



Designation: D8126 – 21

# Standard Test Method for Efficient Basicity Determination by Potentiometric Hydrochloric Acid Titration<sup>1</sup>

This standard is issued under the fixed designation D8126; 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.

## 1. Scope\*

1.1 This test method covers a procedure for the determination of the efficient basicity (EBas) in new marine cylinder lubricants that lubricate the upper part, that is, piston-ring-cylinder area, of two-stroke marine engines.

1.2 This test method has been developed for marine cylinder lubricants, having base number (BN) (measured by Test Method D2896) from 20 mg KOH/g to 100 mg KOH/g, and an EBas from 10 mg KOH/g to 36 mg KOH/g.

1.3 In this test method, only the efficient basicity is determined, corresponding to the components or part of components that have a major role in neutralization of the acidic species formed in the combustion of the fuel in the marine engine. It differentiates between the fastest reacting species and the last one to react like overbasing compounds in detergent (classically mineral calcium carbonate,  $\text{CaCO}_3$ ). 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.

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

1.5 *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. Some specific hazards statements are given in Sections 6 and 7.*

1.6 *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.*

<sup>1</sup> 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.

Current edition approved Nov. 1, 2021. Published November 2021. Originally approved in 2017. Last previous edition approved in 2017 as D8126 – 17. DOI: 10.1520/D8126-21.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- 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
- D4739 Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration
- D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

## 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.

3.1.2 *efficient basicity, EBas, n*—the quantity of hydrochloric acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of sample, required to neutralize the basic components, which are organic species, of the tested lubricant in a specified solvent to a specified buffer endpoint using a specified detection system.

## 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

<sup>2</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

titration curve according to the criteria given in Section 12 and used to calculate the EBAs.

## 5. Significance and Use

5.1 Lubricants 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 measurement of the amount of basic substances in the oil under the conditions of the testing procedure.

5.2 A primary objective of a marine cylinder lubricant is the neutralization of sulfuric acid, produced during fuel combustion, to protect the engine from corrosion. The EBAs method characterizes the more efficient basic species of the lubricant reacting with acids from the beginning of the neutralization (when the lubricant milieu is basic) until an equilibrium state where the lubricant becomes slightly acidic. The use of hydrochloric acid (HCl) allows differentiating basicities of various strengths during titration.

5.3 In marine lubricants, the constituents that can be considered to have basic properties are primarily organic and inorganic bases coming from the detergent. Basicity can also be brought to the lubricant by other components including dispersants, amino compounds, or any organic basic components. This test method uses the same titration system as that of Test Method D4739, however the evaluation and interpretation of the titration result is different. The hydrochloric acid is used as the titrant in this test method and Test Method D4739, whereas Test Method D2896 uses a stronger acid, perchloric acid. While all three methods can be considered as complementary to evaluate the basicity of lubricants, this test method is only used for marine cylinder lubricants.

5.4 This test method measures only the efficient basicity of the lubricant, which represents only the part of the total basicity, until the point of which the lubricant becomes slightly acidic. It will depend on the components of the formulation itself. In that respect, the EBAs cannot be compared to base number given by Test Methods D4739 or D2896. The EBAs is then complementary information to the base number, giving performance in efficiency of neutralization of acidic species.

## 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 titrimer 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  $\pm 0.001$  mL for automatic titrators. For manual buret, it should be  $\pm 0.005$  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 lithium chloride (LiCl) in ethanol.

6.3.1 *Combination Electrode*—Sensing electrodes may have the silver/silver chloride (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.

6.3.1.1 In the reference compartment, the sensing electrode part shall use a glass membrane designed for nonaqueous 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. 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.<sup>3</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*—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 5 buffer solution with a tolerance of  $\pm 0.02$  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 *Chloroform*—Reagent grade. (**Warning**—Toxic and suspected carcinogen.)

7.5 *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 0.1 g (weigh accurately at the nearest 0.0001 g)

<sup>3</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.

of primary standard Tris(hydroxymethyl)aminomethane dissolved in 60 mL CO<sub>2</sub>-free water.

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

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

7.8 *Propan-2-ol (Isopropyl Alcohol)*—Anhydrous, (less than 0.1 % H<sub>2</sub>O). (**Warning**—Flammable.)

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

7.10 Alternative volumes of solutions may be prepared provided the final solution concentration is equivalent.

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

7.12 *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.

7.13 *Tris(hydroxymethyl)aminomethane ((HOCH<sub>2</sub>)<sub>3</sub>CNH<sub>2</sub>), primary standard, dried*—Crush a 1 g to 3 g portion of primary standard Tris(hydroxymethyl)aminomethane to a fine powder using an agate or other nonreactive mortar and pestle for 60 s to 90 s. Take special care to crush any larger crystals. Dry the crushed material at room temperature (22 °C to 23 °C) for 24 h in a vacuum desiccator over anhydrous magnesium perchlorate or equivalent. Drying of this material at elevated temperatures is not recommended, owing to the possibility of decomposition.

