
**Rubber — Determination of
5-ethylidenenorbornene (ENB) or
dicyclopentadiene (DCPD)
in ethylene-propylene-diene (EPDM)
terpolymers**

*Caoutchouc — Détermination du 5-éthylidènenorbornène (ENB)
ou du dicyclopentadiène (DCPD) dans les terpolymers
d'éthylène-propylène-diène (EPDM)*



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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16565 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This second edition cancels and replaces the first edition (ISO 16565:2002), of which it constitutes a minor revision. The main changes concern corrections to the Y-axes in Figures 1 to 3 and to the X and Y-axes in Figure 4.

Rubber — Determination of 5-ethylidenenorbornene (ENB) or dicyclopentadiene (DCPD) in ethylene-propylene-diene (EPDM) terpolymers

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. 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 to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies the methods to be used to determine the content of 5-ethylidenenorbornene (ENB) or dicyclopentadiene (DCPD) in ethylene-propylene-diene (EPDM) terpolymers in the 0,1 % to 15 % range.

ENB and DCPD are dienes introduced into ethylene-propylene rubbers to generate specific cure properties. Since high precision for diene content determination is important, a Fourier transform infrared spectroscopic (FT-IR) method is utilized.

NOTE The procedures for mass fraction of ENB and mass fraction of DCPD differ only in the location in the infrared (IR) peak being quantified.

2 Principle

A test specimen is moulded between two PTFE-coated aluminium or mylar sheets. The ENB content is determined from its infrared absorbance at $1\,681\text{ cm}^{-1}$ to $1\,690\text{ cm}^{-1}$, a measure of the exocyclic double bond in ENB. The DCPD content is determined from its infrared absorbance at $1\,605\text{ cm}^{-1}$ to $1\,610\text{ cm}^{-1}$, a measure of the monocyclic double bond in DCPD.

The second derivative of the absorbance is calculated and ratioed to an internal standard. For ENB, the resulting second-derivative peak near $1\,690\text{ cm}^{-1}$ is related to the ENB mass fraction by calibrating the instrument with known EPDM standards. For DCPD, the resulting second-derivative peak near $1\,610\text{ cm}^{-1}$ is related to the DCPD mass fraction in the same way.

For oil-extended polymers, the oil must be extracted before the diene content is determined.

3 Apparatus

3.1 Carver-type press, capable of compressing films at $150\text{ }^{\circ}\text{C}$ and 10 MPa.

3.2 Mould

3.2.1 The mould primarily used is made of a stainless-steel strip $400\text{ }\mu\text{m}$ thick with an opening which will give a specimen of the appropriate size for the specimen-film holder described in 3.4 (2 cm by 2 cm). The mould shall have approximately the same dimensions as the press platens.

3.2.2 Alternatively, a thinner mould plate may be used. However, precision can be adversely affected at low diene levels. The precision of the method shall be determined when thinner films are utilized. For example, 127- μm -thick stainless-steel foil with a 15 mm by 35 mm opening may be used for the simultaneous determination of ethylene and diene.

3.2.3 For liquid EPDMs, a ring washer of 22 mm outer diameter by 16 mm inner diameter and 400 μm thick is used as a spacer between salt plates (NaBr, NaCl) to set a fixed path length. The spacer is sized to cover only the outer edge of the salt plates.

3.3 PTFE-coated aluminium moulding sheets, type A, 36 μm thick, or **silicone release sheeting**.

3.4 Specimen-film holders: Films may be moulded, cut out and transferred to a film holder. Magnetic-film holders are ideal. Alternatively, a mould sized to fit in the spectrophotometer specimen compartment with an appropriate-size opening, may be used to support the film without removal after compressing. A standard salt plate support is used for liquid samples prepared between salt plates.

