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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

<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.

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.

7.7 *Phenolphthalein Solution, Neutralized*—Dissolve 1.0 ± 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.

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

<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.

7.9 *Potassium Hydrogen Phthalate*—( $C_8H_5KO_4$ ) 0.1 M Standard Solution—Weigh  $2.0422 \pm 0.0002$  g of potassium hydrogen phthalate that has been dried at  $110 \pm 5^\circ C$  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  $25 \pm 0.03$  mL of alcoholic KOH solution and  $25 \pm 1$  mL of butanone (methyl ethyl-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  $25 \pm 1$  mL of butanone or one of the alternative solvents (**Warning**—See 4.1), followed by  $25 \pm 0.03$  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.

## 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 con-

denser. 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

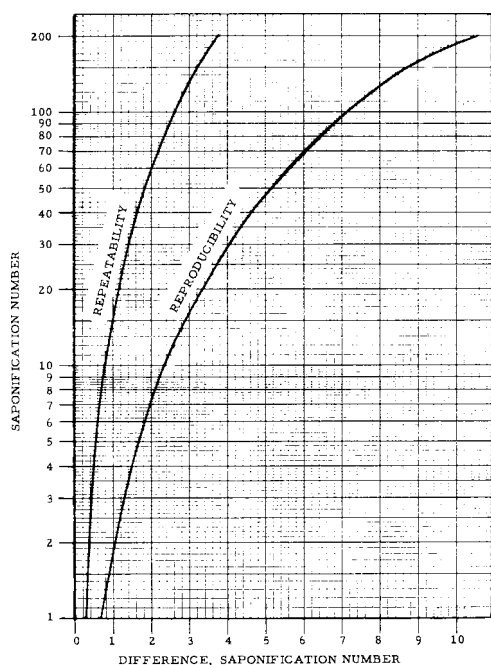


FIG. 1 Precision Data

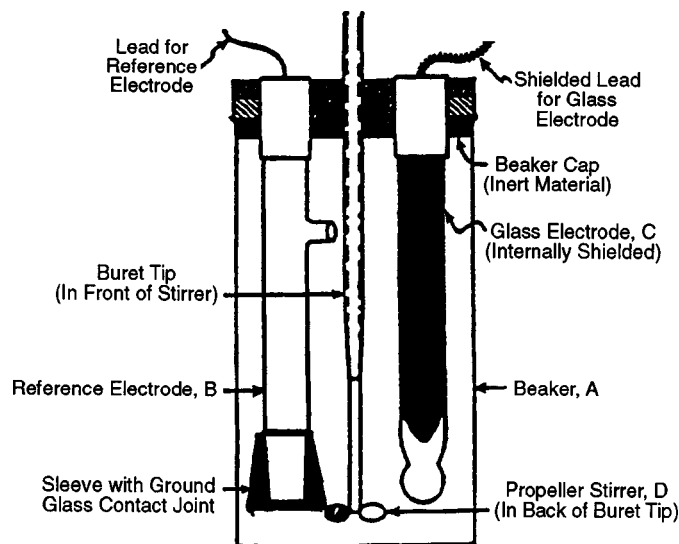


FIG. 2 Cell for Potentiometric Titration



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 electricity, shown by erratic movements of recorder pen or meter indicator, when the titration assembly (beaker and electrodes) is approached by the operator. In that case, surround the beaker closely with a cylinder of copper gauze that is electrically grounded.

## 15. Reagents

15.1 *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 19—Commercially available reagents may be used in place of laboratory preparations, provided they meet the specifications outlined.

15.2 *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.

15.3 *Alcohol*—95 % ethanol (**Warning**—See 7.3) (see Note 4) or 95 % ethanol to which has been added 10 volume % of methanol (see 7.3, Note 4, and Note 5), or absolute alcohol.

15.4 *Aqueous Hydrochloric Acid Standard Solution (0.5 M)*—Standardize frequently enough to detect molarity changes of 0.0005, by titrating with standard alcoholic KOH solution (see 15.7 and Note 6).

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

15.6 *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.

15.7 *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.

15.7.1 Alternatively prepare 0.5 or 0.1 M alcoholic KOH by mixing 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).

15.7.2 The KOH solutions shall be standardized by titrating

with standard potassium hydrogen phthalate solution (see 15.8 and Note 7).

