INTERNATIONAL STANDARD

ISO 12965

First edition
2000-09-15

Butadiene rubber — Determination of microstructure by infra-red spectrometry

Caoutchouc butadiène — Détermination de la microstructure par spectrométrie à infrarouge

Reference number
ISO 12965:2000(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 12965 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses.*

Butadiene rubber — Determination of microstructure by infra-red spectrometry

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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 the determination of the microstructure of butadiene rubber (BR) by infra-red spectrometry using a cast film.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 1407:1992, *Rubber — Determination of solvent extract*.

ISO 1795:2000, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*.

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards.*

3 Principle

3.1 A small quantity of extracted rubber is dissolved in methylene chloride and cast on a salt plate.

3.2 A spectrum is obtained over the range 2 000 cm^{-1} to 600 cm^{-1}. From the absorbances at fixed wavelengths, the *cis*, *trans* and vinyl contents are calculated.

4 Reagent

4.1 Methylene chloride.

5 Apparatus

5.1 Double-beam infrared spectrophotometer or **Fourier-transform infra-red (FTIR) spectrophotometer,** with 2 cm^{-1} resolution. The instrument shall be capable of scale expansion along the absorbance or transmittance axis over the spectral region of 2 000 cm^{-1} to 600 cm^{-1}.

5.2 Salt plate.

5.3 Balance, weighing to 0,1 mg.

5.4 Vacuum oven, operating at 50 °C to 60 °C.

6 Sampling

Sample the raw rubber in accordance with ISO 1795.

7 Procedure

7.1 Mill the test sample to as thin a sheet as possible. Extract the rubber in accordance with ISO 1407 using ethanol/toluene azeotrope (ETA). Dry the extracted rubber under vacuum in the oven at 50 °C to 60 °C.

7.2 Take approximately 100 mg of extracted sample and dissolve it in around 20 ml of methylene chloride. If gel is present, filter the solution.

7.3 Ensure that the salt plate is levelled horizontally before the film is cast. Place 3 or 4 drops of the solution on the plate and spread evenly over the beam area. Allow the solvent to evaporate, preferably at room temperature.

7.4 Check that the transmittance over the measurement range lies between 50 % and 30 %. If grossly outside these limits, clean the salt plate and repeat step 7.3 with more or less solution.

7.5 When 7.4 is satisfied, scan over the range 2 000 cm^{-1} to 600 cm^{-1}.

7.6 Draw a baseline from 2 000 cm^{-1} to 600 cm^{-1}, taking care that no peaks are cut (see Figures 1, 2 and 3 for medium-, low- and high-*cis* polybutadiene).

7.7 Measure the absorbances at 965 cm^{-1} (A_{965}), 909 cm^{-1} (A_{909}) and 728 cm^{-1} (A_{728}). These are an indication of the *trans* (A_{965}), vinyl (A_{909}) and *cis* (A_{728}) contents.

7.8 Normalize the above absorbances using the following equations:

$$\%A_{965} = \frac{A_{965}}{A_{965} + A_{909} + A_{728}} \times 100$$

$$\%A_{909} = \frac{A_{909}}{A_{965} + A_{909} + A_{728}} \times 100$$

$$\%A_{728} = \frac{A_{728}}{A_{965} + A_{909} + A_{728}} \times 100$$

7.9 Calculate the contents of the different isomers, c_{cis}, c_{trans} and c_{vinyl}, in g/dm^3, using the following equations:

$$c_{cis} = 1{,}789\,6 \times \%A_{728} - 0{,}025\,3 \times \%A_{965} - 0{,}008\,5 \times \%A_{909}$$

$$c_{trans} = 0{,}3971 \times \%A_{965} - 0{,}050\,2 \times \%A_{728} - 0{,}014\,2 \times \%A_{909}$$

$$c_{vinyl} = 0{,}295\,4 \times \%A_{909} - 0{,}007\,5 \times \%A_{728} - 0{,}006\,5 \times \%A_{965}$$

