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Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration[1]

This standard is issued under the fixed designation D 2896; 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.

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

1. Scope*

1.1 This test method covers the determination of basic constituents in petroleum products by titration with perchloric acid in glacial acetic acid.

1.2 Procedures A and B use different titration solvent volumes and sample weights.

NOTE 1—A round robin on a series of new and used oils and additive concentrates has shown that the two procedures give statistically equivalent results.

1.3 Appendix X2 provides the use of an alternative solvent system which eliminates the use of chlorobenzene in this test method. The use of the alternative solvent gives statistically equivalent results; however, the precision is worse. Paragraph X2.5.5 provides guidance when comparing results using the two different solvents.

1.4 The constituents that may be considered to have basic characteristics include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, and salts of heavy metals.

NOTE 2—This test method is applicable to both fresh oils and used oils as described in Sections 16, 17, and 19 and Appendix X1.

1.5 This test method can be used to determine base number >300 mg KOH/g. However, the precision statement in Section 19 has been obtained only on base number ≤300 mg KOH/g.

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

1.7 *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 warning statements, see Section 7, Section 10, and X2.2.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 1193 Specification for Reagent Water

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *base number*—the quantity of perchloric acid expressed in terms of the equivalent number of milligrams of potassium hydroxide that are required to titrate 1 g of the sample dissolved in the specified solvent to a well-defined inflection point as specified in this test method.

4. Summary of Test Method

4.1 The sample is dissolved in an essentially anhydrous mixture of chlorobenzene and glacial acetic acid and titrated with a solution of perchloric acid in glacial acetic acid using potentiometric titrimeter. A glass indicating electrode and a reference electrode are used, the latter being connected with the sample solution by means of a salt bridge. The meter readings are plotted against the respective volumes of titrating solution, and the end point is taken at the inflection in the resulting curve.

4.2 Procedure A uses 120 mL of titration solvent. Procedure B uses 60 mL of titration solvent. In addition, the two procedures use different equations for the calculation of appropriate sample weights. Since many portions of the test method are identical for Procedures A and B, only the unique sections will be described separately for the two versions of the test method.

4.3 Occasionally certain used oils give no inflection in the forward titration mode, in which case a back titration modification with sodium acetate titrant is employed.

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

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This test method has been approved by the sponsoring committees and accepted by the cooperating societies in accordance with established procedures.

[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.

***A Summary of Changes section appears at the end of this standard.**

5. Significance and Use

5.1 New and used petroleum products can contain basic constituents that are present as additives. The relative amounts of these materials can be determined by titration with acids. The base number is a measure of the amount of basic substance 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 limits must be empirically established.

6. Apparatus

6.1 *Potentiometric Titrimeters*, either automatic recording or manual.

6.2 *Glass Electrode*, pH 0 to 11, general-purpose type.

6.3 *Reference Electrode*, silver/silver chloride (Ag/AgCl) reference electrode with a nonaqueous bridge as described in Section 10. (See also 19.1.)

NOTE 3—Some reference electrodes with fritted or fiber diaphragms and some combined glass plus reference electrodes systems are commercially available, such as the single-rod glass plus silver/silver chloride electrode assembly. During the development of this test method, the use of electrodes of these types gave problems in some laboratories, but not in others. Accordingly, these electrodes are permitted in this test method, provided that the sodium perchlorate bridge is used; however, when stability or other problems arise with their use, the sleeve-type electrode should be used.

6.4 *Stirrer*, either mechanical or electrical, with variable speeds and with propeller or paddle of chemically inert material. When 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 a titration. A magnetic stirrer with stirring bar can be used provided it meets these conditions.

6.5 *Buret*, 10 or 20-mL, graduated in 0.05-mL divisions and calibrated with an accuracy of ±0.02 mL, or an automatic buret of similar accuracy.

6.6 *Titration Beaker*, made of borosilicate glass or other suitable titration beaker, tall form recommended.

6.6.1 For Procedure A, use a beaker of 250 or 300 mL capacity. For Procedure B, use a beaker of about 150 mL capacity such that 60 mL of titration solvent will cover the electrodes.

NOTE 4—Other beakers of suitable size capacity may be used.

6.7 *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.

NOTE 5—Some apparatus may 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 this case surround the beaker closely with a cylinder of copper gauze that is electrically grounded.

