



# Standard Test Method for Rubber Chemicals—Determination of the Percent Nitrogen in Rubber Antioxidant: Polymerized TMQ<sup>1</sup>

This standard is issued under the fixed designation D 5376; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of the nitrogen content of polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ). It is based on a potentiometric titration of an acetone solution of TMQ with perchloric acid in acetic acid.

1.2 The values stated in 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.* Specific precautionary statements are given in Section 9.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries<sup>2</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *lot sample*—a production sample representative of a standard production unit, normally referred to as “the sample”.

## 4. Summary of Test Method

4.1 A sample of 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) is dissolved in acetone and the nitrogen in TMQ is determined by a potentiometric titration with perchloric acid in acetic acid.

## 5. Significance and Use

5.1 This test method is designed to determine the nitrogen content of oligomeric 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) antioxidant. TMQ is used for heat protection of vulcanized rubber.

5.2 This test method is suitable for assessing product specifications since nitrogen content is related to product

performance, that is, antioxidant efficiency and heat protection. For comparison of product quality at different production facilities sufficient interlaboratory accuracy and precision are required.

## 6. Interferences

6.1 Based on past experience, one significant source of error in this test method is the titration end point assessment. Problems can be avoided by closely following the procedure.

6.2 Theoretically, any material containing basic nitrogen, capable of forming HCl-salt, will be measured by this test method. Extensive high performance liquid chromatograph (HPLC) analyses of the product indicates that the most significant interfering impurities are products formed by side reactions between aniline and acetone, such as those given in Fig. 1.

6.3 Other possible interfering impurities may include the anilino end groups attached to TMQ oligomers, such as those given in Fig. 2.

## 7. Apparatus

7.1 *Standard Laboratory Glassware and Equipment.*

7.2 *Potentiometer.*<sup>3</sup>

7.3 *Reference Electrode,*<sup>4</sup> platinum electrode in an electrolytic glass cell with a frit of porosity 4, filled with a saturated solution of lithium perchlorate in acetic acid (see Fig. 3).

7.4 *Glass Electrode.*<sup>5</sup>

7.5 *Weighing Pipet,* 5 cm<sup>3</sup>.

7.6 *Buret,* 25 cm<sup>3</sup>, Class A, graduated in 0.1 cm<sup>3</sup> increments.

7.7 *Buret,* 50 cm<sup>3</sup>, Class A, graduated in 0.1 cm<sup>3</sup> increments.

7.8 *Magnetic Stirrer.*

7.9 *Erlenmeyer Flask,* 300 cm<sup>3</sup> narrow-neck.

7.10 *Measuring Cylinder,* 50 cm<sup>3</sup>.

7.11 *Beaker,* 150 cm<sup>3</sup>.

7.12 *Beaker,* 400 cm<sup>3</sup>.

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 09.01.

<sup>3</sup> Available from Knick, Berlin, Germany, Type pH62 equipped with a titrator or from Mettler, USA.

<sup>4</sup> Calomel reference electrodes have also been found to be satisfactory, Bechman 39422 or equivalent.

<sup>5</sup> Available from Schott and Gen., Mainz, Germany, or from Mettler, USA.

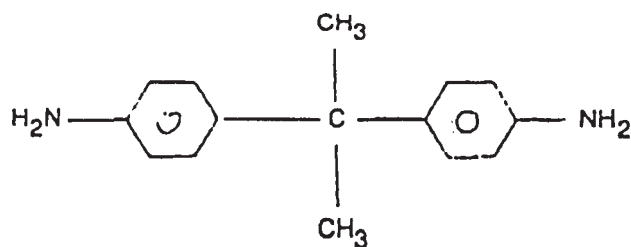
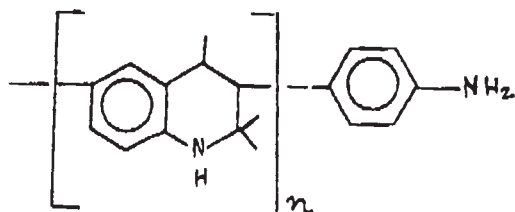