7.10 Determine the microstructure of the rubber, in percent, using the following equations:

$$\%_{cis} = \frac{c_{cis} \times 100}{c_{cis} + c_{trans} + c_{vinyl}}$$

$$\%_{trans} = \frac{c_{trans} \times 100}{c_{cis} + c_{trans} + c_{vinyl}}$$

$$\%_{vinyl} = \frac{c_{vinyl} \times 100}{c_{cis} + c_{trans} + c_{vinyl}}$$

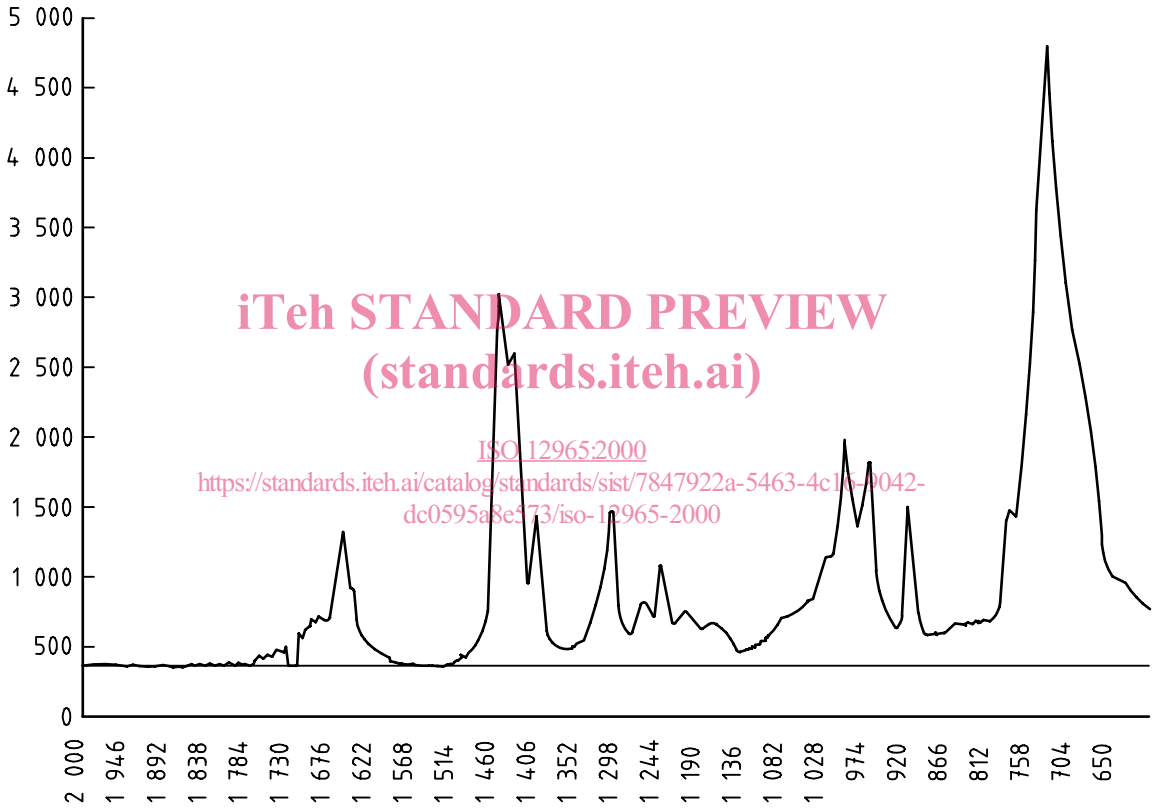

Figure 1 — Sample A (medium-*cis* polybutadiene)

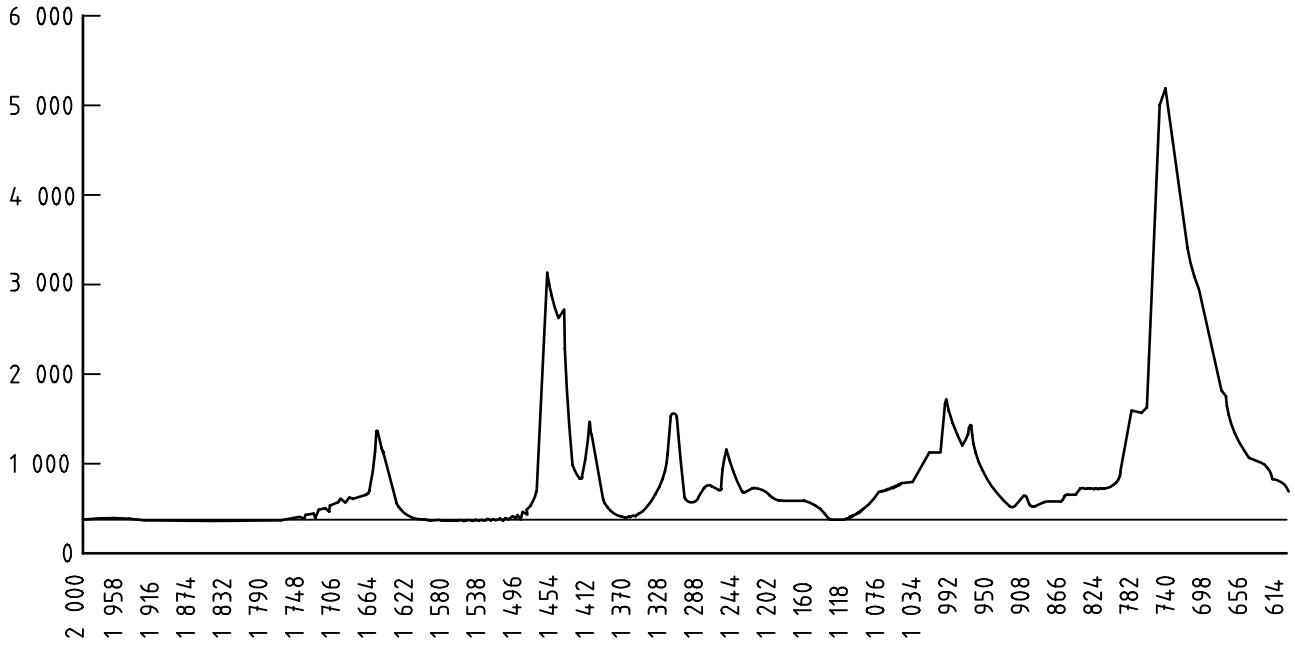

Figure 2 — Sample B (high-*cis* polybutadiene)