3.5 Infrared Fourier transform spectrophotometer, capable of measuring absorbances in the range 4 000 cm^{-1} to 600 cm^{-1} with a transmittance specification (accuracy) of $\pm 1\%$ T or better. The instrument shall be capable of spectral resolution of 2 cm^{-1} . A deuterated triglycine sulfate (DTGS) or, as an alternative, a mercury cadmium telluride (MCT) detector shall be used.

NOTE A specification for the evaluation of the analysis of infrared spectra is given in Reference [1].

The instrument shall be capable of spectral accumulation, averaging and subtracting. Water is the primary source of interference in this method. Methods, physical and electronic, that minimize the moisture level and moisture-level variation are required to obtain the highest precision. The preferred method is to use an instrument equipped with a dry-gas purge and specimen shuttle, which permits alternating and repetitive collection of single-beam specimen and background spectra (see Clause 5). Alternatively, should a specimen shuttle be unavailable, careful purging of the specimen compartment with dry nitrogen can yield satisfactory results. High precision of calibration-standard data is indicative of adequate purging. When moisture interference is not removed by purging, spectral subtraction of water vapour can be used. A procedure for further development of the method is described in Annex A.

4 Test specimen preparation

4.1 Primary method

Place 0,20 g $\pm$ 0,05 g of the material to be analysed between two sheets (see 3.3) in the mould (see 3.2.1). Place the mould between the press platens heated to 125 $^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and apply 4 MPa pressure for 60 s $\pm$ 10 s.

Should the material be highly viscous, the mould may be heated to 175 $^{\circ}\text{C} \pm 5^{\circ}\text{C}$.

Cool the material to ambient temperature. Cut out a piece of film approximately 15 mm by 50 mm. Detach the specimen film from the sheets (see 3.3) and position it on the spectrophotometer specimen compartment window.

4.2 Alternative method

When using the thinner mould described in 3.2.2, place a small piece (0,04 g to 0,06 g) of the material to be analysed in the mould opening between two sheets (see 3.3) and compress as in 4.1. Remove the mould from the press, turn it over and compress it again. Then remove the mould from the press and allow it to cool to ambient temperature. When cool, carefully remove the sheets (see 3.3), allowing the specimen film to remain attached to the mould.

4.3 Alternative method for liquid polymer film preparation

Place a washer (see 3.2.3) on top of a salt plate. Place a small amount (about 0,3 g) of the liquid EPDM polymer to be analysed in the centre of the washer, filling the hole completely. Place a second salt plate on top of the filled washer. Gently place a 1 kg weight on top of the salt plate/washer assembly and allow the weighted assembly to sit for 2 min to 3 min. (For viscous samples, it may be necessary to warm the sample prior to compressing.) Remove the 1 kg weight and, if necessary, allow to cool. Wipe off any excess material that may have been pressed out of the assembly. Hold the assembly up to the light and inspect for bubbles and/or voids. Should there be imperfections, repeat the preparation with a larger amount of material.

5 Acquisition of spectra

5.1 With a specimen shuttle

5.1.1 The data-acquisition parameters shall be:

- resolution: 2 cm⁻¹;
- scans/scan time: total scan time, split between specimen scans and background scans, about 90 s.

5.1.2 Place the test specimen in the specimen compartment, allow purge to re-establish and, in alternating fashion, collect single-beam specimen and empty specimen compartment spectra. Eight passes of the shuttle shall be made (eight specimen and eight empty-compartment collections), collecting four scans at each position.

5.1.3 Calculate the specimen absorbance spectrum as minus log₁₀ of the ratio of the accumulated single-beam specimen to the empty-compartment spectrum.

$$A = -\log_{10}(P/P_0)$$

where

- A is the absorbance of the specimen at a given wavelength;
- P_0 is the empty specimen compartment light-beam intensity at that wavelength;
- P is the single-beam specimen light-beam intensity at that wavelength.

5.2 Without a specimen shuttle

5.2.1 The data-acquisition parameters shall be:

- resolution: 2 cm⁻¹;
- scans/scan time: background scans: 32 scans, 120 s total; specimen scans: 32 scans, 120 s total.

