Designation: D 4795 – 94 (Reapproved 1998)

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Nitrogen Content of Soluble Nitrocellulose—Alternative Method[1]

This standard is issued under the fixed designation D 4795; 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 Test Methods D 301 for measuring nitrogen content in nitrocellulose by nitrometer are the accepted standard. However, the glassware is specialized and the precision is dependent on the development of a high level of skill by the operator. The ferrous-sulfate titration of nitrate is a classical procedure. By controlling critical variables and automating the actual titration, precision equivalent to the nitrometer can be achieved with nitrocellulose. This test method describes such a procedure.

1.2 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

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 hazard statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 301 Test Methods for Soluble Cellulose Nitrate[2]

D 1193 Specification for Reagent Water[3]

3. Summary of Test Method

3.1 A weighed specimen of nitrocellulose is dissolved in sulfuric acid and titrated automatically with ferrous sulfate. The nitrogen content of the specimen is calculated using the equivalence factor of the ferrous sulfate.

4. Significance and Use

4.1 This test method provides a simpler means for measuring the nitrogen content of nitrocellulose than the nitrometer described in Test Method D 301. Under controlled conditions, the procedure described is capable of results equivalent to those obtained by the nitrometer.

5. Interferences

5.1 The presence of moisture (or other volatile components) in the specimen will affect results. It is recommended that only thoroughly dry specimens be used.

5.2 Temperature rise must be controlled during the titration. The cooling bath provides that control. However, if the rate of titrant addition is too fast, temperature may rise out of control. Results may then be erratic. Adherence to the procedure will avoid temperature excursions. For optimum system efficiency, room temperature should be maintained at 23 ± 2°C.

5.3 The strength of the sulfuric acid used to dissolve the specimen is very important. Too low an acid strength slows the rate of solution which, in turn, causes titrations to be abnormally slow. Results then become erratic.

6. Apparatus

6.1 *Acid Bottle Safety Dispenser*.

6.2 *Brinkman 20 Titration System*, or equivalent, with 25 mL amber buret:

6.2.1 *Electrode*, platinum.

6.2.2 *Electrode*, glass.

6.3 *Desiccator*, with drying agent.

6.4 *Weighing bottles*, 12-mL capacity, aluminum (preferred) or glass.

6.5 *Analytical Balance*, accurate to ±0.1 mg.

6.6 *Ovens*—135°C, for drying standards, and 100°C, for drying specimens, having unexposed heating elements and the door latch removed.

6.7 *Circulating Unit*, for chilled water, 5 ± 2°C.

6.8 *Blender*, with 8-oz (0.25-L) blender jar.

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.[4] Other grades may be used, provided it is first ascertained that the reagent is of

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.36 on Cellulose and Cellulose Derivatives.

Current edition approved April 15, 1994. Published June 1994. Originally published as D 4795 – 88. Last previous edition D 4795 – 88.

[2] *Annual Book of ASTM Standards*, Vol 06.03.

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

[4] *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. Pharmacopeiall Convention, Inc. (USPC), Rockville, MD.

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 Type III of Specification D 1193.

7.3 *Sulfuric Acid* (H_2SO_4) 95 to 98 %.

7.4 *Ferrous Sulfate Solution*—Dissolve 350 g of ferrous sulfate crystals ($FeSO_4$) in 1000 mL of distilled water. Add 1000 mL of 1+1 H_2SO_4 solution. Makes 2 L.

7.5 *Potassium Nitrate (KNO_3) Standard* or an equivalent nitrate primary standard.

7.6 *Nitrocellulose Standard*—A sample with a known nitrogen value or other known organic nitrate.

8. Hazards

8.1 Since the sample of nitrocellulose must be dried, it is imperative that care be exercised in storage, handling, and disposal. Dry nitrocellulose is extremely flammable. Refer to the Procedure section for Drying Samples of Methods D 301.

8.2 Strong sulfuric acid used as the solvent for the specimen can burn the skin. The ferrous sulfate titrant is also strongly acidic. Take proper precautions to protect the operator and the equipment.

8.3 To prevent burns from acid dripping off the electrodes and dispenser tip, always wipe the electrodes and dispenser tip with a tissue before reaching under them to retrieve a beaker.

9. Preparation of Apparatus

9.1 If the system has been down for at least 8 h, purge the system with 40 mL of ferrous sulfate solution.

10. Calibration and Standardization

10.1 Weigh a sample bottle containing 0.5000 ± 0.05 g of KNO_3 that has been dried in a 135°C oven for a minimum of 4 h and stored in a dessicator. If KNO_3 has been out of the oven for 4 h or more, redry in a 135°C oven for a minimum of 2 h. (Nitrocellulose specimens are dried in a 100°C oven for a minimum of 1 h. If out of the oven more than 2 h, redry for ½h.) Turn on the pump of the chilled water circulator to start water flowing through the cooling bath.

10.2 Place the magnetic stirring bar into a dry 250-mL beaker and fill the beaker with 150 mL of H_2SO_4 (20± 2°C).

10.3 Place the beaker in the cooling bath on the stirrer unit. Start the stirrer and adjust the speed for a *slight* vortex. Too vigorous a vortex can cause the nitrocellulose to splash onto the sides of the beaker.