FIG. 1 1(a) 2,2-bis(4'-amino-phenyl)-propane



and/or

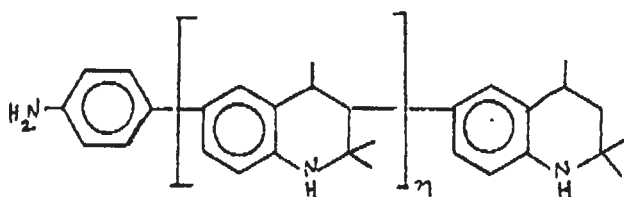


FIG. 2 1(b) (Top)—3-(4'-amino-phenyl)-terminated oligomeric 2,2,4-trimethyl-1,2-dihydroquinoline;  
(Bottom)—6-(4'-amino-phenyl)-terminated oligomeric 2,2,4-trimethyl-1,2-dihydroquinoline

7.13 Dropping Funnel, 50 cm<sup>3</sup>.

7.14 Thermometer, range -20 to +60°C.

7.15 Pipet, 5 cm<sup>3</sup>.

7.16 Volumetric Flask, 2 dm<sup>3</sup>.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>6</sup> 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.

8.2 *Acetic Acid*, p.a.<sup>7</sup>

<sup>6</sup> "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 "Analytical Standards for Laboratory U.K. Chemicals," BHD Ltd., Poole, Dorset, and the "United States Pharmacopoeia."

<sup>7</sup> Available from Merck, Art No. 60 E.

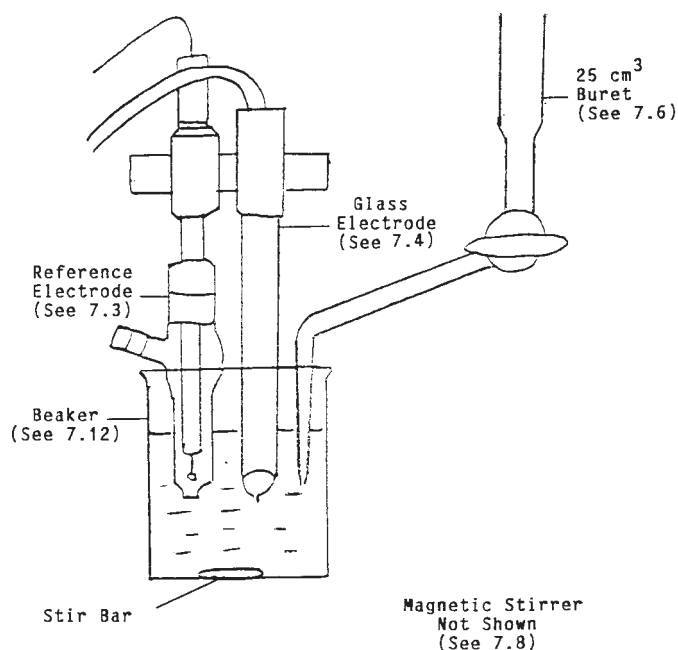


FIG. 3 Titration Vessel

8.3 *Acetic Anhydride*, p.a.<sup>8</sup>

8.4 *Acetone*, p.a.

8.5 *Lithium Perchlorate*, 3 H<sub>2</sub>O p.a.<sup>9</sup>

8.6 *Perchloric acid*, p.a. approx. 70 %.<sup>10</sup>

8.7 *Phenolphthalein*, 1 % dissolved in ethanol.

8.8 *Potassium Hydrogen Phthalate*, p.a.<sup>11</sup>

8.9 *Sodium Hydroxide* (1 N)—Aqueous sodium hydroxide.

## 9. Hazards

9.1 Perchloric acid (70 to 72 %) is a strong oxidant. Care must be exercised to keep it from contacting organic matter. Seventy to 72 % perchloric acid must be kept at or below room temperature. When hot and concentrated it is known to be explosive.