5.2.2 Establish a dry atmosphere inside the empty specimen compartment and collect the empty specimen compartment spectra.

5.2.3 Place the test specimen in the specimen compartment and re-establish a dry atmosphere inside the compartment. Collect the single-beam specimen spectra and calculate the specimen absorption spectrum as described in 5.1.3.

6 Calibration of the spectrophotometer

6.1 Obtain a series of known standards covering the diene content range 0 % to 10 %. Calibration may be based on secondary standards qualified by other laboratories using this method or, more generally, by primary standards whose diene content is well known. Primary standards may be established via use of proton nuclear magnetic resonance ($^1\text{H-NMR}$), in conjunction with other techniques. The ENB calibration standards¹⁾ employed in the development of this method were determined by a combination of refractive index and H-NMR (utilizing samples dissolved in deuterated *o*-dichlorobenzene at 120 °C; the ENB assignment was based exclusively on the exocyclic olefinic protons of ENB). The DCPD standards¹⁾ were determined by a similar H-NMR technique involving the cyclic olefinic protons of DCPD. The use of four standards at the (copolymer) 2 %, 5 % and 10 % levels is the minimum recommended.

6.2 Using the procedure in Clause 5, acquire a minimum of five absorbance spectra for each of the calibration standards described in 6.1. Several repetitions on separate specimens of each standard may be averaged to improve the accuracy of the calibration.

6.3 Using the procedure in Clause 7, calculate the ratio of the second-derivative diene peak height to the internal thickness gauge for each of the spectra acquired.

6.4 Calculate a linear calibration line (diene peak ratio versus assigned values of the standards as mass fraction in percent of diene) by computing a slope and intercept using standard least-squares linear-regression techniques.

7 Diene determination

7.1 Preparation

Prepare the specimen film as described in Clause 5.

7.2 Single absorbance spectrum

Collect a single absorbance spectrum based on the procedure in Clause 6.

7.3 Determination of film thickness

7.3.1 Normalize the spectrum by bringing the lowest point of the spectrum to zero (that is, determine the minimum absorbance in the spectrum and offset the spectrum to bring the minimum absorbance to zero).

7.3.2 To determine the film thickness automatically, subtract the absorbance at 2750 cm^{-1} from the absorbance at 2703 cm^{-1} . If the result is positive, the sample belongs to group 1. Otherwise, it belongs to group 2 (see Figure 1).

Group 1: The thickness gauge is the net absorbance difference between 2708 cm^{-1} (isoptic point) and 2450 cm^{-1} (anchor point) (see Figure 2).

Group 2: The thickness gauge is the net absorbance difference between 2668 cm^{-1} (isoptic point) and 2450 cm^{-1} (anchor point) (see Figure 3).

1) The sole source of supply of the ENB standards is Exxon Chemical Polymer Laboratories, PO Box 5200, Baytown, TX 77522, USA. For DCPD standards, the sole source is Uniroyal Chemical Company, World Headquarters, Chemical Characterization Laboratory, Benson Road, Middlebury, CT 06749, USA.

7.4 Determination of diene content

7.4.1 Normalize the total spectrum to one optical density (OD) unit by multiplying the total spectrum by $1/A$, where A is the net absorbance at thickness gauge.

7.4.2 Calculate the ENB content, as a mass fraction in percent:

$$\text{Peak ht} = A_{1\,681} - (0,75A_{1\,688} + 0,25A_{1\,689})$$

This is subsequently referred to as the ENB peak height. Figure 4 shows a typical second-derivative spectrum for EPDM.

Use the calibration procedure described in Clause 6 to compute a mass fraction of ENB for the sample, using only interpolation (and not extrapolation). If the ENB peak height is lower than the ENB peak height of the lowest, or higher than the ENB peak height of the highest, calibration standard, then report the ENB content as out of range for the calibration standards employed.

