Designation: D5902 – 05 (Reapproved 2015)

Standard Test Method for Rubber—Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Iodine Value[1]

This standard is issued under the fixed designation D5902; 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 This test method covers the Wijs procedure for the determination of unsaturation (iodine value) in hydrogenated nitrile rubbers.

1.2 This test method is applicable only to those hydrogenated nitrile rubbers derived from copolymers of acrylonitrile and butadiene.

1.3 Iodine values are reported in centigrams of iodine per gram of HNBR [cg(I_2)/g]. Higher iodine values indicate higher levels of unsaturation.

1.4 This test method is appropriate for calculating the percent residual unsaturation of hydrogenated nitrile rubber if the iodine value of the base polymer before hydrogenation has been determined.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1959 Test Method for Iodine Value of Drying Oils and Fatty Acids (Withdrawn 2006)[3]

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

3. Summary of Test Method

3.1 A sample of the raw, unvulcanized rubber is dissolved in chloroform.

3.2 The dissolved sample is reacted with Wijs solution.

3.3 When the reaction is completed, potassium iodide solution is added.

3.4 The resultant solution is then back-titrated with sodium thiosulfate solution and the iodine value is calculated.

4. Significance and Use

4.1 Hydrogenated nitrile rubbers are available at different levels of unsaturation and different acrylonitrile content. Highly saturated grades offer optimum resistance to aging, such as exposure to heat, ozone and chemicals, and can be cured effectively only with peroxides or high energy radiation.

4.2 Partially unsaturated grades can be cured by sulfur systems in addition to peroxides and high energy radiation.

4.3 This test method provides a technique to determine the unsaturation level of hydrogenated nitrile rubbers in the raw, unvulcanized state. It can be used for research and development, quality control, and referee purposes.

5. Apparatus

5.1 *Erlenmeyer Flasks,* with ground glass stoppers (300 mL).

5.2 *Flask Shaker.*

5.3 *Pipets.*

5.4 *Constant Temperature Bath.*

6. Reagents

6.1 Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[4]

---

[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.

Current edition approved June 1, 2015. Published September 2015. Originally approved in 1996. Last previous edition approved in 2010 as D5902 – 05 (2010). DOI: 10.1520/D5902-05R15.

[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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I of Specification D1193.

6.3 *Chloroform.*

6.4 *Wiijs Solution* (prepared in accordance with Test Method D1959).

6.5 *Potassium Iodide Solution* (prepared in accordance with Test Method D1959).

6.6 *0.1 N Sodium Thiosulfate Solution* (prepared in accordance with Test Method D1959).

6.7 *Starch Indicator Solution* (prepared in accordance with Test Method D1959).

7. Procedure

7.1 If the approximate level of unsaturation is known, the following sample sizes are recommended:

Approximate unsaturation level	Sample weight in mg
2 %	930–970
5 %	680–720
10 %	430–470

If the approximate level of unsaturation is unknown, a sample weight of 680–720 mg is recommended.

7.2 Weigh the finely divided sample to the nearest 0.1 mg. Add the sample to a 300-mL glass stoppered Erlenmeyer flask containing 50 mL of chloroform. Using the flask shaker, shake until the samples are completely dissolved in the chloroform (approximately 1 h).

7.3 Immediately place the flask containing the dissolved sample into a constant temperature bath maintained at 23 ± 1 °C for 30 min.

7.4 Pipet 25 cm^3 of Wiijs solution into the flask containing the specimen while shaking the flask. Replace the glass stopper and return the flask to the constant temperature bath maintained at 23 ± 1 °C for 2 h.

7.5 Remove the flask from the constant temperature bath and quickly add 10 cm^3 of potassium iodide solution while shaking the flask vigorously.

7.6 Wash off any iodine from the stopper into the flask with distilled water. Wait 5 min before beginning the titration.

7.7 Titrate with the 0.1 N sodium thiosulfate solution, adding it gradually while shaking the flask vigorously. Continue the titration until the yellow coloring is just about to disappear. Add 1 to 2 cm^3 of starch indicator solution and continue the titration until the violet color just disappears.

