



Designation: D3228 – 22

Standard Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method¹

This standard is issued under the fixed designation D3228; 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 U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of nitrogen in lubricating oils when present in the concentration from 0.03 % to 0.10 % by mass, and for the determination of nitrogen in fuel oils when present in the concentration from 0.015 % to 2.0 % by 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 stated in SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 7.6, 7.9, and 9.8.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D1193 Specification for Reagent Water

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Oct. 1, 2022. Published November 2022. Originally approved in 1973. Last previous edition approved in 2020 as D3228 – 20. DOI: 10.1520/D3228-22.

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.

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *digestion, n*—treating a sample with the use of heat or elevated pressures, or both, usually in the presence of chemical additives, to bring analytes of interest into solution or to remove interfering matrix components, or both.

3.2.1.1 *Discussion*—In this test method acid, a catalyst and heat are used to break the carbon nitrogen bonds to form ammonium sulfate.

3.2.2 *lubricating oil, n*—a liquid lubricant, usually comprising several ingredients, including a major portion of base oil and minor portions of various additives.

3.2.3 *titration, n*—quantitative chemical analysis method used to determine the unknown concentration of a specified element by reacting a solution prepared from the sample to be analyzed with a known concentration and volume of specific reagent.

3.2.3.1 *Discussion*—Sensing electrodes or color indicators can be used to follow titrations if they respond to either the species being determined or the titrant ion.

3.2.4 *Total Kjeldahl Nitrogen (TKN), n*—the sum of the nitrogen contained in the free ammonia and other nitrogen compounds which are converted to ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ under the specified digestion conditions.

4. Summary of Test Method

4.1 The sample is digested in a mixture of concentrated sulfuric acid, potassium sulfate, and a catalyst of mercuric

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

oxide, titanium dioxide, or copper sulfate. After digestion, sodium sulfide is added to precipitate the mercury if used as a catalyst, 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.

5. Significance and Use

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

6. Apparatus

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

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

6.3 *Heater*, electrical or gas.

6.4 *Kjeldahl Distillation Apparatus*.

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

6.5 *Kjeldahl Flask*, at least 500 mL volume.

6.6 *Kjeldahl Digestion Apparatus*.

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.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 as defined by Types I of Specification D1193.

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

7.4 *Catalyst Reagent*—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). Other commercially prepared catalyst for Kjeldahl digestion tablets or packets that use a catalyst other than mercury may be used.

7.5 *Methyl Purple Indicator Solution*—Aqueous solution containing approximately 0.1 % active constituent (not methyl violet). Other appropriate indicator solutions such as Sher indicator or an indicator mixture of bromocresol green – methyl red may also be used.

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

7.7 *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.

7.8 *Sucrose*—High purity reagent (for example, NIST SRM 17f).

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

7.10 *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 ($\text{HOOC}_6\text{H}_4\text{COOK}$). Use the procedure outlined in Sections 14 to 19 of Practice E200.

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

7.11 *Sulfuric Acid* (0.005 M)—Prepare by tenfold dilution of the standard 0.05 M sulfuric acid prepared and standardized in 7.10.

7.12 *Quality Control (QC) Sample*, 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 11.

8. Sampling

8.1 Take the sample in accordance with the instructions in Practice D4057.

8.2 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.

9. Procedure

9.1 Transfer 1.0 g 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.

NOTE 4—When using commercially prepared Kjeldahl tablets, it is important to use 1 g of catalyst per 2 mL of sulfuric acid in the digestion.

9.2 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 .

9.3 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

³ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.