



# Standard Test Method for Total Nitrogen In Lubricating Oils and Fuel Oils By Modified Kjeldahl Method<sup>1</sup>

This standard is issued under the fixed designation D 3228; 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 This test method is applicable for the determination of nitrogen in lubricating oils when present in the concentration from 0.03 to 0.10 mass %, and for the determination of nitrogen in fuel oils when present in the concentration from 0.015 to 2.0 mass %. This test method is also applicable to the analysis of additive concentrates and additive packages.

NOTE 1—This test method may not be applicable to certain materials containing N–O or N–N linkage. However, the samples used in the cooperative program to establish the precision of the test method were compounded with currently available ashless additives containing nitrogen. Complete recovery of the nitrogen present in these additives was obtained.

1.2 The values given in acceptable SI units are to be regarded as the standard.

1.3 *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 precautionary statements, see 6.6, 6.9, and 8.8.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.04.

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis<sup>5</sup>

## 3. Summary of Test Method

3.1 The sample is digested in a mixture of concentrated sulfuric acid, potassium sulfate, mercuric oxide, and copper sulfate. After digestion, sodium sulfide is added to precipitate the mercury, and the mixture is made alkaline with caustic. Nitrogen, now in the form of ammonia, is distilled into a boric acid solution. The ammonia is titrated with standard sulfuric acid using methyl purple as an indicator.

## 4. Significance and Use

4.1 The concentration of nitrogen is a measure of the presence of nitrogen-containing additives. Knowledge of its concentration can be used to predict performance.

## 5. Apparatus

5.1 *Buret*, 50-mL, graduated in 0.1-mL subdivisions, one for each titrant. Other size burettes may also be used.

5.2 *Flask*, Erlenmeyer, 300-mL. Other sizes are also acceptable.

5.3 *Heater*, electrical or gas.

5.4 *Kjeldahl Distillation Apparatus*.

NOTE 2—Commercially available semi-automatic Kjeldahl apparatus are acceptable. In such cases manufacturer prescribed sizes of burettes and flasks may be used.

5.5 *Kjeldahl Flask*, at least 500-mL volume.

## 6. Reagents

6.1 *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,

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 15.05.

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

where such specifications are available.<sup>6</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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types II and III of Specification D 1193.

6.3 *Boric Acid Solution* (40 g/L)—Dissolve 40 g of boric acid ( $H_3BO_3$ ) in 1 L of boiling water.

6.4 *Catalyst Reagent*<sup>7</sup>—For each test carefully weigh and mix 9.9 g of potassium sulfate ( $K_2SO_4$ ), 0.41 g of mercuric oxide (HgO), and 0.08 g of copper sulfate ( $CuSO_4$ ).

6.5 *Methyl Purple Indicator Solution*<sup>8</sup>—Aqueous solution containing approximately 0.1 % active constituent (not methyl violet). Other appropriate indicator solutions may also be used.

6.6 *Sodium Hydroxide Solution* (1000 g/L)—Dissolve 1000 g of sodium hydroxide (NaOH) in 1 L of water. (**Warning**—Causes burns. Poison.)

6.7 *Sodium Sulfide Solution* (40 g/L)—Dissolve 40 g of sodium sulfide ( $Na_2S$ ) in warm water 194°F (90°C); cool and dilute to 1 L.

6.8 *Sucrose (NIST)*—Primary standard grade.

6.9 *Sulfuric Acid* (rel dens 1.84)—Concentrated sulfuric acid ( $H_2SO_4$ ). (**Warning**—Causes severe burns. Strong oxidizer.)

6.10 *Sulfuric Acid, Standard* (0.05 M)—Slowly add 3 mL of concentrated sulfuric acid ( $H_2SO_4$ , rel dens 1.84) to 500 mL of water in a suitable size beaker. Mix the acid and water; allow it to cool and transfer to a 1-L volumetric flask. Dilute to the mark with water; mix well. Standardize sulfuric acid to the nearest 0.0005 mol/L against 0.1 mol/L NaOH solution using phenolphthalein indicator. Standardize the NaOH solution against primary standard grade potassium hydrogen phthalate ( $HOOCC_6H_4COOK$ ). Use the procedure outlined in Sections 14 to 19 of Practice E 200.

