer Motor,* variable speed, magnetically linked.

NOTE 3—A propeller may also be used instead of a magnetic stirrer to mix the samples.

6.7 *Stirring Bar,* cylindrical, TFE-fluorocarbon encased, 25.4 mm long and 7.9 mm in diameter.

6.8 *Pipet,* capable of transferring 0.100 mL ± 0.002 mL of titration indicator solution.

6.9 *Titration Solvent Buret*—A 500 mL or larger capacity buret with 5 mL subdivisions. The top of the buret is stoppered and connected with an absorption tube, as in 6.2, to remove atmospheric carbon dioxide and water. An alternative means of dispensing the titration solvent may be used provided a dispensing repeatability within ±1 mL for 40 mL is obtainable and the solvent in the dispenser is isolated from atmospheric carbon dioxide and water.

NOTE 4—An automated photometric device may also be used for detecting the titration end point. However, the precision estimates given in Section 13 may not apply to this mode of titration.

7. Reagents and Materials

7.1 *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 or to other such recognized standards for reagent chemicals.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar 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.