Designation: D4739 – 11 (Reapproved 2017)

Standard Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration[1]

This standard is issued under the fixed designation D4739; 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.

INTRODUCTION

Currently, there are two ASTM test methods under the jurisdiction of Committee D02 used for determining base number by potentiometric titration: Test Method D2896 and Test Method D4739. They are both used throughout the petroleum industry. Test Method D2896 is for new oils and is used in setting specifications since it is more accurate than Test Method D4739. Test Method D4739 shall be used exclusively for the purpose of tracking base number loss as an oil proceeds in service. In many cases, the test methods will provide different results. Some comparisons are given in the Scope and the Significance and Use sections of this test method to distinguish between the two standards and to provide guidance to users.

1. Scope

1.1 This test method covers a procedure for the determination of basic constituents in petroleum products and new and used lubricants. This 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 than that of the next weaker groups. This test method covers base numbers up to 250.

1.2 In new and used lubricants, the constituents that can be considered to have basic properties are primarily organic and inorganic bases, including amino compounds. This test method uses hydrochloric acid as the titrant, whereas Test Method D2896 uses perchloric acid as the titrant. This test method may or may not titrate these weak bases and, if so, it will titrate them to a lesser degree of completion; some additives such as inhibitors or detergents may show basic characteristics.

1.3 When testing used engine lubricants, it should be recognized that certain weak bases are the result of the service rather than having been built into the oil. This test method can be used to indicate relative changes that occur in oil during use under oxidizing or other service conditions regardless of the color or other properties of the resulting oil. The values obtained, however, are intended to be compared with the other values obtained by this test method only; base numbers obtained by this test method are not intended to be equal to values by other test methods. Although the analysis is made under closely specified conditions, this test method is not intended to, and does not, result in reported basic properties that 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.

1.4 This test method was developed as an alternative for the former base number portion of Test Method D664 (last published in Test Method D664 – 81).

1.4.1 Colorimetric test methods for base number are Test Method D974, IP 139, and 5102.1 on acid and base number by extraction (color-indicator titration) of Federal Test Method Standard No. 791b. Test results by these methods may or may not be numerically equivalent to this test method.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.*

1.7 *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.*

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[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.

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2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D974 Test Method for Acid and Base Number by Color-Indicator Titration

D1193 Specification for Reagent Water

D2896 Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

2.2 *IP Standard:*[3]

IP 139 Petroleum products and lubricants—Determination of acid and base number—Colour-indicator titration method

2.3 *U.S. Federal Test Method:*[4]

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

3. Terminology

3.1 *Definitions:*

3.1.1 *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.

3.1.1.1 *Discussion*—In this test method, the sample is titrated to a meter reading corresponding to aqueous acidic buffer solution or appropriate inflection point.

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 basic buffer solution.

4. Summary of Test Method

4.1 The sample is dissolved in a mixture of toluene, propan-2-ol (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 Section 12 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. The relative amount of these materials can be determined by titration with acids. The base number is a measure of the amount of basic substances in the oil always under the conditions of the test. It is sometimes used as a measure of lubricant degradation in service. However, any condemning limit shall be empirically established.

5.2 As stated in 1.2, this test method uses a weaker acid to titrate the base than Test Method D2896, and the titration solvents are also different. Test Method D2896 uses a stronger acid and a more polar solvent system than Test Method D4739. As a result, Test Method D2896 will titrate salts of weak acids (soaps), basic salts of polyacidic bases, and weak alkaline salts of some metals. They do not protect the oil from acidic components due to the degradation of the oil. This test method may produce a falsely exaggerated base number. Test Method D4739 will probably not titrate these weak bases but, if so, will titrate them to a lesser degree of completion. It measures only the basic components of the additive package that neutralizes acids. On the other hand, if the additive package contains weak basic components that do not play a role in neutralizing the acidic components of the degrading oil, then the Test Method D4739 result may be falsely understated.

5.3 Particular care is required in the interpretation of the base number of new and used lubricants.

5.3.1 When the base number of the new oil is required as an expression of its manufactured quality, Test Method D2896 is preferred, since it is known to titrate weak bases that this test method may or may not titrate reliably.

5.3.2 When the base number of in-service or at-term oil is required, this test method is preferred because in many cases, especially for internal combustion engine oils, weakly basic degradation products are possible. Test Method D2896 will titrate these, thus giving a false value of essential basicity. This test method may or may not titrate these weak acids.

