



# 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

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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.

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*.

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

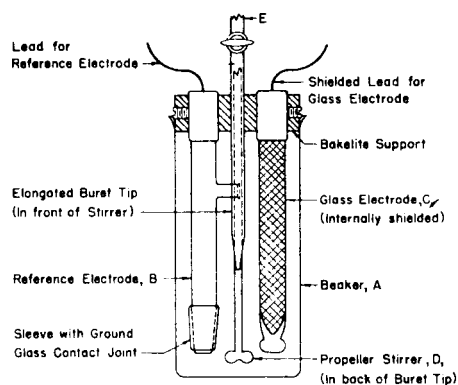
5.1 New and used petroleum products may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with bases. The acid number is a measure of this amount 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:



**FIG. 1 Cell for Potentiometric Titration**

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.

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 ±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 or other suitable material. (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 ±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.

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**—Corrosive, causes burns.).

7.4 *Propan-2-ol, Anhydrous*, (less than 0.1 % H<sub>2</sub>O) (**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.

7.5 *2,4,6-Trimethyl Pyridine (γ Collidine)*—((CH<sub>3</sub>)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N) (mol weight 121.18), (**Warning**—2,4,6-Trimethyl Pyridine (γ collidine) is hazardous if swallowed, breathed, or spilled on skin or eyes.) (**Warning**—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.) conforming to the following requirements:

Boiling range	168 to 170°C
Refractive index, $n_D^{20}$	1.498 2 ± 0.000 5
Color	colorless

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**—*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.):

Melting point	96 to 97°C
Color	pale yellow

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**—Causes severe burns.).

7.9 *Toluene*—(**Warning**—Flammable.).

7.10 *Hydrochloric Acid Solution, Standard Alcoholic* (0.1 mol/L) (**Warning**—Corrosive, causes burns.) (**Warning**—Flammable.) 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

<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 Pharmacopeial and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

with 125 mL of CO<sub>2</sub>-free water.

7.11 *Hydrochloric Acid Solution, Standard Alcoholic* (0.2 mol/L), (**Warning**—Corrosive, causes burns.) (**Warning**—Flammable.). 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**—Flammable.) (**Warning**—2,4,6-Trimethyl Pyridine ( $\gamma$  collidine) is hazardous if swallowed, breathed, or spilled on skin or eyes.) (**Warning**—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.) Accurately weigh  $24.2 \pm 0.1$  g of 2,4,6-trimethyl pyridine ( $\gamma$ -collidine), and transfer to a 1-L volumetric flask containing 100 mL of propan-2-ol. Using a 1-L graduated cylinder, add to the flask, while continuously stirring its contents,  $150/C \pm 5$  mL of 0.2-mol/L alcoholic HCl solution ( $C$  being the exact molarity concentration of the HCl solution found by standardization). Dilute to the 1000-mL mark with propan-2-ol, and mix thoroughly. Use within two weeks.

7.13 *Buffer, Nonaqueous Acidic*—Add 10 mL of buffer stock Solution A to 100 mL of titration solvent. Use within 1 h.

7.14 *Buffer Stock Solution B*—(**Warning**—Flammable.) (**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.) Accurately weigh  $27.8 \pm 0.1$  g of  $m$ -nitrophenol and transfer to a 1-L volumetric flask containing 100 mL of propan-2-ol. Using a 250-mL graduated cylinder, add to the flask while continuously stirring its contents,  $50/C_2 \pm 1$  mL of 0.2-mol/L alcoholic KOH solution ( $C_2$  being the exact molarity concentration of the KOH solution found by standardization). Dilute to the 1000-mL mark with propan-2-ol and mix thoroughly. Use within two weeks.

7.15 *Buffer Nonaqueous Basic*—Add 10 mL of buffer stock Solution B to 100 mL of titration solvent. Use within 1 h.

