INTERNATIONAL STANDARD

ISO 7270-2

Second edition
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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
ISO 7270-2:2012(E)

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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*.

This second edition cancels and replaces the first edition (ISO 7270-2:2005), which has been technically revised.

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.

CAUTION — Certain procedures specified in this part of ISO 7270 might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This part of ISO 7270 specifies a pyrolytic gas-chromatographic method for the determination of the styrene/butadiene/isoprene ratio in copolymers, or blends of homopolymers and/or copolymers, in raw rubbers or in unvulcanized or vulcanized compounds. It is applicable to copolymers/terpolymers consisting of styrene, butadiene and isoprene, and blends of these polymers.

NOTE 1 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.

NOTE 2 The styrene/butadiene/isoprene ratio determined by this test method is affected by the presence of resin and by a high level of sulfur.

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 1407:2011, *Rubber — Determination of solvent extract*

3 Principle

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

Samples of unknown composition are then pyrolysed, and the pyrolysis products are analysed under the same conditions. The styrene/butadiene/isoprene ratio in these samples 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:

— acetone;

- methanol;
- methylethylketone.

4.2 Carrier gas:

- nitrogen;

or

- 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/gas 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 materials, column lengths, column diameters and stationary and liquid phases are suitable for use in this part of ISO 7270, the main requirement being high resolution of the volatile pyrolysis products styrene, butadiene and isoprene.

NOTE 1 Capillary columns, which have a separation efficiency which is better than that of packed columns, 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.

NOTE 3 When using an ordinary (30 m) capillary column, it is difficult to separate isobutene from butadiene completely. The reason is that, in pyrolytic gas-chromatographic methods, isobutene, which is a decomposition product of rubber containing the isoprene unit, is detected close to the retention time of butadiene. It is possible, however, to discriminate between isoprene and butadiene, even without complete separation, by means of the calibration curves.

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 test samples from calibration samples and unknown sample

6.1.1 A minimum of three calibration samples shall be used for the preparation of the calibration curves, including a calibration sample with the composition expected for the unknown sample under test.

6.1.2 The nature (raw, unvulcanized, or vulcanized) of the calibration samples should preferably be the same as that of the unknown sample under test.

6.1.3 Process or extender oil and additives in both the calibration samples and the unknown sample shall be extracted in accordance with ISO 1407:2011, method B, using a solvent suitable for the type of compound concerned (vulcanized or unvulcanized). The solvent chosen shall not affect the polymer and shall remove as much of the process and extender oil and additives as possible. All samples shall be dried after extraction, using the drying procedure specified in method B of ISO 1407:2011.

NOTE Process and extender oils can cause serious interference.

6.1.4 From the extracted samples, take test samples of masses appropriate to the pyrolyser used, and as small and as equal as possible for improved reproducibility.

NOTE Generally, the mass will be between 0,1 mg and 5 mg, depending on the pyrolyser.

6.2 Test conditions

6.2.1 The test conditions, including the pyrolysis temperature, shall be the same for the preparation of the calibration curves and the analysis of the unkown sample.

6.2.2 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.

6.2.3 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.

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

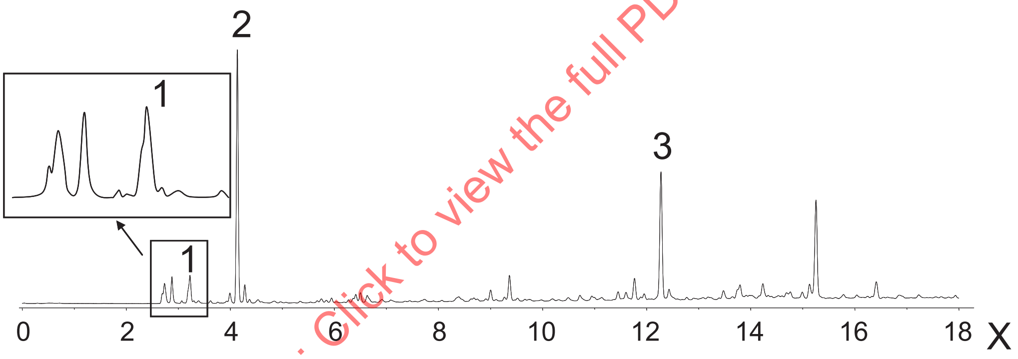
Pyrolysis	
Device	Micro-furnace
Pyrolysis temperature	550 °C
Gas-chromatographic column	
Liquid phase	5 % diphenyldimethylpolysiloxane
Film thickness	1,0 µm
Column diameter/material	0,25 mm ID/stainless steel (deactivated)
Column length	30 m
Chromatographic conditions	
Carrier gas and flow rate	Helium, 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 increase at 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/material	0,25 mm ID/stainless steel (deactivated)
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 increase at 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