5.3.3 When the loss of base number value, as the oils proceed in service, is the consideration, this test method is to be preferred and all values including the unused oil shall be determined by this test method. Base numbers obtained by this test method shall not be related to base numbers obtained by another test method such as Test Method D2896.

5.3.4 In ASTM Interlaboratory Crosscheck Programs for both new and used lubricants, historically Test Method D2896 gives a higher value for base number.

6. Apparatus

6.1 *Potentiometric Titration,* 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

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[2] 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.

[3] Available from Energy Institute, 61 New Cavendish St., London, W1G 7AR, U.K., http://www.energyinst.org.

[4] Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098.

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; it is read from a scale with a manual buret.

6.2 *Sensing Electrode,* standard pH with glass membrane, suitable for non-aqueous titrations.

6.3 *Reference Electrode,* Silver/Silver Chloride (Ag/AgCl) reference electrode with sleeve junction, filled with 1 M to 3 M LiCl in ethanol.

6.3.1 *Combination Electrode*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. The combination electrode shall have a sleeve junction type of reference and shall use an inert ethanol electrolyte, for example, 1 M to 3 M LiCl in ethanol. In the reference compartment, the sensing electrode part shall use a glass membrane designed for non-aqueous titrations. These combination electrodes shall have the same response or better response than a dual electrode system. They shall have removable sleeves for easy rinsing and addition of electrolyte. (**Warning—**When a movable sleeve is part of the electrode system, ensure that the sleeve is unimpaired before every titration.)

6.4 *Stirrer, Buret, Stand, Titration Vessel,* as specified in Annex A1, are required.

7. Reagents

7.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the requirement of either Type I, II, or III of Specification D1193.

7.3 *Buffer, Aqueous Acid*—Commercial pH 3 buffer solution with a tolerance of ±0.02 pH units at 25 °C. This solution shall be replaced at regular intervals consistent with its stability or when contamination is suspected. Information related to the stability should be obtained from the manufacturer.

7.4 *Buffer, Aqueous Basic*—Commercial pH 10 buffer solution with a tolerance of ±0.02 pH units at 25 °C. This solution shall be replaced at regular intervals consistent with its stability or when contamination is suspected. Information related to the stability should be obtained from the manufacturer.

7.5 *Chloroform*—Reagent grade. (**Warning—**Toxic and suspected carcinogen.)

7.6 *Hydrochloric Acid Solution, Standard Alcoholic (0.1 M)*—Mix 9 mL of reagent grade hydrochloric acid (HCl, sp gr 1.19) (**Warning—**Toxic and corrosive), with 1 L of anhydrous isopropyl alcohol. 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 CO_2-free water.

7.7 *Ethanol*—reagent grade. (**Warning—**Flammable and toxic, especially when denatured.)

7.8 *Lithium Chloride Electrolyte* —Prepare a solution of 1 M to 3 M LiCl in ethanol.

7.9 *Potassium Hydroxide*—(**Warning—**Causes severe burns.)

7.10 *Potassium Hydroxide Solution, Standard Alcoholic (0.1 M)*—Add 6 g of reagent grade potassium hydroxide (KOH) (**Warning—**Toxic and corrosive), 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 (CO_2) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbent, and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease. Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in CO_2-free water.

7.11 *Propan-2-ol (Isopropyl Alcohol)*—Anhydrous, (less than 0.1 % H_2O). (**Warning—**Flammable.) 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 by passing the solvent upward through a molecular sieve column using one part of molecular sieve per ten parts of solvent. (**Warning—**It has been reported that, if not inhibited against it, propan-2-ol can contain peroxides. When this occurs, an explosive mixture is possible when the storage vessel or other equipment such as a dispensing bottle, are near empty and approaching dryness.

7.12 Commercially available solutions may be used in place of laboratory preparations provided the solutions have been certified as equivalent.

7.13 Alternate volumes of solutions may be prepared provided the final solution concentration is equivalent.

7.14 *Toluene*—Reagent grade. (**Warning—**Extremely flammable.)

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[5] *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.

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.

