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Designation 177/96

British Standard 4457

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

This standard is issued under the fixed designation D664; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

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

## 1. Scope\*

1.1 This test method covers procedures for the determination of acidic constituents in petroleum products, lubricants, biodiesel and blends of biodiesel.

1.1.1 *Test Method A*—For 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.

1.1.2 *Test Method B*—Developed specifically for biodiesel and biodiesel blends with low acidity and slightly different solubility. This test method requires the use of an automatic titrator with automatic endpoint seeking capability.

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

D974 and D3339. There has not been any attempt to correlate this method with other non-titration methods.

NOTE 3—A few laboratories have made the observation that there is a difference in Test Method D664 results when aqueous versus nonaqueous buffers are used.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:<sup>2</sup>

- D974 Test Method for Acid and Base Number by Color-Indicator Titration
- D1193 Specification for Reagent Water
- D3339 Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

## 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.

<sup>1</sup> 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 D4739 has been developed as an alternative to the base number portion of D664.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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

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 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 titration solvent 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, biodiesel and blends of biodiesel 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 or biodiesel and blends under service conditions. No general correlation is known between acid number and the corrosive tendency of biodiesel and blends or 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  $\pm 0.005$  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 4—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.

6.1.2 *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 5—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  $\pm 0.02$  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<sub>2</sub>-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 6—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.

6.2.3 *Graduated Cylinder*—50 mL, or dispensing device capable of delivering  $50 \pm 0.5$  mL.

6.2.4 *Pipette*—2.0 mL, Class A.

6.2.5 *Titration Beaker*—250 mL, 125 mL, or suitable capacity, made of borosilicate glass or other suitable material.

## 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>3</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.

7.1.1 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, reference to water shall be understood to mean reagent water that meets the requirements of either Type I, II, or III of Specification **D1193**.

7.3 *Primary Standard*—Where specified, these samples, or samples of commercially available primary standards, are to be used in standardizing the volumetric solutions.

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

7.5 *Lithium Chloride*, LiCl.

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

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

7.8 *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.

NOTE 7—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.

7.9 *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.

## 8. Electrode System

8.1 *Preparation of Electrodes*—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, and 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 162 mV (20 to 25°C). If the difference is less than 162 mV, lift the sleeve of the electrode and insure electrolyte flow. Repeat the measurements. If the difference is still less than 162 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 one unit. If one or the other is changed, it shall be considered as different pair and shall be re-tested.

8.3 *Maintenance and Storage of Electrodes*—Cleaning the electrodes 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. 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.

NOTE 8—See **Appendix XI** for a possible procedure to check the electrode performance.

8.3.1 Clean the glass electrode at frequent intervals based on use and type of samples being analyzed (not less than once every week during continual use) by immersing in non-chromium containing, strongly oxidizing cleaning solution. The reference electrode shall be cleaned periodically when in

<sup>3</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 *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.

use or when a new electrode is installed. Drain the reference electrode at least once each week and refill with the fresh LiCl electrolyte as far as the filling hole. Ensure that there are no air bubbles in the electrode liquid. If air bubbles are observed, hold the electrode in a vertical position and gently tap it to release the bubbles. Maintain the electrolyte level in the reference electrode above that of the liquid in the titration beaker or vessel at all times.

8.3.2 Prior to each titration soak the prepared electrodes in water (pH 4.5 to 5.5) for at least 5 min. Rinse the electrodes with propan-2-ol immediately before use, and then with the titration solvent.

8.3.3 When not in use, immerse the lower half of the reference electrode in LiCl electrolyte. When the glass electrode is used, store it in water that has been acidified with HCl to a pH of 4.5 to 5.5. Do not allow electrodes 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.

8.3.3.1 *Electrode Life*—Typically, electrode usage is limited to 3 to 6 months depending, upon usage. Electrodes have a limited shelf life and shall be tested before use (see 8.2).

## 9. Standardization of Apparatus

9.1 *Determination of Meter Readings for the Aqueous Buffer Solutions*—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 aqueous 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 Immerse the electrodes in the pH 4 and the pH 11 aqueous buffers and stir each of them for approximately 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 for each of them. 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.

