Designation: D 3179 – 89 (Reapproved 2002)

Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke[1]

This standard is issued under the fixed designation D 3179; 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.

1. Scope

1.1 These test methods cover the determination of total nitrogen in samples of coal and coke. The analytical data from these test methods shall be reported as part of ultimate analysis where ultimate analysis is requested. If ultimate analysis is not requested, the value shall be reported according to the request. Two methods are included as follows:

	Sections
Test Method A—Kjeldahl-Gunning Macro Analysis, with an alternative technique included	9 to 16
Test Method B—Kjeldahl-Gunning Semi-Micro Determination	17 to 23

1.2 *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.*

1.3 The values stated in SI units are to be regarded as the standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 121 Terminology of Coal and Coke[2]

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Practice for Preparing Coal Samples for Analysis[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3176 Practice for Ultimate Analysis of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System[4]

3. Terminology

3.1 For definitions of terms used in these test methods, refer to Definitions D 121. For an explanation of the metric system including units, symbols, and conversion factors, see IEEE/ASTM SI 10.

4. Summary of Test Methods

4.1 In these procedures, nitrogen is converted into ammonium salts by destructive digestion of the sample with a hot, catalyzed mixture of concentrated sulfuric acid and potassium sulfate. These salts are subsequently decomposed in a hot alkaline solution from which the ammonia is recovered by distillation and finally determined by alkalimetric or acidimetric titration.

5. Significance and Use

5.1 Nitrogen results obtained by these test methods are required to fulfill the requirements of the ultimate analysis, Practice D 3176. Also, results obtained may be used to evaluate the potential formation of nitrogen oxides as a source of atmospheric pollution.

5.2 Nitrogen data are used in comparing coals and in research. When the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination.

6. Interferences

6.1 No significant interferences have been determined using these procedures. However, strict adherence is necessary when using these nitrogen procedures to obtain good reproducible results.

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.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to meet its use without lessening the accuracy of the determination.

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[1] These test methods are under the jurisdiction of ASTM Committee D05 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Sept. 29, 1989. Published February 1990. Originally published as D 3179 – 73. Last previous edition D 3179 – 89 (1997)$^{\epsilon 1}$.

[2] *Annual Book of ASTM Standards*, Vol 05.06.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 14.02. Excerpts appear in the gray pages of all the volumes.

[5] *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.

7.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water, conforming to Specification D 1193.

8. Sampling and Preparation

8.1 The sample shall be the material pulverized to pass No. 60 (250-µm) sieve and well mixed in accordance with Method D 346 or Method D 2013. In the case of coke and anthracite, grinding the sample to pass a No. 200 (75-µm) or finer sieve is recommended.

8.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D 3173, in order to allow calculation of the as-analyzed data to other bases.

TEST METHOD A—MACRO-NITROGEN DETERMINATION WITH ALTERNATIVE METHOD INCLUDED

9. Scope and Application

9.1 This test method describes a macro procedure for the determination of nitrogen in both coal and coke, by two alternative procedures. In both procedures, a 1 g sample is digested with a hot catalyzed mixture of concentrated sulfuric acid and potassium sulfate, which converts the nitrogenous compounds to ammonium salts. The salts are then decomposed in a hot alkaline solution, releasing the ammonia, which is then distilled into either standard sulfuric-acid or boric-acid solution and finally determined by alkalimetric or acidimetric titration.

10. Apparatus

10.1 *Digestion Unit*—An electrically heated digestion rack or a gas burner; either type of heater shall be provided with adequate means of control to maintain digestion rates as described in 12.1. It is essential that an electric digestion rack provides adjustable controls to regulate desirable digestion temperatures. To eliminate emission of sulfur-acid fumes, the digestion process must be carried out under a well-ventilated fume hood. Commercially made multiple-unit digestion racks provided with fume exhaust ducts may be used.

10.2 *Digestion Flasks*—Made of heat-resistant glass,[6] having a capacity of 500 or 800 mL.

10.3 *Distillation Unit*—A suitable glass steam distillation unit with a splash head to trap any entrained caustic soda and also provided with adequate means of control to maintain distillation rates as described in 12.1. Commercially made multiple unit distillation racks provided with water-cooled glass or block-tin condensers may be used.

10.4 *Buret*—Microburet graduated in 0.01 mL. A50 mL microburet is needed for Method A.

