



Standard Test Method for Rubber—Nitrogen Content¹

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1. Scope

1.1 This test method outlines two procedures for the determination of total nitrogen in natural and synthetic rubbers and latexes, using variants of the Kjeldahl process.

1.2 It is applicable to raw rubbers, cured or uncured compounds, and finished articles.

1.3 Procedure A, the referee method, is a macro procedure. Procedure B, the alternative method, is a semimicro procedure using the same reagent as in Procedure A.

1.4 In the absence of other nitrogen-containing materials, the method can be used for the estimation of the NBR content of NBR rubbers and rubber products.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.* Specific warnings are given in 8.2 and 9.2.

2. Referenced Documents

2.1 *ASTM Standards:*²

D 4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

E 147 Specification for Apparatus For Microdetermination Of Nitrogen By Kjeldahl Method

3. Summary of Method

3.1 The procedures used are modifications of the Kjeldahl method using sulfuric acid, potassium sulfate, and catalytic

amounts of copper sulfate and selenium in the digestion mixture. The distillate from a strongly alkaline solution of the digested sample is caught in boric acid solution and titrated with standard acid or in excess standard acid and back titrated with standard base.

4. Significance and Use

4.1 The determination of nitrogen in natural rubber is usually carried out in order to arrive at an estimate of the protein content. Minor amounts of non-proteinous nitrogen-containing constituents are also present, however, and in the dry solids prepared from natural rubber latex, these materials can make a substantial contribution to the total nitrogen content.

4.2 In the absence of other nitrogen-containing materials, the method can be used for the estimation of the NBR content of NBR rubbers and rubber products.

4.3 In the absence of other nitrogen-containing materials and if the acrylonitrile content of the NBR rubber is known, the method can be used to estimate the amount of NBR rubber in mixtures.

4.4 This method may be used for quality control, for purchase and raw material uses, for processing studies, and for research and development.

5. Apparatus

5.1 *Kjeldahl Digestion and Distillation Apparatus:*

5.2 *For Procedure A*—Macro-Kjeldahl apparatus, preferably having ground-glass joints and including an 800-cm³ Kjeldahl flask, with electrical heating equipment for the digestion apparatus.

5.3 *For Procedure B*—Micro-Kjeldahl digestion and distillation apparatus in accordance with Specification **E 147**, or semimicro Kjeldahl digestion and distillation apparatus in which the digestion and distillation are carried out in the same flask (30 to 100-cm³ Kjeldahl flask that may be attached to the distillation apparatus by means of a standard-taper joint).

¹ This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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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.

6. Reagents

6.1 *Boric Acid Solution* (40 g/dm³)—Dissolve 40 g of boric acid (H₃BO₃) in warm water, dilute to nearly 1 dm³, cool to room temperature, and dilute to 1 dm³.

6.2 *Catalyst Mixture*—Prepare a finely divided, intimate mixture of 30 parts by mass of anhydrous potassium sulfate (K₂SO₄), 4 parts of cupric sulfate (CuSO₄·5H₂O) and 1 part of selenium powder. Alternatively, dissolve, with heating, 110 g of K₂SO₄, 14.7 g of CuSO₄·5H₂O and 3.7 g of selenium in 600 cm³ of H₂SO₄ (density 1.89 Mg/m³).

6.3 *Indicator, Methyl Red–Methylene Blue*—Dissolve 0.1 g of methyl red and 0.05 g of methylene blue in 100 cm³ of alcohol.

6.4 *Indicator, Methyl Red–Bromcresol Green*—Dissolve 0.08 g of methyl red and 0.4 g of bromcresol green in 100 cm³ of alcohol.

6.5 *Sodium Hydroxide, Standard Solution (0.02 M), Carbonate-Free*—Prepare a 0.02 M carbonate-free solution of sodium hydroxide (NaOH). Standardize against National Bureau of Standards sample No. 84 of potassium hydrogen phthalate in accordance with instructions furnished with the standard sample.

6.6 *Sodium Hydroxide, Standard Solution (0.1 M), Carbonate-Free*—Prepare a 0.1 M carbonate-free solution of sodium hydroxide (NaOH). Standardize against National Bureau of Standards sample No. 84 of potassium hydrogen phthalate in accordance with the instruction furnished with the standard sample.