10.1.1 When applicable, refer to Practice D4057 (Manual Sampling) or Practice D4177 (Automatic Sampling) for proper sampling techniques.

10.1.2 When sampling used lubricants, the specimen shall be representative of the system sampled and shall be free of contamination from external sources.

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 (see 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 vigorous agitation of portions of the sample in the original container.

NOTE 11—When samples are visibly free of sediment, the heating procedure 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 removal of large contaminating particles.

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

## Test Method A

### 11. Reagents

11.1 See 7.

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

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

11.4 *Hydrochloric Acid Solution, Standard Alcoholic*, (0.1 mol/L). (**Warning**—See 11.2 and 7.8.) 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.

11.5 *Potassium Hydroxide Solution, Standard Alcoholic*, (0.1 mol/L). (**Warning**—See 7.7 and 7.8.) 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<sub>2</sub>) 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<sub>2</sub>-free water.

11.6 *Titration Solvent*—Add  $5 \pm 0.2$  mL of water to  $495 \pm 5$  mL of anhydrous propan-2-ol and mix well. Add  $500 \pm 5$  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.

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

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

12.1 Into a 250-mL beaker or a suitable titration vessel, introduce a weighed quantity of sample as recommended in

**TABLE 1 Recommended 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

**Table 1** (see **Note 13**) and add 125 mL of titration solvent (see **Note 14**). 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 throughout the determination at a rate sufficient to produce vigorous agitation without splattering and without stirring air into the solution.

**NOTE 13**—If it is suspected that the recommended sample size will foul the electrodes, a smaller sample size can be taken. Results using smaller sample size may not be equivalent to results obtained with the recommended sample size. The precision statement does not include results when using a smaller sample size.

**NOTE 14**—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. Results using chloroform may not be equivalent to results obtained using toluene. The precision statement does not include results when using chloroform.

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

### 12.3 Manual Titration Method:

12.3.1 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.

12.3.2 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.

12.3.3 In the intermediate regions (plateau) 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.

12.3.4 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 aqueous basic buffer.

12.3.5 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 starting another titration to restore the aqueous gel layer of the glass electrode. After 5 min in the water, rinse the electrodes with propan-2-ol then the titration solvent before proceeding to the next titration. If the electrodes are found to be dirty and contaminated, proceed as in **8.1**. Store electrodes according to **8.3.3**.

### 12.4 Automatic Titration Method:

12.4.1 Adjust the apparatus in accordance with the manufacturer's instructions to provide a dynamic mode of titrant addition.

12.4.2 Verify that the instrument will determine the amount of strong acid when the initial mV of the test sample, relative to the mV reading of the aqueous acidic buffer, indicates the presence of such acids. Record the volume of KOH added to reach the mV of the pH 4 aqueous buffer. This value is used to calculate the strong acid number. Proceed with the automatic titration and record potentiometric curves or derivative curves as the case may be.

