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Standard Test Method for Acid and Base Number by Color-Indicator Titration¹

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 products² 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*:³

- 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
- D4175** Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- 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.

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee **D02.06** on Analysis of Liquid Fuels and Lubricants.

In the IP, this test method is under the jurisdiction of the Standardization Committee. This test method was adopted as a joint ASTM-IP standard in 1965.

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² 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**.

³ 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

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.⁴ 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.

7.6 *p-Naphtholbenzein Indicator*^{5,6} Solution—The *p*-naphtholbenzein shall meet the specifications given in **Annex**

⁴ 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.

⁵ 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.

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 (CO₂) 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 CO₂. 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 Strict observance of the sampling procedure described in **8.2** is necessary, since the sediment itself is acidic or basic or has adsorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

8.2 Heat the sample (**Note 9**) of used oil to 60 °C ± 5 °C in the original container and agitate until all sediment is homogeneously suspended in the oil (**Note 10**). If the original container is of opaque material, or if it is 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, and transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container. 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 9**).

NOTE 9—When samples are visibly free of sediment, the heating procedure described in **8.2** may be omitted. When samples are visibly free of sediment, the straining procedure may also be omitted.

NOTE 10—As used oil 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 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 11—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 14**). Add 0.1 M KOH solution in increments and mix to disperse the KOH as necessary (see **Note 12**). Shake vigorously near the end point, but avoid dissolving carbon dioxide (CO₂) 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

⁶ 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.

(see **Note 13**) 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.

NOTE 12—When acid numbers about or below one are expected, better precision can be obtained by substituting 0.01 M or 0.05 M solutions in **9.2** and **9.3**. This substitution was not included in the development of a precision statement.

NOTE 13—To observe the end point of dark-colored oil, shake the flask vigorously to produce momentarily a slight foam when the color change occurs as the last few drops of titrant are added and observe the titration under a white fluorescent lamp at bench top level.

NOTE 14—The temperature can be measured by any suitable temperature measuring device.

NOTE 15—An automated photometric device may also be used to detect the titration end point. However, the precision estimates given in Section **15** may not apply to this mode of titration.

9.3 Blank—Perform a blank titration on 100 mL of the titration solvent and 0.5 mL of the indicator solution, adding 0.1 mL or less increments of the 0.1 M KOH solution.

9.3.1 The titration solvent usually contains weak acid impurities which react with the strongly basic components of the sample. To correct the base number for the sample, determine an *acid number* blank upon the solvent.

10. Procedure for Base Number

10.1 If the titration solvent containing the dissolved sample assumes a green or greenish-brown color after the indicator is added (**9.1**), carry out the titration as described in **9.2**, but use 0.1 M HCl and titrate until the green-brown color changes to orange.

10.2 Blank—Perform a blank titration as directed in **9.3**.

11. Procedure for Strong Acid Number

11.1 Introduce approximately 25 g of a representative sample, weighed to the nearest 0.1 g, into a 250 mL separatory funnel and add 100 mL of boiling water. Shake vigorously and drain the water phase, after separation, into a 500 mL titration flask. Extract the sample twice more with 50 mL portions of boiling water, adding both extracts to the titration flask. To the combined extracts add 0.1 mL of methyl orange indicator solution and, if the solution becomes pink or red, titrate with 0.1 M KOH solution until the solution becomes golden brown in color. If the initial color is not pink or red, report the strong acid number as zero. (See **Note 15**.)

11.2 Blank—Into a 250 mL Erlenmeyer flask, introduce 200 mL of the same boiling water as used for the sample titration. Add 0.1 mL of methyl orange indicator solution. If the indicator color is yellow-orange, titrate with 0.1 M HCl to the same depth and shape of color obtained in the titration of the sample. If the indicator color is pink or red, titrate with 0.1 M KOH solution to the same end point as that used in the sample titration.

12. Quality Control Checks

12.1 Confirm the performance of the equipment or the procedure each day it is in use, by analyzing a quality control (QC) sample. It is advisable to analyze additional QC samples as appropriate, such as at the end of a batch of samples or after a fixed number of samples to ensure the quality of the results.

Analysis of results from these QC samples can be carried out using control chart techniques.⁷ When the result of a test on a QC sample exceeds the control limits of the laboratory, corrective action, such as instrument recalibration may be required. An ample supply of QC sample material shall be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions. If possible, the QC sample shall be representative of samples typically analyzed and the average value and control limits of the QC sample shall be determined prior to monitoring the measurements process. The precision for the QC sample must be compared against that given in the Precision and Bias section of this test method in order to verify that the instrument is functioning correctly.

NOTE 16—Because the acid and base numbers 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.

13. Calculation

13.1 Calculate the acid number as follows:

$$\text{Acid number, mg of KOH/g} = [(A - B)M \times 56.1]/W \quad (2)$$

where:

A = KOH solution required for titration of the sample (**9.2**), mL,

B = KOH solution required for titration of the blank (**9.3**), mL,

M = molarity of the KOH solution, and

W = sample used, g.

13.2 Calculate the strong-acid number as follows:

13.2.1 If the blank titration is made with acid:

$$\text{Strong - acid number, mg of KOH/g} = [(CM + Dm) \times 56.1]/W \quad (3)$$

where:

C = KOH solution required to titrate the water extract (**11.1**), mL,

M = molarity of KOH solution,

D = HCl solution required to titrate the blank solution (**11.2**), mL,

m = molarity of the HCl solution, and

W = sample used, g.

13.2.2 If the blank titration is made with base:

$$\text{Strong - acid number, mg of KOH/g} = [(C - D)M \times 56.1]/W \quad (4)$$

where:

C = KOH solution required to titrate the water extract (**11.1**), mL,

D = KOH solution required to titrate the blank solution (**11.2**), mL,

M = molarity of the KOH solution, and

W = sample used, g.

13.3 Calculate the base number as follows:

$$\text{base number, mg of KOH/g} = [(Em + FM) \times 56.1]/W \quad (5)$$

⁷ MNL 7, *Manual on Presentation of Data Control Chart Analysis*, Section 3: Control Charts for Individuals, 6th ed., ASTM International, W. Conshohocken, PA, 1990.