7.16 *Potassium Hydroxide Solution, Standard Alcoholic* (0.1 mol/L)—(**Warning**—Flammable.) (**Warning**—Causes severe burns.). Add 6 g of potassium hydroxide (KOH) to approximately 1 L of anhydrous 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<sub>2</sub>) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbants 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<sub>2</sub>-free water.

7.17 *Potassium Hydroxide Solution, Standard Alcoholic* (0.2 mol/L), (**Warning**—Flammable.) (**Warning**—Causes severe burns.). Prepare, store, and standardize as directed in 7.16, but use 12 to 13 g of KOH to approximately 1 L of propan-2-ol.

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

NOTE 6—Commercially available reagents can be used in place of laboratory preparations.

## 8. Preparation of Electrode System

8.1 *Maintenance of Electrodes*—Clean the glass electrode (Note 7) at frequent intervals (not less than once every week during continual use) by immersing in cold chromic acid cleaning solution (**Warning**—Causes severe burns. A recognized carcinogen. Strong oxidizer. Contact with materials may cause fire. Hygroscopic.) or in other equipment cleaning solutions. Drain the calomel electrode at least once each week and refill with fresh KCl electrolyte as far as the filling hole. Ascertain that crystallized KCl is present. Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker or vessel at all times. When not in use, immerse the lower halves of the electrodes in water. Do not allow them to remain immersed in titration solvent for any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times.

NOTE 7—Cleaning the electrodes<sup>7</sup> thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining repeatable potentials, since contamination may introduce uncertain erratic and unnoticeable liquid contact potentials.<sup>6</sup> While this is of secondary importance when end points are chosen from inflection points in the titration curve, it may be quite serious when end points are chosen at arbitrarily fixed cell potentials.

8.2 *Preparation of Electrodes*—Before and after using, wipe the glass electrode thoroughly with a clean cloth, or a soft absorbent tissue, and rinse with water. Wipe the calomel reference electrode with a cloth or tissue, carefully remove the ground-glass-sleeve and thoroughly wipe both ground surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint (**Warning**—Causes severe burns.). Wet the ground surfaces thoroughly with electrolyte, set the sleeve firmly in place, and rinse the electrode with water. Prior to each titration, soak the prepared electrodes in water for at least 5 min immediately before use, and touch the tips of the electrodes with a dry cloth or tissue to remove the excess of water.

8.3 *Testing of Electrodes*—Test the meter-electrode combination when first put into use, or when new electrodes are installed, and retest at intervals thereafter by dipping the electrodes into a well-stirred mixture of 100 mL of the titration solvent and 1.0 to 1.5 mL of 0.1-mol/L alcoholic KOH solution. For the meter-electrode combination to be suitable for use, the potential between the electrodes should change by more than 480 mV from the potential between the same

<sup>7</sup> For a detailed discussion of the need for care in preparation of the electrodes, see Lykken, L., Porter, P., Ruliffson, H. D., and Tuemmler, F. D., "Potentiometric Determination of Acidity in Highly Colored Oils," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol 16, 1944, pp. 219–234.

electrodes when dipped in the nonaqueous acidic buffer solution (Note 8).

NOTE 8—Considerably more sensitive electrodes are now available that will show a potential change of at least 590 mV under these conditions, and their use is recommended. When combination electrodes are used, test as in 8.3.

## 9. Standardization of Apparatus

9.1 *Determination of Meter Readings for the Nonaqueous Buffer Solutions Corresponding to Acid End Points*—To ensure comparable selection of end points when definite inflection points are not obtained in the titration curve, determine daily, for each electrode pair, the meter readings obtained with freshly prepared nonaqueous acidic and basic buffer solutions.

NOTE 9—The response of different glass electrodes to hydrogen ion activity is not the same. Therefore, it is necessary to establish regularly for each electrode system the meter readings corresponding to the buffer solutions arbitrarily selected to represent acidic or basic end points.