10.5 *Erlenmeyer Flask*—Having a capacity of 250 to 300 mL.

10.6 *Rubber Tubing*—Sufficient for attaching condenser to cooling water supply and drain.

10.7 *Pipets*—As required.

11. Reagents

11.1 *Alkali Solution*—Cautiously dissolve 8.0 g of potassium sulfide (K_2S) and 500 g of sodium hydroxide (NaOH) (**Warning—**This solution becomes very hot. Cool the solution and dilute to 1 L. The use of appropriate amounts of sodium sulfide (Na_2S) or potassium hydroxide (KOH) may be substituted (Note 13).)

11.2 *Ethyl Alcohol* (95 %)—Ethyl alcohol conforming to Formula No. 30 or 2A of the U.S. Bureau of Internal Revenue. Methyl alcohol may be used.

11.3 *Mercury*.

NOTE 1—Other satisfactory and permissible catalysts for the digestion, together with the quantities of K_2SO_4 required in their use are as follows:
(1) Five grams of a mixture containing 32 parts by weight of K_2SO_4, 5 parts by weight of mercuric sulfate ($HgSO_4$), and one part by weight of selenium.
(2) Three-tenths gram of mercuric selenite ($HgSeO_3$) with 7 to 10 g of K_2SO_4.
(3) Three-tenths gram of cupric selenite dihydrate ($CuSeO_3 \cdot 2H_2O$) with 7 to 10 g of K_2SO_4. When this mixture is used, the addition of a sulfide to the alkali solution is not necessary.

11.4 *Potassium Permanganate* ($KMnO_4$), crystals.

11.5 *Potassium Sulfate* (K_2SO_4), crystals.

11.6 *Sucrose*, National Institute of Standards and Technology primary-standard grade.

11.7 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

11.8 *Zinc*, mossy or granular.

REAGENTS REQUIRED ONLY FOR KJELDAHL-GUNNING METHOD

11.9 *Methyl Red Indicator Solution* (0.4 to 1 g/L)—Dissolve 0.04 to 0.1 g of methyl red in 50 mL of 95 % ethyl alcohol or methyl alcohol and add 50 mL of water. Bromcresol green solutions to equal concentrations may be used.

11.10 *Sodium Hydroxide, Standard Solution* (0.1 to 0.2 *N*)—Prepare and accurately standardize a 0.1 to 0.2 *N* sodium hydroxide (NaOH) solution against a primary standard.

11.11 *Sulfuric Acid* (0.2 *N*)—Prepare and standardize a 0.2 *N* sulfuric acid (H_2SO_4) solution. The solution need not be standardized against a primary standard.

REAGENTS REQUIRED ONLY FOR ALTERNATIVE METHOD

11.12 *Boric Acid Solution* (50 g/L)—Dissolve 5 g of boric acid (H_3BO_3) in 100 mL of boiling water. Allow to cool before use.

11.13 *Mixed Indicator Solution*—Prepare a solution containing 0.125 % methyl red and 0.083 % methylene blue in 95 % ethyl alcohol or in methyl alcohol. Prepare a fresh solution at bimonthly intervals.

11.14 *Sulfuric Acid* (0.1 to 0.2 *N*)—Prepare and accurately standardize a 0.1 to 0.2 *N* sulfuric acid (H_2SO_4) solution against a primary standard; hydrochloric acid (HCl) of similar concentration may be substituted.

12. Procedure

12.1 Weigh approximately 1 g (weighed to nearest 1 mg) of the analysis sample and carefully transfer into a 500 or 800-mL Kjeldahl flask containing 7 to 10 g of K_2SO_4 and 0.6 to 0.8 of mercury (Note 1). Add 30 mL of H_2SO_4(sp gr 1.84) to the

[6] Borosilicate glass has been found satisfactory for this purpose.

mixture by pouring down the neck of the flask with rotation, in order to wash any adherent sample material into the mixture. Swirl the contents of the flask several times to ensure thorough mixing and wetting of the sample. Incline the flask at an angle of 45 to 60° on the digestion heater in a fume hood (Note 2), and heat the contents to boiling; controlling the heat so the H_2SO_4 vapors condense no more than halfway up the neck of the flask. Continue the boiling until all sample particles are oxidized, as evidenced by a nearly colorless solution, or for at least 2 h after the solution has reached a straw-colored stage. The total time of digestion will require 3 to 6 h, except in the case of coke and anthracite, which may require 12 to 16 h (Note 3). When the digestion is completed and the solution has cooled, a few crystals of $KMnO_4$ may be added to ensure complete oxidation; further heating may be necessary to destroy the excess permanganate and decolorize the solution.

