INTERNATIONAL STANDARD

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Rubber — Analysis by pyrolytic gas-chromatographic methods —

Part 2: Determination of styrene/butadiene/isoprene ratio

Caoutchouc — Méthodes d'analyse par pyrolyse et chromatographie en phase gazeuse —

Partie 2: Détermination du rapport styrène/butadiène/isoprène

Reference number
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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 7270-2 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

ISO 7270 consists of the following parts, under the general title *Rubber — Analysis by pyrolytic gas-chromatographic methods*:

— *Part 1: Identification of polymers (single polymers and polymer blends)*

— *Part 2: Determination of styrene/butadiene/isoprene ratio*

Rubber — Analysis by pyrolytic gas-chromatographic methods —

Part 2: Determination of styrene/butadiene/isoprene ratio

WARNING — Persons using this part of ISO 7270 should be familiar with normal laboratory practice. This part of ISO 7270 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 part of ISO 7270 specifies the principles and procedures for determining, by pyrolysis and subsequent gas chromatography, the styrene (STY)/butadiene (BD)/isoprene (IP) ratio in copolymers, or blends of homopolymers and/or copolymers, in raw rubbers or vulcanized or unvulcanized compounds.

It is applicable to copolymers/terpolymers consisting of styrene, butadiene and isoprene, and blends of these polymers.

NOTE The use of this part of ISO 7270 pre-supposes sufficient working knowledge of the principles and techniques of gas chromatography for the analyst to perform the operations described and interpret the results correctly.

2 Normative references

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

ISO 1407, *Rubber — Determination of solvent extract*

3 Principle

Calibration curves are first prepared by pyrolysing samples with known STY/BD/IP ratios and analysing the pyrolysis products by gas chromatography to determine the percentage content of each component (STY, BD and IP), relative to the total of the three components, in the pyrolysis products.

Samples of unknown composition are then pyrolysed and the pyrolysis products analysed under the same conditions. The STY/BD/IP ratio in the original sample is determined from the calibration curves.

4 Reagents

All reagents shall be of analytical grade.

4.1 Solvents for extraction purposes

The following solvents are suitable (see 6.1.1):

— acetone;

— methanol;

— methylethylketone.

4.2 Carrier gas

— nitrogen;

— helium.

4.3 Gas for flame-ionization detector: hydrogen plus purified compressed air.

5 Apparatus

5.1 Extraction apparatus

As specified in ISO 1407.

5.2 Pyrolysis/chromatography system

5.2.1 General

The apparatus utilized to obtain pyrograms consists of four parts: the pyrolysis device, the gas chromatograph, the gas-chromatographic column and the data-handling equipment.

5.2.2 Pyrolysis device

The following types of pyrolysis device are suitable:

— micro-furnace pyrolyser;

— Curie-point pyrolyser;

— platinum-filament pyrolyser.

5.2.3 Gas chromatograph

A wide variety of gas chromatographs using either a flame-ionization detector (FID) or a thermal-conductivity detector (TCD) are suitable for use in this part of ISO 7270. An FID is preferable for use with capillary columns.

5.2.4 Chromatographic columns

A variety of column lengths and diameters and stationary and liquid phases are suitable for use in this part of ISO 7270, the main requirement being good resolution of the volatile pyrolysis products styrene, butadiene and isoprene.

NOTE 1 Capillary columns with good separation efficiency are suitable, but not essential.

NOTE 2 Capillary columns containing non-polar polydimethylsiloxanes and partially modified (diphenyl-, cyanopropylphenyl- or other) semi-polar silicones are suitable.

5.2.5 Data-handling equipment

A recorder, an integrator or a computer data-analysis system may be used.

6 Procedure

6.1 Preparation of calibration curves

6.1.1 Prepare calibration samples of known compositions close to that assumed for the unknown (test) sample.

6.1.2 Take a test portion of mass appropriate to the apparatus used. Generally, this will be between 0,1 mg and 5 mg. For good reproducibility, the size of the test portion should be as small as practicable.

6.1.3 Place the test portion in the pyrolysis device and pyrolyse it. An appropriate pyrolysis temperature is 500 °C to 600 °C for a micro-furnace or Curie-point pyrolyser, and 600 °C to 750 °C for a platinum-filament pyrolyser. Use the same pyrolysis temperature for all of a series of related measurements.

The gas-chromatographic conditions will depend on the column used. Typical operating conditions are given in Tables 1 to 3 and examples of chromatograms obtained using each set of conditions are given in Figures 1 to 3.

NOTE The type of pyrolysis device used and the pyrolysis temperature will affect the results.

6.1.4 Record the peak areas X, Y and Z for STY, BD and IP, respectively, in the pyrolysis products and calculate, for each of these components, the percentage peak area relative to their total, as follows:

percentage peak area for styrene $[X/(X + Y + Z)] \times 100$

percentage peak area for butadiene $[Y/(X + Y + Z)] \times 100$

percentage peak area for isoprene $[Z/(X + Y + Z)] \times 100$

6.1.5 For each of the three components STY, BD and IP, prepare a calibration curve by plotting the known percentage of the component (relative to the total of the three) in the unpyrolysed sample against the percentage peak area for the component in the pyrolysis products. An example of one such calibration curve (for butadiene) is shown in Figure 4.