7. Reagents and Materials

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.[3] 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 D 1193.

7.3 *Acetic Acid*, glacial (**Warning**—Toxic and irritant).

7.4 *Acetic Anhydride* (**Warning**—Toxic and irritant).

7.5 Chlorobenzene (**Warning**—Toxic and irritant).

7.6 *Perchloric Acid, Standard Solution in Acetic Acid* (0.1 *N*)[4] (**Warning**—Powerful oxidant when dry or heated. Great care should be taken to avoid contact with organic matter under conditions that may result in subsequent drying or heating, and spills should be washed immediately and thoroughly with water)—Mix 8.5 mL of 70 to 72 % perchloric acid ($HClO_4$, 70 to 72 %) (or 10.2 mL of 60 to 62 % $HClO_4$ solution) with 500 mL of glacial acetic and 30 mL (or 35 mL if the 60 to 62 % $HClO_4$ solution is used) of acetic anhydride. Dilute to 1 L with glacial acetic acid. Allow the solution to stand for 24 h.

NOTE 6—Excess acetic anhydride should be avoided to prevent acetylation of any primary or secondary amines that may be present.

7.7 *Potassium Hydrogen Phthalate*—($KHC_8H_4O_4$).

7.8 *Sodium Perchlorate Electrolyte*—(**Warning**—Sodium perchlorate is toxic and an irritant. It is also a powerful oxidizing agent when heated. Great care should be taken to avoid contact with organic matter under conditions that may result in subsequent drying or heating, and spills should be washed immediately and thoroughly with water.) Prepare a saturated solution of sodium perchlorate ($NaClO_4$) in glacial acetic acid. An excess of undissolved $NaClO_4$ shall always be present at the bottom of the solution.

7.9 *Titration Solvent*—Add one volume of glacial acetic acid to two volumes of chlorobenzene.

7.10 *Sodium Carbonate*, anhydrous (Na_2CO_3).

7.11 *Sodium Acetate Solution*, 0.1 *N* in acetic acid (for back titration, see Sections 16 and 17)—Dissolve 5.3 g of anhydrous Na_2CO_3 in 300 mL of glacial acetic acid. Dilute to 1 L with acetic acid after solution is complete.

8. Standardization of Reagents

8.1 *Perchloric Acid Solution*—The standardization of the perchloric acid solution ($HClO_4$) differs for the two procedures as follows:

8.1.1 *Procedure A (120 mL)*—Heat a quantity of potassium hydrogen phthalate in an oven at 120°C for 2 h and allow it to cool. Take 0.1 to 0.2 g of the potassium hydrogen phthalate weighed to the nearest 0.1 mg and dissolve it in 40 mL of warm

[3] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] Available commercially for purchase already prepared.

glacial acetic acid. Add 80 mL of chlorobenzene, cool, and titrate with 0.1 *N* $HClO_4$ solution, using the electrode system and procedures given in 10.1 to 10.4 and 11.4 to 11.7. Detect the end point by the same procedure used for base number determination (see 14.2). Carry out a blank titration on 40 mL of glacial acetic acid plus 80 mL of chlorobenzene (see 11.8).

8.1.2 *Procedure B (60 mL)*—Heat a quantity of potassium hydrogen phthalate in an oven at 120°C for 2 h and allow it to cool. Take 0.05 to 0.1 g of the potassium hydrogen phthalate weighed to the nearest 0.1 mg and dissolve it in 20 mL of warm glacial acetic acid. Add 40 mL of chlorobenzene, cool, and titrate with 0.1 *N* $HClO_4$ solution as described in 8.1.1. Carry out a blank titration on 20 mL of glacial acetic acid and 40 mL of chlorobenzene (see 11.8).

8.1.3 Calculate the normality, N_A, of the $HClO_4$ solution as follows:

$$N_A = 1000W/[204.23\cdot(V - b)] \quad (1)$$

where:

W = potassium hydrogen phthalate, g,
V = $HClO_4$ solution used, mL, and
b = volume corresponding to V for the blank titration, mL.

NOTE 7—Because of the relatively large coefficient of volumetric expansion of organic liquids, the acetous $HClO_4$ solution should be used within ± 5°C of the temperature at which it was standardized. If used at a temperature more than 5°C higher, multiply the volume used by the factor $1 - (t\cdot0.001)$. If used at a temperature more than 5°C lower, multiply by the factor $1 + (t\cdot0.001)$, where t is the difference in degrees Celsius between temperatures of standardization and use and is always positive.

