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## Standard Test Method for Acid and Base Number by Color-Indicator Titration<sup>1,2</sup>

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 ( $\epsilon$ ) 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<sup>3</sup> 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

<sup>1</sup> 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.

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

<sup>2</sup> 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.

<sup>3</sup> 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**.

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:<sup>4</sup>

**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

<sup>4</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

## 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.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—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.

<sup>5</sup> 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<sup>6,7</sup> 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  $\pm$  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)<sub>2</sub>) (**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<sub>2</sub>) 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  $\pm$  1 °C and dissolve in 40 mL  $\pm$  1 mL of water, free of CO<sub>2</sub>. 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

<sup>6</sup> 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.

<sup>7</sup> 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.

**TABLE 1 Size of Sample<sup>A</sup>**

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

<sup>A</sup> 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.

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.

## 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<sub>2</sub>) 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.

NOTE 11—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 12—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 13—The temperature can be measured by any suitable temperature measuring device.

NOTE 14—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 14.)

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.<sup>8</sup> 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 15—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:

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

<sup>8</sup> MNL 7, *Manual on Presentation of Data Control Chart Analysis*, Section 3: Control Charts for Individuals, 6th ed., ASTM International, W. Conshohocken, PA, 1990.

where:

$E$  = HCl solution required for titration of the sample (Section 10), mL,  
 $m$  = molarity of the HCl solution,  
 $F$  = KOH required for titration of the acid number blank, mL,  
 $M$  = molarity of the KOH solution, and  
 $W$  = sample used, g.

## 14. Report

14.1 Report the result as acid number, strong acid number, or base number as follows:

Acid number (D974) = (result)  
 Strong acid number (D974) = (result)  
 Base number (D974) = (result)

14.2 Report the acid or base number values as follows:

Acid Number	Report Results
< 0.02	< 0.02
0.02 to < 1.0	Report to the nearest 0.01
1.0 to 2.0	Report to the nearest 0.1

## 15. Precision and Bias

15.1 *Precision*—This precision section applies only to new, light-colored, straight mineral oils and new and used inhibited steam turbine oils. Insufficient data are available on other oils coming within the scope of this test method so that no precision is given for such oils.

15.1.1 *Repeatability*—The difference between two 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:

Acid or Base Number	Repeatability
0.00 to 0.1	0.03
Over 0.1 to 0.5	0.05
Over 0.5 to 1.0	0.08
Over 1.0 to 2.0	0.12

15.1.2 *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:

Acid or Base Number	Reproducibility
0.00 to 0.1	0.04
Over 0.1 to 0.5	0.08
Over 0.5 to 2.0	15 % of the neutralization number level

NOTE 16—These precision values do not apply to oils that are so highly colored as to obscure the end point color change.

NOTE 17—For precision applicable to electrical insulating liquids, refer to Guide D117.

NOTE 18—The precision statements were based on the use of manual burets only. The user is cautioned that the precision statements may or may not be applicable to titrations performed with the use of automated burets, since no interlaboratory study has been conducted to date to statistically evaluate results determined by both techniques.

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

## 16. Keywords

16.1 acid number; base number; color indication titration; petroleum products

# ANNEXES

## (Mandatory Information)

### A1. SPECIFICATIONS FOR *p*-NAPHTHOLBENZEIN

A1.1 *p*-Naphtholbenzein shall conform to the following requirements:

A1.1.1 *Appearance*—Red amorphous powder.

A1.1.2 *Chlorides*—Less than 0.5 %.

A1.1.3 *Solubility*—Ten grams shall dissolve completely in 1 L of titration solvent (see A2.7.2).

A1.1.4 *Minimum Absorbance*—Dissolve exactly 0.1 g of sample in 250 mL of methanol. (**Warning**—Flammable. Vapor harmful. Can be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous.) Five millilitres of this solution is made up to 100 mL with pH 12 buffer. This final dilution should have a minimum absorbance of 1.20 when read

at the 650 nm peak using a Beckman DU or alternative type spectrophotometer, 1 cm cells, and water as the blank.

A1.1.5 *pH Range*:

A1.1.5.1 Indicator turns to the first clear green at a relative pH of  $10.0 \pm 0.5$  when tested by the method for pH range of *p*-naphtholbenzein indicator as described in Note A2.3.

A1.1.5.2 Requires not more than 0.5 mL of 0.01 *M* KOH solution above that for blank to bring indicator solution to the first clear green.

A1.1.5.3 Requires not more than 1.0 mL of 0.01 *M* KOH solution above that for blank to bring indicator solution to a blue color.

A1.1.5.4 Initial pH of indicator solution is at least as high as that of the blank.

## A2. TEST METHOD FOR DETERMINING pHr RANGE OF *p*-NAPHTHOLBENZEIN INDICATOR

### A2.1 Scope

A2.1.1 This test method is intended for determining the acceptability of *p*-naphtholbenzein indicator for use in Test Method D974 with regard to color change over a pHr range.

