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

This standard is issued under the fixed designation D5670; 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 percentage of residual unsaturation (double bonds in unhydrogenated butadiene) in hydrogenated nitrile rubber and is based on infrared examination of rubber films cast from solution.

1.2 This test method is applicable to all grades of hydrogenated nitrile rubber in the raw state.

1.3 This test method assumes that specimens and infrared spectra are prepared and analyzed by experienced personnel and that the equipment is operated according to the manufacturer's direction for optimum performance. No details for operation of infrared spectrophotometers are included in this test method.

1.4 Since it is customary in infrared spectrophotometry to use wavenumbers (cm^{-1}) rather than Hertz (Hz), the unit for frequency in the SI system, the former is employed throughout this test method.

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]

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

E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

3. Summary of Test Method

3.1 A specimen of the raw rubber is purified by precipitation with methanol from a solution in methyl ethyl ketone or by extraction of the solid rubber with methanol in a Soxhlet apparatus.

3.2 The purified rubber specimen is again dissolved in methyl ethyl ketone and a film is cast on a potassium bromide (KBr) disc.

3.3 The infrared spectrum of the film is obtained with a Fourier Transform Infrared Spectrophotometer (FT-IR) or a dispersive infrared spectrophotometer.

3.4 The corrected absorbance of the specific absorption bands for acrylonitrile (ACN), butadiene (BD), and hydrogenated butadiene (HBD) are determined using the baseline method and the percentage of residual unsaturation (double bonds in unhydrogenated butadiene) is calculated with the aid of absorbance factors from the referenced literature.[3]

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 effectively cured 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 an infrared technique to determine the unsaturation level of hydrogenated nitrile rubbers in the raw state. It can be used for research and development, quality control, and referee purposes.

---

[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 Aug. 1, 2014. Published November 2014. Originally approved in 1995. Last previous edition approved in 2009 as D5670 – 95 (2009). DOI: 10.1520/D5670-95R14.

[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] Brück, D., Kautschuk, Gummi, *Kunststoffe*, Vol 42, 1989, pp. 107–110 and 194–197.

5. Apparatus

5.1 *Preparation of Rubber Solution:*

5.1.1 *Erlenmeyer Flask with Ground Glass Stopper,* (50 cm^3).

5.1.2 *Flask Shaker.*

5.2 *Precipitation of Rubber from Solution:*

5.2.1 *Beaker,* (250 cm^3).

5.2.2 *Magnetic Stirrer.*

5.2.3 *Dropping Funnel,* (150 cm^3).

5.3 *Extraction of Rubber:*

5.3.1 *Soxhlet Extraction Apparatus with Flask,* (150 cm^3).

5.3.2 *Extraction Thimbles,* (27 by 100 mm).

5.4 *Kofler Heating Bench or Other Heating Device,* with temperature control.

5.5 *Spectrophotometer,* required resolution capability of 2 cm^{-1}. The instrument must be in good operating condition as defined by the manufacturer and Practices E932 and E1421. The instrument shall be capable of scale expansion along the absorbance or transmittance axis. The spectral region of 2500–600 cm^{-1} is used in this test method.

6. Reagents

6.1 Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society.[4] Other grades may be used, provided they are of sufficiently high purity as not to lessen the accuracy of the determination.

6.2 *Methyl Ethyl Ketone.*

6.3 *Methanol.*

6.4 *Dry Compressed Nitrogen,* (in cylinders or provided as a laboratory service).

6.5 *Potassium Bromide (KBr) Discs.*

7. Procedure

7.1 *Specimen Preparation:*

7.1.1 *Specimen Purification by Precipitation (see Note 1):*

7.1.1.1 Weigh 1.0 g of the finely divided rubber specimen and dissolve in 20 cm^3 methyl ethyl ketone using a 50-cm^3 Erlenmeyer flask with ground glass stopper on a flask shaker.

7.1.1.2 Transfer the solution into a 250-cm^3 beaker and precipitate the rubber by slowly dropping 150 cm^3 methanol from a dropping funnel into the solution under agitation with a magnetic stirrer.

7.1.1.3 Decant the solvent, wash the precipitated rubber with 50 cm^3 methanol and redissolve in 20 cm^3 methyl ethyl ketone.

7.1.2 *Specimen Purification by Extraction (see Note 1):*

7.1.2.1 Extraction is an alternative to the precipitation method.

7.1.2.2 Weigh 1.0 g of the finely divided rubber specimen into an extraction thimble and extract for 6 h in a Soxhlet apparatus (150-cm^3 flask) with 120 cm^3 methanol.

7.1.2.3 Remove the extracted rubber sample from the thimble and dissolve in 20 cm^3 methyl ethyl ketone as described in 7.1.1.1.

7.1.3 *Preparation of Cast Rubber Films:*

7.1.3.1 Cast a smooth rubber film from the solution in methyl ethyl ketone onto a potassium bromide (KBr) disc.

7.1.3.2 Evaporate the solvent on a Kofler bench or similar heating device at a maximum temperature of 100°C under a stream of nitrogen.