8.2 *Sodium Acetate Solution*—The standardization of the sodium acetate solution (Na_2CO_3) differs for the two procedures as follows:

8.2.1 *Procedure A (120 mL)*—Use 120 mL of titration solvent and 8.00 mL of 0.1 *N* $HClO_4$ solution. Titrate with 0.1 *N* sodium acetate solution, using the electrode system and procedure given in 10.1 to 10.4 and 11.4 to 11.7. Detect the end point by the same procedure as will be used for base number determination (see 14.2). Calculate the normality, N_B, of the sodium acetate solution as follows:

$$N_B = [(8.00 - b)N_A]/G \quad (2)$$

where:

b = volume corresponding to V for the blank titration,
N_A = normality of the $HClO_4$ solution, and
G = volume of standard sodium acetate used in the standardization, mL.

8.2.2 *Procedure B (60 mL)*—Use 60 mL of titration solvent and 4.00 mL of 0.1 *N* $HClO_4$ solution. Titrate as described in 8.2.1. Calculate the normality, N_B, of the sodium acetate solution as follows:

$$N_B = [(4.00 - b)N_A]/G \quad (3)$$

where:

b = volume corresponding to V for the blank titration,
N_A = normality of the $HClO_4$ solution, and
G = volume of standard acetous sodium acetate used in the standardization, mL.

9. Preparation of Sample

9.1 It is essential to ensure that the sample is representative since any sediment can be acidic or basic or have adsorbed acidic or basic material from the sample. When necessary, samples are warmed to aid mixing. Used oils should be vigorously shaken to ensure homogeneity before sampling.

NOTE 8—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.

10. Preparation of Electrode System

10.1 *Preparation of Electrodes*—When the reference electrode is to be changed from aqueous bridge to nonaqueous, drain out the aqueous solution, wash out all crystals of KCl with water, then rinse the outer jacket (salt bridge) several times with $NaClO_4$ electrolyte solution. Finally fill the outer jacket with $NaClO_4$ electrolyte solution up to the filling hole. 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 $NaClO_4$ electrolyte solution, and rinse the electrode with chlorobenzene. When in use, the electrolyte level in the reference 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 reference electrode with the $NaClO_4$ 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.

10.2 *Testing of Electrodes*—Test the meter-electrode combination when first put into use or when new electrodes are installed and retest at intervals thereafter as follows:

10.2.1 *Procedure A*—Dip the electrodes into a well-stirred mixture of 100 mL of glacial acetic acid plus 0.2 g of $KHC_8H_4O_4$ and record the reading given by the meter. Rinse the electrodes with chlorobenzene and immerse in 100 mL of glacial acetic acid plus 1.5 mL of 0.1 *N* $HClO_4$ solution. The difference between readings is to be at least 0.3 V.

10.2.2 *Procedure B*—Dip the electrodes into a well-stirred mixture of 60 mL of glacial acetic acid plus 0.1 g of $KHC_8H_4O_4$ and record the reading vein by the meter. Rinse the electrodes with chlorobenzene and immerse in 50 mL of glacial acetic acid plus 0.75 mL of 0.1 *N* $HClO_4$ solution. The difference between readings is to be at least 0.3 V.

NOTE 9—See Appendix X4 for a possible procedure to check the electrode performance.

10.3 *Cleaning of Electrodes*—Following a titration, first wash the electrodes with titration solvent to remove any adhering oily material from the previous titration. Then wash the electrodes with water to dissolve any $NaClO_4$ that may have formed around the sleeve of the reference electrode and to restore the aqueous gel layer of the glass electrode. Rinse again with the titration solvent. Before starting a series of sample titrations, follow this rinsing procedure, then run one or two blank titrations on the solvent to condition the electrodes. Repeat the blank titrations if necessary.

10.4 *Maintenance of Electrodes*—When there is reason to believe that the glass electrode has become contaminated, it can be cleaned by immersion in cold chromic acid (**Warning**—Corrosive and carcinogenic) or an alternative non-chromium-containing strongly-oxidizing acid cleaning solution for 5 min, followed by thorough water washing. After this cleaning treatment, test the electrode as described in 10.2. The reference electrode can be cleaned by draining and refilling with fresh $NaClO_4$ solution. Maintain the electrolyte level in the reference electrode above that of the liquid in the titration beaker at all times. Do not allow the electrodes 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 and particularly avoid scratching the glass electrode.