15.8 *Potassium Hydrogen Phthalate*—( $C_8H_5KO_4$ ) 0.1 M *Standard Solution*—Weigh  $2.0422 \pm 0.0002$  g of potassium hydrogen phthalate that has been dried at  $110 \pm 5^\circ C$  for 1 h into a 100-mL volumetric flask. Dissolve in distilled or deionized water. Some heating can be necessary to dissolve the solid. Dilute to 100 mL with distilled or deionized water after the solution has cooled.

15.9 *Stoddard Solvent*, technical grade. (**Warning**—See 7.10.)

15.10 *Potassium Chloride, Aqueous (3.0 M)*—Prepare by dissolving 225.2 g reagent grade KCl in 1.0 L of distilled or deionized water.

15.11 *Xylene*, reagent grade. (**Warning**—See 7.11.) See 15.1.

15.12 *Chlorobenzene*, reagent grade. See 15.1.

## 16. Preparation, Testing, and Maintenance of Electrode System

### 16.1 *Preparation of Electrodes:*

16.1.1 If the calomel electrode is to be changed from nonaqueous to aqueous bridge, drain out the nonaqueous solution, wash with water and methanol, then rinse the outer jacket (salt bridge) several times with 3.0 M aqueous KCl electrolyte solution. Finally, fill the outer jacket with 3.0 M aqueous KCl electrolyte solution up to the filling hole.

16.1.2 When using the sleeve-type electrode, carefully remove the ground-glass sleeve 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 and to wet the ground surfaces thoroughly with electrolyte. Set the sleeve firmly in place, refill the outer jacket with the 3.0 M aqueous KCl electrolyte solution, and rinse the electrode with chlorobenzene.

16.1.3 When in use, the electrolyte level in the calomel electrode should be kept above that of the liquid in the titration beaker to prevent entry of contaminants into the salt bridge. When not in use, fill the calomel electrode with 3.0 M aqueous KCl electrolyte solution, leave the bung in the filling orifice, and immerse both electrodes in distilled water, keeping the level of the electrolyte above that of the distilled water.

16.2 *Testing of Electrodes*—Test when new electrodes are installed, and retest once a month thereafter by standardizing 10 mL of 0.5 M alcoholic KOH using 0.5 M aqueous HCl.

### 16.3 *Maintenance of Electrodes:*

16.3.1 Clean the glass electrode (see Note 17) at least once every week during continual use by immersing in cold chromic acid cleaning solution (**Warning**—See 16.3.3) or Nochromix solution.

16.3.2 Drain the calomel electrode at least once each week and refill with fresh 3.0 M aqueous KCl electrolyte as far as the filling hole. Ascertain that crystallized KCl is present. Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker of vessel at all times.

16.3.3 Immerse the lower halves of the electrodes in water when not in use. Do not allow them to remain immersed in titration solvent for any appreciable period of time between titrations. Although the electrodes are not extremely fragile,

handle them carefully at all times. (**Warning**—Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regularly testing the electrodes are very important in obtaining repeatable potentials because contamination can introduce uncertain erratic and unnoticeable liquid contact potentials, resulting in nonrepeatable results.)

16.3.4 At the end of the blank titration and between successive titrations a thin film of KCl crystals coats the electrode and the titrant delivery tip. Use a jet of water from a plastic squeeze bottle to remove it. Then rinse the electrode by immersion in a beaker full of distilled water for a few seconds. Dry the electrode by blotting with a paper towel; do *not* rub the electrode.

16.3.5 At the end of a set of sample titrations a mixture of KCl crystals and of sample fractions coats the electrode and titrant delivery tip. Cleaning is performed by immersion in a titration beaker containing the following:

- 50 mL of Stoddard Solvent
- 38 mL of 2-Propanol
- 38 mL of Distilled Water

Stir the solution for a time long enough to dissolve the coating; typically less than 1 min. Remove the traces of washing solution from the electrode with a jet of water from a plastic squeeze bottle. Then rinse the electrode further by immersion in a beaker full of water stirred for a few seconds. Dry the electrode by blotting with a paper towel; do *not* rub the electrode.

16.3.6 The electrode must be held firmly in a steady holder so that it does not wobble when the liquid is vigorously stirred. Electrode wobbling creates electrical noise, which interferes with the determination of the end points, resulting in nonrepeatable results.