8. Preparation of Electrode System

8.1 *Maintenance and Storage of Electrodes*—Cleaning the electrode thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining repeatable potentials, since the contamination may introduce uncertain erratic and unnoticeable liquid contact potentials. While this is of secondary importance when end points are chosen from inflection points in the titration curve, it may be very serious when end points are chosen at experimentally determined cell potentials as outlined in the procedure.

8.1.1 Clean the pH indicating electrode or the pH indicating part of the combination electrode at frequent intervals based on use and type of samples being analyzed by immersing in non-chromium containing, strongly oxidizing cleaning solution. The electrode shall be cleaned periodically when in use or when a new electrode is installed. Drain the LiCl electrolyte from the electrode at least once each week, and refill with fresh LiCl electrolyte as far as the filling hole. Ensure that there are no air bubbles in the electrode liquid. If air bubbles are observed, hold the electrode in a vertical position and gently tap it to release the bubbles. Maintain the electrolyte level in the electrode above that of the liquid in the titration beaker at all times.

8.1.2 When not in use, immerse the lower halves of the electrodes in either water (sensing) 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.

8.1.3 *Electrode Life*—Typically, electrode usage is limited to 3 to 6 months, depending upon usage. Electrodes have a limited shelf life and shall be tested before use (8.3).

8.2 *Preparation of Electrodes:*

8.2.1 When Ag/AgCl reference electrode is used for the titration and it contains an electrolyte that is not 1 M to 3 M LiCl in ethanol, replace the electrolyte. Drain the electrolyte from the electrode, wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with the LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve, ensure that there will be a free flow of electrolyte into the system. A combination electrode shall be prepared in the same manner. The electrolyte in a combination electrode can be removed with the aid of a vacuum suction.

8.2.2 Prior to each titration, soak the prepared electrodes in water, pH 4.5 – 5.5 acidified with HCL, for at least 5 min. Rinse the electrode with propan-2-ol immediately before use, and then with the titration solvent.

8.3 *Testing of Electrodes*—See Appendix X2 for the procedure to check electrode performance.

9. Standardization of Apparatus

9.1 *Determination of Meter Readings for the Aqueous Buffer Solution*—Ensure comparable selection of end points when definite inflection points are not obtained in the titration curve. Determine daily, for each electrode pair, the meter readings obtained with the aqueous acidic buffer solution to be used for the determination of base numbers and with the aqueous basic buffer solution to be used for the determination of strong base numbers.

9.2 Prepare the electrodes as described in 8.2, immerse them in the appropriate aqueous buffer solution, and stir for at least 2 min, maintaining the temperature of the buffer solution at a temperature within 2 °C of that at which the titrations are to be made. Read the cell voltage. The reading so obtained in the acidic buffer solution is taken as the end point for the base number if an inflection is not observed as specified in 12.1, and the reading obtained in the basic buffer solution is taken as the end point for the strong base number.

10. Preparation of Sample of Used Oil

10.1 Strict observation of the sampling procedure is necessary, since the sediment itself is acidic or basic or has absorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

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

10.1.2 When sampling used lubricants, the specimen shall be representative of the system samples and shall be free of contamination from external sources. As used oil can change appreciably in storage, test samples as soon as possible after removal from the lubricating system, and note the dates of sampling and testing.

10.2 Heat the sample (Note 1) of used oil to 60 °C ± 5 °C in the original container, and agitate the sample until all of the sediment is homogeneously suspended in the oil. If the original container is a can, or if it is glass and 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. Transfer all traces of sediment from the original container to the bottle by vigorous agitation of portions of the sample in the original container.

10.3 After complete suspension of all sediment, strain the sample or a convenient aliquot through a 100 mesh screen for the removal of large particles.

NOTE 1—When samples are visibly free of sediment, the heating procedures described may be omitted.

11. Procedure for Base Number and Strong Base Number

11.1 Calculate the quantity of sample required for its expected base number as follows:

$$A = 7/E \tag{1}$$

where:

A = approximate mass of sample, g and
E = expected base number.

11.1.1 Take a maximum of 5 g and a minimum of 0.1 g for analysis. The precision of weighing is as follows:

Size of Sample, g	Precision of Weighing, g
1–5	0.005
0.1–1	0.002

11.2 Into a suitable titration vessel, introduce a weighed quantity of sample as prescribed in 11.1.1, and add 75 mL of titration solvent. If 75 mL of solvent is not sufficient to properly cover the electrodes, add just enough additional solvent to do so. Ensure the electrodes are properly immersed. Prepare the electrodes as directed in 8.2. Place the beaker or titration vessel on the titration stand, and adjust its position so that the electrodes are about half immersed. Start the stirrer, and stir throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution.

