



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

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 (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 ~~is applicable for~~ covers 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~~ stated 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~~ warning statements, see 6.6, 6.9, and 8.8.

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

Current edition approved Nov. 10, 2004³. Published December 2004³. Originally ~~published as D 3228–73~~; approved in 1973. Last previous edition ~~D 3228–96~~; approved in 2001 as D 3228–01.

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

2. Referenced Documents

2.1 ASTM Standards:²

D 1193 Specification for Reagent Water

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

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, 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.

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*⁴—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*⁵—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

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*, Vol 11.01, volume information, refer to the standard's Document Summary page on the ASTM website.

³ *Annual Book Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of ASTM Standards, reagents not listed by the American Chemical Society, see *Vol 05.02: Annual 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 The sole source of supply of commercially prepared catalyst reagent mixture, brand name Kel-Pak #1, known to the committee at this time is Matheson Scientific, 1850 Greenleaf Ave., Elk Grove Village, IL 60007. If you are aware of alternative suppliers, please provide this information to ASTM Standards, Vol 05.04, International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹, which you may attend.

⁵ 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.

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 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.

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 solution is added to the cooled digestion flask, considerable hydrogen sulfide is evolved. Therefore, conduct 8.8 and 8.9 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.)

8.9 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.

8.9.1 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.

8.9.2 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.

8.10 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.

8.11 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 6—The total volume in the receiving flask is approximately 150 mL. For convenience the receiving flask can be marked at the 130 and 150-mL volume points.

NOTE 7—Commercially available digestion–distillation apparatus may be used as long as the same chemical reactions occurring in Section 8 are maintained. In such cases, follow the manufacturer’s instructions for the details of digestion and distillation sequences.

8.12 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 8—Commercially available automated colorimetric titrators may be used instead of the manual titration described in 8.12.

8.13 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.

9. Calculation

9.1 Calculate the nitrogen content of the sample as follows:

$$\text{Nitrogen content, mass \%} = [(A - B) \times M1 + C \times M2] \times 2 \times 0.01401 \times 100/W \quad (1)$$

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,
- 0.01 = normality of 0.005 M H_2SO_4 ,
- 0.1 = normality of 0.05 M H_2SO_4 ,
- 0.01401 = equivalent weight, g/mL,
- 100 = factor to convert to percent, and
- W = weight of sample used, g.

10. Quality Control

10.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (6.12).

10.1.1 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.

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

11. Precision and Bias

11.1 *Precision:*

NOTE 9—The precision of commercially available digester-distillation units and automated colorimetric titrators mentioned in Note 2, Note 7, and Note 8 is not known at present. It is anticipated that Subcommittee D02.03.03 will conduct cross-checks in the future to determine the precision.

11.1.1 ~~For~~ *Lubricating Oils*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1.1 *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:

$$0.01 \text{ mass \%} \quad (2)$$

11.1.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators 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:

$$0.02 \text{ mass \%} \quad (3)$$

11.1.2 ~~For Fuel~~ *Fuel Oils*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.2.1 *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:

$$0.066 \sqrt{M} \quad (4)$$

where M = the mean of the values.

11.1.2.2 *Reproducibility*—The difference between two single and independent results obtained by different operators 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:

$$0.190 \sqrt{M} \quad (5)$$

where M = the mean of the two values.

11.2 *Bias*—Bias has not yet been determined.

12. Keywords

12.1 fuel oils; Kjeldahl; lubricating oils; nitrogen

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL MONITORING

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practice D 6299 and *ASTM MNL 7*⁶).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D 6299 and *ASTM MNL 7*).⁶ Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

NOTE X1.1—In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

X1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM method precision to ensure data quality (see Practice D 6299 and *ASTM MNL 7*).⁶

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X1.6 See Practice D 6299 and *ASTM MNL 7*⁶ for further guidance on QC and Control Charting techniques.

⁷ *Reagent Chemicals, American Chemical Society Specifications ASTM MNL 7*, American Chemical Society, Washington, DC. For suggestions *Manual on the Testing Presentation of reagents not listed by the American Chemical Society; see Analar Standards for Laboratory Chemicals Data Control Chart Analysis*, 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. Section 3, 6th ed., ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Sub-Committee D02.03 has identified the location of selected changes to this standard since the last issue (~~D 3228–96~~) (D 3228–01) that may impact the use of this standard.

(1) ~~Added a QC sample to Section 6, Reagents.~~

(2) ~~Added a QC Section 10.~~

(1) Added new Note 7 allowing the use of commercial digester-distillation apparatus.

(2) Added new Note 8 allowing the use of automated colorimetric titrators.

(3) Added new Note 9 explaining that the precision of the automated digestion-distillation-titration systems is not known at present.

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