11. Procedure A (120 mL)

11.1 Calculate the quantity of sample required from its expected base number, *BN*, as follows:

$$\text{Approximate weight of sample, g} = 28/\text{expected } BN \quad (4)$$

NOTE 10—For the back titration procedure (see 16.2), or when analyzing used oils, it may be necessary to use a smaller sample weight.

11.1.1 Weigh the sample into the titration beaker, applying the limits shown as follows. A maximum of 20 g should be taken for analysis.

Sample Weight, g	Precision of Weighing, g
10 to 20	0.05
5 to 10	0.02
1 to 5	0.005
0.25 to 1.0	0.001
0.1 to 0.25	0.0005

11.2 Add 120 mL of titration solvent to the sample.

11.3 Place the beaker on the titration stand and stir the solution until the sample is dissolved.

NOTE 11—If solution of the sample proves difficult, dissolve it in 80 mL of chlorobenzene in the titration beaker, then add 40 mL of glacial acetic acid. Many used oils contain some solid materials that will not dissolve. This is a frequently observed condition.

11.4 Prepare the electrodes as directed in 10.1, 10.2, and 10.3. Position the electrodes in the solution so that they are immersed as far as possible. Continue stirring throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution. Adjust the meter so that it reads in the upper part of the millivolt scale; for example, 700 mV. For simple meters without this adjustment, it is necessary to incorporate a source of potential in series with the electrode. A 1.5-V dry cell and potential divider is suitable.

11.5 Fill the buret with 0.1 *N* $HClO_4$ solution and place the buret in position in the titration assembly, taking care that the tip is immersed below the level of the surface of the liquid in the beaker. Record the initial buret and meter (cell potential) readings.

11.6 *Titration*:

11.6.1 *Manual Titration*—Add suitable small portions of titrant and, after waiting until a constant potential has been established (Note 12), record the buret and meter readings. At the start of the titration and in any subsequent regions (inflections) where 0.1 mL of titrant consistently produces a total change of more than 0.03 V (corresponding to 0.5 pH scale unit) in the cell potential, add 0.05-mL portions. In the intermediate regions (plateaus) where 0.1 mL increments change the potential by less than 0.03 V, add large portions sufficient to produce a total potential change approximately equal to, but not greater than, 0.03 V. Titrate in this manner until the potential changes less than 0.005 V (corresponding to 0.1 pH scale unit) per 0.1 mL.

NOTE 12—Consider the cell potential constant when it changes less than 0.005 V/min.

11.6.2 *Automatic Recording Titration*—Adjust the instrument in accordance with the manufacturer's instructions and set the titration speed at 1.0 mL/min maximum.

11.7 On completion of the titration, remove the beaker and rinse the electrodes and buret tip with titration solvent, then with water, then again with titration solvent (see 10.3). Store in water when not in use (see 10.1).

11.8 For each set of samples make a blank titration using 120 mL of titration solvent. For a manual titration add 0.1 *N* $HClO_4$ solution in 0.05-mL increments, waiting between each addition until a constant cell potential is established. Record meter and buret readings after each increment. Follow the procedure in 11.6.2 for an automatic titration.

12. Procedure B (60 mL)

12.1 Calculate the quantity of sample required from its expected base number as follows:

$$\text{Approximate weight of sample, g} = 10/\text{expected } BN \quad (5)$$

NOTE 13—For the back titration procedure (see 17.2) it may be necessary to use a smaller sample weight.

12.1.1 Weigh the sample into the titration beaker, applying the limits shown as follows. A maximum of 10 g should be taken for analysis.

Sample Weight, g	Precision of Weighing, g
5 to 10	0.02
1 to 5	0.005
0.25 to 1.0	0.001
0.1 to 0.25	0.0005

NOTE 14—It is especially important for Procedure B that great care be exercised in obtaining accurate weights particularly for the high base number samples which require small sample weights.

12.2 Add 60 mL of titration solvent to the sample.

12.3 Place the sample on the titration stand and stir the solution until the sample is dissolved.

NOTE 15—If the solution of the sample proves difficult, dissolve it in 40 mL of chlorobenzene in the titration beaker, then add 20 mL of glacial acetic acid.