NOTE 2—When fume exhaust ducts or hoods are not available, a Hengar tube may be inserted in the neck of the flask.

NOTE 3—Addition of 0.1 g of chromic trioxide (CrO_3) to the digestion mixture has been found very helpful in reducing the time of digestion for coke.

12.2 Dilute the cooled digestion mixture to about 300 mL with cold water, and remove any heat of dilution by cooling with water. Meanwhile, pipet into the 250 or 300-mL Erlenmeyer flask, 20.0 mL of 0.2 *N* H_2SO_4 and add 6 drops of methyl red or bromcresol green indicator solution. Attach the glass connecting tube to the discharge end of the condenser, using the short piece of rubber tubing as a seal. Incline the Erlenmeyer flask at a suitable angle, and insert this tube so that the end is immersed to the maximum depth in the acid. Add 1 to 2 g of granular zinc to the mixture in the Kjeldahl flask (two or three small pieces of mossy zinc is used), and slowly add 100 mL of the alkali solution so that it forms a distinct layer under the acid solution. (**Warning—**If the layers are mixed, considerable heat may be generated with subsequent spray of the flask contents. The flask opening should be directed away from the operator and others during this step.) This may be accomplished by inclining the flask at an angle of 45 to 60° and pouring the alkali solution down the neck. Failure to maintain discrete layers during this operation may lead to loss of ammonia. Quickly connect the flask to the distilling condenser through the Kjeldahl connecting bulb, and then swirl the contents to promote thorough mixing.

12.3 Bring the contents of the Kjeldahl flask to a boil carefully, in order to avoid violent bumping, and then distill the ammonia over into the acid solution in the Erlenmeyer flask. Continue the distillation at a maximum rate of approximately 350 mL/h until 150 to 175 mL of distillate have been collected. Discontinue the boiling, and remove the glass connecting tube from the condenser and Erlenmeyer flask. Rinse the tube with distilled water, collecting the washings in the Erlenmeyer flask, and then back-titrate the excess acid with 0.1 to 0.2 *N* NaOH solution.

12.4 Run a blank determination in the same manner as described in 12.1-12.3 using approximately 1 g of sucrose (weighed to the nearest 1 mg) as the sample material.

13. Calculation and Report

13.1 Calculate the percentage of nitrogen in the analysis sample as follows:

$$\text{Nitrogen, \%} = [(B - A)N \times 0.014/C] \times 100 \quad (1)$$

where:

A = millilitres of NaOH solution required for titration of the sample,
B = millilitres of NaOH solution required for titration of the blank,
N = normality of the NaOH solution, and
C = grams of sample used.

14. Procedure for Alternative Technique

14.1 Digest the sample as described in 12.1.

14.2 Dilute and cool the digestion mixture as described in 12.2. Add to the 250 or 300-mL Erlenmeyer flask approximately 20 mL of H_3BO_3 solution and 5 drops of mixed indicator solution. Then proceed as described in the remainder of 12.2.

14.3 Distill the ammonia into the H_3BO_3 solution exactly as described in 12.3 and finally titrate the ammonia with 0.2 *N* H_2SO_4.

14.4 Run a blank determination in the same manner as described in 14.1-14.3, using approximately 1 g (weighed to the nearest 1 mg) of sucrose as the sample material. Blank determinations must be made to correct for nitrogen from sources other than the sample. A blank determination shall be made whenever a new batch of any one reagent is used in the analysis.

14.5 *Calculation*—Calculate the percentage of nitrogen in the sample as follows:

$$\text{Nitrogen, \%, in the analysis sample} = [(A - B)N \times 0.014/C] \times 100 \quad (2)$$

where:

A = millilitres of H_2SO_4 required for titration of the sample,
B = millilitres of H_2SO_4 required for titration of the blank,
N = normality of the H_2SO_4, and
C = grams of the sample used.

15. Report

15.1 The results of the nitrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

15.2 Use the percentage of moisture in the sample passing a No. 60 (250-µm) sieve to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D 3176 and D 3180.

16. Precision and Bias

16.1 The permissible differences between duplicate determinations shall not exceed the following values in more than 5 of 100 instances.