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Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration[1]

This standard is issued under the fixed designation D 664; 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.

This standard has been approved for use by agencies of the Department of Defense.

ε[1] NOTE—Variable *C* in 12.3.1 was corrected editorially in September 2004.

1. Scope*

1.1 This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and propan-2-ol. It is applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9}; extremely weak acids whose dissociation constants are smaller than 10^{-9} do not interfere. Salts react if their hydrolysis constants are larger than 10^{-9}. The range of acid numbers included in the precision statement is 0.1 mg/g KOH to 150 mg/g KOH.

NOTE 1—In new and used oils, the constituents that may be considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents.

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

NOTE 2—The acid number obtained by this standard may or may not be numerically the same as that obtained in accordance with Test Methods D 974 and D 3339. There has not been any attempt to correlate this method with other non-titration methods.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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]

2.1 *ASTM Standards:*

D 974 Test Method for Acid and Base Number by Color-Indicator Titration
D 1193 Specification for Reagent Water
D 3339 Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions:*

3.1.1 *acid number*, *n*—the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified end point.

3.1.1.1 *Discussion*—This test method expresses the quantity of base as milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in a mixture of toluene and propan-2-ol to which a small amount of water has

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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This test method was adopted as a joint ASTM-IP standard in 1964. ASTM Test Method D 4739 has been developed as an alternative to the base number portion of D 664.

[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.**

been added from its initial meter reading in millivolts to a meter reading in millivolts corresponding to an aqueous basic buffer solution or a well-defined inflection point as specified in the test method.

3.1.1.2 *Discussion*—This test method provides additional information. The quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading in millivolts to a meter reading in millivolts corresponding to a freshly prepared aqueous acidic buffer solution or a well-defined inflection point as specified in the test method shall be reported as the *strong acid number.*

3.1.1.3 *Discussion*—The causes and effects of the so-called strong acids and the causes and effects of the other acids can be very significantly different. Therefore, the user of this test method shall differentiate and report the two, when they are found.

4. Summary of Test Method

4.1 The sample is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained and for used oils, end points are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions.

5. Significance and Use

5.1 New and used petroleum products may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with bases. The acid number is a measure of this amount of acidic substance in the oil, always under the conditions of the test. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

5.2 Since a variety of oxidation products contribute to the acid number and the organic acids vary widely in corrosion properties, the test method cannot be used to predict corrosiveness of oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils toward metals.

6. Apparatus

6.1 *Manual Titration Apparatus*:

6.1.1 *Meter*, a voltmeter or a potentiometer that will operate with an accuracy of ±0.005 V and a sensitivity of ±0.002 V over a range of at least ±0.5 V when the meter is used with the electrodes specified in 6.1.2 and 6.1.3 and when the resistance between the electrodes falls within the range from 0.2 to 20 MΩ. The meter shall be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching, with a grounded lead, any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand, or the meter.

NOTE 3—A suitable apparatus could consist of a continuous-reading electronic voltmeter designed to operate on an input of less than 5×10^{-12} A, when an electrode system having 1000-MΩ resistance is connected across the meter terminals and provided with a metal shield connected to the ground, as well as a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interference from any external electrostatic field.

6.1.2 *Sensing Electrode*, Standard pH, suitable for nonaqueous titrations.

6.1.3 *Reference Electrode*, Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1M–3M LiCl in ethanol.

6.1.3.1 *Combination Electrodes*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. The combination electrode shall have a sleeve junction on the reference compartment and shall use an inert ethanol electrolyte, for example, 1M–3M LiCl in ethanol. These combination electrodes shall have the same response or better response than a dual electrode system. They shall have removable sleeves for easy rinsing and addition of electrolyte.

NOTE 4—A third electrode, such as a platinum electrode, may be used to increase the electrode stability in certain systems.

6.1.4 *Variable-Speed Mechanical Stirrer*, a suitable type, equipped with a propeller-type stirring paddle. The rate of stirring shall be sufficient to produce vigorous agitation without spattering and without stirring air into the solution. A propeller with blades 6 mm in radius and set at a pitch of 30 to 45° is satisfactory. A magnetic stirrer is also satisfactory.

6.1.4.1 If an electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in the meter reading during the course of the titration.

6.1.5 *Burette*, 10-mL capacity, graduated in 0.05-mL divisions and calibrated with an accuracy of ±0.02 mL. The burette shall have a tip that extends 100 to 130 mm beyond the stopcock and shall be able to deliver titrant directly into the titration vessel without exposure to the surrounding air or vapors. The burette for KOH shall have a guard tube containing soda lime or other CO_2-absorbing substance.

6.1.6 *Titration Beaker*, 250 mL capacity, made of borosilicate glass or other suitable material.