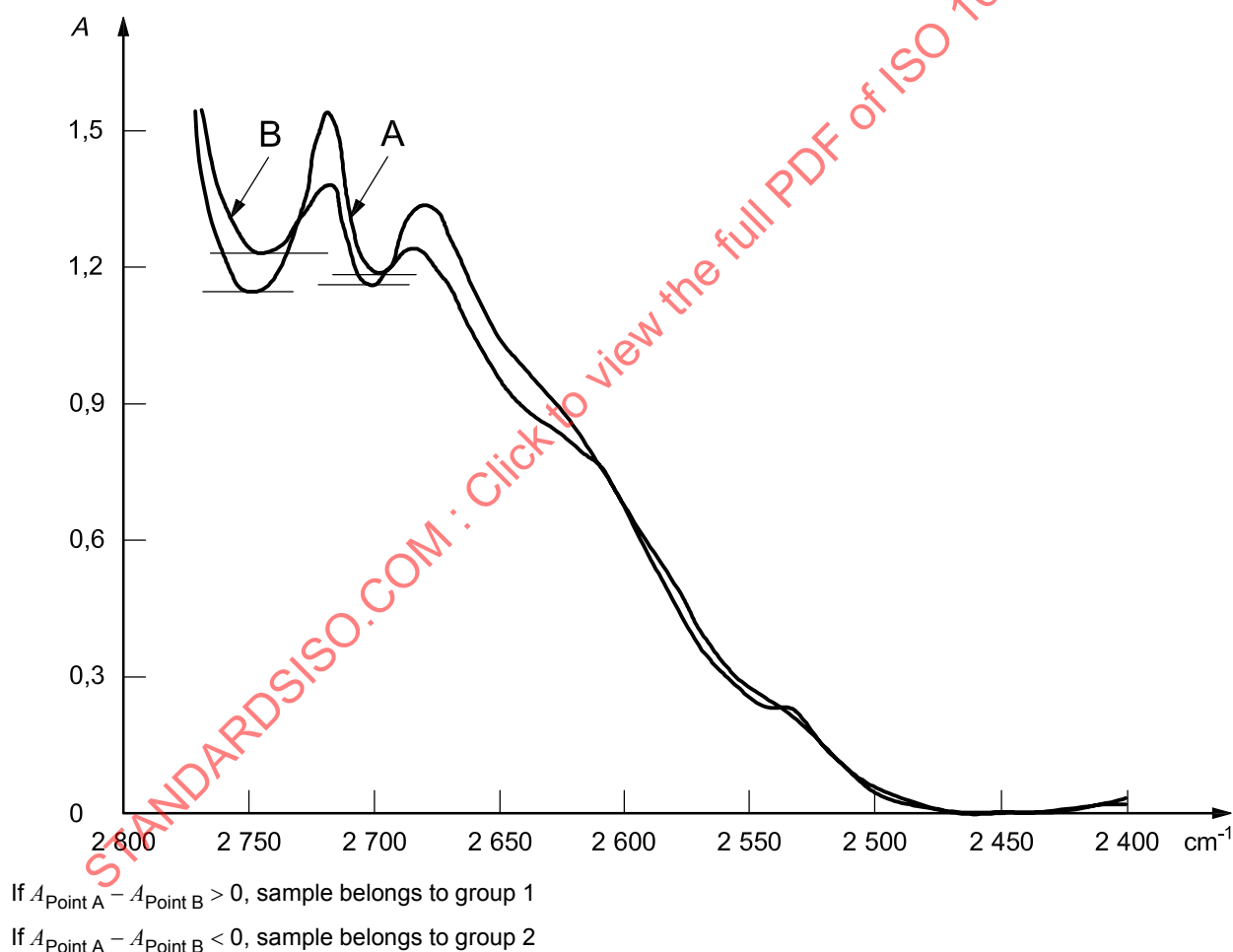


Figure 1 — FT-IR thickness