9.2 Acetic anhydride is a noxious chemical and corrosive to the skin. Avoid breathing vapors and use gloves and goggles for protection. Acetone is flammable and vapors form explosive mixtures. Consult appropriate texts for further information on the use and disposal of these chemicals.

## 10. Sampling

10.1 To ensure sample homogeneity, grind a minimum of 10 g of a "lot" sample with a mortar and pestle. Take test unit (0.4 g) from this composite.

## 11. Reagent Preparation and Standardization

11.1 As is the case with any titration method, it is extremely important that the titrants are accurately standardized.

<sup>8</sup> Available from Merck, Art. No. 42.

<sup>9</sup> Available from Merck, Art. No. 10538.

<sup>10</sup> p.a. = pro analysi, means analytical grade reagent available from Merck, Art. No. 519.

<sup>11</sup> Available from Merck, Art. No. 4876.

11.2 Prepare the primary titrant (0.1 *N* perchloric acid) by diluting 70 % perchloric acid with acetic acid, having first eliminated the water content by reaction with acetic anhydride.

11.2.1 The exact concentration of the approximately 70 % perchloric acid is determined as follows: weigh about 3 g of the approximately 70 % perchloric acid to the nearest 0.1 mg in a weighing pipet, dissolve in 50 cm<sup>3</sup> water and titrate with 1 *N* NaOH using phenolphthalein as indicator. Determine the concentration of perchloric acid as follows:

$$C_1 = \frac{V \times N \times M}{W} \times \frac{100}{1000} \quad (1)$$

where:

- $C_1$  = % concentration of perchloric acid,
- $V$  = volume of NaOH, cm<sup>3</sup>,
- $N$  = normality of the NaOH solution,
- $M$  = molecular mass of perchloric acid, 100.5, and
- $W$  = sample mass of approximately 70 % perchloric acid, g.

11.2.2 To prepare 2 dm<sup>3</sup> of 0.1 *N* perchloric acid solution in acetic acid, the mass ( $W_1$ ) of perchloric acid to be taken is:

$$W_1 = \frac{2 \times 10.05 \times 100}{C_1} \quad (2)$$

where:

- $W_1$  = mass of perchloric acid, g, and
- $C_1$  = % concentration of perchloric acid from 11.2.1.

11.2.2.1 The amount of acetic anhydride ( $W_2$ ) required to eliminate the water content in  $W_1$  g of perchloric acid is calculated thus:

$$W_2 = \frac{(100 - C_1) \times 10.05 \times 2 \times 100 \times Ma}{C_1 \times 18 \times C_2} \quad (3)$$

where:

- $Ma$  = molecular mass of acetic anhydride = 102,
- $C_1$  = % concentration of perchloric acid, and
- $C_2$  = % concentration of acetic anhydride.

11.2.3 Add 8.5 cm<sup>3</sup> of 70 to 72 % perchloric acid to 100 to 200 cm<sup>3</sup> glacial acetic acid. Add 20 cm<sup>3</sup> of acetic anhydride and allow the solution to stand for at least 0.5 h. Dilute to 1 dm<sup>3</sup> with glacial acetic acid. To standardize, weigh to the nearest 0.1 mg, about 0.4 g of potassium hydrogen phthalate, dissolve completely in 50 cm<sup>3</sup> acetone and titrate potentiometrically with perchloric acid.

11.2.4 These solutions are stable over a long period of time.

## 12. Procedure

12.1 Assemble appropriate glassware from Section 1 according to Fig. 3 and place this assembly on the magnetic stirrer.

12.2 Prepare the specimen according to Section 10 and weigh 0.4 g to the nearest 0.1 mg into a 150-cm<sup>3</sup> beaker, dissolve with 50 cm<sup>3</sup> of acetone and titrate potentiometrically with 0.1 *N* perchloric acid using a 25 cm<sup>3</sup> buret as illustrated in Fig. 3.

