Designation: ~~D3228 – 20~~ D3228 – 22

Standard Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method[1]

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 ~~6.6~~7.6, ~~6.9~~7.9, and ~~8.8~~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
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:*

[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 ~~July 1, 2020~~Oct. 1, 2022. Published ~~July 2020~~November 2022. Originally approved in 1973. Last previous edition approved in ~~2019~~2020 as ~~D3228 – 19~~.D3228 – 20. DOI: ~~10.1520/D3228-20~~.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.

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

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 [$(NH_4)_2SO_4$] 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 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 ($HOOCC_6H_4COOK$). 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 ~~6.10~~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 ~~10~~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.

[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.

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 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.

NOTE 5—When using commercial block digestors, swirling of the flask is not necessary but use of intermediate heating may be necessary to mitigate sample foaming.

9.4 Maintain a minimum volume of 15 mL of liquid in the Kjeldahl flask during the digestion period. Add volumes of 5 mL 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 6—For some samples, a two hour digestion period may be unnecessary, if the solution has completely cleared.

9.5 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.

9.6 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 immersed in the boric acid to minimize any loss of ammonia during the distillation.

9.7 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. Alternate volumes of water may be used when using a steam distillation apparatus with block digestion tubes.

NOTE 7—It can be necessary to warm the contents in the Kjeldahl flask to facilitate solution of the salt cake.

9.8 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 solution is added to the cooled digestion flask, considerable hydrogen sulfide is evolved. Therefore, conduct ~~8.8~~9.8 and ~~8.9~~9.9 in a hood with a suitable draft.) (**Warning**—In addition to other precautions, care must be exercised in the disposal of the mercuric sulfide. Laboratories processing large volumes of Kjeldahl nitrogen determinations should consider the use of a recovery trap for mercury.)

9.9 Place the Kjeldahl flask in a slurry of ice and water. Cool the contents in the Kjeldahl flask to approximately 40 °F (4.5 °C). Slowly add 75 mL of NaOH solution (1000 g/L) down the inclined neck of the Kjeldahl flask, without agitation, to form two layers.

9.9.1 Carefully remove the Kjeldahl flask from the ice bath so that mixing of the layers does not occur. Carefully place the Kjeldahl flask on the Kjeldahl distillation rack.

9.9.2 Immediately connect the Kjeldahl flask to the distillation apparatus and mix the contents of the Kjeldahl flask thoroughly by swirling. The digestion flask must be connected to the distillation apparatus immediately after the alkali has been added and

layered, but before swirling to mix the acid and alkali. When any mixing is permitted to occur before the digestion flask is connected, the heat generated can be sufficient to release some of the ammonia which can be lost. This loss results in low recovery of ammonia, and thus low values for the nitrogen content of the sample.

9.10 Promptly apply full heat to the digestion flask. Reduce the heat just before the solution begins to boil and maintain at low boiling for 5 min. Heat must be applied promptly to prevent sucking of the H_3BO_3 solution into the condenser as the digestion solution cools. The initial distillation rate must not be too rapid because most of the ammonia is distilled during the first few minutes, and if too large an amount is present it can not all be absorbed in the H_3BO_3 solution. Increase the heat to rapid boiling, until the volume in the receiving flask reaches a volume of approximately 130 mL.

9.11 Lower the receiving flask to expose the condenser delivery tube tip. Rinse the tip with water. After approximately 1 min of additional distillation, turn off the heat and allow the condenser to drain.

NOTE 8—The total volume in the receiving flask is approximately 150 mL. For convenience the receiving flask can be marked at the 130 mL and 150 mL volume points.

NOTE 9—Commercially available digestion–distillation apparatus may be used as long as the same chemical reactions occurring in Section ~~8~~9 are maintained. In such cases, follow the manufacturer's instructions for the details of digestion and distillation sequences.

9.12 Titrate the contents in the receiving flask with standard H_2SO_4 (0.005 *M*) to an end point where the gray color of the solution just disappears and only the purple color remains. If the titration exceeds 50 mL, continue the titration with standard H_2SO_4 (0.05 *M*). Read the volume of the standard acid to the nearest 0.05 mL.

NOTE 10—Commercially available automated colorimetric titrators may be used instead of the manual titration described in ~~8.1~~9.12.

9.13 Determine a blank with every set of samples, identical in every way with the regular determinations, except 1.0 g of sucrose is added in place of the sample. The initial volume of 20 mL of H_2SO_4 (rel dens 1.84) is all that is used for the digestion of the sucrose.

10. Calculation

10.1 Calculate the nitrogen content of the sample as follows:

$$\text{Nitrogen content, mass \%} = \frac{(A - B) \times M1 \times 2 \times 1.401}{W} \quad (1)$$

When two concentrations of acid are used to titrate the sample:

$$\text{Nitrogen content, mass \%} = \frac{[((A - B) \times M1) + (C \times M2)] \times 2 \times 1.401}{W} \quad (2)$$

where:

A = millilitres of 0.005 M H_2SO_4 required to titrate the sample,
B = millilitres of 0.005 M H_2SO_4 required to titrate the blank,
C = millilitres of 0.05 M H_2SO_4 required to titrate the sample,
M1 = 0.005 (molarity of 0.005 M H_2SO_4),
M2 = 0.05 (molarity of 0.05 M H_2SO_4),
2 = number of equivalents of H_2SO_4,
1.401 = equivalent weight, g/mL,
W = weight of sample used, g.

11. Quality Control

11.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (~~6.1~~7.12).

11.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

11.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.