6.7 *Sodium Hydroxide Solution (40 %)*—Dissolve 400 g of sodium hydroxide (NaOH) in 600 cm³ of water.

6.8 *Sulfuric Acid* (density 1.89 Mg/m³)—Concentrated sulfuric acid (H₂SO₄).

6.9 *Sulfuric Acid, Standard (0.01 M)*—Prepare a 0.1 M solution of sulfuric acid (H₂SO₄). Standardize against 0.02 M carbonate-free NaOH solution, using 2 drops of methyl red-methylene blue indicator.

6.10 *Sulfuric Acid, Standard (0.05 M)*—Prepare a 0.05 M solution of sulfuric acid (H₂SO₄). Standardize against 0.1 M carbonate-free NaOH solution, using 2 drops of methyl red-methylene blue indicator.

6.11 *Zinc, Granulated or Mossy.*

7. Sampling

7.1 Depending upon the use to which this test method will be put, sampling shall be at the discretion of the analyst, to obtain as representative a sample as possible of the lot to be tested.

8. Procedure A, Referee Method (Macro Method)

8.1 Weigh a 2-g test specimen to the nearest 1 mg, cut into small pieces, and place in a Kjeldahl flask. To the Kjeldahl flask add about 13 g of catalyst mixture (see 6.2) and 60 cm³ of H₂SO₂ (6.8) or, alternatively, about 65 cm³ of catalyst solution in H₂SO₄. Swirl the flask until the contents are well mixed. Then boil gently until the solution is clear and continue heating for 1 h longer.

8.2 Cool the flask and its contents to room temperature and dilute with 200 cm³ of water. Add 150 cm³ of 40 % NaOH

solution to the contents of the flask, pouring slowly down the side of the flask so that the contents do not mix. Without mixing the contents of the flask, slide several pieces of mossy or granulated zinc metal down into the flask and quickly connect the flask to the trap connected to the condenser. (**Warning**—The addition of base (NaOH) to an acid solution (H₂SO₄) will produce an exothermic reaction. Protect hands and eyes adequately.)

8.3 Into a suitable receiving flask place either 75 cm³ of water and 25.0 cm³ of 0.05 M H₂SO₄ or 100 cm³ of H₃BO₃ solution. Mount the flask with the acid solution (see 6.1) so that the end of the delivery tube projects below the surface of the solution. While holding the stopper of the Kjeldahl flask in place, swirl the contents of the flask and mix thoroughly. Start distilling at once and continue distilling evenly until 200 cm³ of distillate have been collected.

NOTE 1—This amount of H₂SO₄ is sufficient for nitrogen content only up to 1.75 %. For samples of higher nitrogen content, use a larger volume of H₂SO₄. Do not use a smaller sample.

8.4 Titrate the contents of the receiving flask with 0.1 N NaOH solution, using methyl red-methylene blue (see 6.3) as indicator when H₂SO₄ is used as the receiving solution, or with 0.05 M H₂SO₄ using bromcresol green-methyl red indicator (see 6.4) when H₃BO₃ solution is used.

8.5 *Blank*—Make a blank determination by carrying out the entire procedure, using only the reagents, with the digestion mixture being heated until the volume is reduced to the same size as obtained with a digested rubber sample.

9. Procedure B, Alternative Method (Semimicro)

9.1 Weigh accurately, to 0.1 mg, about 0.1 g of the sample into the micro or semimicro Kjeldahl flask. Add about 0.65 g of the catalyst mixture (see 6.2) and 3 cm³ of H₂SO₄ (6.8), or, alternatively, add 3.5 cm³ of the catalyst solution in H₂SO₄, to the flask. Boil gently by electrical heating and continue boiling for about 30 min after the digest has become a clear green color with no yellow tint.

9.2 Cool the digest. If the micro apparatus requiring a transfer to the distillation apparatus has been used, dilute the digest with 10 cm³ of water and transfer with two or three 3-cm³ portions of water to the distillation apparatus which has been steamed out for 2 min. If the semimicro apparatus has been used, dilute the digest with 16 to 20 cm³ of water and attach the flask to the distillation apparatus which has been steamed out for 2 min by using an empty digestion flask in place of the sample digestion flask. (**Warning**—The addition of water to concentrated acid (H₂SO₄) will produce a violent reaction unless the water is added carefully. Pour the required amount of water slowly down the side of the tilted flask. At the same time gently rotate the flask to facilitate mixing. This is an exothermic reaction; therefore, hands and eyes should be adequately protected.)

