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Second edition
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Rubber — Determination of residual unsaturation of hydrogenated nitrile butadiene rubber (HNBR) by infrared spectroscopy

Caoutchouc — Détermination de la non-saturation résiduelle du caoutchouc nitrile butadiène hydrogéné (HNBR) par spectroscopie à infrarouge

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This second edition cancels and replaces the first edition (ISO 14558:2000), of which it constitutes a minor revision where the normative references were updated and the precision data were moved to an informative Annex B.

Rubber — Determination of residual unsaturation of hydrogenated nitrile butadiene rubber (HNBR) by infrared spectroscopy

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies a method for determining the residual unsaturation in hydrogenated nitrile rubber (HNBR) by measuring the infrared (IR) absorbance of HNBR films cast from solution.

This International Standard assumes that samples and IR spectra are prepared and analysed by experienced personnel and that equipment is operated in accordance with the manufacturer's instructions. Details for operating an IR spectrometer are not included in this method.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

3 Principle

Raw, unvulcanized HNBR is purified by precipitation with methanol from a solution in methyl ethyl ketone (MEK) or by extraction of the solid HNBR with methanol in a Soxhlet apparatus.

The purified sample is dissolved in MEK and a film is cast on a potassium bromide (KBr) disc.

The IR spectrum of the film is obtained with a Fourier-transform (FT) or dispersive IR spectrometer.

The "corrected absorbance" of the specific absorbance bands for acrylonitrile (AN), 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 literature (see 8.5).

4 Reagents

Reagent grade chemicals should preferably be used in all determinations. Other grades may be used provided that they are of sufficiently high purity not to lessen the accuracy of the determination.

4.1 Methyl ethyl ketone (MEK).

4.2 Methanol.

4.3 Dry, compressed nitrogen.

4.4 Potassium bromide discs.

5 Sampling

Sample the raw rubber in accordance with ISO 1795.

6 Apparatus

Ordinary laboratory equipment and the following.

6.1 Conical flask, 50 cm^3, with ground-glass stopper.

6.2 Flask shaker.

6.3 Beaker, 250 cm^3.

6.4 Magnetic stirrer.

6.5 Soxhlet extraction apparatus, with 150 cm^3 flask.

6.6 Extraction thimbles, 25 mm × 100 mm.

6.7 Koffler heating bench, or other heating device, with temperature control to ±2 °C.

6.8 Fourier-transform IR (FTIR) spectrometer, with 2 cm^{-1} resolution or a dispersive IR spectrometer capable of equivalent spectral resolution. The instrument shall be capable of scale expansion along the absorbance or transmittance axis over the special region of 2 500 cm^{-1} to 600 cm^{-1}.

7 Procedure

7.1 Sample preparation

7.1.1 Purification by precipitation

7.1.1.1 Transfer 1 g of the finely divided HNBR rubber sample into a 50 cm^3 conical flask. Add 20 cm^3 of MEK to the flask. Tightly stopper the flask and place it on a flask shaker and shake until the sample has completely dissolved.

7.1.1.2 Precipitate the rubber by slowly pouring the MEK solution into a 250 cm^3 beaker containing 150 cm^3 of methanol, while rapidly stirring the methanol with a magnetic stirrer.

7.1.1.3 Decant the solvent and wash the precipitated rubber with 50 cm^3 of methanol. Decant the methanol washings and redissolve the precipitated rubber in 20 cm^3 of MEK.

7.1.2 Purification by extraction

Transfer 1 g of finely divided rubber into an extraction thimble and extract for 6 h in a Soxhlet apparatus with 100 cm^3 of methanol.

Remove the extracted sample from the thimble and dissolve in 20 cm^3 of MEK.

7.1.3 Preparation of cast HNBR film

Cast a smooth film from the MEK solution (see 7.1.1.3 or 7.1.2) on a KBr disc.

On a Koffler, or similar, heating device, in a well-ventilated hood under a stream of nitrogen, carefully evaporate the MEK solvent from the cast film, taking care not to heat the film over 100 °C.

The thickness of the film shall be chosen so that the absorbance A of the band at 2 236 cm^{-1} is <0,8 A. With dispersion spectrometers and an unsaturation of <1 %, films shall exhibit an A (2 236) of between 0,7 and 0,8.

7.2 Obtaining the IR spectrum

Obtain the spectrum with an FTIR spectrometer with 2 cm^{-1} resolution, collecting 50 scans, or with a dispersive IR spectrometer and appropriate scan parameters.

NOTE Appearance of a band at approximately 1 730 cm^{-1} indicates residual MEK and a band at 696 cm^{-1} indicates inadequate purification.

