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## Standard Test Methods for Saponification Number of Petroleum Products<sup>1</sup>

This standard is issued under the fixed designation D 94; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 These test methods<sup>2</sup> cover the determination of the amount of constituents in petroleum products such as lubricants, additives, and transmission fluids that will saponify under the conditions of the test.

1.1.1 Two test methods are described: Method A—Color Indicator Titration (Sections 6-13), and Method B—Potentiometric Titration (Sections 14-23).

1.2 Because compounds of sulfur, phosphorus, the halogens, and certain other elements that are sometimes added to petroleum products also consume alkali and acids, the results obtained indicate the effect of these extraneous materials in addition to the saponifiable material present. Results on products containing such materials, on used internal-combustion-engine crankcase oils, and on used turbine oils must be interpreted with caution.

NOTE 1—The materials referred to above, which are not normally considered saponifiable matter, include inorganic or certain organic acids, most nonalkali soaps, and so forth. The presence of such materials increases the saponification number above that of fatty saponifiable materials for which the test method is primarily intended. The odor of hydrogen sulfide near the end of the back-titration in the saponification test is an indication that certain types of reactive sulfur compounds are present in the sample. In the case of other reactive sulfur, chlorine, and phosphorus compounds and other interfering materials, no simple indication is given during the test. A gravimetric determination of the actual amount of fatty acids is probably the most reliable method for such compounds. Test Methods D 128 or IP Method 284/86 can be used to determine fatty acids gravimetrically.

1.3 The values stated in SI units are to be regarded as the 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. For specific hazard statements, see Sections 6, 7, 8, 10, 15, 16, 17, and 19.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 117 Guide to Test Methods, Specifications, and Guides for Electrical Insulating Oils of Petroleum Origin<sup>3</sup>

D 128 Test Methods for Analysis of Lubricating Grease<sup>4</sup>

D 1193 Specification for Reagent Water<sup>5</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>6</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>6</sup>

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance<sup>7</sup>

#### 2.2 Institute of Petroleum Standards:

IP 136 Method of Test for Saponification Number of Petroleum Products<sup>8</sup>

IP 284 Method of Test for Fatty Acids<sup>8</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *saponification number, n*—the number of milligrams of potassium hydroxide consumed by 1 g of a sample under the conditions of the test.

3.1.1.1 *Discussion*—The value of the saponification number in these test methods can be affected by the presence of other alkali-reactive species, as described in Note 1.

3.1.2 *saponify, v*—to hydrolyze a fat with alkali to form an alcohol and the salt of a fatty acid.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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<sup>2</sup> Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in Guide D 117. Experience has shown that for transformer oils, Test Method D 94, modified by use of 0.1 M KOH solution and 0.1 M HCl, is more suitable.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 10.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>7</sup> *Annual Book of ASTM Standards*, Vol 05.03.

<sup>8</sup> Available from Institute of Petroleum, 61 New Cavendish St., London, W.I., England.

#### 4. Summary of Test Method

4.1 A known mass of the sample is dissolved in a suitable solvent, such as butanone (methyl ethyl ketone), xylenes, or Stoddard Solvent, or a combination thereof (**Warning**—Extremely flammable. Vapors can cause flash fire), and is heated with a known amount of alcoholic potassium hydroxide (KOH). The excess alkali is titrated with standard acid, and the saponification number is calculated.

4.2 The titration end point can be detected either colorimetrically (Method A) or potentiometrically (Method B).

#### 5. Significance and Use

5.1 Petroleum products can contain additives that react with alkali to form metal soaps. Fats are examples of such additives. Also, certain used engine oils, especially from turbine or internal combustion engines, can contain chemicals that will similarly react with alkali. The saponification number expresses the amount of base that will react with 1 g of sample when heated in a specific manner. This then gives an estimation of the amount of acid present in the sample, that is, any free acid originally present plus any combined (for example, in esters) that have been converted to metal soaps during the heating procedure.

5.2 Saponification numbers are also used in setting product specifications for lubricants and additives.

#### METHOD A—COLOR INDICATOR TITRATION

#### 6. Apparatus

6.1 *Erlenmeyer Flask and Condenser*—An Erlenmeyer flask, 250 or 300-mL capacity, alkali-resistant (see **Note 2**) and (**Warning**—Causes severe burns; a recognized carcinogen; strong oxidizer—contact with other material can cause fire; hygroscopic), to which is attached a straight or mushroom-type reflux condenser. The straight-type condenser is fitted to the flask with a ground-glass joint; the mushroom-type condenser must fit loosely to permit venting of the flask. Water reflux condensers can also be used instead of air condensers.

**NOTE 2**—Do not use scratched or etched Erlenmeyer flasks because KOH will react with them. The glassware shall be chemically clean. It is recommended that flasks be cleaned with chromic acid cleaning solution (Alternatively, Nochromix or similar products can be used.)