NOTE 1 When using an ordinary (30 m) length of capillary column, it is difficult to completely separate isobutene from butadiene. In pyrolytic gas-chromatographic methods, isobutene, which is a decomposition product of rubber containing the isoprene unit, is detected in the near retention range of butadiene. It is possible, however, to discriminate between isoprene and butadiene even without complete separation by means of the calibration curves.

NOTE 2 A longer (60 m) capillary column with a thicker film affords better separation of these components.

Table 1 — Recommended operating conditions for micro-furnace pyrolysis followed by chromatography with a 30 m capillary column

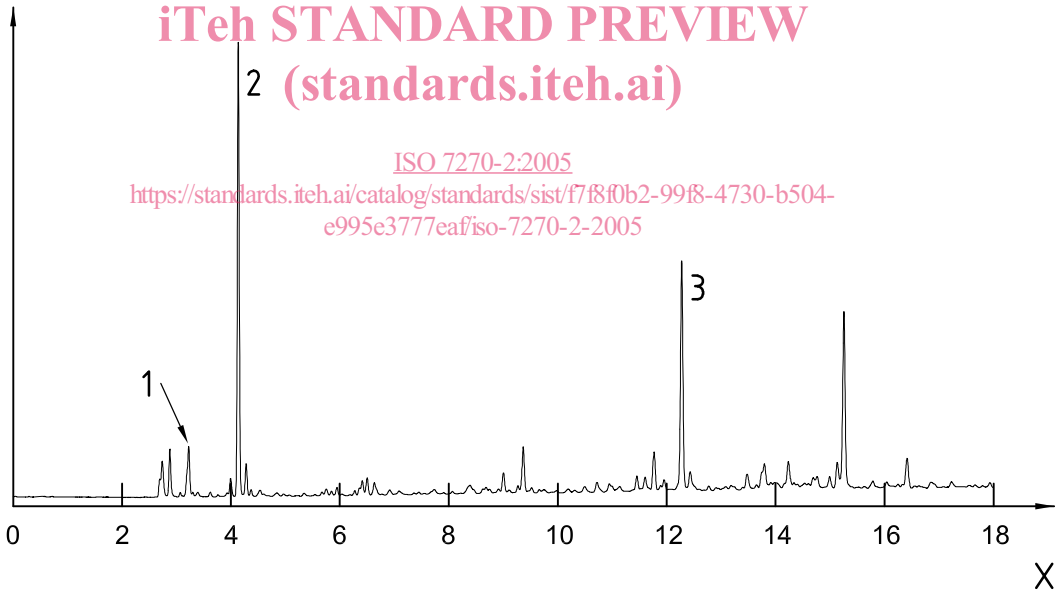
Pyrolysis	
Device	Micro-furnace
Pyrolysis temperature	550 °C
Gas-chromatographic column	
Liquid phase	5 % diphenyldimethylpolysiloxane
Film thickness	1,0 µm
Column diameter	0,25 mm ID
Column length	30 m
Chromatographic conditions	
Carrier gas and flow rate	Helium, 0,8 ml/min
Injector temperature	250 °C
Type of detector	FID
Detector temperature	300 °C
Temperature programme	Isothermal for 2 min at 50 °C then 20 °C/min from 50 °C to 280 °C then isothermal for 10 min at 280 °C

Table 2 — Recommended operating conditions for micro-furnace pyrolysis followed by chromatography with a 60 m capillary column

Pyrolysis	
Device	Micro-furnace
Pyrolysis temperature	550 °C
Gas-chromatographic column	
Liquid phase	5 % diphenyldimethylpolysiloxane
Film thickness	1,0 µm
Column diameter	0,25 mm ID
Column length	60 m
Chromatographic conditions	
Carrier gas and flow rate	Helium, 0,8 ml/min
Injector temperature	250 °C
Type of detector	FID
Detector temperature	300 °C
Temperature programme	Isothermal for 7 min at 50 °C then 10 °C/min from 50 °C to 280 °C then isothermal for 10 min at 280 °C

Table 3 — Recommended operating conditions for Curie-point pyrolysis followed by chromatography with a packed column

Pyrolysis	
Device	Curie-point pyrolyser
Pyrolysis temperature	590 °C (3 s)
Gas-chromatographic column	
Liquid phase	20 % silicone 710/Chromosorb W60 to W80 mesh
Column diameter/material	3 mm ID/stainless steel
Column length	3 m
Chromatographic conditions	
Carrier gas	Helium
Type of detector	FID
Temperature programme	Isothermal for 2 min at 50 °C then 10 °C/min from 50 °C to 220 °C then isothermal for 10 min at 220 °C



Key

X time (minutes)

1 butadiene

2 isoprene

3 styrene

Figure 1 — Example of chromatogram obtained with 30 m capillary column