12.4 Prepare the electrodes as directed in 10.1, 10.2, and 10.3. Position the electrodes in the solution so that they are immersed as far as possible. Continue stirring throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution. Adjust the meter so that it reads in the upper part of the millivolt scale; for example, 700 mV. For simple meters

without this adjustment, it may be necessary to incorporate a source of potential in series with the electrode. A 1.5-V dry cell and potential divider is suitable.

12.5 Fill the buret with 0.1 *N* $HClO_4$ solution and place the buret in position in the titration assembly, taking care that the tip is immersed below the level of the surface of the liquid in the beaker. Record the initial buret and meter (cell potential) readings.

12.6 *Titration*:

12.6.1 *Manual Titration*—Add suitable small portions of titrant and after waiting until a constant potential has been established (Note 12), record the buret and meter readings. At the start of the titration and in any subsequent regions (inflections) where 0.1 mL of titrant consistently produces a total change of more than 0.03 V (corresponding to 0.5 pH scale unit) in the cell potential, add 0.05-mL portions. In the intermediate regions (plateaus) where 0.1 mL increments change the potential by less than 0.03 V, add large portions sufficient to produce a total potential change approximately equal to, but not greater than, 0.03 V. Titrate in this manner until the potential changes less than 0.005 V (corresponding to 0.1 pH scale unit) per 0.1 mL.

12.6.2 *Automatic Recording Titration*— Adjust the instrument in accordance with the manufacturer's instructions and set the titration speed at 1.0 mL/min maximum.

12.7 On completion of the titration, remove the beaker and rinse the electrodes and buret tip with titration solvent, then with water, then again with titration solvent (see 10.3). Store the electrodes in water when not in use (see 10.1).

12.8 For each set of samples make a blank on 60 mL of titration solvent. For a manual titration add 0.1 *N* $HClO_4$ solution in 0.05-mL increments, waiting between each addition until a constant cell potential is established. Record meter and buret readings after each increment. Follow the procedure in 12.6.2 for an automatic titration.

13. Quality Control Checks

13.1 Confirm the performance of the equipment or the procedure each day it is in use, by analyzing a quality control (QC) sample. It is advisable to analyze additional QC samples as appropriate, such as at the end of a batch of samples or after a fixed number of samples. Analysis of result(s) from these QC samples can be carried out using control chart techniques.[5] When the result of a test on a QC sample exceeds the control limits of the laboratory, corrective action such as instrument recalibration, may be required. An ample supply of QC sample material shall be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions. If possible, the QC sample shall be representative of samples typically analyzed and the average value and control limits of the QC sample shall be determined prior to monitoring the measurement process. The precision for the QC sample must be compared against that given in the Precision and Bias section of this test method in order to verify that the instrument is functioning correctly.

[5] ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, Section 3: Control Charts for Individuals, 6th ed, ASTM International, W. Conshohocken, PA.

NOTE 16—Because the base number can vary while the QC sample is in storage, when an out-of-control situation arises, the stability of the QC sample can be a source of the error.

14. Calculation

14.1 For a manual titration, plot the volumes of the acid added against the corresponding meter readings.

14.2 Interpret the end point from the graph obtained from the manual or automatic titration. The end point is the midpoint of the inflection, that point at which the curve changes from concave to convex. A useful but not mandatory guide is that the end point is preceded and followed by a deflection of a least 50 mV/0.1 mL of titrant.

14.3 When there is no inflection point or only a very poor one, proceed to Section 16 or Section 17 on back titration. The inflection obtained during back titration preferably is to meet the criteria described in 14.2.

14.4 Calculate the base number, *BN*, as follows:

$$BN,\ \text{mg KOH/g} = [(E - F) \cdot N_A \cdot 56.1]/S \quad (6)$$

where:

E = $HClO_4$ solution used to titrate the sample to the inflection point on the titration curve, mL,
F = volume corresponding to E for blank titration at same potential as sample, mL
N_A = normality of $HClO_4$ solution, and
S = sample, g.

15. Report

15.1 Report the result as follows:

$$\text{Base Number (D 2896}-\text{Procedure A or B)} = \text{Result} \quad (7)$$

This report format may not be used when using the alternative solvent described in Appendix X2. Instead, use the format described in X2.4.

