



Standard Test Method for Base Number Determination by Potentiometric Titration¹

This standard is issued under the fixed designation D 4739; 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.

1. Scope

1.1 This test method covers a procedure for the determination of basic constituents in petroleum products and lubricants (Note 1). The test method resolves these constituents into groups having weak-base and strong-base ionization properties, provided the dissociation constants of the more strongly basic compounds are at least 1000 times that of the next weaker groups.

1.1.1 This test method covers base numbers up to 70. While it can be extended to higher base numbers, the precision of the test method for base numbers greater than 70 has not been determined.

NOTE 1—In new and used oils, the constituents which can be considered to have basic properties are primarily organic and inorganic bases, including amino compounds, although certain salts of heavy metals, salts of weak acids, basic salts of polyacidic compounds, and some additives such as inhibitors or detergents may show basic characteristics.

1.2 This test method can be used to indicate relative changes that occur in an oil during use under oxidizing or other service conditions regardless of the color or other properties of the resulting oil (Note 2). Although the analysis is made under closely specified conditions, the method is not intended to, and does not, result in reported basic properties which can be used under all service conditions to predict performance of an oil; for example, no overall relationship is known between bearing corrosion or the control of corrosive wear in the engine and base number.

NOTE 2—A color indicator titration method is also available in the Test Method D 974 and IP 139. The base numbers obtained by the potentiometric method may or may not be numerically the same as those obtained by Test Method D 974 or equivalent color indicator methods such as given in Federal Test Method Std. No. 791b. Potentiometric methods for base number are also available in Test Method D 2896.

NOTE 3—Test Method D 4739 was developed as an alternative for the former base number portion of Test Method D 664. Base numbers obtained by this method may or may not be numerically the same as those obtained by the former base number portion of Test Method D 664.²

1.3 The values stated in acceptable metric units are to be regarded as the standard.

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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² The base number portion was last published in the 1981 version.

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:

D 664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration³

D 974 Test Method for Acid and Base Number by Color-Indicator Titration³

D 1193 Specification for Reagent Water⁴

D 2896 Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration⁵

2.2 IP Standard:

IP 139 Test Method for Neutralization Number by Color-Indicator Titration⁶

2.3 U.S. Federal Test Method:

Federal Test Method Standard No. 791b Lubricants Liquid Fuels and Related Products; Methods of Testing⁷

3. Terminology

3.1 Definitions:

3.1.1 *base numbers, n*—the quantity of acid, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample to a specified end point.

3.1.1.1 *Discussion*— In this test method, the sample is titrated to a meter reading corresponding to a freshly prepared nonaqueous acidic buffer solution.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *strong base number, n*—the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample dissolved in the specified solvent from the initial meter reading to a meter reading corresponding to a freshly prepared basic buffer solution.

4. Summary of Test Method

4.1 The sample is dissolved in a mixture of toluene,

³ Annual Book of ASTM Standards, Vol 05.01.

⁴ Annual Book of ASTM Standards, Vol 11.01.

⁵ Annual Book of ASTM Standards, Vol 05.02.

⁶ IP Standards for Petroleum and Its Products, Part 1. Methods for Analysis and Testing.

⁷ Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

isopropyl alcohol, chloroform, and a small amount of water and titrated potentiometrically with alcoholic hydrochloric acid solution. The test results of this procedure are obtained by titration mode of fixed increment and fixed time additions of the titrant. An endpoint is selected from a titration curve according to the criteria given in 13.1 and used to calculate a base number.

5. Significance and Use

5.1 New and used petroleum products can contain basic constituents that are present as additives or as degradation products formed during service. The relative amount of these materials can be determined by titrating with acids. The base number is a measure of the amount of basic substances in the oil—always under the conditions of the test. The base number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

6. Apparatus

6.1 *Potentiometric Titrimeter*, automatic or manual, with capability of adding fixed increments of titrant at fixed time intervals (see Annex A1).

6.1.1 The titrimeter must automatically (or manually) control the rate of addition of titrant as follows: Delivery of titrant will be incremental; after delivery of precisely a 0.100-mL increment (see 6.1.2), the delivery is stopped and a fixed time period of 90 s is allowed to pass before another 0.100-mL increment of titrant is delivered. This procedure is repeated until the titration is completed.

6.1.2 The precision of addition of the 0.100-mL increments of titrant must be ± 0.001 mL for automatic titrators. For manual buret, it should be ± 0.005 mL. A higher incremental precision is required for an automatic buret because the total volume to the end point is summed from the individual increments, whereas with a manual buret it is read from a scale.

