Designation: D974 – 22

Designation: 139/98 (2017)

Standard Test Method for Acid and Base Number by Color-Indicator Titration[1,2]

This standard is issued under the fixed designation D974; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

1. Scope*

1.1 This test method covers the determination of acidic or basic constituents (Note 1) in petroleum products[3] and lubricants soluble or nearly soluble in mixtures of toluene and isopropyl alcohol. It is applicable for the determination of acids or bases whose dissociation constants in water are larger than 10^{-9}; extremely weak acids or bases 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 considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, and addition agents such as inhibitors and detergents. Similarly, constituents considered to have basic properties include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, salts of heavy metals, and addition agents such as inhibitors and detergents.

NOTE 2—This test method is not suitable for measuring the basic constituents of many basic additive-type lubricating oils. Test Method D4739 can be used for this purpose.

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

NOTE 3—Oils, such as many cutting oils, rustproofing oils, and similar compounded oils, or excessively dark-colored oils, that cannot be analyzed for acid number by this test method due to obscurity of the color-indicator end point, can be analyzed by Test Method D664. The acid numbers obtained by this color-indicator test method need not be numerically the same as those obtained by Test Method D664, the base numbers obtained by this color indicator test method need not be numerically the same as those obtained by Test Method D4739, but they are generally of the same order of magnitude.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D117 Guide for Sampling, Test Methods, and Specifications for Electrical Insulating Liquids

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

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

[1] This test method is under the jurisdiction of ASTM International Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of ASTM Subcommittee D02.06 on Analysis of Liquid Fuels and Lubricants. The technically equivalent standard as referenced is under the jurisdiction of the Energy Institute Subcommittee SC-C-4.

Current edition approved Nov. 1, 2022. Published January 2023. Originally approved in 1948. Last previous edition approved in 2021 as D974 – 21. DOI: 10.1520/D0974-22.

This test method was adopted as a joint ASTM-IP standard in 1965.

[2] This test method has been developed through the cooperative effort between ASTM and the Energy Institute, London. ASTM and IP standards were approved by ASTM and EI technical committees as being technically equivalent but that does not imply both standards are identical.

[3] Statements defining this test method, its modification, and its significance when applied to electrical insulating oils of mineral origin will be found in Guide D117.

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

D4739 Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration

3. Terminology

3.1 *Definitions:*

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

3.1.1.1 *Discussion*—In this test method, the indicator is *p*-naphtholbenzein titrated to a green/green-brown end point in a toluene-water-isopropanol solvent.

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

3.1.2.1 *Discussion*—In this test method, the indicator is *p*-naphtholbenzein titrated to an orange end point in a toluene-water-isopropanol solvent.

3.1.3 *used oil, n*—any oil that has been in a piece of equipment (for example, an engine, gearbox, transformer, or turbine) whether operated or not. **D4175**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *strong acid number, n*—the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a boiling water extract of the sample to a golden-brown end point using methyl orange solution.

4. Summary of Test Method

4.1 To determine the acid or base number, the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end point indicated by the color change of the added *p*-naphtholbenzein solution (orange in acid and green-brown in base). To determine the strong acid number, a separate portion of the sample is extracted with boiling water and the aqueous extract is titrated with potassium hydroxide solution, using methyl orange as an indicator.

5. Significance and Use

5.1 New and used petroleum products can contain basic or 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 acids or bases. This number, whether expressed as *acid number* or *base number*, is a measure of this amount of acidic or basic substances, respectively, in the oil—always under the conditions of the test. This 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; however, 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 corrosive properties, the test 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. Compounded engine oils can and usually do have both acid and base numbers in this test method.

6. Apparatus

6.1 *Burets (with the following dimensions):*

50 mL buret graduated in 0.1 mL subdivisions
10 mL buret graduated in 0.05 mL or smaller subdivisions
5 mL with 0.02 mL subdivisions

NOTE 4—An automated buret capable of delivering titrant amounts in 0.05 mL or smaller increments can be used but the stated precision data were obtained using manual burets only.

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.[5] 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*—References 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 *Isopropyl Alcohol,* anhydrous (less than 0.9 % water). (**Warning**—Flammable.)

7.4 *Hydrochloric Acid Solution, Standard Alcoholic*—(0.1 *M*)—Mix 9 mL of concentrated hydrochloric acid (**Warning**—Corrosive, fumes cause irritation) (HCl, sp gr 1.19) with 1000 mL of anhydrous isopropyl alcohol (2-propanol) (**Warning**—See 7.3). Standardize frequently enough to detect molarity changes of 0.0005 (Note 6), preferably by electrometric titration of approximately 8 mL (accurately measured) of the 0.1 *M* alcoholic KOH solution diluted with 125 mL of carbon dioxide-free water. When an electrometric titration is used for the standardization, the end point shall be a well-defined inflection point closest to the cell voltage for the acidic buffer solution. When a colorimetric titration is used for the standardization, titrate to the first stable appearance of the orange color with methyl orange indicator.

NOTE 5—Commercially available reagents may be used in place of the laboratory preparations when they are certified to be in accordance with 7.1.

NOTE 6—To simplify calculations, both the standard KOH and HCl solutions can be adjusted so that 1.00 mL is equivalent to 5.00 mg of KOH.

7.5 *Methyl Orange Indicator Solution*—Dissolve 0.1 g of methyl orange in 100 mL of water.