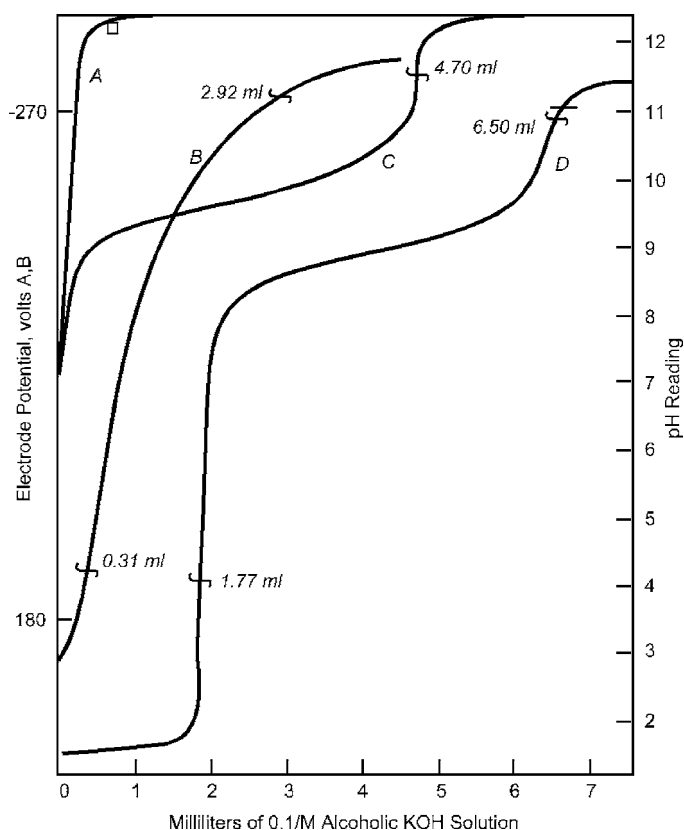
12.4.3 Titrate with the 0.1-mol/L alcoholic KOH solution. The apparatus shall be adjusted or programmed such that, when an inflection point, suitable for use in the calculation is approached, the rate of addition of titrant and volume of titrant added are based on the change in slope of the titration curve. The titrant shall be added in increments of a suitable size to achieve a potential difference of 5 to 15 mV per increment. Increment volume shall vary between 0.05 and 0.5 mL. The next increment shall be added if the signal does not change more than 10 mV in 10 s. The maximum waiting time in between increments shall not exceed 60 s.

12.4.4 The titration can be terminated when the signal reaches the pH 11 buffer potential past 200 mV. An equivalence point is recognizable if the first derivative of the titration curve produces a maximum, which is significantly higher than the noise produced by electrostatic effects. See also **13.1.1**.

12.4.5 The goal of cleaning is to rinse the residue from the previous sample and to rehydrate the electrode. On completion of the titration, rinse the electrodes and burette tip with titration solvent. If clean, then rinse with 2-propanol and then with water. Immerse the electrodes in pH 4.5–5.5 water for at least 3 to 5 min to rehydrate the aqueous gel layer of the glass electrode. Rinse with 2-propanol prior to beginning the next sample to remove the water. If sample residue remains after the rinse with titration solvent, another solvent such as toluene, xylene, heptane, or chloroform may be used for rinse. The rinse may be more effective if a beaker of solvent is used with strong stirring. Using automated equipment, cleaning may be done by rinsing with titration solvent, soaking with stirring in a solvent such as toluene, xylene, heptane, or chloroform for 45 s, soaking briefly in 2-propanol to remove the solvent, then soaking in pH 4.5–5.5 water 3 to 5 min to rehydrate. Dip in 2-propanol briefly to remove water before beginning the next sample. The same solvent cleaning beaker, 2-propanol beaker and water beaker may be used for a short series of samples. They should be changed at reasonable intervals, before contamination builds up. The user shall ensure that the electrode is adequately cleaned and hydrated. If electrodes are found dirty and contaminated, proceed as in **8.1**. Store electrodes according to **8.3.3**.

**NOTE 15**—When acid numbers about or below 0.1 are expected, better precision can be obtained by modifying the method in one or more ways, such as by substituting a 0.01 or 0.05 M alcoholic KOH solution; increasing the sample size above 20 g; or switching from a manual operated burette (that is, graduated in 0.05 mL divisions) to an automated burette that can dispense smaller increments of the KOH solution, if samples are being analyzed by manual titration.

### 12.5 Blanks:



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 aqueous 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. 1 Illustrative Titration Curves

12.5.1 For each set of samples and for every new batch of titration solvent, perform a blank titration of 125 mL of the solvent. For manual titration, add 0.1-mol/L alcoholic KOH solution in 0.01 to 0.05-mL increments, waiting between each addition until a constant cell potential is reached. Record the meter and readings when the former becomes constant after each increment. For automatic titration, use the same mode of titration as for the determination of the acidic property of the sample but use smaller increments of titrant addition, 0.01 to 0.05-mL. Recheck the blank periodically based on the sample load.

12.5.2 When strong acids are present and a strong acid number is to be determined, perform a blank titration of 125 mL of the titration solvent, adding 0.1 mol/L alcoholic HCl solution in 0.01 to 0.05-mL increments in a manner comparable to that specified in 12.5.1.