9.2 Prepare the electrodes as described in 8.2, immerse them in the nonaqueous buffer solution, and stir for 5 min, maintaining the temperature of the buffer solution at a temperature within 2°C of that at which the titrations are to be made. Read the cell voltage. The readings so obtained are taken as the end points in titration curves having no inflection points.

## 10. Preparation of Sample of Used Oil

10.1 Strict observance of the sampling procedure is necessary since the sediment itself is acidic or basic or has absorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

NOTE 10—As used oil can change appreciably in storage, test samples as soon as possible after removal from the lubricating system; and note the dates of sampling and testing.

10.2 Heat the sample (Note 11) of used oil to  $60 \pm 5^\circ\text{C}$  in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can or if it is glass and more than three-fourths full, transfer the entire sample to a clear-glass bottle having a capacity at least one third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

NOTE 11—When samples are visibly free of sediment, the heating procedures described can be omitted.

10.3 After complete suspension of all sediment, strain the sample or a convenient aliquot through a 100-mesh screen for the removal of large contaminating particles.

NOTE 12—When samples are visibly free of sediment, the straining procedure described can be omitted.

## 11. Procedure for Acid Number and Strong Acid Number

11.1 Into a 250-mL beaker or a suitable titration vessel, introduce a weighed quantity of sample as prescribed in Table 1 and add 125 mL of titration solvent (Note 13). Prepare the electrodes as directed in 8.2. Place the beaker or titration vessel on the titration stand and adjust its position so that the electrodes are about half immersed. Start the stirrer, and stir

**TABLE 1 Size of Test Portion**

Acid Number	Mass of Test Portion, g	Accuracy of Weighing, g
0.05 – < 1.0	20.0 ± 2.0	0.10
1.0 – < 5.0	5.0 ± 0.5	0.02
5 – < 20	1.0 ± 0.1	0.005
20 – < 100	0.25 ± 0.02	0.001
100 – < 260	0.1 ± 0.01	0.0005

throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution. If feasible, adjust the meter so that it reads in the upper part of the millivolt scale, for example 700 mV.

NOTE 13—A titration solvent that contains chloroform (**Warning**—May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned.) can be used in place of toluene to completely dissolve certain heavy residues of asphaltic materials.

11.2 Select the right burette, fill with the 0.1-mol/mL alcoholic KOH solution, and place the burette in position on the titration assembly, ensuring that the tip is immersed about 25 mm in the liquid in titration vessel. Record the initial burette and meter (cell potential) readings.

### 11.3 Manual Titration Method:

11.3.1 Add suitable small portions of 0.1-mol/L alcoholic KOH solution and wait until a constant potential has been established, record the burette and meter readings.

11.3.2 At the start of the titration and in any subsequent regions (inflections) where 0.1 mL of the 0.1-mol/L KOH solution consistently produces a total change of more than 30 mV in the cell potential, add 0.05-mL portions.

11.3.3 In the intermediate regions (plateaux) where 0.1 mL of 0.1-mol/L alcoholic KOH changes the cell potential less than 30 mV, add larger portions sufficient to produce a total potential change approximately equal to, but not greater than 30 mV.

11.3.4 Titrate in this manner until the potential changes less than 5 mV/0.1 mL of KOH and the cell potential indicates that the solution is more basic than the freshly prepared nonaqueous basic buffer.

11.3.5 Remove the titration solution, rinse the electrodes and burette tip with the titration solvent, then with propan-2-ol and finally with reagent grade water. Immerse the electrodes in water for at least 5 min before using for another titration to restore the aqueous gel layer of the glass electrode. Store the electrodes in reagent water when not in use. If the electrodes are found to be dirty and contaminated, proceed as in 8.1.

### 11.4 Automatic Titration Method:

11.4.1 Adjust the apparatus in accordance with the manufacturer's instructions to comply with the potential equilibrium mode requirements established for the manual titration as explained in 11.3.1 or to provide a variable continuous delivery rate mode of titration of less than 0.2 mL/min during the titration and preferably 0.05 mL/min through the region of inflections and at the end point corresponding to that found for the freshly prepared standard nonaqueous basic buffer solution.