7.1.3.3 The thickness of the rubber film must be chosen so that the strongest band to be evaluated from the infrared spectrum has an absorbance of less than 0.8.

7.2 *Infrared Spectrum:*

7.2.1 Obtain a 50-scan spectrum with an FT-IR instrument with 2 cm^{-1} resolution or with a dispersive infrared spectrophotometer and appropriate scan parameters.

7.2.2 In case the repeatability and standard deviation of the absorbance must be determined, test up to six different films of the same specimen.

7.2.3 If only a transmittance mode operation is possible with the instrument being used, the spectrum shall be scanned in that mode.

7.3 *Calculation of Results:*

7.3.1 Calculate the corrected absorbance $A(i)$ by subtracting the baseline absorbance from the peak absorbance at the point below the peak (see Fig. X1.1).

7.3.2 When the transmittance mode is used, calculate the corrected absorbance $A(i)$ by taking the log10 of the quotient of percent transmittance of the baseline at the point above the peak and the percent transmittance of the peak (see Fig. X1.2).

7.3.3 Draw baselines to approximately the following wavenumbers (all values are in cm^{-1}):

ACN: 2280–2200 for the peak 2236 (see Note 2)
BD: 1010–910 for the peak 970
HBD: 840–670 for the peak 723

7.3.4 If repeatability and standard deviation $s(i)$ must be determined, use the normalized absorbance ratios

$$\bar{A}(970) = A(970)/A(2236), \text{ and} \tag{1}$$

$$\bar{A}(723) = A(723)/A(2236) \tag{2}$$

from spectra of different films produced from each specimen (see Note 2).

7.3.5 Calculate the molar concentrations $c(i)$ using absorbance factors from the referenced literature[3] and the measured normalized absorbance ratios $\bar{A}(970)$ and $\bar{A}(723)$ (see Eq 1 and Eq 2).

7.3.6 The absorbance factors from the referenced literature[3] are given below:

$$k(2236) = 1;\ k(970) = 2.3 \pm 0.03;\ k(723) = 0.255 \pm 0.002 \tag{3}$$

7.3.7 Calculate the molar concentrations according to the following equations:

$$c(ACN) = \frac{1}{\sum_i \bar{A}(i)} \tag{4}$$

---

[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.

$$c(BD) = \frac{A(970)}{k(970)} \times \frac{1}{\sum A(i)} \tag{5}$$

$$c(HBD) = \frac{A(723)}{k(723)} \times \frac{1}{\sum A(i)} \tag{6}$$

where

$$\sum A(i) = 1 + \frac{A(970)}{k(970)} + \frac{A(723)}{k(723)} \tag{7}$$

7.3.8 Calculate the percent unsaturation (double bonds in unhydrogenated butadiene) according to:

$$\%\ \text{Unsaturation} = \frac{c(BD)}{c(BD) + c(HBD)} \times 100 \tag{8}$$

7.3.9 An example of the infrared spectrum interpretation and calculation is given in Table X1.1 and Figs. X1.1 and X1.2.

8. Limitation

8.1 This test method is valid when the absorbance factors for the absorption bands at wavenumbers 2236 and 2214 cm^{-1} in the spectra of some grades of hydrogenated nitrile rubber are equal. When they are not equal, *c*(ACN) calculated only from *A*(2236) will be too small and *c*(BD), *c*(HBD), and percent unsaturation will be too large.

9. Report

9.1 Report the following information:

9.1.1 Proper specimen identification,

9.1.2 Number of data points used to obtain the result,

9.1.3 The residual unsaturation of the HNBR specimen(s) reported to the nearest 0.1 percentage point, and

9.1.4 Identification of any deviation from the specified standard method.

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 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 below. 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 these test methods.

10.3 A Type 1 interlaboratory test program was conducted to evaluate precision. Both repeatability and reproducibility are short term; a period of a few days separates test results. Each determination (measurement) is a test result.

10.4 Three different materials, (grades of HNBR), with different degrees of unsaturation were used for the interlaboratory program. These were tested in seven laboratories on two different days one week apart. On each test day duplicate test values were obtained. The analysis for precision followed the general procedure as set forth in Annex A5 of Practice D4483. Each cell of the Practice D4483 Table 1 basic data format contained four values (two test days, two test results each day). The estimates for the repeatability parameters therefore contain two undifferentiated sources of variation: replicates within days and between days. The final precision parameters are given in Table 1 of this test method.

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, *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 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*—The 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.

NOTE 1—Appearance of a band at wavenumber 696 cm^{-1} in the infrared spectrum indicates inadequate purification.

NOTE 2—Some grades of hydrogenated nitrile rubber exhibit an additional nitrile band at wavenumber 2214 cm^{-1}. In this case, calculate *A*(ACN) = *A*(2236) + *A*(2214) and use *A*(ACN) for further calculations.