### 13. Calculation

13.1 *Manual Titration*—Plot the volumes of the 0.1-mol/L alcoholic KOH solution added against the corresponding meter readings (see Fig. 1). Mark as an end point only a well-defined inflection point (see Note 16) that is closest to the cell voltage

corresponding to that obtained with the aqueous acidic or basic buffer. If inflections are ill defined or no inflection appears (see Fig. 1, Curve B), mark the end point at the meter reading corresponding to that obtained with the appropriate aqueous buffer.

NOTE 16—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.

13.1.1 Some additive chemistry may produce an inflection point beyond the buffer endpoint. For additives, take the last inflection point for calculation. *If using an automatic titrator, a change in the instrument parameters may be required to detect this type of endpoint.*

13.1.2 For all acid titrations on used oils, mark as an end point, the point on the curve that corresponds to the meter reading for an aqueous basic buffer (pH 11) and the meter reading for the aqueous acid buffer (pH 4) when strong acids are indicated.

NOTE 17—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.

13.2 *Automatic Titration Method*—Mark the end points on the curves obtained in 12.4, in the same way as for the manual titration method.

13.3 *Method of Calculation*—The method of calculation in 13.3.1 is applicable to both manual and automatic methods.

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

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

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

where:

- A = volume of 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 the pH 11 aqueous buffer, or in case of ill-defined or no inflection point, to the meter reading corresponding to the pH 11 aqueous buffer, mL. For additives, A is the volume of alcoholic KOH at the last inflection point,
- 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 the pH 4 aqueous buffer, mL, and
- D = alcoholic HCl solution used to titrate solvent blank to end point corresponding to C, mL.

### 14. Quality Control Checks

14.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

NOTE 18—Because used oils, particularly used engine oils, are known to change during storage, such samples may not be suitable for this purpose.

14.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.<sup>4</sup>

14.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the total testing process.<sup>4</sup> Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

14.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC precision should be periodically checked against the precision listed in the Precision and Bias section of this test method to ensure data quality.

14.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. Because the base number can vary while the QC sample is in storage, when an out-of-control situation arises, the stability of the QC sample can be a source of the error.

## 15. Report

15.1 Given there are two different ways to determine the endpoint, report the type of endpoint used: inflection point or buffer endpoint. Report sample size used if differs from the recommended sample size. Also, report if chloroform was used as solvent. Report the results as acid number or strong acid number as follows:

$$\text{Acid number (Test Method D664, Test Method A)} = (\text{result}) \quad (3)$$

$$\text{Strong acid number (Test Method D664, Test Method A)} = (\text{result}) \quad (4)$$

15.2 For used oil samples report also the date of testing and, when available, the date the sample was taken (see 10.2).

## 16. Precision and Bias<sup>5</sup>

### 16.1 Acid Number:

16.1.1 *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.

$$\text{Fresh Oils} = 0.044(X + 1) \quad (5)$$

$$\text{Used Oils Buffer end point} = 0.117 X \quad (6)$$

where:

$X$  = the average of the two test results.

16.1.2 *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.

$$\text{Fresh Oils} = 0.141(X + 1) \quad (7)$$

$$\text{Used Oils Buffer end point} = 0.44X \quad (8)$$

where:

$X$  = the average of the two test results.

### 16.2 Strong Acid Number:

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

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

## Test Method B

### 17. Reagents

17.1 See Section 7.

17.2 *Potassium Hydroxide Solution, Standard Alcoholic (0.01 mol/L)*—(Warning—See 7.7 and 7.8.) Add 0.56 g of potassium hydroxide (KOH) to approximately 1 L of propan-2-ol or weigh  $1.122 \pm 0.02$  g of 50 % KOH into 1 L of propan-2-ol. Boil gently for 10 min to effect solution. Allow the solution to stand protected from carbon dioxide (CO<sub>2</sub>) 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 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 mol/L by potentiometric titration of pipetted quantities of potassium acid phthalate solution dissolved in CO<sub>2</sub>-free water.