8 Calculations

8.1 Draw baselines between approximately the following:

— for AN: 2 280 cm^{-1} to 2 200 cm^{-1} for the peak at 2 236 cm^{-1};

— for BD: 1 010 cm^{-1} to 910 cm^{-1} for the peak at 970 cm^{-1};

— for HBD: 840 cm^{-1} to 670 cm^{-1} for the peak at 723 cm^{-1}.

8.2 Calculate the corrected absorbance $A(i)$ of each band i by subtracting the baseline absorbance at the point below the peak from the peak absorbance.

Some grades of HNBR exhibit an additional nitrile band at 2 214 cm^{-1}. Should this band appear, calculate the absorbance of the AN band from $A(AN) = A(2\ 236) + A(2\,214)$ and use this value of $A(AN)$ in further calculations.

8.3 Should transmittance be used, calculate $A(i)$ by taking the $\log_{10}$ of the quotient of "percent transmittance of the baseline at the point below the peak divided by the percent transmittance of the peak".

8.4 When calculating reproducibility and standard deviations, use the following "normalized absorbance ratios":

$$A(970) = \frac{A(970)}{A(2\,236)} \tag{1}$$

$$A(723) = \frac{A(723)}{A(2\,236)} \tag{2}$$

8.5 Calculate the molar concentrations, using absorbance factors from the literature (see NOTE 1) together with the calculated normalized absorbance ratios [see Formulae (1) and (2)], as follows:

$$c(AN) = \frac{1}{\sum A(i)} \tag{3}$$

$$c\left(BD\right) = \frac{A\ \left(970\right)}{k\ \left(970\right)} \times \frac{1}{\sum A\left(i\right)} \tag{4}$$

$$c\left(HBD\right) = \frac{A\ \left(723\right)}{k\ \left(723\right)} \times \frac{1}{\sum A\left(i\right)} \tag{5}$$

where

$$\sum A\left(i\right) = \ 1 + \frac{A\ \left(970\right)}{k\ \left(970\right)} + \frac{A\ \left(723\right)}{k\ \left(723\right)} \tag{6}$$

NOTE 1 The absorbance factors can be found in Reference [1]. These factors are the following:

— k (2 236) = 1;

— k (970) = 2,3 ± 0,03;

— k (723) = 0,255 ± 0,002.

NOTE 2 This determination is valid only when the absorbance factors for the absorption bands at 2 236 cm^{-1} and 2 214 cm^{-1} are equal. When they are not equal, $c\ \left(AN\right)$ calculated only from $A\ \left(2\,236\right)$ is too small and $c\ \left(BD\right)$, $c\ \left(HBD\right)$ and hence, the calculated residual unsaturation is too large.

8.6 Calculate the percent unsaturation, U (the percentage of double bonds in the hydrogenated butadiene), as follows:

$$U\ = \frac{c\left(BD\right)}{c\left(BD\right)\ + c\left(HBD\right)} \times 100 \tag{7}$$

8.7 An example of infrared spectrum interpretation and calculation is given in Annex A.

9 Precision

See Annex B.

10 Test report

The test report shall contain the following information:

a) a reference to this International Standard, i.e. ISO 14558;

b) all details necessary for identification of each sample;

c) the number of data points used to obtain the result;

d) the residual unsaturation of each HNBR sample, reported to the nearest 0,1 %;

e) any deviation from the method specified;

f) the date of the analysis.

Annex A
(informative)

Example of infrared spectrum interpretation and calculation

A.1 Example of infrared spectrum interpretation

An example of infrared spectrum interpretation is given in Table A.1.

Table A.1 — HNBR, medium ACN, partially unsaturated

	Corrected absorbance			Normalized absorbance ratio[a]	
	A **(AN)** (baseline 2 280 to 2 200)	***A*** **(BD)** (baseline 1 005 to 935)	***A*** **(HBD)** (baseline 840 to 670)	***A*** **(970)**	***A*** **(723)**
	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				**+0,001**	**+0,01**
[a] From Formulae (1) and (2).					

A.2 Sample calculation of unsaturation

$$\sum A(i) = 1 + \frac{0,119}{2,3} + \frac{0,431}{0,255} = 2,742 \quad \text{(A.1)}$$

$$c(AN) = \frac{1}{2,742} = 0,365 \quad \text{(A.2)}$$

$$c(BD) = \frac{0,119}{2,3 \times 2,762} = 0,019 \quad \text{(A.3)}$$

$$c(HBD) = \frac{0,431}{0,255 \times 2,742} = 0,616 \quad \text{(A.4)}$$

$$U = \frac{0,019}{0,019 + 0,616} \times 100 = 3\ \% \quad \text{(A.5)}$$