6.2 *Glass Indicating Electrode*, pH 0 to 14, general purpose.

6.3 *Reference Electrode*, sleeve type, saturated calomel electrode, or Ag/AgCl electrode, with inner and outer electrolyte filling solutions of saturated LiCl in isopropyl alcohol.

NOTE 4—Certain alternative electrode-electrolyte combinations have been found to give satisfactory results although the precision using these alternatives has not been determined. Combination electrodes may be used provided they conform to 8.3 and have a sufficient fast response time.

6.4 *Stirrer, Buret, Stand, Titration Vessel*, as specified in Annex A1 are required. A typical cell assembly is shown in Fig. 1.

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,

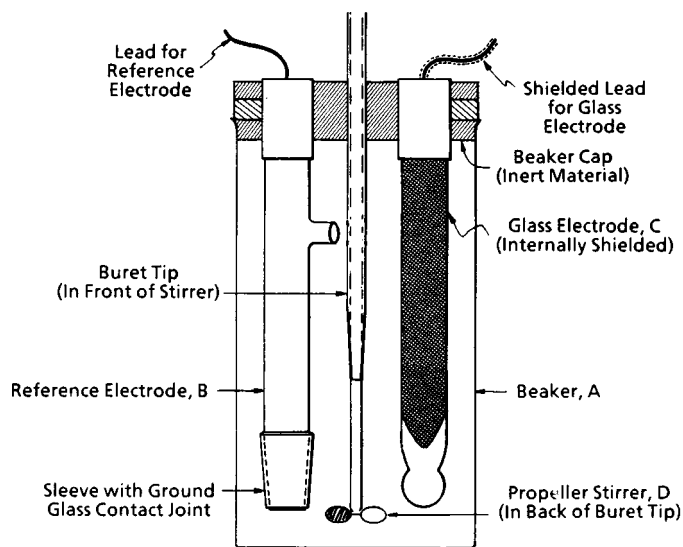


FIG. 1 Cell for Potentiometric Titration

where such specifications are available.⁸ 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*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification D 1193.

7.3 *Buffer Stock Solution A*—Accurately weigh 24.2 ± 0.1 g of 2,4,6-trimethyl pyridine (γ -collidine), and transfer to a 1-L volumetric flask containing 100 mL of anhydrous isopropyl alcohol. Using a 250-mL graduated cylinder, add to the flask, while continuously stirring its contents, $150/N_{\text{HCl}} \pm 5$ mL of 0.2 M alcoholic HCl solution (N_{HCl} being the exact molarity of the HCl solution found by standardization). Dilute to the 1000-mL mark with anhydrous isopropyl alcohol, and mix thoroughly. Use within 2 weeks.

7.4 *Buffer Stock Solution B*—Accurately weigh 27.8 ± 0.1 g of *m*-nitrophenol and transfer to a 1-L volumetric flask containing 100 mL of anhydrous isopropyl alcohol. Using a 250-mL graduated cylinder, add to the flask while continuously stirring its contents, $50/N_{\text{KOH}} \pm 1$ mL of 0.2 M alcoholic KOH solution (N_{KOH} being the exact molarity of the KOH solution found by standardization). Dilute to the 1000-mL mark with anhydrous isopropyl alcohol and mix thoroughly. Use within 2 weeks.

7.5 *Buffer, Nonaqueous Acid*—Add 10 mL of buffer stock solution A (see 7.3) to 100 mL of titration solvent. Use within 1 h.

7.6 *Buffer, Nonaqueous Base*—Add 10 mL of buffer stock solution B (see 7.4) to 100 mL of titration solvent. Use within 1 h.

7.7 *Chloroform*, (**Warning**—See Note 5) reagent grade.

⁸ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.



NOTE 5—**Warning:** Toxic and suspected carcinogen.

7.8 *Hydrochloric Acid Solution, Standard Alcoholic*—(0.1 M)—Mix 9 mL of reagent grade hydrochloric acid (HCl, sp gr 1.19), (**Warning**—see Note 6), with 1 L of anhydrous isopropyl alcohol. (See Note 7). Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of approximately 8 mL (accurately measured) of the 0.1 M alcoholic KOH solution diluted with 125 mL CO₂-free water.

NOTE 6—**Warning:** Toxic and corrosive.

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

7.9 *Hydrochloric Acid Solution, Standard Alcoholic*—(0.2 M)—Prepare and standardize as described in 7.8, but use 18 mL of HCl (sp gr 1.19) (see Note 8).

NOTE 8—Commercially available reagents may be used in place of laboratory preparations.