6.2 *Hot Plate*—A suitable hot plate heated by either electricity or steam. (**Warning**—Thermal hazard; in addition to other precautions, avoid contact with exposed skin.)

#### 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>9</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.

**NOTE 3**—Commercially available reagents may be used in place of laboratory preparations, provided they meet the specifications outlined.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III in Specification **D 1193**.

7.3 *Alcohol*<sup>10</sup>—95 % ethanol (**Warning**—Flammable. Denatured—Cannot be made nontoxic) (see **Note 4**) and (**Warning**—Flammable) or 95 % ethanol to which has been added 10 volume % of methanol (see **Note 4** and **Note 5**) or absolute alcohol.

**NOTE 4**—It has been found that 99 % 2-propanol (isopropyl alcohol) can be substituted for the purified ethanol with entirely satisfactory results. This substitution is not permissible, however, in referee tests.

**NOTE 5**—This composition is available under the name of “U.S. Department of Treasury Specially Denatured Formula 30 (Regulation No. 3-1938).”<sup>10</sup> Formula 3A plus 5 % methanol is an equivalent.

7.4 *Aqueous Hydrochloric Acid Standard Solution (0.5 M)*—Standardize to detect molarity changes of 0.0005 by titrating with standard alcoholic KOH solution (see **7.8** and **Note 6**).

**NOTE 6**—Where saponification numbers below one are expected, better precision can be obtained by substituting 0.1 M KOH solution and HCl for the 0.5 M reagents in Sections **7, 8, 10, 17, and 19**.

7.5 *Butanone (Methyl Ethyl Ketone)*, technical grade. Store in dark or brown bottles. (**Warning**—See **4.1**.)

7.6 *Naphtha*, (**Warning**—Extremely flammable. Harmful if inhaled. Vapors can cause flash fire.) ASTM Precipitation Grade (or *Petroleum Spirit-60/80* or hexanes) (**Warning**—Combustible. Vapor harmful.) Petroleum spirit shall conform to the current **IP 136**. <https://standards.iteh.ai/catalog/standards/sist/b69445741783/astm-d94-02>

7.7 *Phenolphthalein Solution, Neutralized*—Dissolve  $1.0 \pm 0.1$  g of phenolphthalein in 100 mL of alcohol (see **7.3**). Neutralize to faint pink color with dilute (0.1 M) alcoholic KOH solution.

7.8 *Alcoholic Potassium Hydroxide Standard Solution (0.5 M)*—Prepare approximately 0.5 M solution by dissolving KOH in the alcohol specified in **7.3**. Allow the solution to settle in a dark place. Filter the solution, and allow to stand for 24 h before using.

7.8.1 Alternatively prepare 0.5 or 0.1 M alcoholic KOH by mixing a commercially available KOH ampule (which is carbonate free) with 95 % alcohol. Using this type solution gives consistent blanks and does not give multiple breaks (see **Note 7**).

**NOTE 7**—Because of the relatively large coefficient of cubic expansion of organic liquids such as 2-propanol (isopropyl alcohol), the standard alcoholic solution has to be standardized at temperatures close to those employed in the titrations of samples.

<sup>9</sup> *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.

<sup>10</sup> Available from the U.S. Bureau of Alcohol, Tobacco, and Firearms, Distilled Spirits and Tobacco Branch, 1200 Pennsylvania Avenue, NW, Washington, DC 20226.

7.8.2 The KOH solutions shall be standardized by titrating with standard potassium hydrogen phthalate solution (see 7.9 and Note 7).

7.9 *Potassium Hydrogen Phthalate*—(C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>) 0.1 M Standard Solution—Weigh 2.0422 ± 0.0002 g of potassium hydrogen phthalate that has been dried at 110 ± 5°C to a constant weight into a 100-mL volumetric flask. Dissolve in reagent water. Some heating may be necessary to dissolve the solid. Dilute to 100 mL with distilled or deionized water, after the solution has cooled.

7.10 *Stoddard Solvent*, technical grade. (**Warning**—Extremely flammable. Harmful if inhaled.)

7.11 *Xylene*, reagent grade. (**Warning**—Extremely flammable. Harmful if inhaled.)

## 8. Blank Determinations

8.1 Perform a blank determination concurrently with each set (see Note 8) (one or more) of samples as follows: measure accurately from a buret or volumetric pipet (see Note 9) into the Erlenmeyer flask 25 ± 0.03 mL of alcoholic KOH solution and 25 ± 1 mL of butanone (methylethyl-ketone) or one of the alternative solvents. Connect the condenser to the flask, and heat for the same amount of time as that used for the sample after refluxing begins. (**Warning**—The reflux condenser should be clamped securely to prevent it from tipping over onto the hot plate with possible breakage of glassware. See also Note 10.) Immediately add 50 mL of ASTM precipitation naphtha (**Warning**—See 7.6, also Note 11 and Note 12) by cautiously pouring the naphtha down the condenser (disconnect condenser if mushroom-type is used), and titrate the blank while hot, without reheating, with 0.5 M hydrochloric acid (HCl) using three drops of neutralized phenolphthalein indicator solution.