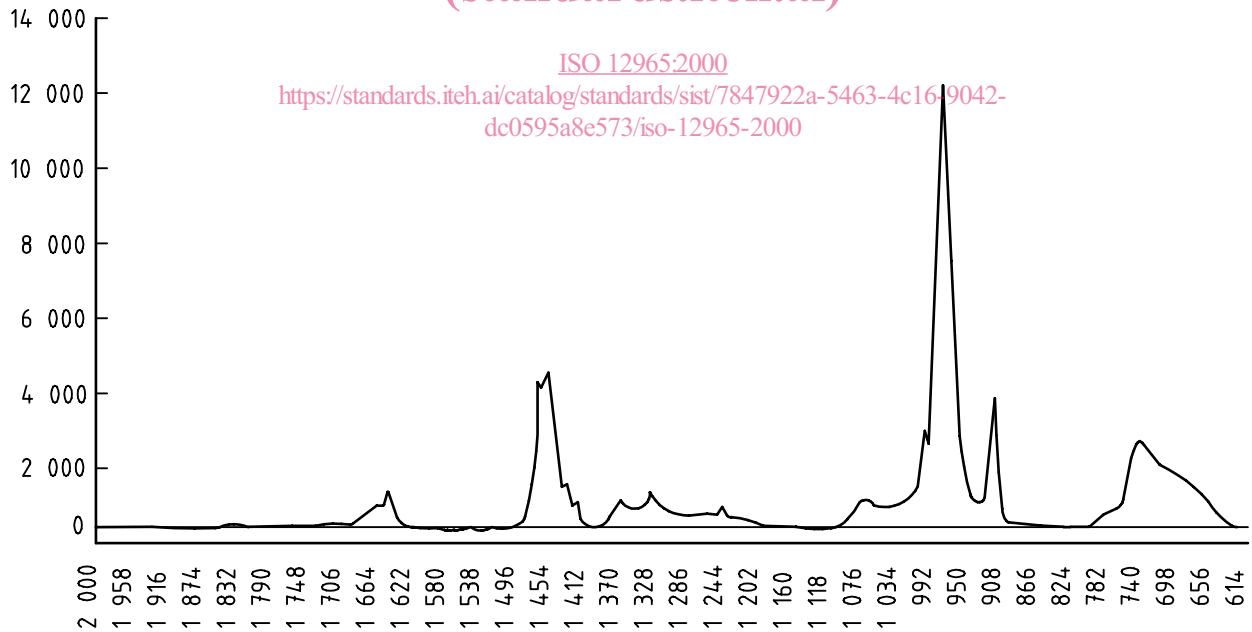

Figure 3 — Sample C (low-*cis* polybutadiene)

8 Precision

8.1 The precision calculations to express repeatability and reproducibility were performed in accordance with ISO/TR 9272. Consult this for precision concepts and nomenclature.

8.2 A type 1 interlaboratory test programme was organized in 1994. Three polybutadiene materials (A, B and C) with different microstructures (see Figures 1, 2 and 3) were sent to the participating laboratories where they were analysed using the test procedure.

8.3 The precision results for the *cis* content are given in Table 1, the precision results for the *trans* content are given in Table 2, while Table 3 shows the precision results for the vinyl content.

For all data, p = 6, q = 3 and n = 5.

8.4 Repeatability for *cis* content: The repeatability r for the *cis* content of polybutadiene has been established as 1,00 percentage points. Two single test results (or determinations) that differ by more than 1,00 percentage points shall be considered suspect and dictate that some appropriate investigative action be taken.

8.5 Reproducibility for *cis* content: The reproducibility R for the *cis* content of polybutadiene has been established as 1,86 percentage points. Two single test results (or determinations), obtained in separate laboratories, that differ by more than 1,86 percentage points shall be considered suspect and dictate that some appropriate investigative action be taken.

8.6 Repeatability for *trans* content: The repeatability r for the *trans* content of polybutadiene has been established as 0,72 percentage points. Two single test results (or determinations) that differ by more than 0,72 percentage points shall be considered suspect and dictate that some appropriate investigative action be taken.

8.7 Reproducibility for *trans* content: The reproducibility R for the *trans* content of polybutadiene has been established as 0,94 percentage points. Two single test results (or determinations), obtained in separate laboratories, that differ by more than 0,94 percentage points shall be considered suspect and dictate that some appropriate investigative action be taken.

8.8 Repeatability for vinyl content: The repeatability r for the vinyl content of polybutadiene has been established as 0,30 percentage points. Two single test results (or determinations) that differ by more than 0,30 percentage points shall be considered suspect and dictate that some appropriate investigative action be taken.

8.9 Reproducibility for vinyl content: The reproducibility R for the vinyl content of polybutadiene has been established as 0,64 percentage points. Two single test results (or determinations), obtained in separate laboratories, that differ by more than 0,64 percentage points shall be considered suspect and dictate that some appropriate investigative action be taken.