12.3 Determine the blank value of the solvent following the same procedure.

NOTE 1—The water introduced with the perchloric acid is removed by adding a calculated amount of acetic anhydride to combine with the water.

The acid-catalyzed reaction of acetic anhydride with water is fairly rapid. When titrating a primary or secondary amine that might react with acetic anhydride, it is important to avoid any excess acetic anhydride in the titrant.

## 13. Calculation

13.1 Determine the percent total basic nitrogen content as follows:

$$\% \text{ nitrogen} = \frac{(V_1 - V_0) \times N \times 14}{1000} \times \frac{100}{S} \quad (4)$$

where:

- $V_1$  = volume of perchloric acid required for titration of the sample, cm<sup>3</sup>
- $V_0$  = volume of perchloric acid required for blank titration, cm<sup>3</sup>,
- $N$  = normality of the perchloric acid solution, and
- $S$  = specimen mass, g.

## 14. Report

14.1 Report the following information:

14.1.1 Proper identification of the sample, and

14.1.2 Results obtained from the two individual determinations and their average as percent nitrogen to the nearest 0.1 %.

## 15. Precision and Bias

15.1 This precision and bias section has been prepared in accordance with Practice D 4483. Refer to Practice D 4483 for terminology and other statistical calculation details.

15.2 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials used in the particular interlaboratory programs as described in this section. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

15.3 A Type 1 (interlaboratory) precision was evaluated in 1990. Both repeatability and reproducibility are short term. A period of a few days separates replicate test results. A test result is the mean value of two determinations, as specified by this test method, of the assay results.

15.4 Three sources of TMQ differing slightly in percent nitrogen were analyzed in six laboratories on two different days.

15.5 The results from one laboratory were eliminated from the analysis since they were substantially different in value than the other five taken as a whole.

15.6 The results of the precision calculation for repeatability and reproducibility are given in Table 1.

15.7 *Repeatability*—The repeatability,  $r$ , of this test method has been established as the appropriate value in Table 1. Two single test results, obtained under normal test method procedures, that differ by more than the tabulated  $r$  (for any given level) must be considered as derived from different or nonidentical sample populations.

15.8 *Reproducibility*—The reproducibility,  $R$ , of this test method has been established as the appropriate value in Table 1. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than

**TABLE 1 Precision of Percent Nitrogen Analysis for TMQ<sup>A</sup>**

Material	Average	Within Laboratories			Between Laboratories		
		$S_r$	$r$	( $r$ )	$S_R$	$R$	( $R$ )
No. 3	7.30	0.0187	0.052	0.71	0.112	0.314	4.30
No. 1	7.41	0.0330	0.092	1.24	0.122	0.342	4.62
No. 2	7.78	0.0195	0.055	0.71	0.101	0.284	3.65
Pooled	7.50	0.0237	0.066	0.87	0.112	0.313	4.19

<sup>A</sup> $S_r$  = repeatability standard deviation,  
 $r$  = repeatability = 2.83 times the square root of the repeatability standard deviation,  
( $r$ ) = repeatability (as percent of material average),  
 $S_R$  = reproducibility standard deviation,  
 $R$  = reproducibility = 2.83 times the square root of the reproducibility standard deviation, and  
( $R$ ) = reproducibility (as percent of material average).

the tabulated  $R$  (for any given level) must be considered to have come from different or nonidentical sample populations.

15.9 Repeatability and reproducibility expressed as a percent of the mean level, ( $r$ ) and ( $R$ ), have equivalent application statements as above for  $r$  and  $R$ . For the ( $r$ ) and ( $R$ ) statements, the difference in the two single test results is expressed as a percent of the arithmetic mean of the two test results.

15.10 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values have not been evaluated for this test method. Bias, therefore, cannot be determined.

15.11 The full details and test results of the interlaboratory test program used for this precision section are complete and in the process of being prepared in the proper format for submission as a research report to ASTM.

## 16. Keywords

16.1 2,2,4-trimethyl-1,2-dihydroquinoline; antioxidant; nitrogen; TMQ

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