NOTE 8—Run blank determinations in duplicate on samples requiring the highest accuracy. The precision data are based on duplicate blank determinations. A single blank is sufficient for routine work.

NOTE 9—If a volumetric pipet is used to measure the alcoholic KOH solution, wait 30 s after delivery to allow for complete drainage.

NOTE 10—Although standard procedure requires 30 min of reflux, some fats are readily saponified and complete saponification takes place within 10 min. On the other hand, difficult saponifiable materials require more than 2 h. Neither the shortened period nor the longer period should be used except by mutual consent of the interested parties.

NOTE 11—Pouring 50 mL of naphtha down the condenser at the end of the saponification not only rinses the condenser but also cools the reaction mixture.

NOTE 12—In the case of insulating oils, the addition of ASTM precipitation naphtha or petroleum spirit is not necessary.

8.2 After the indicator color has been discharged, add, dropwise, more indicator solution. If this addition of indicator restores the color, continue the titration, making further dropwise additions of indicator, if necessary, until the end point is reached (Note 13). The end point is reached when the indicator color is completely discharged and does not immediately reappear upon further dropwise addition of the indicator solution. Record as  $V_1$  in 11.1.

NOTE 13—Avoid emulsification of titration mixture, but ensure phase contact by swirling the flask vigorously as the end point is approached.

## 9. Sample

9.1 Using Practice D 4057 (manual sampling) or Practice D 4177 (automatic sampling) as a guideline for obtaining a representative sample, make sure that the portion of the sample to be tested appears homogenous. Choose the size of the sample so that the back-titration volume is from 40 to 80 % of the blank, but do not exceed a 20-g sample weight (see Note 14).

NOTE 14—The following sample sizes are suggested:

Saponification Number	Sample Size, g
181 to 400	1
111 to 180	2
71 to 110	3
31 to 70	5
16 to 30	10
0 to 15	20

## 10. Procedure

10.1 Weigh the specimen to the nearest 0.01 g (record as  $W$  in 11.1), such as by difference, from a small beaker into the Erlenmeyer flask. Add 25 ± 1 mL of butanone or one of the alternative solvents (**Warning**—See 4.1), followed by 25 ± 0.03 mL of alcoholic KOH solution (**Warning**—See 7.3) measured accurately from a buret or volumetric pipet (see Note 6).

10.2 Dissolve the difficult to dissolve samples, such as lubricants and additives, first in 15 to 25 mL of Stoddard Solvent (**Warning**—See 7.10) or xylene (**Warning**—See 7.11) before adding butanone (**Warning**—See 4.1).

10.3 Connect the condenser to the flask and heat for 30 min after refluxing begins (see Note 10). Immediately add 50 mL of ASTM precipitation naphtha (**Warning**—Do not pour naphtha while the flask is on the hot plate) and (see 7.6) by cautiously pouring the naphtha down the condenser (see Note 11) (disconnect condenser if mushroom-type before adding the naphtha).

10.4 Titrate the solution while hot (without reheating) with 0.5 M HCl using three drops of neutralized phenolphthalein indicator solution (**Warning**—See 7.3). When the indicator color is discharged, add, dropwise, more indicator solution. If this addition of indicator restores the color, continue the titration, making further dropwise additions of indicator, if necessary, until the end point is reached (Note 13). The end point is reached when the indicator color is completely discharged and does not immediately reappear upon further dropwise addition of the indicator solution. (Record as  $V_2$  in 11.1.) When testing waxes, it may be necessary to reheat the solution during titration to prevent solidification of the sample.

## 11. Calculation

11.1 Calculate the saponification number,  $A$ , as follows:

$$A = 56.1 M (V_1 - V_2)/W \quad (1)$$

where:

- $M$  = molarity of the hydrochloric acid,
- $V_1$  = volume of acid used in titrating the blank, mL,
- $V_2$  = volume of acid used in titrating the sample, mL,
- $W$  = sample, g, and
- 56.1 = molecular weight of KOH.



**12. Report**

12.1 For saponification numbers of less than 50, report the saponification number to the nearest 0.5 mg KOH/g sample.

12.2 For saponification number of 50 or more, report to the nearest whole number.

12.3 For electrical insulating oils, report the values to the nearest 0.1 mg KOH/g sample.

12.4 Report the saponification numbers as obtained by Test Methods D 94, Method A.

**13. Precision and Bias**

13.1 *Precision*—The data shown in Fig. 1 shall be used for judging the acceptability of results (95 % probability) (see Note 15).