gauge — Determination of group

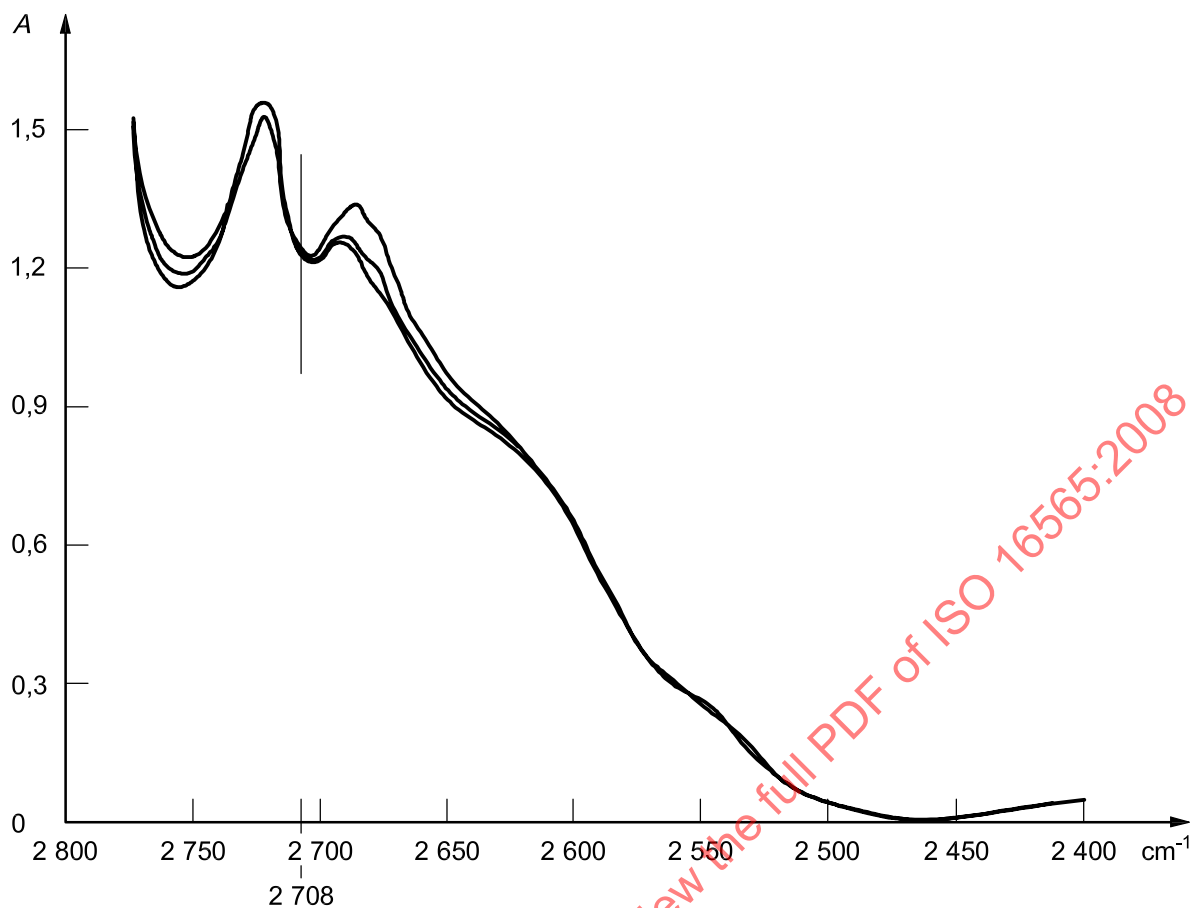