11.3 Select and fill a suitable buret with the 0.1 M alcoholic HCl solution, and place the buret in position on the titration assembly, taking care that the tip is immersed about 25 mm in the liquid in titration vessel. Record the initial buret and meter (cell potential) readings.

11.4 *Titration*—The reaction of the hydrochloric acid with the basic components is very slow with most titrations for base number. As a result, these titrations are not at equilibrium. Because of this, the titration conditions are tightly specified and must be strictly adhered to in order to achieve the precision as stated.

NOTE 2—When best precision of titration is desired, if the titrant tip has been sitting for more than 30 min without being used, it is best to purge the tips by dispensing a few millilitres of titrant before beginning a titration.

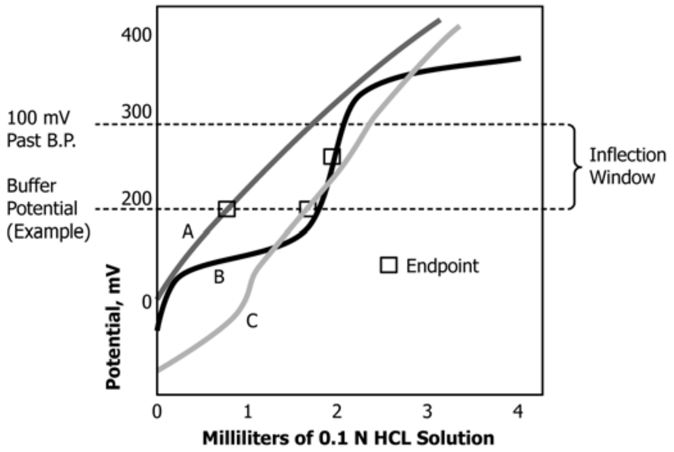
NOTE 3—See Appendix X1 for techniques for reducing the titration time of a sample. Pre-dosing techniques have been found to provide satisfactory results, although the precision using these techniques has not been determined.

11.4.1 Whether the titration is carried out manually or automatically, the following procedure of *fixed increment, fixed time* addition of titrant shall be followed. Add 0.1 M HCl in increments of 0.100 mL throughout the titration with a 90 s pause between each incremental addition. Take millivolt readings at the end of each 90 s interval.

11.4.1.1 The meter readings of potential difference are plotted manually or automatically against the respective volumes of titrant, and the end point is taken as described in 12.1.

11.4.2 On completion of the titration, remove the titration vessel and rinse the electrodes and buret tip with the titration solvent, then with water, then again with titration solvent. (*Soak electrodes in distilled water for at least 5 min before using for another titration.*) Store the sensing electrode in deionized or distilled water and the reference electrode in a saturated solution of LiCl in isopropyl alcohol when not in use (see 8.1).

11.4.3 *Blanks*—For each set of samples, make a blank titration of the same volume of titration solvent used for the sample. For the base number blank, add 0.1 M alcoholic HCl solution in 0.01 mL increments, waiting 12 s between each addition, until a potential which is 100 mV past the buffer potential (see 11.4) is reached. For the strong base number blank, add KOH titrant under the same conditions until the potential corresponding to the basic buffer solution is reached.



(A) Titration curve has no inflections. Take end point at the buffer potential.

(B) Titration curve has well-defined inflection within prescribed window. Take well-defined inflection as the end point.

(C) Titration curve has inflection prior to buffer potential but not in prescribed window. Take end point at buffer potential.

FIG. 1 Example Titration Curves to Illustrate Selection of End Points

12. Calculation

12.1 If an inflection (see Note 4) occurs in the potential region between the pH 3 buffer potential (see 11.4) and a point 100 mV past this potential, mark this inflection as the end point. If more than one inflection points are observed, use the last well-defined inflection point. If no well-defined inflection occurs in the above mentioned potential region, mark as the end point the point on the curve that corresponds to the acidic aqueous pH 3 buffer potential. See Fig. 1 for examples of end points.

