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## Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This test method was adopted as a joint ASTM-IP standard in 1964.*

*This test method has been adopted for use by government agencies to replace Method 5106 of Federal Test Method Standard No. 791b. ASTM Test Method D 4739 has been developed as an alternative to the base number portion of D 664.*

### 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 (Note 1). 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  $10^{-9}$ .

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 an 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 an 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.

1.3 The values stated in acceptable SI units are to be regarded as the standard.

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

#### 2.1 ASTM Standards:

D 974 Test Method for Acid and Base Number by Color-Indicator Titration<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

D 3339 Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration<sup>4</sup>

### 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 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 the solvent from its initial meter reading in millivolts to a meter reading in millivolts corresponding to a freshly prepared non-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 nonaqueous acidic buffer solution or a well-defined inflection point as specified in the test method shall be reported as the *strong acid number*.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

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 calomel reference 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, end points are taken at meter readings corresponding to those found for freshly prepared nonaqueous 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 an oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils toward metals.

#### 6. Apparatus

6.1 The cell assembly used for the potentiometric titration is shown in Fig. 1.

##### 6.2 Manual Titration Apparatus:

6.2.1 *Meter*, a voltmeter or a potentiometer that will operate with an accuracy of  $\pm 0.005$  V and a sensitivity of  $\pm 0.002$  V over a range of at least  $\pm 0.5$  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 M $\Omega$ . 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  $5 \times 10^{-12}$  A, when an electrode system having 1000-M $\Omega$  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.

6.2.2 *Glass Electrode*, pencil type, 125 to 180 mm in length and 8 to 14 mm in diameter (C in Fig. 1).

6.2.2.1 The body of the electrode shall be made of a chemically resistant glass tube with a wall thickness of 1 to 3 mm.

6.2.2.2 The end dipping into the solution shall be closed with a hemisphere of glass sealed on to the electrode tube and the radius of this hemisphere shall be about 7 mm. The thickness of the glass in the hemisphere shall be great enough so that the resistance of the hemisphere is 100 to 1000 M $\Omega$  at 25°C.

6.2.2.3 The electrode shall contain a reproducible, permanently sealed liquid cell for making electrical connection with the inner surface of the hemisphere.

6.2.2.4 The entire electrical connection from the sealed contact cell to the meter terminal shall be surrounded by an electrical shield that will prevent electrostatic interference when the shield is grounded.

6.2.2.5 The shield shall be insulated from the electrical connection by insulating material of the highest quality, such as rubber and glass, so that the resistance between the shield and the entire length of the electrical connection is greater than 50 000 M $\Omega$ .

6.2.3 *Calomel Reference Electrode*, pencil type, 125 to 180 mm in length and 8 to 14 mm in diameter (B in Fig. 1).

6.2.3.1 This electrode shall be made of glass and shall be provided with an external, removable glass sleeve on the sealed end that is dipped into the titration solution.

6.2.3.2 The glass sleeve shall be 8 to 25 mm in length, shall be slightly tapered, and shall be ground to fit the electrode so that the sealed end of the electrode protrudes 2 to 20 mm beyond the sleeve. The ground surface shall be continuous and free of smooth spots.

6.2.3.3 At a point between the extremities of the ground surface, the electrode tube shall be pierced by a hole or holes 1 mm in diameter. The electrode shall contain the necessary mercury, calomel, and electrical connection to the mercury, all arranged in a permanent manner.

6.2.3.4 The electrode shall be filled almost to capacity with saturated KCl electrolyte and shall be equipped with a stoppered port through which the electrolyte may be replenished.

6.2.3.5 When suspended in the air and with the sleeve in place, the electrode shall not leak electrolyte at a rate greater than one drop in 10 min.

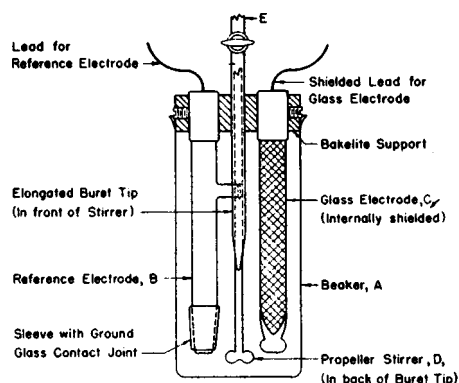


FIG. 1 Cell for Potentiometric Titration

NOTE 4—Certain alternative electrode-electrolyte combinations have been shown to give satisfactory results although the precision using these alternatives has not been determined. Combination electrodes can be used for this test method provided they have sufficiently fast response time.<sup>5</sup>

6.2.4 *Variable-Speed Mechanical Stirrer*, a suitable type, equipped with a glass, propeller-type stirring paddle (D in Fig. 1). 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.