## 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.

8.1.1.1 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 months 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 Prepare the electrodes as described in 8.2, immerse them in the pH 5 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 pH 5 acidic buffer solution is taken as the end point for the EBAs.

## 10. Preparation of Lubricant Samples

10.1 When applicable, refer to Practice [D4057](#) (Manual Sampling) or Practice [D4177](#) (Automatic Sampling) for proper sampling techniques.

10.1.1 When sampling used lubricants, the specimen shall be representative of the system sampled and shall be free of contamination from external sources.

10.1.2 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 1—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.

## 11. Procedure for EBAs Measurement

11.1 Weigh 0.8 g ± 0.08 g sample into a suitable titration vessel and record the weight to the nearest 0.0001 g.

11.2 Add 75 mL of titration solvent. 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 splattering 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 milliliters of titrant before beginning a titration.

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 EBAs 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 is reached.

## 12. Calculation

12.1 Mark as the end point the point on the curve that corresponds to the acidic aqueous pH 5 buffer potential. See Fig. 1 for examples of end points.

NOTE 3—The extensive work done on EBAs determinations on several marine cylinder lubricants indicated that pH 5 aqueous acid buffer was the best choice to discriminate the efficient basicity.

12.2 Calculate the EBAs as follows:

$$EBas, \text{ mg KOH/g} = [(A - B) \times M \times 56.1] / W \quad (1)$$

where:

A = alcoholic HCl solution used to titrate the sample to the end point (aqueous acidic pH 5 buffer), mL,

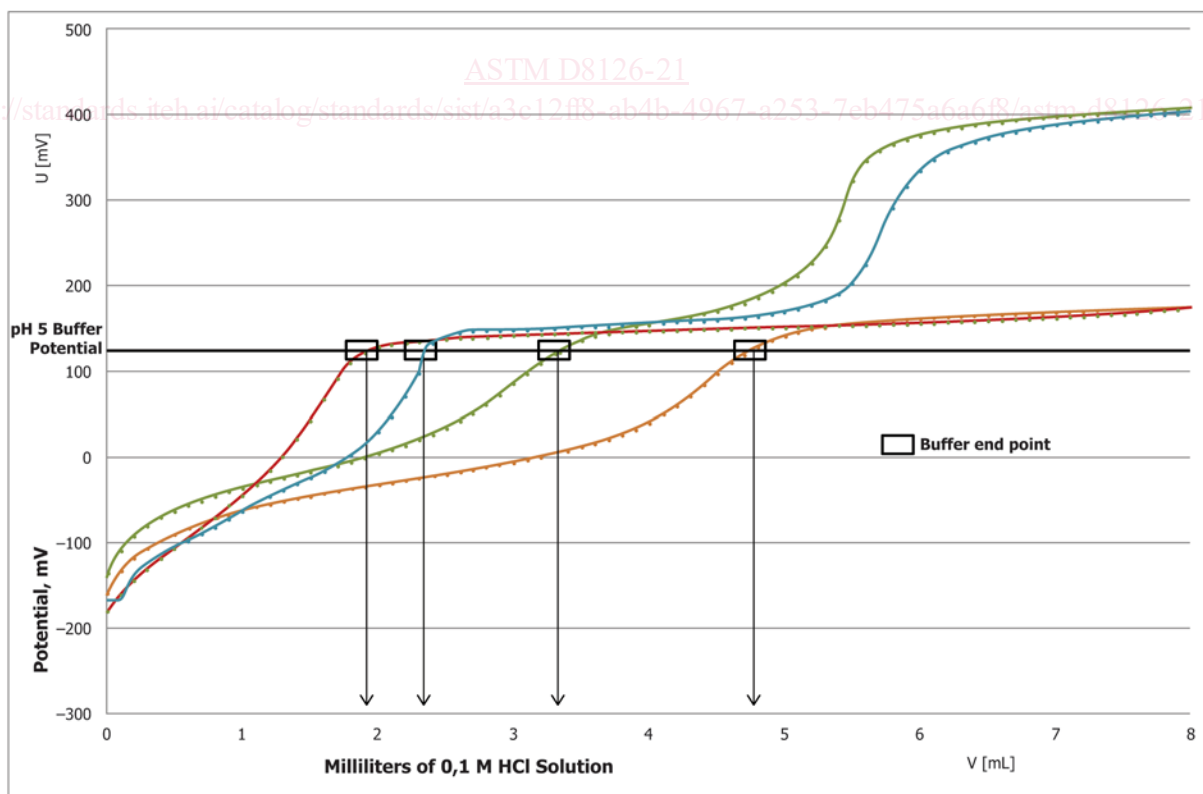


FIG. 1 Example Titration Curves to Illustrate Selection of End Points