NOTE 4—An inflection point is generally recognizable by inspection whenever at least five successive cell potential changes, Δ, caused by the addition of the corresponding five increments of titrant, exhibit a maximum illustrated as follows:

Titrant, mL	Δ, mV
1.8	8.3
1.9	10.7
2.0	11.3
2.1	10.0
2.2	7.9

The Δ at the maximum should be at least 5 mV, and the *difference* in Δ between the maximum and *both* the first and last Δ should be at least 2 mV.

12.2 Calculate the base number and strong base number as follows:

$$\text{Base number, mg KOH/g} = \left[(A - B) \times M \times 56.1\right]/W \tag{2}$$

$$\text{Strong base number, mg KOH/g} = \left[(CM + Dm) \times 56.1\right]/W \tag{3}$$

where:

A = alcoholic HCl solution, mL, used to titrate the sample to the end point (aqueous acidic pH 3 buffer or inflection—see 7.3 and 12.1),

B = alcoholic HCl, mL, used to titrate the solvent blank to the *same potential at which the sample end point occurs*,
M = molarity of the alcoholic HCl solution,
W = sample, g,
C = alcoholic HCl solution, mL, used to titrate the sample to an end point that occurs at a meter reading corresponding to the aqueous basic pH 10 buffer (see 7.4 and 12.1),
D = alcoholic KOH solution, mL, used to titrate the solvent blank to the potential corresponding to C, and
m = molarity of the alcoholic KOH solution.

13. Report

13.1 Report the results as base number and strong base number, Test Method D4739.

13.2 Report the base number values less than 10 mg/g to 0.1 mg/g KOH; and values between 10 and greater than 10 mg/g to 1 mg KOH.

14. Quality Control Checks

14.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

14.2 Prior to monitoring the measurement process, the user of this test method needs to determine the average value and control limits of the QC sample.

14.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the total testing process. Any out of control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

14.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirement. Generally, a QC sample should be analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced.

15. Precision and Bias

15.1 *Precision*—The precision of this test method as determined by statistical examination of results on 11 fresh samples, and 6 used oils samples run in duplicates by 14 different laboratories is as follows:[6,7]

15.1.1 *Base Number:*

15.1.1.1 *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 value only in one case in twenty:

$$\text{Fresh oils and additives:} r = 0.11\,(X+0.0268)^{0.79}$$

$$\text{Used oils:} r = 0.22\,X^{0.47}$$

15.1.1.2 *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 value only in one case in twenty:

$$\text{Fresh oils and additives:} R = 0.42\,(X+0.0268)^{0.79}$$

$$\text{Used Oils: } R = 1.53\,X^{0.47}$$

15.1.1.3 X is the mean of two or more results, in mg/g KOH.

15.1.2 *Strong Base Number*—Precision data have not been developed for strong base number because of its rare occurrence.

15.2 *Bias*—A statement of bias is not applicable since a standard reference material for this property is not available.

16. Keywords

16.1 base number; lubricants; petroleum products; potentiometric titration

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1217. Contact ASTM Customer Service at service@astm.org.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1638. Contact ASTM Customer Service at service@astm.org.

ANNEX

(Mandatory Information)

A1. APPARATUS

A1.1 Apparatus for Manual Titration

A1.1.1 *Meter*—A voltmeter or potentiometer that will operate with an accuracy of ±0.005 V and a sensitivity of ±0.002 V, over a range of at least ±0.5 V, when the meter is used with the electrodes specified in A1.1.2 and A1.1.3, and when the resistance between the electrodes falls within the range from 0.2 MΩ to 20 MΩ. The meter shall be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching with a grounded lead (Note A1.1), any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand, or the meter. A desirable apparatus may consist of a continuous-reading electronic voltmeter with specified range, accuracy, and sensitivity, that is designed to operate on an input of less than 5×10^{-12} A when an electrode system having 1000 MΩ resistance is connected across the meter terminals, and that is provided with a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interferences from the presence of external electrostatic field.

NOTE A1.1—*Grounded* or *connected to the ground* means connected through a resistance of not more than 100 Ω to a standard ground potential such as that of a water-service pipe.

A1.1.2 *Electrodes*—See 6.2 and 6.3.

