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Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration¹

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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 \leq 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 applica-*

bility 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 (HClO₄, 70 to 72 %) (or 10.2 mL of 60 to 62 % HClO₄ solution) with 500 mL of glacial acetic and 30 mL (or 35 mL if the 60 to 62 % HClO₄ 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*—(KHC₈H₄O₄).

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 (NaClO₄) in glacial acetic acid. An excess of undissolved NaClO₄ 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 (Na₂CO₃).

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 Na₂CO₃ 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 (HClO₄) 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* HClO₄ 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* HClO₄ 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 HClO₄ solution as follows:

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

where:

- W = potassium hydrogen phthalate, g,
- V = HClO₄ 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 HClO₄ 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 $1 - (t-0.001)$. If used at a temperature more than 5°C lower, multiply by the factor $1 + (t-0.001)$, 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 (Na₂CO₃) 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* HClO₄ 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 HClO₄ 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* HClO₄ 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 HClO₄ 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 NaClO₄ electrolyte solution. Finally fill the outer jacket with NaClO₄ 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 NaClO₄ 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 NaClO₄ 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 KHC₈H₄O₄ 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* HClO₄ 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 KHC₈H₄O₄ and record the reading given 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* HClO₄ 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 NaClO₄ 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.