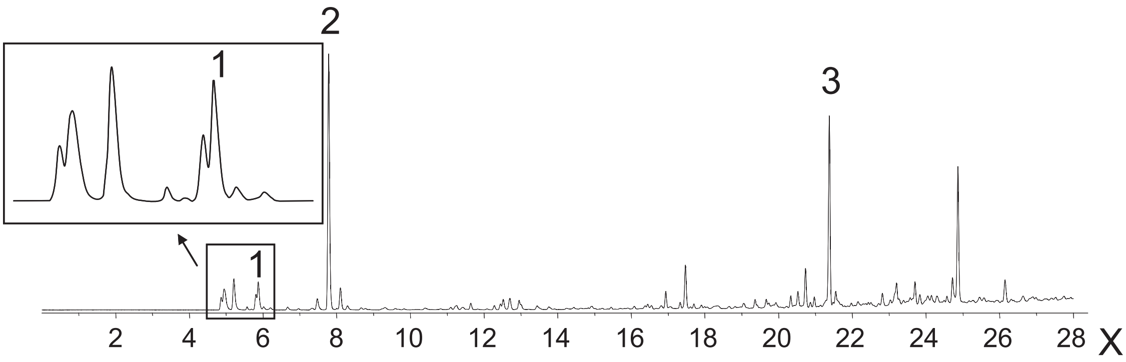
Pyrolysis	
Device	Curie-point pyrolyser
Pyrolysis temperature/time	590 °C/3 s
Gas-chromatographic column	
Liquid phase	20 % silicone 710/Chromosorb W (60 to 80 mesh)
Column diameter/material	3 mm ID/stainless steel
Column length	3 m
Chromatographic conditions	
Carrier gas	Helium
Type of detector	FID
Temperature programme	Isothermal for 2 min at 50 °C then increase at 10 °C/min from 50 °C to 220 °C then isothermal for 10 min at 220 °C



Key

X time (min)
1 butadiene
2 isoprene
3 styrene

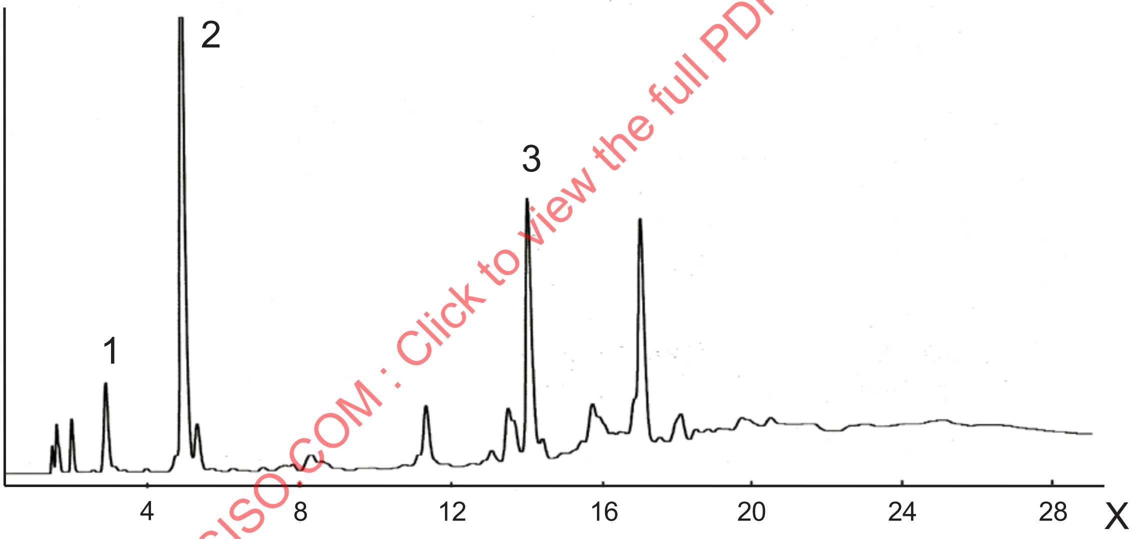
Figure 1 — Example of chromatogram obtained with 30 m capillary column



Key

X time (min)
1 butadiene
2 isoprene
3 styrene

Figure 2 — Example of chromatogram obtained with 60 m capillary column



Key

X time (min)
1 butadiene
2 isoprene
3 styrene

Figure 3 — Example of chromatogram obtained with packed column

6.3 Preparation of calibration curves

6.3.1 Place a test sample taken from one of the extracted calibration samples in the pyrolysis device, pyrolyse it, and analyse the pyrolysis products with the gas chromatograph to obtain the pyrogram. Repeat this step for the other calibration samples in order to prepare the calibration curves.