11.4.2 Proceed with the automatic titration and record potentiometric curves or derivative curves as the case may be.

11.4.3 Titrate in this manner with the 0.1-mol/L alcoholic

KOH solution until the potential becomes constant, for example, changing less than 5 mV/0.1 mL (automatic end point) or until the potential reading indicates that the solution is more basic than the freshly prepared nonaqueous basic buffer solution (preselected end point).

11.4.4 On completion of the titration, rinse the electrodes and burette tip with the titration solvent, then with propan-2-ol, and finally with reagent grade water. Keep the electrodes immersed in water for at least 5 min before reusing for another titration to restore the aqueous gel layer of the glass electrode. If electrodes are found dirty and contaminated proceed as in 8.1. Store the electrodes in reagent grade water when not in use.

#### 11.5 Blanks:

11.5.1 For each set of samples, make a blank titration of 125 mL of the titration solvent. For manual titration, add 0.1-mol/L alcoholic KOH solution in 0.05-mL increments, waiting between each addition until a constant cell potential is reached. Record the meter and burette readings when the former becomes constant after each increment. For automatic titration proceed as in 11.4.

11.5.2 For each set of samples, make a blank titration of 125 mL of titration solvent, adding 0.1 mol/L alcoholic HCl solution in 0.05-mL increments in a manner comparable to that specified in 11.5.1.

## 12. Calculation

12.1 *Manual Titration*—Plot the volumes of the 0.1-mol/L alcoholic KOH solution added against the corresponding meter readings (see Fig. 2). Mark as an end point, only well-defined inflection point (Note 14) that is closest to the cell voltage corresponding to that obtained with the freshly prepared nonaqueous acidic and basic buffers. If inflections are ill-defined or no inflection appears (see Fig. 2, Curve B), mark the end point at the meter reading corresponding to that obtained with the appropriate freshly prepared nonaqueous buffer.

NOTE 14—One inflection point is generally recognizable by inspection whenever several successive 0.05-mL increments each produce a cell potential change greater than 15 mV at least 30 % greater than those produced by previous or subsequent increments of the same size. Generally, definite inflection points may be discerned only in regions where increments of the same size are used.

12.1.1 For all acid titrations on used oils, mark as an end point, the point on the curve that corresponds to the freshly prepared nonaqueous basic buffer end point (Note 15).

NOTE 15—The cooperative work done on acid number determinations on fresh oils, additive concentrates, and used oils indicated well-defined inflection points for fresh oils and additive concentrates, and generally ill-defined inflections, or no inflection points at all, for used oils.

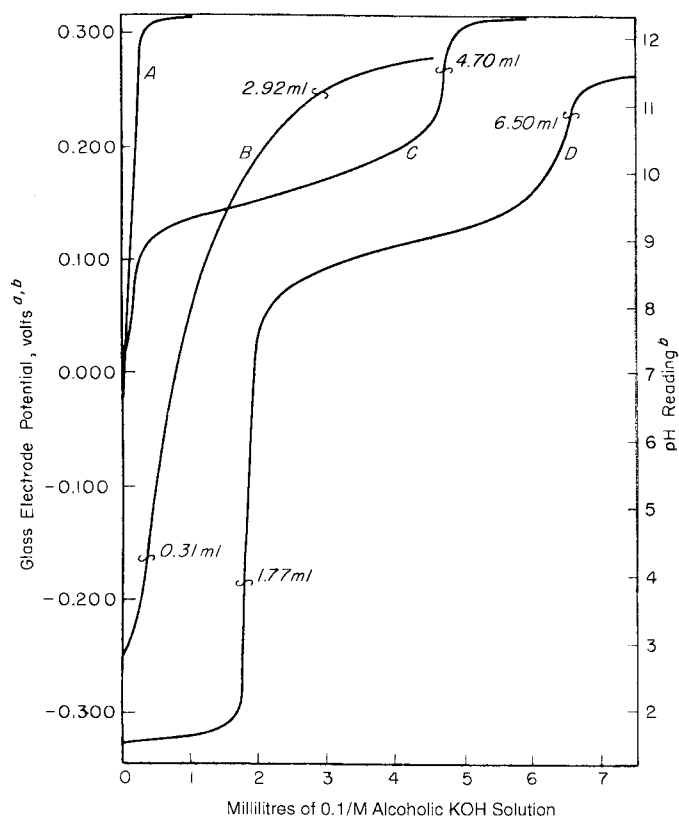
12.2 *Automatic Titration Method*—Mark the end points on the curves obtained in 11.4, in the same way as for the manual titration method.