A1.1.3 *Stirrer*—A variable-speed mechanical stirrer of any suitable type, equipped with a glass, propeller-type-stirring paddle.A propeller with blades 6 mm in radius and set at a pitch of 30° to 45° is satisfactory. A magnetic stirrer is also satisfactory. If electrical stirring apparatus is used, it must be grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in meter reading during the courses of titration.

A1.1.4 *Buret*—A 5 mL buret graduated in 0.01 mL divisions and calibrated with an accuracy of ±0.005 mL. The buret shall have a chemically-resistant stopcock and shall have a tip that extends 100 mm to 130 mm beyond the stopcock.

A1.1.5 *Titration Beaker*—A 250 mL beaker made of borosilicate glass, or other suitable titration beaker.

A1.1.6 *Titration Stand*—A suitable stand to support the electrodes, stirrer, and buret. An arrangement that allows the removal of the beaker without disturbing the electrodes, buret, and stirrer is desirable.

A1.2 Apparatus for Automatic Titration

A1.2.1 Automatic titration system shall be generally in accordance with A1.1 and provide the following technical performance characteristics of features:

A1.2.1.1 The addition of titrant must be automatically controlled to dispense discontinuously 0.100 mL ± 0.001 mL increments of titrant, with a waiting period of 90 s between increments.

A1.2.1.2 Interchangeable precision motor-driven burets with volume dispensing accuracy of ±0.001 mL.

A1.2.1.3 A record of the complete course of a titration by continuously printing out the potential or change in potential, with the addition of each increment of titrant versus volume of titrant added.

APPENDIXES

(Nonmandatory Information)

X1. REDUCING TITRATION TIME

X1.1 A long, equilibration period of 90 s/increment was selected for the base number titration because the titration reaction and electrode equilibration are generally slow. This, of course, can lead to long titration time/sample, with a maximum time of 1 h based on a maximum volume of titrant of 4 mL and a rate of titrant addition of 0.1 mL/90 s. It is possible to substantially reduce the titration time by predosing with rapid addition of titrant until a potential within 25 mV of the buffer potential is reached, then allowing 90 s for equilibration and completing the titration under normal conditions. This procedure is not expected to have an adverse affect on the precision of this test method; however, the precision under these conditions has not been determined.

X1.2 There are many cases where the optimum in precision in the base number is not required, and in these cases the titration time can be shortened by taking a smaller sample. For example, for a base number of 2 and using a sample size calculated from Eq 1, a total titration time of 24 min would be required. By taking only one half of the prescribed sample size the titration time would be reduced to 12 min. The affect of halving the sample size on the precision of this test method has not been determined, but it would be expected to be small.

X2. CHECK FOR ELECTRODE PERFORMANCE

X2.1 The kinetic electrode test measures the kinetic response of the electrode. Electrodes can calibrate with acceptable slope and intercept values yet still not have a response good enough for titration. The speed of response and subsequent stability is important for a titration electrode. A manual method is described in X2.3 that can be carried out with a pH meter or titrator set to read millivolts continuously.

X2.2 The essence of the test method is to challenge the electrode coming from rest in a water solution with buffers and measure the potential after 30 s and 60 s. A fast electrode reaches a stable point in less than 30 s and changes little from 30 s to 60 s. Use buffers pH 4, pH 7, and pH 11 for this check, as needed.

X2.3 Procedure

X2.3.1 Set the titrator or pH meter to read millivolts continuously. Have provision for stirring the buffer solution at the same speed used for the titrations.

X2.3.2 Allow the electrode to stabilize for 1 min in distilled or equivalent deionized water.

X2.3.3 Remove the electrodes from the water, and place them in the pH 4 buffer. Start a stopwatch at about the moment when the buffer touches the electrode. After 30 s, note the potential.

X2.3.4 After another 30 s, note the potential again. The difference between the two potentials is termed the drift.

X2.3.5 Repeat the procedure for pH 7 buffer and pH 11 buffer.

X2.4 Calculate the drift for each of the three buffers. The electrode response may be judged as follows:

drift < 1 excellent
1 < drift < 2 good
2 < drift < 3 acceptable
3 < drift < 4 questionable
4 < drift unacceptable

X2.5 The difference between the 60 s potentials for pH 4 buffer and pH 7 buffer should be greater than 162 mV, or 54 mV ⁄pH number. Electrodes with a slope less than 54 mV ⁄pH number are not reliable for titration.