16. Back Titration, Procedure A (120 mL)

16.1 Some used oils give no inflection point or only a very poor one with the test method described in Section 11. When this situation is encountered, the following modified test method may be used. In this modified test method, excess standard $HClO_4$ solution is added to the sample, then the excess $HClO_4$ solution is back titrated with standard sodium acetate solution.

16.2 Accurately weigh the amount of sample specified in 11.1 into the titration beaker. (See Note 17.)

NOTE 17—The sample size for the back titration modification does not exceed 5 g. When, with a 5-g sample, no inflection point is found, reduce the sample size to 3 g and repeat the analysis. Reducing the sample size generally improves the clarity of the inflection point. However, it should be noted that the cooperative work that led to the precision statement (see 19.2) employed a sample size of 5 g maximum.

16.3 Dissolve the sample in 80 mL of chlorobenzene and add 40 mL of acetic acid.

16.4 Use a volumetric buret or pipet to add accurately 8.00 mL of standard 0.1 *N* $HClO_4$ solution to the beaker. (The standard $HClO_4$ solution must be in excess. If necessary, add more than 8.00 mL and correct accordingly (16.7).)

16.5 Stir the contents of the beaker for 2 min.

16.6 Titrate the unneutralized $HClO_4$ solution with standard 0.1 *N* sodium acetate solution. Carry out the titration in the same manner as described in Section 11. For the back titration, the starting point will be in the range from 0 to 100 mV.

16.7 Instead of weighing out a separate sample and proceeding through 16.6, the back titration procedure can be used on a sample being titrated as in 11.1 to 11.6.2, provided that the sample size did not exceed 5 g (see Note 17). When it is apparent from the forward titration that a satisfactory inflection is not present, note the volume of standard $HClO_4$ solution used, then proceed with 16.6. The standardization (8.2.1) should be modified to coincide with the volume of standard $HClO_4$ solution.

16.8 Calculate the base number, *BN*, as follows:

$$BN,\ \text{mg KOH/g} = [(G - H) \cdot N_B \cdot 56.1]/S \quad (8)$$

where:

G = volume of standard sodium acetate used in the standardization, mL (see 8.2.1 or 8.2.2),
N_B = normality of the sodium acetate solution,
H = volume of standard sodium acetate used in the sample back titration, mL, and
S = weight of sample, g.

17. Back Titration, Procedure B (60 mL)

17.1 Some used oils give no inflection point or only a very poor one with the test method described in Section 12. When this situation is encountered, the following modified test method may be used. In this modified test method, excess standard $HClO_4$ solution is added to the sample, then the excess $HClO_4$ solution is back titrated with standard sodium acetate solution.

17.2 Accurately weigh the amount specified in 12.1 into the titration beaker (see Note 18).

NOTE 18—The sample size for the back titration modification does not exceed 2.5 g. When, with a 2.5-g sample, no inflection point is found, reduce the sample size to 1.5 g and repeat the analysis. Reducing the sample size generally improves the clarity of the inflection point.

17.3 Dissolve the sample in 40 mL chlorobenzene and add 20 mL of acetic acid.

17.4 Use a volumetric buret or pipet to add accurately 4.00 mL of standard 0.1 *N* $HClO_4$ solution to the beaker. (The standard $HClO_4$ solution must be in excess. If necessary, add more than 4.00 mL and correct accordingly (17.7).)

17.5 Stir the contents of the beaker for 2 min.

17.6 Titrate the unneutralized $HClO_4$ solution with standard 0.1 *N* sodium acetate solution. Carry out the titration in the same manner as described in Section 12. For the back titration, the starting point will be in the range from 0 to 100 mV.

17.7 Instead of weighing out a separate sample and proceeding through 17.6, the back titration procedure can be used on a sample being titrated as in 12.1 to 12.6.2, provided that the sample size did not exceed 2.5 g (see Note 18). When it is apparent from the forward titration that a satisfactory inflection is not present, note the volume of standard $HClO_4$ solution used, then proceed with 17.6. The standardization (8.2.2) should be modified to coincide with the volume of standard $HClO_4$ solution used.