10.4 With the stirrer operating and the electrodes up in the air away from the acid, slowly pour the specimen into the vortex of the swirl. Be careful not to touch the dispensing tip or electrodes with the weighing bottle. Reweigh the weighing bottle to find the weight of the standard by difference.

10.5 Allow most of the KNO_3 to dissolve. Visually inspect the solution until no more chunks or chips of KNO_3 remain. The solution may be cloudy.

10.6 Lower the electrodes and the dispensing tip into the H_2SO_4.

10.7 Set the controls to the desired settings.

10.8 As the KNO_3 dissolves and HNO_3 is formed by the reaction of H_2SO_4 and the specimen, a millivolt potential change is evident by a rising recorder pen.

10.8.1 When the pen shows a leveling off, it is an indication that the majority of the KNO_3 is in solution. Visually inspect the solution to verify the fact that chips are no longer present.

10.9 Set the buret control to a rate of about 5 mL/min. Allow 10 ± 0.1 mL to dispense at this rate.

10.10 Stop the buret, switch the dispense-rate switch to automatic, and restart. Allow the titration to proceed automatically to the end point.

10.11 At the completion of the automatic titration, immediately record the millilitre reading. Switch the electrode setting to STANDBY.

10.12 Raise the electrodes from the acid and allow most of the acid to drip into the titration beaker. Carefully wipe by dabbing the electrodes and dispensing tip with a tissue. (**Precaution**—See Section 8.) Discard the tissue into a container of water. *DO NOT* allow acid to drip into the circulating-bath water.

10.13 Remove the completed titration beaker from the cooling bath.

10.14 Lower the electrodes and pipet into a beaker of clean H_2SO_4 for soaking. Make sure the acid is not contaminated with $FeSO_4$. (It may bleed from the dispenser tip giving a reddish tint to the acid.) Replace with clean H_2SO_4 if this occurs.

NOTE 1—It is important to soak the electrodes in between each analysis and while the titrators are not in use. Cleanliness of equipment is of the utmost importance in this method of analysis.

10.15 Calculate the nitrogen equivalence factor F for the standard KNO_3 as follows:

$$F = (A \times 13.855)/B \quad (1)$$

where:

A = weight of KNO_3, g,
13.855 = nitrogen equivalence of nitrogen in KNO_3 or in the standard material used, and
B = amount of $FeSO_4$ used to titrate KNO_3, mL.

11. Specimen Preparation

11.1 *Cutting*:

11.1.1 Use a sample size of approximately 2 heaping tablespoons of wet nitrocellulose.

11.1.2 For high viscosity types, place the sample into a small 8-oz (0.25-L) plastic blender jar. Fill to the fill line with tap water, and screw on the cap with a 4-blade cutter unit inside.

11.1.3 Place on the blender base and blend for 7 min at high speed.

11.1.4 For 11 % nitrogen and low viscosity types, grind in a tissue disintegrator using a 16-oz (0.5-L) glass jar about ¾ full of tap water.

11.1.5 Grind each sample at high speed for their respective times as follows:

Hercules Designation	Time, min
SS, all	5
RS ½	4
RS ¼	4
RS ⅛	3
AS, all	3

11.2 At the completion of cutting, remove the sample container and draw off the excess water from the nitrocellulose by filtering on a Büchner funnel through a circular filter paper.

11.3 Dry the material in accordance with the paragraph on small quantities in the Procedure section for Drying Samples of Methods D 301.

11.4 After drying, weigh 3 replicate specimens of 0.4500± 0.0075 g each into a weighing can or bottle.

11.5 It is desirable to analyze the specimens as soon as they are taken out of the oven. Allow time for cooling in a desiccator before weighing. If specimens are out of the oven for more than 2 h, redry for ½ h at 100°C.

12. Procedure

12.1 Prepare specimens in accordance with Section 11.

12.2 Repeat 10.1-10.15, using the settings for the specimen given in Table 1.

12.3 Dispose of any excess H_2SO_4 standard down the sink and rinse with large quantities of water.

13. Calculation

13.1 Calculate the percent of nitrogen *N* as follows:

$$N = (C \times F)/D \quad (2)$$

TABLE 1 Suggested Settings for Brinkman 20

	EP-1	Select	EP-1 Setting, mV	Proposed Band[A]	Minimum Delivery[A]
Standardizations with KNO_3	-mV	EP-1	350	80	100
Analysis of nitrocellulose	-mV	EP-1	200	80	100

[A] These are approximations only. Settings can vary between instruments.

where:

C = $FeSO_4$ to titrate specimen, mL,
F = equivalence factor from 10.15, and
D = weight of specimen, g.

14. Precision and Bias [5]

14.1 *Precision*—Tests by two laboratories on two samples gave results equivalent to the nitrometer in precision and bias. No more extensive interlaboratory testing has been undertaken as yet.

14.2 *Bias*—No statement on bias can be made as no suitable reference material is available as a standard.

15. Keywords

15.1 nitrogen content; soluble nitrocellulose

[5] Supporting data available from ASTM Headquarters. Request RR: D01-1056.