17.3 *Potassium Acid Phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), primary standard, dried*—Place 10 to 20 g of primary standard potassium acid phthalate (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) of 100-mesh fineness, in a weighing bottle at 120°C for 2 h. Stopper the container and cool it in a desiccator.

17.4 *Potassium Acid Phthalate (KHP) Solution (0.01 mol/L)*—For a volumetric standard, weigh approximately 1.0 g and record the weight to the nearest  $\pm 0.0001$  g of dried potassium acid phthalate primary standard (KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) and make up to the mark with DI Type II water in a 500 mL volumetric flask. Alternatively for a weight-based standard, weigh the KHP and record the weight to the nearest 0.0001 g and record the total amount of water and KHP to the nearest

<sup>4</sup> ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th edition, ASTM International, W. Conshohocken, PA.

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1551.

±0.01 g and express the concentration as mg KHP/g of solution. Mix thoroughly to dissolve the solution.

## 18. Procedure

### 18.1 Standardization of the Titrant 0.01 M Alcoholic KOH:

18.1.1 Weigh 2 g of KHP solution into a 125 mL or suitable size beaker and record the weight to the nearest 0.0001 g if using weight-based standard or pipette 2 mL of KHP solution into a vessel and add approximately 50 mL of CO<sub>2</sub> free water. Titrate the solution to determine the titer of 0.01M KOH. This volume of KHP solution will use approximately 2 mL of the 0.01 M KOH.

18.1.2 Prepare two additional KHP solutions to standardize the titrant as in 18.1.

18.1.3 Use the three determinations to calculate the average concentration (mol/L) of the KOH. The average of the titrant mol/L determinations should agree ±0.0005 M.

18.2 *Determination of the Solvent Blank*—Adjust the apparatus in accordance with the manufacturer's instructions to provide a dynamic mode of titration. Addition of titrant volume increments should not be greater than 0.2 mL. Measure precisely 50 mL of propan-2-ol using a graduated cylinder, pipet or automated dispensing device capable of dispensing 50 ± 0.5 mL into a 125 mL or suitable size beaker. Stir the solution and titrate. Record the volume (mL) of KOH to ±0.01 mL used to titrate to the inflection point.

### 18.3 Analysis of the Sample:

18.3.1 Adjust the apparatus in accordance with the manufacturer's instructions to provide a dynamic mode of titrant addition.

18.3.2 Weigh 5 g of biodiesel into a 125 mL or suitable size beaker on an analytical balance and record the weight to the nearest 0.0001 g. Measure 50 ± 0.50 mL of IPA using a pipet or automated dispensing device into a suitable beaker. Prepare the electrodes as directed in 8.1. 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 throughout the determination at a rate sufficient to produce vigorous agitation without splattering and without stirring air into the solution.

NOTE 19—It is important that the same volume of titration solvent ±0.5 mL is used for the blank and samples or inconsistent results can occur.

18.3.3 Select the right burette, fill with 0.01-mol/L alcoholic KOH solution, and place the burette in position on the titration assembly, ensuring that the tip is immersed about 25 mm in titration vessel liquid and titrate.

18.3.4 On completion of the titration, rinse the electrodes and burette tip with propan-2-ol, followed by water. Immerse the electrodes in water for at least 2 min before starting another titration to restore the aqueous gel layer of the glass electrode. Rinse the electrodes with propan-2-ol prior to running the next sample. If electrodes are found dirty and contaminated, proceed as in 8.1. Store electrodes according to 8.3.3.

18.3.5 Multiple titration inflection points are often found during the analysis associated with organic acids which form over time due to the oxidation of biodiesel over prolonged

storage periods. The volume of titrant for the last well defined endpoint should be used to calculate the total acidity.