**17. Blank Determination**

17.1 Make 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 (methyl ethyl ketone) or one of the alternative solvents. Connect the condenser to the flask, and heat for 30 min (see 8.1 and Note 10) after refluxing begins. Immediately add 50 mL of ASTM precipitation naphtha (**Warning**—See 7.6) (see also Note 11 and Note 12) by cautiously pouring the naphtha down the condenser (disconnect condenser if mushroom type is used), and potentiometrically titrate the blank while hot, without reheating, with 0.5 M HCl.

17.2 Transfer the solution into a 200-mL borosilicate beaker, taking care to wash the flask with two 10-mL portions of naphtha (see 7.6).

17.3 Place the titration solution with a magnetic stir bar on a magnetic stir plate. Immerse the electrodes as far as possible without touching the magnetic stir bar. Adjust the speed of stirring to maximum possible without causing excessive aeration or splattering of solution.

17.4 Titrate the blank solution with 0.5 M aqueous HCl added at the rate of 2 mL/min, using potentiometric titrator. Two inflections with corresponding equivalence points are expected. The first one corresponds to the free KOH (record as

$V_B$  in 21.1) and the second one to the small amount of potassium carbonate ( $K_2CO_3$ ) generally present in commercial (KOH) (see Fig. 3).

17.5 A pre-addition of titrant used in the blank to expedite the titration time.

**18. Sample**

18.1 Make sure that the sample 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).

**19. Procedure**

19.1 Weigh the specimen to the nearest 0.01 g (record as  $W$  in 21.1) 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).

19.2 Dissolve the difficult to dissolve samples such as lubricants and additive first in 15 to 25 mL of Stoddard Solvent (**Warning**—See 7.10) or xylene (**Warning**—See 7.9) before adding butanone (**Warning**—See 4.1).

19.3 Connect the condenser to the flask and heat for 30 min after refluxing begins (see 8.1 and 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).

19.4 Titrate the solution while hot (without reheating) with 0.5 M aqueous HCl. Follow the titration procedure used for the blank (see Section 17) using the potentiometric titrator. Fig. 3 shows a complete titration curve for a sample. The titration of the sample differs from the blank in that no pre-addition of titrant is made and the titration conditions are much less critical.

19.4.1 The potential readings are fairly constant. The reading before any addition of titrant is -520 mV. The first inflection is moderately sharp and takes place around -300 mV.

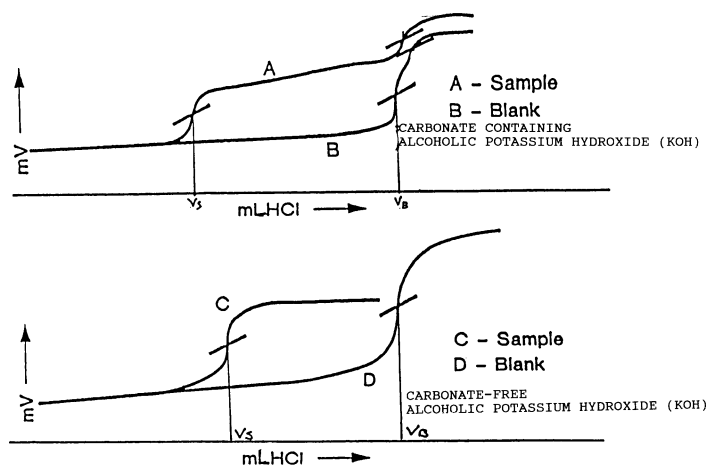


FIG. 3 Complete Titration Curve for a Sample

The second inflection is extremely sharp and takes place around 50 mV.

## 20. Quality Control Checks

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

20.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and the control limits of the QC sample (see *ASTM MNL 7*).<sup>11</sup>

20.3 Record the QC results and analyze by control charts or other statistical equivalent technique to ascertain the statistical control status of the total testing process (see *ASTM MNL 7*).<sup>11</sup> Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in process recalibration.

20.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. 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. The QC precision should be periodically checked against the precision listed in the Precision and Bias section of this method to ensure data quality.

20.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

20.6 See *ASTM MNL 7*,<sup>11</sup> and Practice D 6299 for further guidance on QC and Control Charting techniques.

## 21. Calculation

21.1 Calculate the saponification number, *A*, as follows:

$$A = \frac{56.1 M (V_B - V_S)}{W} \quad (2)$$

where:

56.1 = molecular weight of KOH,

*M* = molarity of HCl,

$V_B$  = volume of acid used in titrating the blank, mL,

$V_S$  = volume of acid used in titrating the sample, mL,  
and

*W* = sample weight, g.