12.3 *Method of Calculation*—The method in 12.3.1 is applicable to both manual and automatic methods.

12.3.1 Calculate the acid number and strong acid number as follows:

$$\text{Acid number, mg KOH/g} = (A - B) \times M \times 56.1/W \quad (1)$$

$$\text{Strong acid number, mg KOH/g} = (CM + Dm) \times 56.1/W \quad (2)$$



NOTE 1—Key: Curve A—Blank on 125 mL of titration solvent.  
 Curve B—10.00 g of used crankcase oil plus 125 mL of titration solvent. Since no sharp inflections are apparent, the end points are chosen at the meter readings obtained with the two nonaqueous buffer solutions.  
 Curve C—10.00 g of oil containing a weak acid plus 125 mL of titration solvent. The end point is chosen as the point at which the curve is most nearly vertical.  
 Curve D—10.00 g of oil containing weak and strong acids plus 125 mL of titration solvent. The end points are chosen as the points at which the curve is most nearly vertical.

**FIG. 2 Illustrative Titration Curves**

where:

- A = alcoholic KOH solution used to titrate sample to end point that occurs at the meter reading of the inflection point closest to the meter reading corresponding to basic nonaqueous buffer, or in case of ill-defined or no inflection point, to the meter reading corresponding to the basic nonaqueous buffer, mL,
- B = volume corresponding to A for blank titration, mL,
- M = concentration of alcoholic KOH solution, mol/L,
- m = concentration of alcoholic HCl solution, mol/L,
- W = sample, mass, g,
- C = alcoholic KOH solution used to titrate the sample to end point that occurs at a meter reading corresponding to acid nonaqueous buffer, mL, and
- D = alcoholic HCl solution used to titrate solvent blank to end point corresponding to C, mL.

## 13. Report

13.1 Report the results as acid number or strong acid number as follows:

$$\text{Acid number (Test Method D 664)} = (\text{result}) \quad (3)$$

Strong acid number (Test Method D 664) = (result) (4)

13.2 No modifications to this test method are permitted.

## 14. Precision and Bias

### 14.1 Acid Number:

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty. See Table 2.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test

method, exceed the following values only in one case in twenty. See Table 3.

### 14.2 Strong Acid Number:

14.2.1 Precision data have not been developed for strong acid number because of its rare occurrence in sample analysis.

14.3 *Bias*—The procedures in this test method have no bias because the acid values can be defined only in terms of the test method.

## 15. Keywords

15.1 acid number; lubricants; petroleum products; potentiometric; strong acid number; titration

**TABLE 2 Repeatability of Acid Number Determination**

Titration Mode	Fresh Oils and Additive Concentrates at Inflection Points		Used Oils at Buffer End Points	
	Manual	Automatic	Manual	Automatic
	Percentage of mean	7	6	5

**TABLE 3 Reproducibility of Acid Number Determination**

Titration Mode	Fresh Oils and Additive Concentrates at Inflection Points		Used Oils at Buffer End Points	
	Manual	Automatic	Manual	Automatic
	Percentage of mean	20	28	39

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