## 19. Calculation or Interpretation of Results

### 19.1 Calculation of KOH solution molarity, mol/L:

19.1.1 Calculation of KOH molarity, mol/L by Volume of mol/L of KHP Solution:

$$\text{KHP solution concentration, } \frac{\text{mol}}{\text{L}} \quad (9)$$

$$= \frac{(\text{weight of KHP, g})}{204.23 * (\text{total volume of KHP solution, L})}$$

$$\text{KOH molarity, } \frac{\text{mol}}{\text{L}} \quad (10)$$

$$= \frac{(2.00 \text{ mL KHP solution}) \left( \text{concentration of KHP solution, } \frac{\text{mol}}{\text{L}} \right)}{\text{volume of KOH, mL}}$$

19.1.2 Calculation of KOH mol/L by Weight of mg/g of KHP Solution:

$$\text{KHP solution concentration, } \frac{\text{mg}}{\text{g}} \quad (11)$$

$$= \frac{(\text{weight of KHP, g}) * 1000}{204.23 * (\text{total weight of KHP solution, g})}$$

$$\text{KOH molarity, } \frac{\text{mol}}{\text{L}} \quad (12)$$

$$= \frac{(\text{weight of KHP solution, g}) \left( \text{concentration of KHP solution, } \frac{\text{mg}}{\text{g}} \right)}{\text{volume of KOH, mL}}$$

NOTE 20—The average mol/L of three determinations should be used for the determination of the Acid number. The average should agree within ±0.0005 M.

### 19.2 Calculation of the Acid Number:

$$\text{Acid number, mg KOH/g} = (A - B) * M * 56.1 / W \quad (13)$$

where:

*A* = Volume of alcoholic KOH solution used to titrate sample to last inflection end point, mL,

*B* = volume corresponding to *A* for blank titration, mL,

*M* = concentration of alcoholic KOH solution, mol/L, and

*W* = sample, mass, g.

## 20. Quality Control Checks

20.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is, representative of the samples typically analyzed, if possible.

NOTE 21—Because biodiesel is known to change during long-term storage, such samples may not be suitable for this purpose. The analyst may use the Potassium Acid Phthalate solution 0.01M as an acceptable QC standard. When used as a QC standard, the KHP solution will provide a good indicator when restandardization of the titrant (0.01M KOH in IPA) is necessary. No data is available on the shelf life of the KHP solution. Commercially prepared standard solutions may also be used.

20.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.<sup>4</sup>

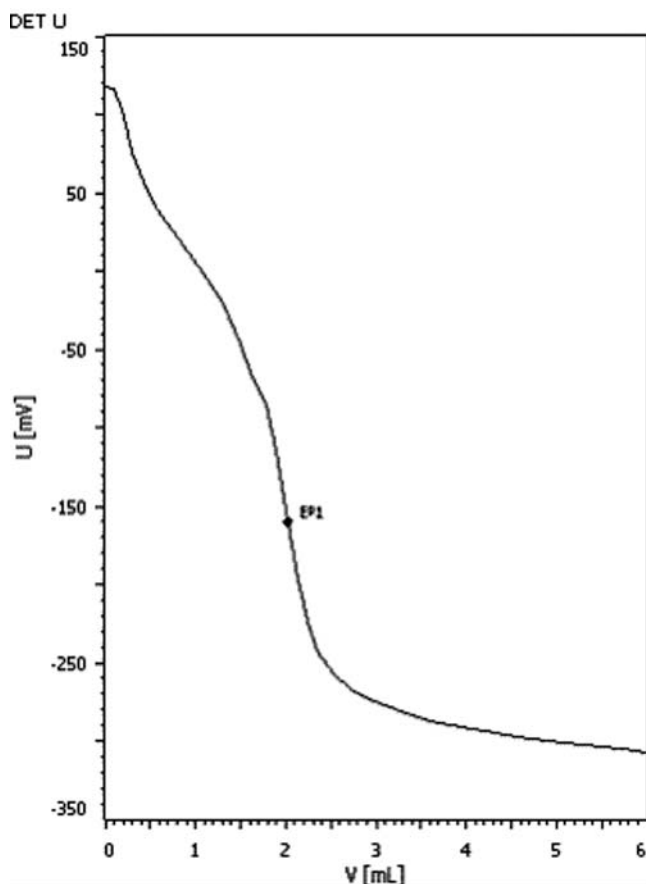


FIG. 2 Illustrative Titration Curve of Biodiesel Sample

20.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the total testing process.<sup>4</sup> Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

20.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC precision should be periodically checked against the precision listed in the Precision and Bias Section of this test method to ensure data quality.