### A2.2 Terminology

A2.2.1 *Definitions of Terms Specific to This Standard:*

A2.2.1.1 *pHr*; *n*—an arbitrary term which expresses the relative hydrogen ion activity in the toluene-isopropanol-water medium.

A2.2.1.1.1 *Discussion*—For the purpose of this test method, the pHr acidity scale is defined by two or three (see **Note A2.1**) standard buffer solutions which have been designated pHr 4, pHr 7, and pHr 10; pHr 7 being the optional third buffer. The exact relation between pHr and the true pH of a toluene-isopropanol-water solution is not known and cannot be readily determined.

### A2.3 Summary of Test Method

A2.3.1 A prescribed amount of indicator is titrated electrometrically through the various color changes with alcoholic (**Warning**—Flammable) potassium hydroxide and results plotted against meter readings converted to pHr units.

### A2.4 Significance and Use

A2.4.1 This procedure is used to establish the pHr values of the various color changes of the *p*-naphtholbenzein indicator.

### A2.5 Apparatus

A2.5.1 *Meter, Electrode, Stirrer, Beaker and Stand*, as specified in the Apparatus section of Test Method D664.

**NOTE A2.1**—It is acceptable to use an automated titration system meeting the requirements of Test Method D664.

### A2.6 Purity of Reagents

A2.6.1 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>5</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.

A2.6.2 References to water shall be understood to mean distilled water.

### A2.7 Reagents

A2.7.1 *Potassium Hydroxide Solution, Standard Alcoholic (0.01 M)*—Prepare, store, and standardize in accordance with Test Method D664.

A2.7.2 *Titration Solvent*—Add 500 mL of toluene and 5 mL of water to 495 mL of anhydrous isopropyl alcohol (2-propanol). The titration solvent should be made up in large quantities.

A2.7.3 *Commercial Aqueous pH 4, pH 7, and pH 10 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.

A2.7.4 *Lithium Chloride Electrolyte*—Prepare a 1 M – 3 M solution of lithium chloride (LiCl) in ethanol. Alternatively, commercial solutions may be purchased.

A2.7.5 *Naphtholbenzein Indicator Solution*—Prepare as described in 7.6.

### A2.8 Preparation of Electrode System

A2.8.1 Prepare the electrode system in accordance with Section 8, Electrode System, of Test Method D664.

### A2.9 Standardization of Apparatus

A2.9.1 Prepare the apparatus in accordance with Section 9, Standardization of Apparatus, of Test Method D664.

**NOTE A2.2**—The resolution of the apparatus standardization may be improved with the use of a third aqueous buffer at pH 7.

### A2.10 Procedure

A2.10.1 Titrate 100 mL of titration solvent (**Warning**—Flammable) with 0.01 M KOH solution until the meter indicates a pHr between 13 and 14.

A2.10.2 Add 0.5 mL of indicator solution to a fresh portion of titration solvent, and after cleaning the electrodes titrate with 0.01 M KOH solution until the meter indicates a pHr between 13 and 14.

A2.10.3 During the titration, plot the volume of titrant against the pHr or meter reading and note on the curve the various color changes at the corresponding pHr values.

**NOTE A2.3**—The following color changes, in order, are intended as a guide:

Amber to olive green  
Olive green to clear green  
Clear green to bluish green  
Bluish green to blue

A2.10.4 Plot the blank titration on the same paper used for the indicator.

### A2.11 Calculation

A2.11.1 Subtract the volume of titrant used in the blank titration from that used for the indicator solution titration at the same pHr corresponding to the definite color changes between 10 pHr to 12 pHr.

A2.11.2 The resulting amount is the volume of 0.01 M KOH solution required to bring a blank indicator solution from an amber to an olive green color change. This value is then used to establish the acceptance criteria for A1.1.5.2 and A1.1.5.3.

**A2.12 Precision and Bias**

A2.12.1 *Precision*—The precision of this procedure has not been determined, and there are no plans to develop one.

A2.12.2 *Bias*—The procedures in this test method have no bias because the values can only be defined in terms of the test method.

**SUMMARY OF CHANGES**

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D974 – 21) that may impact the use of this standard. (Approved Nov. 1, 2022.)

(1) Revised Section 8.

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D974 – 14<sup>e2</sup>) that may impact the use of this standard. (Approved July 1, 2021.)

- (1) Revised subsections 3.2.1 and 4.1 description of water to align with subsection 11.1 procedural requirements.
- (2) Removed optional substitutions for KOH and HCl from Note 6.
- (3) Adjusted subsection A1.1.4 mass requirement for indicator.
- (4) Revised subsection A1.1.5.1 to align with D664 revision.
- (5) Revised subsections A2.5 through A2.9 to align with D664 revisions and included option to improve resolution of method with the use of three aqueous pH buffers.

- (6) Adjusted KOH concentration requirement in subsection A2.7.1 to reflect procedure in A2.10 and removed A2.7.2 as not used in the A2.10 procedure. Revised numbering in Annex A2 as appropriate.
- (7) Removed former Fig. A2.1.

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