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.6 *p-Naphtholbenzein Indicator*[6,7] Solution—The *p*-naphtholbenzein shall meet the specifications given in Annex A1. Prepare a solution of *p*-naphtholbenzein in titration solvent equal to 10 g/L ± 0.01 g/L.

7.7 *Potassium Hydroxide Solution, Standard Alcoholic* (0.1 *M*)—Add 6 g of solid KOH (**Warning**—Highly corrosive to all body tissue) to approximately 1 L of anhydrous isopropyl alcohol (containing less than 0.9 % water) in a 2 L Erlenmeyer flask. Boil the mixture gently for 10 min to 15 min, stirring to prevent the solids from forming a cake on the bottom. Add at least 2 g of barium hydroxide ($Ba(OH)_2$) (**Warning**—Poisonous if ingested, strongly alkaline, causes severe irritation producing dermatitis) and again boil gently for 5 min to 10 min. Cool to room temperature, allow to stand for several hours, and filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide (CO_2) during filtration. Store the solution in a chemically resistant dispensing bottle out of contact with cork, rubber, or saponifiable stopcock lubricant and protected by a guard tube containing soda lime or soda nonfibrous silicate absorbent (Ascarite, Carbosorb, or Indecarb).

7.7.1 *Standardization of Potassium Hydroxide Solution*—Standardize frequently enough to detect changes of 0.0005 *M*. One way to do this is as follows: Weigh, to the nearest 0.1 mg approximately 0.2 g of potassium acid phthalate, which has been dried for at least 1 h at 110 °C ± 1 °C and dissolve in 40 mL ± 1 mL of water, free of CO_2. Titrate with the potassium hydroxide alcoholic solution to either of the following end points: (*1*) When the titration is electrometric, titrate to a well-defined inflection point at the voltage that corresponds to the voltage of the basic buffer solution, or (*2*) When titration is colorimetric, add six drops of phenolphthalein indicator solution and titrate to the appearance of a permanent pink color. Perform the blank titration on the water used to dissolve the potassium acid phthalate. Calculate the molarity using the following equation:

$$\text{Molarity} = \frac{W_p}{204.23} \times \frac{1000}{V - V_b} \quad (1)$$

where:

W_p = weight of the potassium acid phthalate, g,
204.23 = molecular weight of the potassium acid phthalate,
V = volume of titrant used to titrate the salt to the specific end point, mL, and
V_b = volume of titrant used to titrate the blank, mL.

7.7.2 *Phenolphthalein Indicator Solution*—Dissolve 0.10 g of solid pure phenolphthalein in 50 mL of water and 50 mL of ethyl alcohol.

NOTE 7—Commercially available reagents may be used in place of the laboratory preparations.

NOTE 8—Because of the relatively large coefficient of cubic expansion of organic liquids, such as isopropyl alcohol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of samples.

7.8 *Titration Solvent*—Prepare by mixing toluene, water, and anhydrous isopropyl alcohol in the ratio 100:1:99.

TABLE 1 Size of Sample[A]

Acid Number or Base Number	Size of Sample, g	Sensitivity of Weighing, g
New or Light Oils		
0.0 to 3.0	20.0 ± 2.0	0.05
Over 3.0 to 25.0	2.0 ± 0.2	0.01
Over 25.0 to 250.0	0.2 ± 0.02	0.001
Used or Dark-Colored Oils		
0.0 to 25.0	2.0 ± 0.2	0.01
Over 25 to 250.0	0.2 ± 0.02	0.001

[A] Light-colored samples of low acid number permit the use of 20 g samples to obtain more precise results. The sample size for dark-colored oils is limited to the quantity specified to minimize possible interference by the dark color.

8. Preparation of Used Oil Samples

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

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

8.1.2 Agitate used oil samples thoroughly to ensure that any sediment present is homogeneously suspended before analysis, as the sediment can be acidic or basic or have adsorbed acidic or basic material from the sample. When necessary, samples are warmed to aid mixing.

NOTE 9—As used oils can change appreciably in storage, samples should be tested as soon as possible after removal from the lubricating system and the dates of sampling and testing, if known, should be noted.

9. Procedure for Acid Number

9.1 Into an appropriate size Erlenmeyer flask or a beaker, introduce a weighed quantity of the sample as given in Table 1. Add 100 mL of the titration solvent and 0.5 mL of the indicator solution, and without stoppering, swirl until the sample is entirely dissolved by the solvent. If the mixture assumes a yellow-orange color, proceed as directed in 9.2; if it becomes green or green-black, and base number analysis is required, proceed as directed in Section 10.

NOTE 10—In routine analysis, the indicator may be pre-mixed with the titration solvent before adding to the sample.

9.2 Without delay, titrate at a temperature below 30 °C (Note 13). Add 0.1 *M* KOH solution in increments and mix to disperse the KOH as necessary (see Note 11). Shake vigorously near the end point, but avoid dissolving carbon dioxide (CO_2) in the solvent. (In the case of acidic oils, the orange color changes to a green or green-brown as the end point is approached.) When the solution first turns green or green-brown, reduce the increment size to dropwise (manual buret) or between 0.01 mL and 0.05 mL (automated buret). Continue until a persistent green or green-brown end point is reached (see Note 12) and held for a minimum of 15 s after the addition of the last increment or if it reverses with two drops of 0.1 *M* HCl.

[6] In a 2006 study, only Kodak, Baker (Mallinkrodt), Fluka, and Aldrich were found to meet the specifications in Annex A1. However, Kodak brand is no longer available.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1626. Contact ASTM Customer Service at service@astm.org.