Figure 2 — FT-IR thickness gauge — Group 1

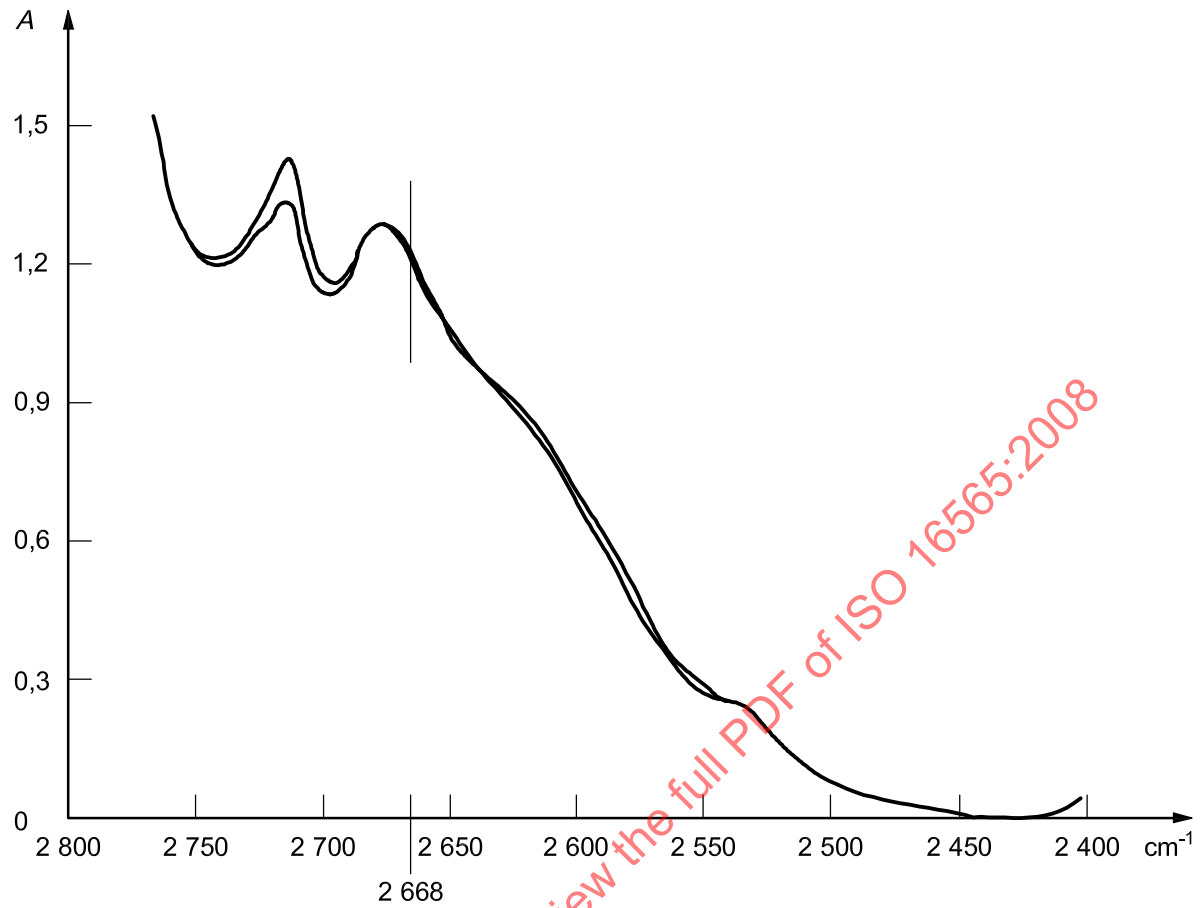
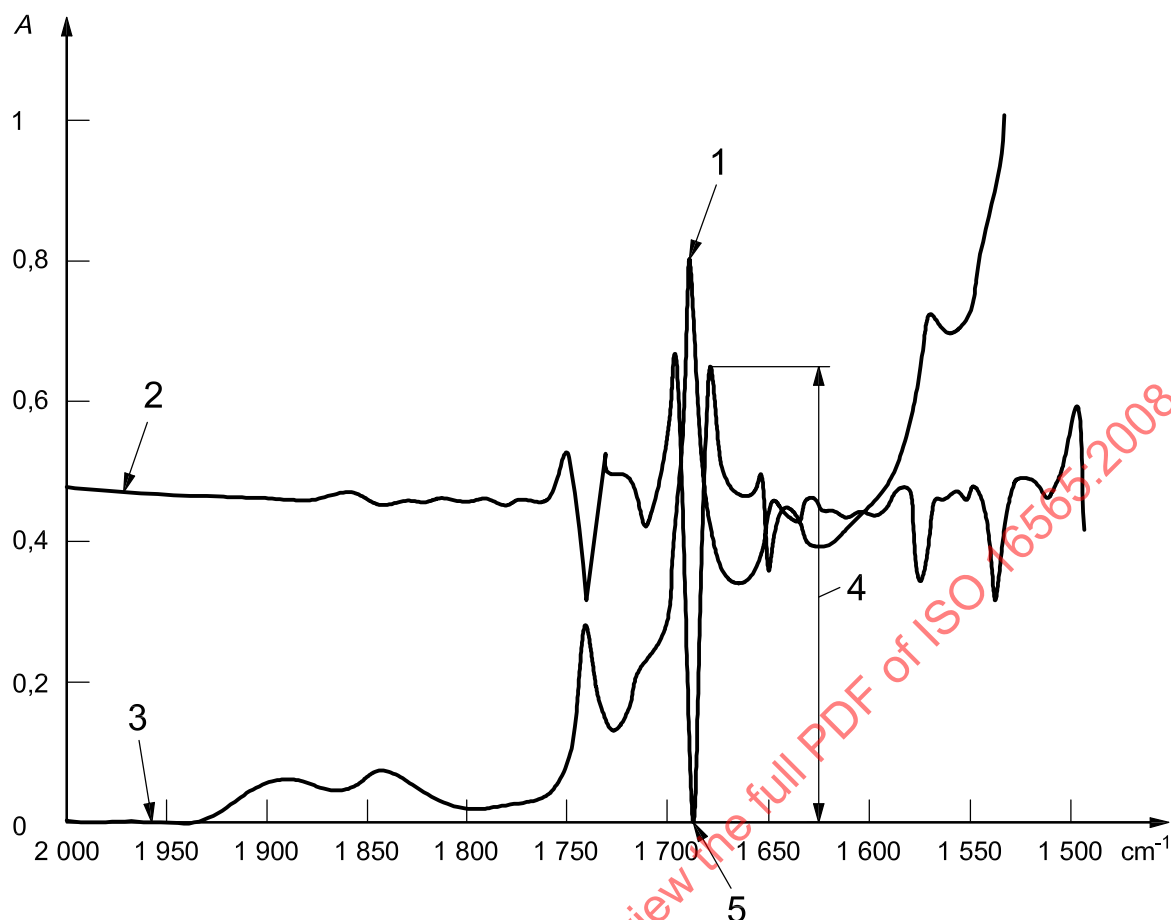