NOTE 15—No precision intervals can be given for highly colored new or used oils, or for oils that produce dark-colored solutions upon saponification, as color can interfere with the detection of the end point of the titration. In such cases, potentiometric titration (Method B) can be used.

13.1.1 *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 Fig. 1 values only in one case in twenty.

13.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the Fig. 1 values only in one case in twenty.

13.2 *Bias*—This is an empirical test method, and there are no accepted reference materials that can be compared; hence, bias cannot be determined.

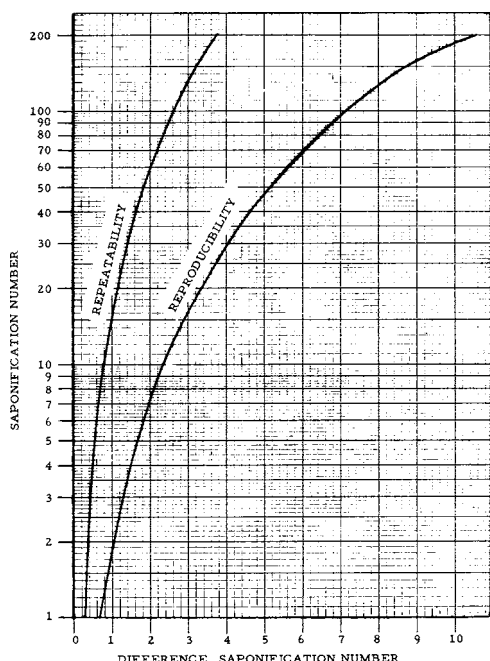


FIG. 1 Precision Data

**METHOD B—POTENTIOMETRIC TITRATION**

**14. Apparatus**

14.1 *Erlenmeyer Flask and Condenser*—An Erlenmeyer flask, 250 or 300-mL capacity, alkali-resistant (see Note 2), to which is attached a straight or mushroom-type reflux condenser. The straight-type condenser is fitted to the flask with a ground-glass joint; the mushroom-type condenser must fit loosely to permit venting of the flask. Water reflux condensers can also be used instead of air condensers.

14.2 *Hot Plate*—A suitable hot plate heated by either electricity or steam (see 6.2).

14.3 *Potentiometric Titrator Automatic, Recording or Manual*—High-precision titrator capable of distinguishing the carbonate from pure caustic in the titration of ACS reagent grade KOH by hydrochloric acid (HCl).<sup>9</sup>

14.4 *Electrodes*—High-quality electrodes must be used. Cleaning and maintenance of the electrodes are vital to their satisfactory operation.

14.4.1 *Combination Glass Electrode*, or a suitable glass electrode and a suitable reference electrode; either silver chloride (AgCl)/saturated alcoholic lithium chloride (LiCl) or saturated potassium chloride (KCl) inverted glass sleeve calomel electrode can be used.

14.5 *Magnetic Stirring Bars*—Because, on titration, two immiscible liquid phases appear, and potassium chloride (KCl) is precipitated, stirring conditions are critical, and very vigorous stirring is essential (see Note 16).

NOTE 16—If a large magnetic stir bar is used, only slow speeds are possible, and if too small a stir bar is used, the highest rotational speeds cause insufficient agitation of the bulk of the liquid. The optimum magnetic stir bar has been found to be a 2.5 by 0.5-cm plain polytetrafluoroethylene (PTFE)-coated cylinder. This magnetic stirrer is not needed if a propeller or paddle stirrer is used.

14.6 *Tall Form Beakers*—250 or 300-mL size Berzelius type tall-form glass beaker with or without a spout (see Note 17).

NOTE 17—The potentiometric titration cannot be performed in the Erlenmeyer flask used in digestion. The small opening of this flask will not accommodate the electrodes, unless a combination electrode is used.

14.7 *Stirrer, Buret Stand, Titration Vessel*—A typical cell assembly is shown in Fig. 2. The propeller or paddle stirrer is not needed if a magnetic stirrer is used.

14.7.1 *Stirrer*, either mechanical or electrical, with variable speeds and with propeller or paddle of chemically inert material. If an electrical stirrer is used, it must be grounded so that disconnecting or connecting the power to the motor will not produce a permanent change in meter reading during the course of titration. A magnetic stirrer with stirring bar can be used provided it meets the above conditions.

14.7.2 *Buret*, 10 or 20-mL, graduated in 0.05-mL divisions and calibrated with an accuracy of  $\pm 0.02$  mL, or an automatic buret of similar accuracy.

14.7.3 *Titration Stand*, suitable to support the beaker, electrodes, stirrer, and buret. An arrangement that allows for the removal of the beaker without disturbing the electrodes, buret, and stirrer is desirable (see Note 18).

NOTE 18—Some apparatus can be sensitive to interference by static