Designation: D974 – 12

Designation: 139/98

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

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 Department of Defense.

1. Scope*

1.1 This test method covers the determination of acidic or basic constituents (Note 1) in petroleum products[2] 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D117 Guide for Sampling, Test Methods, and Specifications for Electrical Insulating Oils of Petroleum Origin
D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration
D1193 Specification for Reagent Water
D4175 Terminology Relating to Petroleum, Petroleum Products, 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.

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

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[1] 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.

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.**

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 hot 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 hot 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. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) can be substituted for KOH and HCl, respectively.

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 A1. Prepare a solution of *p*-naphtholbenzein in titration solvent equal to 10 ± 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 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**—

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[4] *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.

[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.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1626.

Poisonous if ingested, strongly alkaline, causes severe irritation producing dermatitis) and again boil gently for 5 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 ± 1°C and dissolve in 40± 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:

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

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 Prepare a 0.1 ± 0.01 m% solution of phenolphthalein by dissolving pure solid phenolphthalein in a 1:1 mixture of water, free of CO_2, and ethanol.

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.

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 ± 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).

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.

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, 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 (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 and 0.05 mL (automated buret). Continue until a persistent green or green-brown end point is reached (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 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:

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

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:

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[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.

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

NOTE 18—For precision applicable to electrical insulating liquids, refer to Guide D117.

NOTE 19—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 A2.7.3).

A1.1.4 *Minimum Absorbance*—Exactly 0.1000 g of sample is dissolved 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 11 ± 0.5 when tested by the method for pHr range of *p*-naphtholbenzein indicator as described in Note A2.1.

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 pHr of indicator solution is at least as high as that of the blank.

A1.1.5.5 Buffer is made by mixing 50 mL of 0.05 *M* diabasic sodium phosphate solution with 26.9 mL of 0.1 *M* sodium hydroxide solution.

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 standard buffer solutions which have been designated pHr 4 and pHr 11. 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, Glass Electrode, Calomel Electrode, Stirrer, Beaker and Stand*, as specified in the Apparatus section 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.[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.

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

A2.7 Reagents

A2.7.1 *Potassium Hydroxide Solution, Standard Alcoholic (0.2 M)*—Prepare, store, and standardize in accordance with Test Method D664.

A2.7.2 *Hydrochloric Acid Solution, Standard Alcoholic (0.2 M)*—Prepare and standardize in accordance with Test Method D664.

A2.7.3 *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.

A2.7.4 *Acidic Buffer Solution (pHr = 4.0)*—Prepare a stock solution in accordance with Test Method D664. Add 10 mL of buffer stock solution to 100 mL of titration solvent. Use the diluted solution within 1 h.

A2.7.5 *Alkaline Buffer Solution (pHr = 11.0)*—Prepare a stock solution in accordance with Test Method D664. Add 10 mL of buffer stock solution to 100 mL of titration solvent. Use the diluted solution within 1 h.

A2.7.6 *Potassium Chloride Electrolyte*—Prepare a saturated solution of potassium chloride (KCl) in water.

A2.7.7 *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, Preparation of the Electrode System, of Test Method D664.

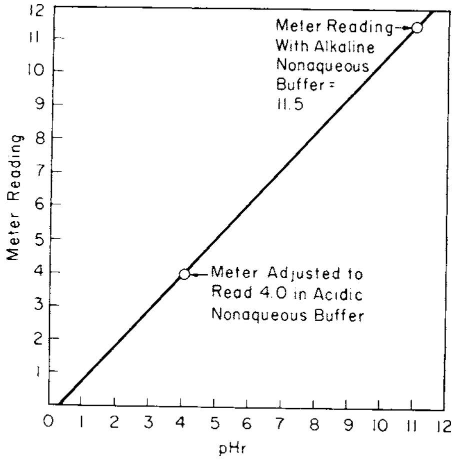

FIG. A2.1 Calibration Curve for Conversion of pH Meter Readings to pHr

A2.9 Standardization of Apparatus

A2.9.1 Prior to each test or series of tests, set the meter to read on the pH scale, insert the electrodes into a beaker containing the acidic nonaqueous buffer solution at a temperature of 25 ± 2°C, and stir the solution vigorously. When the pH meter reading becomes constant adjust the asymmetry potential dial of the instrument so that the meter reads 4.0.

A2.9.2 Remove the acidic buffer, clean the electrodes, and immerse them in water for several minutes. Dry the electrodes and insert them in a beaker containing alkaline nonaqueous buffer solution at 25 ± 2°C. When the pH meter reading has become steady, record the exact value. If the reading is within 0.2 pH units of 11.0, the initial acidity, pHr, of unknown solutions may be read directly from the dial of the meter. If the reading is not within 0.2 units of 11.0, prepare a correction graph as shown in Fig. A2.1. Use this graph to convert pH meter readings to initial acidity, pHr.

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 A2.1—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 to 12 pHr.

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 (D974–11) that may impact the use of this standard. (Approved April 15, 2012.)

(*1*) Added significant figures in 14.2.

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D974–08$^{\varepsilon 1}$) that may impact the use of this standard. (Approved May 15, 2011.)

(*1*) Updated 3.1.1 and 3.1.2.

(*2*) Replaced "casserole" with "titration flask" in 11.1.

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