Figure 3 — FT-IR thickness gauge — Group 2



Key

- 1 Peak for 1 690 cm⁻¹ double bond
- 2 SD of normal spectrum
- 3 V 5600 normal spectrum
- 4 SD peak height
- 5 SD = 0 at peak

Figure 4 — Second-derivative (SD) peak height calculation

7.4.3 Calculate the DCPD content, as a mass fraction, as the peak height (in OD units) of the second derivative (the second-derivative algorithm shall use nine-point smoothing) between 1 601 cm⁻¹ and 1 620 cm⁻¹, using the following equation:

$$\text{Peak ht} = A_{1\,601} - A_{1\,610}$$

This is subsequently referred to as the DCPD peak height.

Use the calibration procedure described in Clause 6 to compute a mass fraction of DCPD for the sample, using only interpolation (and not extrapolation). If the DCPD peak height is lower than the DCPD peak height of the lowest, or higher than the DCPD peak height of the highest, calibration standard, then report the DCPD content as out of range for the calibration standards employed.

8 Precision and bias

8.1 The precision and bias data given in this clause were obtained for the primary method (see 4.1) in accordance with ISO/TR 9272:1986. This gives terminology and other statistical calculation details.

8.2 The precision results presented in this clause give an estimate of the precision of the test method with the materials (rubbers, etc.) used in the particular interlaboratory programme described in 8.3 and 8.4. The precision parameters shall not be used for acceptance or rejection testing of any group of materials without documentation that the parameters are applicable to the particular group of materials and the specific testing protocol of the test method used.

8.3 A type 1 interlaboratory test programme was conducted in 1996. Five materials (polymers) with different levels of ENB were supplied to three laboratories. In each laboratory, two replicate tests were conducted on each of two successive test days. A test result is defined as a single measurement of the mass percent of ENB.

8.4 A preliminary analysis to determine if the combined between-replicate/between-day variance was significantly greater than the between-replicate (on one day) variance showed that the between-replicate/between-day variance was not greater than the between-replicate variance. This demonstrates that, in this programme, testing on successive days did not add a significant source of variation over and above that inherent in duplicate testing on one day. The repeatability and reproducibility results generated by the programme therefore apply to short-term replicate testing.

8.5 The precision results for the ENB grades tested are given in Table 1 (see also the footnotes to the table).

NOTE Precision and bias testing for DCPD is currently being undertaken.

Precision can be expressed in the form of the following statements that use an appropriate value of r and R or (r) and (R) associated with a mean level or material in the table closest to the mean level under consideration for any material in routine testing operations.

8.6 The **repeatability limit** r (expressed as mass fraction in percent) of this test method has been established as the appropriate value tabulated in Table 1. Two single test results, obtained under normal test method procedures, that differ by more than the tabulated value of r (for any given level) must be considered as derived from different or non-identical sample populations.

8.7 The **reproducibility limit** R (expressed as mass fraction in percent) of this test method has been established as the appropriate value tabulated in Table 1. Two single test results, obtained in two different laboratories under normal test method procedures, that differ by more than the tabulated value of R (for any given level) must be considered to have come from different or non-identical sample populations.

8.8 The relative repeatability (r) and the relative reproducibility (R) are approximately equal over the range 3,0 % to 11,0 % (actual) ENB, at 2,6 % (relative) and 11,0 % (relative), respectively (see pooled values in Table 1).

8.9 In test method terminology, bias is the difference between an average test value and a 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.

Table 1 — Type 1 precision results for mass fraction of ENB

Material	Average ENB content	s_r	r	(r)	s_R	R	(R)
ENB003	0,08	0,110	0,311	— ^a	0,137	0,388	— ^a
ENB005	3,70	0,030	0,083	2,26	0,167	0,473	12,77
ENB002	4,99	0,059	0,168	3,36	0,171	0,484	9,70
ENB004	6,78	0,062	0,177	2,60	0,259	0,733	10,81
ENB001	10,92	0,066	0,186	1,70	0,404	1,143	10,47
Pooled values	— ^b	—	0,159	2,60	—	0,758	11,00

where

- s_r is the repeatability standard deviation;
- s_R is the reproducibility standard deviation;
- r is the repeatability limit, in measurement units;
- R is the reproducibility limit, in measurement units;
- (r) is the repeatability (relative), in percent;
- (R) is the reproducibility (relative), in percent.

^a Relative precision is not meaningful for very low ENB contents.

^b ENB003 excluded.

9 Test report

The test report shall include the following information:

- a) a reference to this International Standard;
- b) the ENB content and the DCPB content, as a mass fraction in percent, giving the result to two decimal places in each case;
- c) the type of mould utilized;
- d) whether spectra were acquired with or without a specimen shuttle;
- e) the date of the analysis.