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

National foreword

This British Standard is the UK implementation of ISO 14558:2016. It supersedes BS ISO 14558:2000 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PRI/50, Raw materials (including latex) for use in the rubber industry.

A list of organizations represented on this committee can be obtained on request to its secretary.

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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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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 $A\left(i\right)$ 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 $A\left(AN\right) = A\left(2\ 236\right) + A\left(2\,214\right)$ and use this value of $A\left(AN\right)$ 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”:

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

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

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:

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

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

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

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:

— $k\ (2\ 236) = 1$;

— $k\ (970) = 2{,}3 \pm 0{,}03$;

— $k\ (723) = 0{,}255 \pm 0{,}002$.

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

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

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

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

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

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

Annex B
(informative)

Precision

The precision parameters shall not be used for acceptance/rejection of materials without documentation that they are applicable to those materials and the testing protocols that include these test methods.

Interlaboratory precision was evaluated (see Table B.1). Both repeatability and reproducibility were short-term. A period of one week separated replicate test results.

Three different materials (grades of hydrogenated nitrile rubber) with different degrees of unsaturation were used in the interlaboratory programme. These were tested in seven laboratories on two different days one week apart. Duplicate tests were run on each day.

When the procedure is correctly performed, accurate and reproducible results are obtained.

Table B.1 — Residual unsaturation *U* of HNBR

HNBR	***U*** (mean)	**Within-laboratory**			**Between laboratories**		
		s_r	*r*	*(r)*	s_R	*R*	*(R)*
Material 1	0,65	0,119	0,337	51,8	0,172	0,486	74,8
Material 2	2,3	0,111	0,316	13,7	0,149	0,421	18,3
Material 3	5,1	0,179	0,506	3,5	0,348	0,984	19,3

s_r is the within-laboratory standard deviation;
r is the repeatability limit (in measurement units);
(r) is the repeatability (as percent of material average);
s_R is the between-laboratory standard deviation;
R is the reproducibility limit (in measurement units);
(R) is the reproducibility (as percent of material average).

Bibliography

[1] Bruck, *Kautschuk, Gummi, Kunststoffe*, 42 (1989), pp. 107-110, pp. 194-197

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