7.10 *Isopropyl Alcohol (2-Propanol), Anhydrous*, (less than 0.1 % H₂O) (**Warning**—see Note 9). If dry reagent cannot be procured, dry it by distillation through a multiple plate column, discarding the first 5 % of material distilling over and using the 95 % remaining. Also, drying can be accomplished using molecular sieves such as Linde Type 4A, by passing the solvent upward through a molecular sieve column using 1 part of molecular sieve per 10 parts of solvent.

NOTE 9—**Warning:** Flammable.

7.11 *Lithium Chloride Electrolyte*—Prepare a saturated solution of lithium chloride (LiCl) in isopropyl alcohol.

7.12 *m-Nitrophenol, NO₂C₆H₄OH*, (**Warning**—see Note 10), (mol weight 139.11), conforming to the following requirements:

Melting point	96 to 97°C
Color	Pale Yellow

NOTE 10—**Warning:** Toxic.

7.12.1 Store the reagent in a brown glass bottle.

7.13 *Potassium Hydroxide Solution, Standard Alcoholic* (0.1 M)—Add 6 g of reagent grade potassium hydroxide (KOH) (**Warning**—see Note 6), to approximately 1 L of anhydrous isopropyl alcohol. Boil gently for 10 min to effect solution. Allow the solution to stand for 2 days and then filter the supernatant liquid through a fine sintered-glass funnel. Store the solution in a chemically resistant bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide (CO₂) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbent (Ascarite, Carbosorb, or Indicarb), and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease (see Note 11). Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in CO₂-free water.

NOTE 11—Commercially available reagents may be used in place of laboratory preparations.

7.14 *Potassium Hydroxide Solution, Standard Alcoholic* (0.2 M)—Prepare, store, and standardize as directed in 7.13, but use 12 to 13 g of KOH to approximately 1 L of anhydrous isopropyl alcohol (see Note 12).

NOTE 12—Commercially available reagents may be used in place of laboratory preparations.

7.15 *Titration Solvent*—In a brown reagent bottle, add 30 mL of water to 1 L of isopropyl alcohol and mix thoroughly. Add 1 L each of toluene and chloroform and mix thoroughly.

7.16 *Toluene*, reagent grade.

NOTE 13—**Warning:** Extremely flammable.

7.17 *2,4,6-Trimethyl Pyridine (γ-Collidine)*, (CH₃)₃C₅H₂N, (**Warning**—see Note 10) (mol weight 121.18), conforming to the following requirements:

Boiling range	168 to 170°C
Refractive index N _D 20	1.4982 ± 0.0005
Color	colorless

7.17.1 Store the reagent over activated alumina and keep it in a brown glass bottle.

7.18 *Chromic Acid Solution*—(**Warning**—See Note 14.)

NOTE 14—**Warning:** Causes severe burns. Recognized carcinogen. Strong oxidizer.

8. Preparation of Electrode System

8.1 *Maintenance of Electrodes*—Clean the glass electrode (Note 15) at frequent intervals (not less than once every week during continual use) by immersing in cold chromic acid cleaning solution (**Warning**—see Note 14). Drain the calomel electrode at least once each week and refill with fresh LiCl electrolyte as far as the filling hole. Make sure that crystallized LiCl is present in the solution. Maintain the electrolyte level in the reference electrode above that of the liquid in the titration beaker at all times. When not in use, immerse the lower halves of the electrodes in either water (glass) or the LiCl in isopropyl alcohol electrolyte (reference). Do not allow them to remain immersed in titration solvent for any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times.

NOTE 15—Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are important in obtaining repeatable potentials, since contamination can introduce uncertain, erratic, and unnoticeable liquid contact potentials.⁹ While this is of secondary importance when end points are chosen from inflection points in the titration curve, it is quite serious when end points are chosen at arbitrarily-fixed cell potentials (that is, the nonaqueous acidic buffer potential).

8.2 *Preparation of Electrodes*, Before and after using, blot-dry the glass electrode thoroughly with a clean cloth or a soft absorbent tissue and rinse with water. Wipe the reference electrode with a cloth or tissue, carefully remove the ground-glass sieve, and thoroughly wipe both ground surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint (Note 15). Wet the ground surfaces thoroughly with electrolyte, set the sleeve firmly in place, and rinse the electrode with water. Prior to each titration, soak the prepared electrodes in water for at least 5

⁹ For a detailed discussion of the need for care in preparation of the electrodes, see Lykken, L., Porter, P., Ruliffson, H. D., and Tuemmler, F. D., "Potentiometric Determination of Acidity in Highly Colored Oils," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol 16. 1944, pp. 219–234.