17.8 Calculate the base number as described in 16.8.

TABLE 1 Preliminary Precision Derived from Log Distribution

	Silver/Silver Chloride	Glass/Calomel
Repeatability	0.004*X	0.013*X
where: X is the mean of at least two determinations		

18. Report of Result for Back Titration

18.1 Report the result as follows:

Base Number by Back Titration
(Test Method D 2896−Procedure A or B) = Result

19. Precision and Bias [6]

19.1 *Preliminary Precision*[7]—Preliminary repeatability of this test method using a silver/silver chloride reference electrode has been found to be equal to or better than using the reference electrode specified in the current test method. Preliminary results appear in Table 1. The subcommittee will continue to determine the precision within the next five years.

19.2 *Procedure A (120 mL)*:

19.2.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows (see Note 15 and Note 17):

19.2.1.1 *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 values only in one case in twenty:

	% of Mean
All oils with forward titration	3
Used oils requiring back titration	24

NOTE 19—Since there were insufficient data from the 1986 cooperative study to determine the precision for the back titration procedure for used oils, the back titration precision data are those obtained in the 1972 study. A new cooperative study is planned to determine the back titration precision using modern instrumentation.

19.2.1.2 *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 values only in one case in twenty:

	% of Mean
All oils with forward titration	7
Used oils requiring back titration	32

NOTE 20—The ranges of base number values for which these precision values were established are given in Appendix X1.

19.2.2 *Bias*—This procedure in this test method for measuring base numbers has no bias because the base numbers can be defined only in terms of the test method.

19.3 *Procedure B (60 mL)*:

19.3.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows: (see Note 15 and Note 17):

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D02-1011 and RR:D02-1237.

[7] The preliminary repeatability in Table 1 was obtained from one laboratory using four measurements each of four samples with base numbers ranging up to 17.

19.3.1.1 *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 values only in one case in twenty:

	% of Mean
All oils with forward titration	5

19.3.1.2 *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 values only in one case in twenty:

	% of Mean
All oils with forward titration	7

19.3.2 *Bias*—This procedure in this test method for measuring base numbers has no bias because the base numbers can be defined only in terms of the test method.

20. Keywords

20.1 base number; perchloric acid; petroleum products; potentiometric titration

APPENDIXES

(Nonmandatory Information)

X1. TEST COVERAGE

X1.1 During the developments of the original test method (Procedure A) and the test method for the reduced titration solvent volume (Procedure B), cooperative testing was done on samples covering a wide range of types of oils, of additive concentrates which are used to prepare these oils, and of services for the oils. Even so, however, it was not possible to cover the complete range of base numbers. It is believed that reasonable interpolation and extrapolation from the ranges used will not introduce serious errors in the precision.

X1.2 The ranges used for the precision were as follows:

X1.2.1 *Fresh Oils*—Base numbers from 6 to 70.

X1.2.2 *Additive Concentrates*—Base numbers from 5 to 300.

X1.2.3 *Used Oils on Which Were Employed the Forward Titration*—Base numbers from 5 to 27.

X2. ALTERNATIVE SOLVENT

X2.1 In order to eliminate the chlorobenzene from this test method, an alternative solvent was developed. Cooperative testing was done on samples covering a wide range of types of oils, both new and used, and of additive concentrates used to prepare these oils. Results have shown that the two solvents provide statistically equivalent results; however, the precision of the alternative solvent is worse than the original. Paragraph X2.5.5 describes how to compare results using the two different solvents.

X2.2 Reagents

X2.2.1 *Xylenes*, mixed. (**Warning**—Flammable. Vapor harmful.)

X2.2.2 *Alternative Titration Solvent*—Add one volume of glacial acetic acid to two volumes of mixed xylenes.

X2.3 Procedure

X2.3.1 Procedure A of this test method is followed exactly, except that mixed xylenes replace chlorobenzene and the alternative titration solvent replaces the titration solvent.

NOTE X2.1—The addition of approximately 10 % acetone by volume to the alternative titration solvent has been shown to reduce electrode noise and may be used. However, the test method precision using the acetone addition to the alternative titration solvent has not been determined.

X2.4 Report

X2.4.1 Report the result as follows:

Base Number (Test Method D 2896–Alternative Solvent, X2) = Result

X2.5 Precision and Bias

X2.5.1 The precision and bias of this alternative solvent test method was determined through a round robin using new and used oils as well as additive concentrates. The base number values covered a range from approximately 0.5 to 400. Statistical analysis of round robin results are available in the research report.[8]

X2.5.2 *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 values only in one case in twenty:

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1345.