9.3 *Distillation:*

9.3.1 *H₃BO₃ Solution in Receiving Flask*—Add 5 cm³ of the H₃BO₃ solution and about 5 cm³ of water to the receiving flask, add 2 drops of methyl red-bromcresol green indicator, (see 6.4), and place the receiver so that the end of the condenser dips below the surface of the H₃BO₃ solution. Add about 10

cm³ of 40 % NaOH solution to the digestion flask, washing it with not more than 5 cm³ of water. Pass steam from the generating flask through the distillation apparatus until the total volume of solution in the receiver is about 30 cm³. This will require about 4 min with the micro apparatus; the time will vary with the semimicro apparatus, and some mild flame heating of the distillation may be necessary during the first minute of the distillation. Lower the receiver until the condenser tip is well above the solution and continue distilling for 1 min. The total volume should be about 35 cm³ with the micro apparatus and 35 to 40 cm³ with the semimicro apparatus. Wash the end of the condenser with water.

9.3.2 *H₂SO₄ in Receiving Flask*—Accurately pipet 10 cm³ of 0.01 M H₂SO₄ into the receiving flask. Alternatively, use smaller volumes (below 5 cm³) delivered accurately from a 5-cm³ buret graduated in 0.2-cm³ divisions. Do not pipet volumes below 10 cm³. Add 2 drops of methyl red-methylene blue indicator (see 6.3) to the receiver and distill as described in 9.3.1.

NOTE 2—This volume of acid will be an excess up to about 2.5 % nitrogen in a 0.1-g test specimen.

9.4 Titration:

9.4.1 *H₃BO₃ Solution in Receiving Flask*—Titrate the distillate with standardized 0.01 M H₂SO₄ using a 5 or 10-cm³ buret graduated in 0.02-cm³ divisions.

9.4.2 *H₂SO₄ in Receiving Flask*—Titrate the distillate with 0.02 M NaOH solution using a 5 or 10-cm³ buret graduated in 0.02-cm³ divisions.

9.4.3 *Blank*—Carry a blank determination through the entire procedure, using all of the reagents but omitting the sample.

10. Calculation

10.1 When H₃BO₃ solution is used as the receiving solution, calculate the nitrogen content as follows:

$$\text{Nitrogen, \%} = [(V_1 - V_2)M \times 0.0140/W] \times 100 \quad (1)$$

where:

- V_1 = cubic centimetres of H₂SO₄ required for titration of contents of the receiving flask (8.4 or 9.4.1),
- V_2 = cubic centimetres of H₂SO₄ required for titration of the blank (8.5 or 9.4.3),
- M = molarity of the H₂SO₄,
- W = grams of sample used, and
- 0.0140 = millimole mass of nitrogen.

10.2 When H₂SO₄ is used as the receiving solution, calculate the nitrogen content as follows:

$$\text{Nitrogen, \%} = [(V_2 - V_1)M \times 0.0140/W] \times 100 \quad (2)$$

where:

- V_1 = cubic centimetres of NaOH solution required for titration of the contents of the receiving flask (8.4 or 9.4.2),
- V_2 = cubic centimetres of NaOH solution required for titration of the blank (8.5 or 9.4.3),
- M = molarity of the NaOH solution,
- W = grams of sample used, and
- 0.0140 = millimole mass of nitrogen.

10.3 Calculate the percentage of NBR rubber present in the sample if the composition of the copolymer used in the rubber product is known.

11. Report

11.1 The test report shall include the following information:

- 11.1.1 Identification of the sample,
- 11.1.2 The average of two determinations, and
- 11.1.3 The method used—micro, semimicro, or macro.

12. Precision

12.1 Precision statements according to the 1988 edition of Practice D 4483 have not been prepared for this method at the date of this revision. When available, they will be added to this method.

13. Keywords

- 13.1 Kjeldahl; nitrogen; rubber

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