NOTE 3—S_r = within-laboratory standard deviation; *r* = repeatability (in measurement units); (*r*) = repeatability (as percent of material average); S_R = between-laboratory standard deviation; *R* = reproducibility (in measurement units); (*R*) = reproducibility (as percent of material average).

TABLE 1 Type 1 Precision: Residual Unsaturation (RU) of HNBR (see Note 3)

HNBR	Nominal% ACN	% RU Mean	Within Laboratory			Between Laboratory		
			S_r	*r*	(*r*)	S_R	*R*	(*R*)
#1	33	0.65	0.119	0.337	51.8	0.172	0.486	74.8
#2	36	2.3	0.111	0.314	13.7	0.149	0.421	18.3
#3	36	5.1	0.179	0.506	9.9	0.348	0.984	19.3

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1072.

11. Keywords

11.1 HNBR; hydrogenated nitrile rubber; infrared spectrometry (IR); unsaturation

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE

X1.1 *HNBR, Medium ACN, Partially Unsaturated:*

X1.2 *Calculation of Unsaturation:*

$$\sum A(i) = 1 + \frac{0.119}{2.3} + \frac{0.431}{0.255} = 2.742 \quad (X1.1)$$

$$c(ACN) = \frac{1}{2.742} = 0.365 \quad (X1.2)$$

$$c(BD) = \frac{0.119}{2.3 \times 2.742} = 0.019 \quad (X1.3)$$

$$c(HBD) = \frac{0.431}{0.255 \times 2.742} = 0.616 \quad (X1.4)$$

$$\text{Unsaturation} = \frac{0.019}{0.019 + 0.616} \times 100 = 3\ \% \quad (X1.5)$$

TABLE X1.1 HNBR, Medium ACN, Partially Unsaturated

	Corrected Absorbance			Normalized Absorbance Ratio[A]	
	$A(2236)$	$A(970)$	$A(723)$	$\bar{A}(970)$	$\bar{A}(723)$
Baseline	2280–2200	1005–935	840–670		
	0.278	0.033	0.117	0.119	0.421
	0.127	0.015	0.056	0.118	0.441
	0.134	0.016	0.059	0.119	0.440
	0.193	0.023	0.082	0.119	0.425
	0.102	0.012	0.045	0.118	0.441
	0.310	0.037	0.130	0.119	0.419
Average				0.119	0.431
Standard deviation $s(i)$				±0.001	±0.01

[A] See Eq 1 and Eq 2.

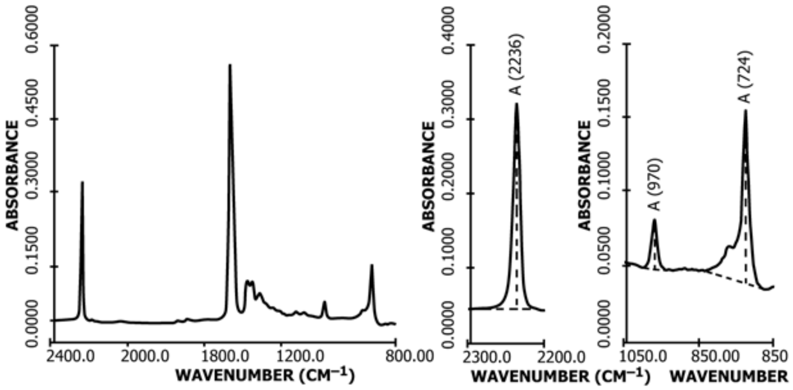

FIG. X1.1 Absorbance Spectrum HNBR, Medium ACN, Partially Unsaturated

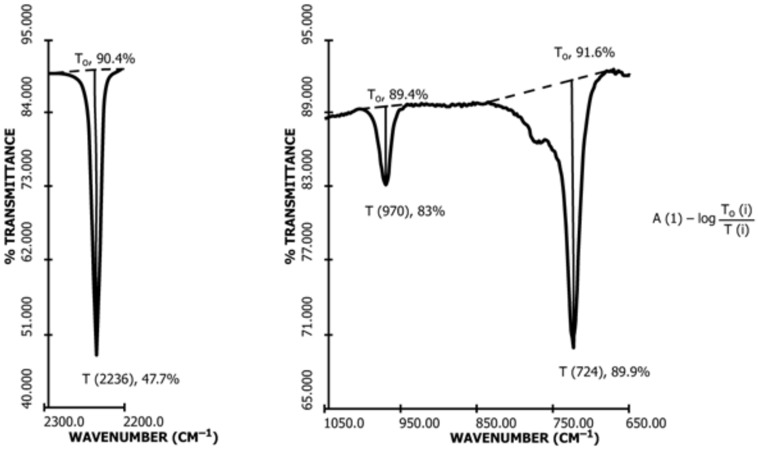

FIG. X1.2 Transmittance Spectrum HNBR, Medium ACN, Partially Unsaturated

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/