6.2 % of the mean

NOTE X2.2—As part of the same round robin, these samples were analyzed using chlorobenzene. The repeatability using chlorobenzene was calculated to be 3.4 % of the mean.

X2.5.3 *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 values only in one case in twenty:

16.2 % of the mean

NOTE X2.3—As part of the same round robin, the same samples were analyzed using chlorobenzene. The reproducibility using chlorobenzene was calculated to be 8.7 % of the mean.

X2.5.4 *Relative Bias*—No systematic bias was detected between the chlorobenzene and mixed xylenes methods.

X2.5.5 To compare results obtained using different solvents, use the following:

X2.5.5.1 *Repeatability*—The difference between two test results using the two different solvent systems, 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 values only in one case in twenty:

5.0 % of the mean

X2.5.5.2 *Reproducibility*—The difference between two single and independent results using the two different solvent systems, 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 values only in one case in twenty:

13.0 % of the mean

X3. ALTERNATIVE ELECTROLYTES

X3.1 The use of alternative electrolytes has been studied in certain laboratories. Limited data on various types of oils and additives have shown that the two alternative electrolytes studied provide statistically equivalent data as sodium perchlorate in glacial acetic acid.

X3.2 Reagents

X3.2.1 Tetraethylammonium Bromide (TEABr).

X3.2.2 Ethylene Glycol.

X3.2.3 Tetraethylammonium Bromide Electrolyte—Prepare a 0.4 M solution of TEABr in ethylene glycol.

X3.2.4 Ethanol. (**Warning**—Flammable and toxic, especially when denatured.)

X3.2.5 Lithium Chloride, LiCl.

X3.2.6 Lithium Chloride Electrolyte—Prepare a 1 M – 3 M solution of lithium chloride (LiCl) in ethanol.

X3.3 Procedure

X3.3.1 Procedures A and B of this test method are followed exactly, except LiCl in ethanol or TEABr in ethylene glycol replaces $NaClO_4$ in acetic acid as the electrolyte in the reference electrode.

X3.4 Report

X3.4.1 Report the result as follows:

Base Number (Test Method D 2896—Alternative Electrolyte, X3) = Result

X3.5 Precision and Bias

X3.5.1 The precision and bias of these alternative electrolytes are not established. Preliminary data shows good correlation when compared to the data obtained from the perchlorate electrolyte specified in this test method.

X4. CHECK FOR ELECTRODE PERFORMANCE

X4.1 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 below which can be carried out with a pH meter or titrator set to read millivolts continuously.

X4.2 The essence of the method is to challenge the electrode coming from rest in a water solution with buffers and measure the potential after 30 and 60 s. A fast electrode reaches a stable point in less than 30 s and changes little from 30 to 60 s. Use buffers pH 4, pH 7, and pH 11 for this check as needed.

X4.3 The procedure for carrying out the test is as follows. 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. Allow the electrode to stabilize for one minute in distilled or equivalent deionized water. Remove the electrodes from the water and place them in the pH 4 buffer, starting a stop watch at about the moment when the buffer touches the electrode. After 30 s, note the potential. After another 30 s, note the potential again. The difference between the two potentials is termed the drift. Repeat the procedure for pH 7 buffer and pH 11 buffer.

X4.4 Calculate the drift for each of the three buffers. The electrode response may be judges as follows:

(1) drift < 1, excellent
(2) 1 < drift < 2, good
(3) 2 < drift < 3, acceptable
(4) 3 < drift < 4, questionable
(5) 4 > drift, unacceptable

X4.5 The difference between the 60-second 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.

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue, D 2896–07, that may impact the use of this standard. (Approved July 15, 2007.)

(*1*) Revised 6.3.
(*2*) Removed "calomel" and replaced with "reference" electrode throughout.
(*3*) Added new 19.1 and renumbered subsequent sections.
(*4*) Added Table 1.
(*5*) Added Footnote 7.

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue, D 2896–06, that may impact the use of this standard. (Approved Jan. 15, 2007.)

(*1*) Clarified the requirements for quality of water to be used in 7.2.
(*2*) Added a new non-mandatory Appendix X3 for using alternative electrolytes