21.2 The first inflection point is due to hydroxide and serves as the end point in the titration. If the added KOH titrant contains carbonate contamination, a second inflection point may be present (see Fig. 3). If this occurs, use the first inflection point as the titration end point for the blank ( $V_B$ ) and the sample ( $V_S$ ).

## 22. Report

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

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

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

22.4 Report the saponification test numbers as obtained by Test Methods D 94, Method B.

## 23. Precision and Bias

23.1 Based on the round robin conducted using seven lube oil additives and automatic transmission fluids and 16 laboratories, the following precision estimates were obtained:<sup>12</sup>

23.1.1 *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 2.76 mg KOH/g saponification number only in one case in twenty.

23.1.2 *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 10.4 mg KOH/g saponification number only in one case in twenty.

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

## 24. Keywords

24.1 additives; lubricating oils; potentiometric titration; saponification number

<sup>11</sup> *ASTM MNL 7*, "Manual on Presentation of Data Control Chart Analysis," 6th ed., ASTM International, W. Conshohocken, PA.

<sup>12</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1340.

## APPENDIX

## (Nonmandatory Information)

## X1. ANALYTICAL HINTS FOR PERFORMING TEST METHODS D 94

X1.1 The following is a helpful list of analytical hints for performing this test method. In no way does it replace the full text of this test method.

X1.1.1 Do not use scratched or etched Erlenmeyer flasks because KOH is more likely to react with them. Flasks should be cleaned with chromic acid or some other non-chromium, strongly oxidizing cleaning solution.

X1.1.2 Standardize aqueous HCl against alcoholic KOH to be able to detect molarity changes of 0.0005.

X1.1.3 Standardize alcoholic KOH solution against standard K-H-Phthalate solution.

X1.1.4 During prolonged storage, alcoholic KOH solution becomes discolored, and in such cases, it should be discarded.

X1.1.5 It is preferable to prepare the KOH solution from a commercially available KOH ampule. This type of solution gives consistent blanks. Since it does not contain carbonate, it does not give multiple inflection points.

X1.1.6 When saponification numbers below one are expected, better precision can be obtained by using 0.1 M KOH and HCl instead of 0.5M solutions.

X1.1.7 Run blanks in duplicate with all samples.

X1.1.8 Use the sample masses suggested in Note 14, but do not exceed 20 g sample limit.

X1.1.9 Some samples may require digestion for longer than the 30 min period suggested. For unknown samples, the required optimum period should be checked out.

X1.1.10 For colored dark samples, the potentiometric method is preferred over the colorimetric method because of its ability to clearly distinguish the end point.

X1.1.11 Since on titration, two immiscible phases appear and KCl is precipitated, stirring conditions are critical and vigorous stirring is essential. Use a polytetrafluorethylene

(PTFE) - 1 coated 2.5 × 0.5 cm stir bar.

X1.1.12 The titration apparatus may need grounding if the meter shows erratic movements when approached by an operator.

X1.1.13 Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regularly testing the electrodes are very important in obtaining repeatable potentials.

X1.1.14 At the end of blank titration and between successive titrations, a thin film of KCl crystals may coat the electrode and the titrant delivery tip. Use a water jet to remove it, and rinse with distilled water.

X1.1.15 Dry the electrodes by blotting with a paper towel: do *NOT* rub the electrodes.

X1.1.16 At the end of a set titrations, clean the deposited KCl crystals and sample residue by washing with water, and then rinse the electrodes in a beaker of 50 mL middle distillate plus 38 mL isopropanol plus 38 mL water for 1 min. Clean the electrodes further with distilled water, and blot-dry with paper towel.

X1.1.17 Hold the electrodes firmly in a steady holder during the titration. Wobbling electrodes create nonrepeatable results by generating electrical noise.

X1.1.18 Two inflection points may be obtained in the titration curve if the KOH solution is contaminated with a small amount of K<sub>2</sub>CO<sub>3</sub>. The first inflection point from KOH, the second from K<sub>2</sub>CO<sub>3</sub>.

X1.1.19 SAP numbers should not be calculated from TAN numbers. Many times these calculated results are higher than the true SAP numbers, due to the presence of free acid by way of hydrolysis of the products.

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