20.5 It is recommended that a QC standard be routinely analyzed at a concentration level in the same range as the samples analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

TABLE 2 Acid Number of Biodiesel<sup>A</sup>

Repeatability = $0.264E-01 * X^{0.4}$ mg/kg KOH
Reproducibility = $0.177 * X^{0.4}$ mg/kg KOH

<sup>A</sup> The degree of freedom for R is less than 30 but greater than 15. Samples 4,5,6,9 were excluded as these samples were below the Limit of Quantitation of the test method.

## 21. Report

21.1 Report acid number of biodiesel and blends to the 0.01 as mg KOH/g of sample (Test Method D664, Test Method B).

## 22. Precision and Bias<sup>6</sup>

22.1 The precision of this test method is based on an interlaboratory study of D664 conducted in 2009. Seven laboratories participated in this study, however the results from one laboratory were excluded from the precision calculations due to a fairly consistent bias in their reported values. Each of the laboratories was asked to report replicate test results for eleven different diesel and biodiesel blends and a blank. Every “test result” reported represents a single determination or measurement. D2PP was used for the analysis of the study data; the details are given in ASTM Research Report RR:D02-1727.

22.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the “r” value for that material; “r” is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory. Repeatability limits are listed in Table 2.

22.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the “R” value for that material; “R” is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories. Reproducibility limits are listed in Table 2.

22.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

22.1.4 Any judgment in accordance with statements 22.1.1 and 22.1.2 would have an approximate 95% probability of being correct.

22.2 The precision statement was determined through statistical examination of 138 results, from six laboratories, on a total of eleven different petroleum blends and a blank.

22.3 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

## 23. Keywords

23.1 acid number; B5; B10; B20; B100; biodiesel; biodiesel blend; lubricants; petroleum products; potentiometric; strong acid number; titration

<sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1727.

**APPENDIX**
**(Nonmandatory Information)**
**X1. CHECK FOR ELECTRODE PERFORMANCE**

X1.1 The kinetic electrode test measures the kinetic response of the electrode. Electrodes can calibrate with acceptable slope and intercept values yet still not have a response good enough for titration. The speed of response and subsequent stability is important for a titration electrode. A manual check is described in this Appendix that can be carried out with a pH meter or titrator set to read millivolts continuously.

X1.2 The essence of this check is to challenge the electrode coming from rest in a water solution with buffers and measure the potential after 30 and 60 s. A fast electrode reaches a stable point in less than 30 s and changes little from 30 to 60 s. Use buffers pH 4, pH 7, and pH 11 for this check, as needed.

**X1.3 Procedure**

X1.3.1 Set the titrator or pH meter to read millivolts continuously. Have provision for stirring the buffer solution at the same speed used for the titrations.

X1.3.2 Allow the electrode to stabilize for 1 min in distilled or equivalent deionized water.

X1.3.3 Remove the electrodes from the water, and place them in the pH 4 buffer. Start a stopwatch at about the moment when the buffer touches the electrode.

X1.3.4 After 30 s, note the potential. After an additional 30 s, note the potential again. The difference between the two potentials is termed the drift.

X1.3.5 Repeat the procedure for pH 7 buffer and pH 11 buffer.

X1.4 Calculate the drift for each of the three buffers. The electrode response may be judged as follows:

- drift < 1 excellent
- 1 < drift < 2 good
- 2 < drift < 3 acceptable
- 3 < drift < 4 questionable
- 4 < drift unacceptable

X1.5 The difference between the 60-s potentials for pH 4 buffer and pH 7 buffer should be greater than 162 mV, or 54 mV / pH number. Electrodes with a slope less than 54 mV / pH number are not reliable for titration.

**SUMMARY OF CHANGES**

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D664–11) that may impact the use of this standard. (Approved July 15, 2011.)

- (1) Updated Section 22.
- (2) Added Table 2.

- (3) Added new research report.

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D664–09a) that may impact the use of this standard. (Approved May 15, 2011.)

- (1) Updated 3.1.1.

- (2) Corrected equation formatting in 19.1.

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