Designation: D 3533 – 90 (Reapproved 2001)

Standard Test Method for Rubber—Nitrogen Content[1]

1. Scope

1.1 This 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 the 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:*

D 1076 Specification for Rubber—Concentrated, Ammonia Preserved, Creamed, and Centrifuged Natural Latex[2]

D 3040 Practice for Preparing Precision Statements for Standards Related to Rubber and Rubber Testing[3]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

E 147 Specification for Apparatus for Microdetermination of Nitrogen by Kjeldahl Method[4]

NOTE 1—The specific dated edition of Practice D 3040 that prevails in this method is referenced in the Precision section.

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-cm^3 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[5] in which the digestion and distillation are carried out in the same flask (30 to 100-cm^3 Kjeldahl flask that may be attached to the distillation apparatus by means of a standard-taper joint).

6. Reagents

6.1 *Boric Acid Solution* (40 g/dm^3)—Dissolve 40 g of boric acid (H_3BO_3) in warm water, dilute to nearly 1 dm^3, cool to

---

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

Current edition approved Oct. 26, 1990. Published May 1991. Originally published as D 3533 – 76. Last previous edition D 3533 – 82.

[2] *Annual Book of ASTM Standards*, Vol 09.01.

[3] Discontinued—see *1986 Annual Book of ASTM Standards*, Vols 09.01 and 09.02.

[4] *Annual Book of ASTM Standards*, Vol 14.04.

[5] Suitable semimicro apparatus may be obtained from the American Instrument Co., 8030 Georgia Ave., Silver Spring, Md., 20910, and from the Scientific Glass Apparatus Co., 737 Broad St., Bloomfield, NJ 07003.

room temperature, and dilute to 1 dm^3.

6.2 *Catalyst Mixture*—Prepare a finely divided, intimate mixture of 30 parts by mass of anhydrous potassium sulfate (K_2SO_4), 4 parts of cupric sulfate ($CuSO_4{\cdot}5H_2O$) and 1 part of selenium powder. Alternatively, dissolve, with heating, 110 g of K_2SO_4, 14.7 g of $CuSO_4{\cdot}5H_2O$ and 3.7 g of selenium in 600 cm^3 of H_2SO_4 (density 1.89 Mg/m^3).

6.3 *Indicator, Methyl Red–Methylene Blue*—Dissolve 0.1 g of methyl red and 0.05 g of methylene blue in 100 cm^3 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 cm^3 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 cm^3 of water.

6.8 *Sulfuric Acid* (density 1.89 Mg/m^3)—Concentrated sulfuric acid (H_2SO_4).

6.9 *Sulfuric Acid, Standard* (0.01 M)—Prepare a 0.1 *M* solution of sulfuric acid (H_2SO_4). 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 (H_2SO_4). 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 cm^3 of H_2SO_2 (6.8) or, alternatively, about 65 cm^3 of catalyst solution in H_2SO_4. 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 cm^3 of water. Add 150 cm^3 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 (H_2SO_4) will produce an exothermic reaction. Protect hands and eyes adequately.)

8.3 Into a suitable receiving flask place either 75 cm^3 of water and 25.0 cm^3 of 0.05 *M* H_2SO_4 or 100 cm^{3}of H_3BO_3 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 cm^3 of distillate have been collected.

NOTE 2—This amount of H_2SO_4 is sufficient for nitrogen content only up to 1.75 %. For samples of higher nitrogen content, use a larger volume of H_2SO_4. 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 H_2SO_4 is used as the receiving solution, or with 0.05 *M* H_2SO_4 using bromcresol green-methyl red indicator (see 6.4) when H_3BO_3 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 cm^3 of H_2SO_4(6.8), or, alternatively, add 3.5 cm^3 of the catalyst solution in H_2SO_4, 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 cm^3 of water and transfer with two or three 3-cm^3 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 cm^3 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 (H_2SO_4) 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 *H_3BO_3 Solution in Receiving Flask*—Add 5 cm^3 of the H_3BO_3 solution and about 5 cm^3 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 H_3BO_3 solution. Add about 10 cm^3 of 40 % NaOH solution to the digestion flask, washing it with not more than 5 cm^3 of water. Pass steam from the generating flask through the distillation apparatus until the total volume of solution in the receiver is about 30 cm^3. 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 cm^3 with the micro apparatus and 35 to 40 cm^3 with the semimicro apparatus. Wash the end of the condenser with water.

9.3.2 *H_2SO_4 in Receiving Flask*—Accurately pipet 10 cm^3 of 0.01 *M* H_2SO_4 into the receiving flask. Alternatively, use smaller volumes (below 5 cm^3) delivered accurately from a 5-cm^3 buret graduated in 0.2-cm^3 divisions. Do not pipet volumes below 10 cm^3. Add 2 drops of methyl red-methylene blue indicator (see 6.3) to the receiver and distill as described in 9.3.1.

NOTE 3—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 *H_3BO_3 Solution in Receiving Flask*—Titrate the distillate with standardized 0.01 *M* H_2SO_4 using a 5 or 10-cm^3 buret graduated in 0.02-cm^3 divisions.

9.4.2 *H_2SO_4 in Receiving Flask*—Titrate the distillate with 0.02 *M* NaOH solution using a 5 or 10-cm^3 buret graduated in 0.02-cm^3 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 H_3BO_3 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 H_2SO_4 required for titration of contents of the receiving flask (8.4 or 9.4.1),
V_2 = cubic centimetres of H_2SO_4 required for titration of the blank (8.5 or 9.4.3),
M = molarity of the H_2SO_4,
W = grams of sample used, and
0.0140 = millimole mass of nitrogen.

10.2 When H_2SO_4 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 Complete identification of the sample,

11.1.2 The average of two individual 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