6.3.2 Record the peak areas P_{ST}, P_{BD} and P_{IP} for styrene, butadiene and isoprene, respectively, obtained from the data-handling equipment (5.2.5). Calculate the percentage peak area for each of these components, A_{ST}, A_{BD} and A_{IP}, relative to their total, as follows:

$$A_{ST} = \frac{P_{ST}}{P_{ST} + P_{BD} + P_{IP}} \times 100$$

$$A_{BD} = \frac{P_{BD}}{P_{ST} + P_{BD} + P_{IP}} \times 100$$

$$A_{IP} = \frac{P_{IP}}{P_{ST} + P_{BD} + P_{IP}} \times 100$$

where

A_{ST} is the percentage peak area for styrene;

A_{BD} is the percentage peak area for butadiene;

A_{IP} is the percentage peak area for isoprene;

P_{ST} is the peak area for styrene;

P_{BD} is the peak area for butadiene;

P_{IP} is the peak area for isoprene.

6.3.3 For each of the three components, styrene, butadiene and isoprene, prepare a calibration curve. For styrene, for example, plot the known percentage of styrene (relative to the total of the three) on the X-axis against the percentage peak area obtained for styrene in the pyrolysis products on the Y-axis. Prepare a regression line for styrene by the least-squares method, and obtain the slope a and Y-intercept b. Using the same procedure, prepare the calibration curves for butadiene and isoprene, and obtain the slopes (c and e) and Y-intercepts (d and f).

6.4 Analysis of the unknown sample

6.4.1 Pyrolyse a test sample prepared from the extracted unknown sample under the same conditions as for the calibration samples.

6.4.2 Record the peak areas Q_{ST}, Q_{BD} and Q_{IP} for styrene, butadiene and isoprene, respectively, obtained from the data-handling equipment (5.2.5).

Calculate C_{ST}, C_{BD} and C_{IP}, the percentage peak areas relative to the total, as follows:

$$C_{ST} = \frac{Q_{ST}}{Q_{ST} + Q_{BD} + Q_{IP}} \times 100$$

$$C_{BD} = \frac{Q_{BD}}{Q_{ST} + Q_{BD} + Q_{IP}} \times 100$$

$$C_{IP} = \frac{Q_{IP}}{Q_{ST} + Q_{BD} + Q_{IP}} \times 100$$

where

C_{ST} is the percentage peak area for styrene;

C_{BD} is the percentage peak area for butadiene;

C_{IP} is the percentage peak area for isoprene;

Q_{ST} is the peak area for styrene;

Q_{BD} is the peak area for butadiene;

Q_{IP} is the peak area for isoprene.

7 Expression of results

Determine the styrene/butadiene/isoprene ratio in the unknown sample using the following formulas:

$$B_{ST} = \frac{C_{ST} - b}{a}$$

$$B_{BD} = \frac{C_{BD} - d}{c}$$

$$B_{IP} = \frac{C_{IP} - f}{e}$$

where

B_{ST} is the percentage of styrene in the test sample;

B_{BD} is the percentage of butadiene in the test sample;

B_{IP} is the percentage of isoprene in the test sample;

a, b, c, d, e and f are the values determined in 6.3.3;

C_{ST}, C_{BD} and C_{IP} are as defined in 6.4.2.

8 Precision

See Annex A.

9 Test report

The test report shall include the following particulars:

a) a full description of the unknown sample and its origin;

b) test method:

  1) a full reference to the test method used, i.e. the number of this part of ISO 7270;

  2) the apparatus and operating conditions used (type of pyrolysis device, pyrolysis temperature, gas-chromatographic apparatus and gas-chromatographic conditions);

c) details of any operations not specified in this part of ISO 7270;

d) the styrene/butadiene/isoprene ratio, expressed as a whole number, for the unknown sample analysed.