6.1.7 *Titration Stand*, suitable for supporting the electrodes, stirrer, and burette.

NOTE 5—An arrangement that allows the removal of the beaker without disturbing the electrodes and stirrer is desirable.

6.2 *Automatic Titration Apparatus*:

6.2.1 Automatic titration systems shall be able to carry out the necessary analyses as prescribed in the method. As a minimum, the automatic titration system shall meet the performance and specification requirements listed in 6.1 as warranted.

6.2.2 A dynamic mode of titrant addition shall be used. During the titration, the speed and volume of the addition shall vary depending on the rate of change of the system. The recommended maximum volume increment is 0.5 mL and the recommended minimum volume increment is 0.05 mL.

7. Reagents

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.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 Commercially available solutions may be used in place of laboratory preparations provided the solutions have been certified as being equivalent.

7.1.2 Alternate volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water at least at the level of Type III of Specification D 1193.

7.3 *Ethanol*, (**Warning**—Flammable and toxic, especially when denatured.)

7.4 *Hydrochloric Acid (HCl)*—Relative density 1.19. (**Warning**—Corrosive, causes burns.)

7.5 *Lithium Chloride*, LiCl.

7.6 *Lithium Chloride Electrolyte*, Prepare a 1M–3M solution of lithium chloride (LiCl) in ethanol.

7.7 *Methanol*, (**Warning**—Flammable. Toxic if swallowed.)

7.8 *Potassium Hydroxide*, (**Warning**—Causes severe burns.)

7.9 *Propan-2-ol, Anhydrous*, (less than 0.1 % H_2O). (**Warning**—Flammable.) If adequately dry reagent cannot be procured, it can be dried by distillation through a multiple plate column, discarding the first 5 % of material distilling overhead and using the 95 % remaining. Drying can also be accomplished using molecular sieves such as Linde Type 4A, by passing the solvent upward through a molecular sieve column using one part of molecular sieve per ten parts of solvent.

NOTE 6—It has been reported that, if not originally inhibited against it, propan-2-ol can contain peroxides. When this occurs, an explosion is possible when the storage of the vessel or other equipment such as a dispensing bottle, is near empty and approaching dryness.

7.10 *Toluene*, (**Warning**—Flammable.)

7.11 *Hydrochloric Acid Solution, Standard Alcoholic*, (0.1 mol/L). (**Warning**—See 7.4 and 7.9.) Mix 9 mL of hydrochloric (HCl, relative density 1.19) acid with 1 L of anhydrous propan-2-ol. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of approximately 8 mL (accurately measured) of the 0.1-mol/L alcoholic KOH solution diluted with 125 mL of CO_2-free water.

7.12 *Commercial Aqueous pH 4, pH 7 and pH 11 Buffer Solutions*—These solutions shall be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability should be obtained from the manufacturer.

7.13 *Potassium Hydroxide Solution, Standard Alcoholic*, (0.1 mol//L). (**Warning**—See 7.8 and 7.9.) Add 6 g of potassium hydroxide (KOH) to approximately 1 L of propan-2-ol. Boil gently for 10 min to effect solution. Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered-glass funnel. Store the solution in a chemically resistant bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide (CO_2) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbents and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in CO_2-free water.

7.14 *Titration Solvent*—Add 5 ± 0.2 mL of water to 495 ± 5 mL of anhydrous propan-2-ol and mix well. Add 500 ± 5 mL of toluene. (**Warning**—Flammable.) The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.

7.15 *Chloroform*, (**Warning**—Flammable. Hazardous material.)

8. Electrode System

8.1 *Preparation of Electrodes*:

8.1.1 When a Ag/AgCl reference electrode is used for the titration and it contains an electrolyte which is not 1M–3M LiCl in ethanol, replace the electrolyte. Drain the electrolyte from the electrode, wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with the LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve ensure that there will be a free flow of electrolyte into the system. A combination electrode shall be prepared in the same manner. The electrolyte in a combination electrode can be removed with the aid of a vacuum suction.

8.2 *Testing of Electrodes*—Test the meter-electrode combination when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Rinse the electrodes with solvent then with water. Dip them into a pH 4 aqueous buffer solution. Read the mV value after stirring one minute. Remove the electrodes and rinse with water. Dip the electrodes into a pH 7 aqueous buffer. Read the mV value after stirring one minute. Calculate the mV difference. A good electrode system will have a difference of at least 158 mV (20 to 25°C). If the difference is less than 158 mV, lift the sleeve of the electrode and insure electrolyte flow. Repeat the measurements. If the difference is still less than 158 mV, clean or replace the electrode(s).

8.2.1 When the sensing electrode and the reference electrode are separate, one pair of electrodes shall be considered as

[3] *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.