NOTE 3—Commercially available pre-standardized  $H_2SO_4$  and NaOH solutions may be used.

6.11 *Sulfuric Acid* (0.005 M)—Prepare by ten-fold dilution of the standard 0.05 M sulfuric acid prepared and standardized in 6.10.

6.12 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 10.

<sup>6</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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD. Other commercial catalyst reagent mixtures that provide equivalent results, such as copper and titanium compounds, are also acceptable.

<sup>7</sup> Commercially prepared catalyst reagent mixture, brand name Kel-Pak #1 may be used and is available from Matheson Scientific, 1850 Greenleaf Ave., Elk Grove Village, IL 60007.

<sup>8</sup> Fleisher Methyl Purple Indicator, U.S. Patent No. 241669, may be obtained from Harry Fleisher Chemical Co., Benjamin Franklin Station, Washington, DC 20004, or from any chemical supply company handling Fleisher Methyl Purple.

## 7. Sampling

7.1 Take the sample in accordance with the instructions in Practice D 4057.

7.2 Ensure that the sample is thoroughly representative of the material to be tested and that the portion of the sample used for test is thoroughly representative of the whole sample.

## 8. Procedure

8.1 Transfer 1.0 to 1.5 g of sample, weighed to the nearest 0.1 mg, into a Kjeldahl flask. Avoid contact of the sample with the neck of the Kjeldahl flask. Add the catalyst reagent mixture to the Kjeldahl flask. Add two or three beads to prevent bumping.

8.2 Wash down the neck of the Kjeldahl flask with 20 mL of  $H_2SO_4$  (rel dens 1.84). Swirl the contents of the Kjeldahl flask to facilitate the mixing of the sample, catalyst reagent, and  $H_2SO_4$ .

8.3 Warm the contents of the Kjeldahl flask on the digestion rack and repeat the swirling. Apply low heat until the frothing has stopped. Samples that do not froth or char shall be subjected to a 20-min low-heating period. Careful periodic swirling of the solution in the Kjeldahl flask shall also be made. Gradually apply intermediate heat to raise the temperature of the solution to boiling.

8.4 Maintain a minimum volume of 15 mL of liquid in the Kjeldahl flask during the digestion period. Add volumes of 5 to 15 mL of  $H_2SO_4$  (rel dens 1.84) when the volume does not conform to this condition. Use the  $H_2SO_4$  to wash down the neck of the Kjeldahl flask after the contents have been allowed to cool sufficiently so that sulfur trioxide ( $SO_3$ ) fumes have subsided. The volume of  $H_2SO_4$  (rel dens 1.84) added will depend upon the carbonaceous material in the Kjeldahl flask. After all of the carbonaceous material has been digested and the solution has cleared, continue the digestion for two more hours at rapid rate of boiling. The total volume of liquid remaining in the Kjeldahl flask after digestion approximates the volume in the Kjeldahl flask for the blank.

NOTE 4—For some samples, a two hour digestion period may be unnecessary, if the solution has completely cleared.

8.5 Turn off the heat, but allow the Kjeldahl flask to remain in the fume duct or hood until the evolution of  $SO_3$  fumes has subsided. Remove the Kjeldahl flask from the rack and cool to approximately room temperature.

8.6 Place a 300-mL receiving flask containing 25 mL of  $H_3BO_3$  solution and 5 drops of methyl purple indicator solution under the condenser with the delivery tube tip extending to the bottom of the receiving flask.

8.7 Measure approximately 275 mL of water and add a portion of this water to the Kjeldahl flask and swirl the contents until the salt cake has dissolved (Note 2). Add the remainder of the water and cool the contents of the Kjeldahl flask to room temperature.

NOTE 5—It can be necessary to warm the contents in the Kjeldahl flask to facilitate solution of the salt cake.

8.8 Add 25 mL of  $Na_2S$  solution to the cooled contents of the Kjeldahl flask, to precipitate the mercury, and swirl to mix. (**Warning**—In addition to other precautions, when the  $Na_2S$