6.2.4.1 If 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.

6.2.5 *Burette*, 10-mL capacity, graduated in 0.05-mL divisions and calibrated with an accuracy of  $\pm 0.02$  mL (E in Fig. 1). The burette shall have a glass stopcock and shall have a tip that extends 100 to 130 mm beyond the stopcock. The burette for KOH shall have a guard tube containing soda lime or other CO<sub>2</sub>-absorbing substance.

6.2.6 *Titration Beaker*, 250-mL capacity, made of borosilicate glass (A in Fig. 1).

6.2.7 *Titration Stand*, suitable for supporting the electrodes, stirrer, and burette in the positions shown in Fig. 1.

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

### 6.3 Automatic Titration Apparatus:

6.3.1 Automatic titration systems shall be generally in accordance with 6.2 and provide the following technical performance characteristics or features.

6.3.1.1 Automatic adaptation of the titration speed in the continuous titrant delivery mode to the slope of the titration curve with the capability of complying with the potential equilibrium specified and providing titration rates of less than 0.2 mL/min during titration and preferably 0.05 mL/min at inflections and at nonaqueous acid and base end points.

6.3.1.2 Interchangeable precision motor-driven burettes with a volume dispensing accuracy of  $\pm 0.01$  mL.

6.3.1.3 A record of the complete course of the titration by continuously printing out the relative potential versus volume of titrant added.

## 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.<sup>6</sup> 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.

<sup>5</sup> Examples; of suitable electrodes are: (a) Glass electrodes: Beckman 41263, Corning 476022, and Metrohm E107, (b) Reference electrodes: Beckman 40463, Corning 476012, and Metrohm EA430, and (c) Combination electrodes: Metrohm EA121 and EA157.

<sup>6</sup> *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification D 1193.

7.3 *Hydrochloric Acid (HCl)*—Relative density 1.19 (**Warning**—See Note 6).

NOTE 6—**Warning:** Corrosive, causes burns.

7.4 *Propan-2-ol, Anhydrous*, (less than 0.1 % H<sub>2</sub>O) (**Warning**—See Note 7). 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 7—**Warning:** Flammable.

7.5 *2,4,6-Trimethyl Pyridine ( $\gamma$  Collidine)*—((CH<sub>3</sub>)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N) (mol weight 121.18), (**Warning**—See Note 8) conforming to the following requirements:

Boiling range	168 to 170°C
Refractive index, $n_D^{20}$	1.4982 $\pm$ 0.0005
Color	colorless

NOTE 8—**Warning:** 2,4,6-Trimethyl Pyridine ( $\gamma$  collidine) is hazardous if swallowed, breathed, or spilled on skin or eyes. **Precaution**—Wear chemical safety goggles, neoprene or rubber gloves and apron. Use only in a well-ventilated hood, or wear an approved respirator for organic vapor or a supplied-air respirator. Do not take internally.

7.5.1 Store the reagent over activated alumina and keep in a brown glass bottle.

7.6 *m-Nitrophenol*—(NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OH) (mol weight 139.11), conforming to the following requirements (**Warning**—See Note 9):

Melting point	96 to 97°C
Color	pale yellow

NOTE 9—**Warning:** *m*-Nitrophenol can be hazardous if swallowed, breathed, or spilled on skin or eyes. Wear chemical-safety goggles, neoprene or rubber gloves, and apron. Use only in a well-ventilated hood, or wear an approved respirator for organic vapor or a supplied-air respirator. Do not take internally.

7.6.1 Store the reagent in a brown glass bottle.

7.7 *Potassium Chloride Electrolyte*—Prepare a saturated solution potassium chloride (KCl) in water.

7.8 *Potassium Hydroxide*—(**Warning**—See Note 10).

NOTE 10—**Warning:** Causes severe burns.

7.9 *Toluene*—(**Warning**—see Note 7).

7.10 *Hydrochloric Acid Solution, Standard Alcoholic* (0.1 mol/L) (**Warning**—See Note 6 and Note 7). 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<sub>2</sub>-free water.

7.11 *Hydrochloric Acid Solution, Standard Alcoholic* (0.2 mol/L), (**Warning**—See Note 6 and Note 7). Prepare and standardize as directed in 7.10 but use 18 mL of HCl (relative density 1.19).

7.12 *Buffer Stock Solution A*—(**Warning**—See Note 7 and