7.8 Allow the flask to stand for 30 min after the titration, then shake the flask, and if color returns, continue the titration.

7.9 Run a blank determination following the titration steps as described in 7.2 through 7.8 concurrently with the sample under test.

8. Calculation

8.1 Calculate the iodine value as follows:

$$\text{Iodine value} = \frac{0.1 \times f \times (B - A) \times 126.9 \times 100}{1000 \times M} \quad (1)$$

$$= \frac{0.1 \times f \times (B - A) \times 12.69}{M}$$

where:

f = normality factor of the 0.1 N sodium thiosulfate solution,
A = cm^3 of sodium thiosulfate solution required for titration of the sample,
B = cm^3 of sodium thiosulfate solution required for titration of the blank,
M = mass of the sample in grams,
126.9 = atomic mass of iodine,
1000 = conversion factor from the mg equivalent of sodium thiosulfate to the g equivalent, and
100 = conversion factor from g to cg.

8.2 Calculate the percent of residual unsaturation if the iodine value of the base polymer prior to hydrogenation is known, as follows:

$$\%\ \text{Residual unsaturation} \quad (2)$$

$$= \frac{\text{Iodine value measured}}{\text{Iodine value of the base polymer}} \times 100$$

9. Report

9.1 The report shall include the following information:
9.1.1 Proper sample identification,
9.1.2 Number of data points used to obtain the result,
9.1.3 The iodine value obtained, and
9.1.4 The percent of residual unsaturation to the nearest 0.1 %, if applicable.

10. Precision and Bias[5]

10.1 This precision and bias section has been prepared in accordance with Practice D4483. Refer to Practice D4483 for terminology and other statistical calculation details.

10.2 *Precision*—The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (rubbers) used in the particular interlaboratory program as described in 10.3 and 10.4. The precision parameters should not be used for acceptance/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.

10.3 A Type I/Class II interlaboratory precision was evaluated. Both repeatability and reproducibility are short term. A period of one week separates replicate test results. Each determination (measurement) is a test result.

10.4 Three different materials (grades of hydrogenated nitrile rubber) with different degrees of unsaturation were used in

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D11-1078.

TABLE 1 Type 1 Precision

Residual Unsaturation of HNBR by Iodine Value

HNBR	Nominal Content	ACN, %	Mean (cgI_2/g)	Within Laboratory[A]			Between Laboratory[A]		
				S_r	r	(r)	S_R	R	(R)
#1	33		6.39	0.282	0.800	12.50	0.324	0.916	14.30
#2	36		12.57	0.181	0.512	4.07	0.344	0.973	7.74
#3	36		28.75	0.262	0.741	2.58	0.496	1.400	4.87

[A] Symbols are defined as follows:
S_r = within-laboratory standard deviation,
r = repeatability, measurement units,
(r) = repeatability, %
S_R = between-laboratory standard deviation,
R = reproducibility, measurement units, and
(R) = reproducibility,% .

the interlaboratory program. These materials were tested in four laboratories on two different days one week apart. Duplicate tests were run on each day. The analysis for precision followed the general procedure as set forth in Annex of Practice D4483. Each cell of Table A5.1 in Practice D4483 contained four values (two test days, two results each day). The estimates for repeatability parameters contain two undifferentiated sources of variation, replicates within days and between days. The final precision parameters are given in Table 1.

10.5 The precision of this test method may be expressed in the format of the following statements that use what is called an "appropriate value" of *r, R*, (*r*) or (*R*), that is, that value obtained from Table 1 to be used in decisions about test results of this test method.

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

10.7 *Reproducibility, R,* of this test method has been established as the appropriate value for any parameter as tabulated in Table 1. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than this tabulated *R* must be considered as derived from different or nonidentical sample populations.

10.8 Repeatability and reproducibility expressed as a percentage of the mean level (*r*) and (*R*) have equivalent application statements as 10.6 and 10.7 for *r* and *R*. For the (*r*) and (*R*) statements the difference in the two single test results is expressed as a percentage of the arithmetic mean of the two test results.

10.9 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias, therefore, cannot be determined.

11. Keywords

11.1 HNBR; iodine value; residual unsaturation