International
Standard

ISO 7270-2

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

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Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 7270-2:2012), of which it constitutes a minor revision.

The main changes are as follows:

- the Normative references have been updated;
- the CAS numbers of the chemicals have been added.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Rubber — Analysis by pyrolytic gas-chromatographic methods —

Part 2:
Determination of styrene/butadiene/isoprene ratio

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document 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 determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document can 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 document 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 document 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 1407:2023, *Rubber — Determination of solvent extract*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 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 (CAS Registry Number®[1] 100-42-5), butadiene (CAS 106-99-0) and isoprene (CAS 78-79-5)], 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.

5 Reagents

All reagents shall be of analytical grade.

5.1 Solvents for extraction purposes.

The following solvents are suitable:

- acetone (CAS 67-64-1);
- methanol (CAS 67-56-1);
- methylethylketone (CAS 78-93-3).

5.2 Carrier gas:

- nitrogen (CAS 7727-37-9);

or

- helium (CAS 7440-59-7).

5.3 Gas for flame-ionization detector: hydrogen (CAS 1333-74-0) plus purified compressed air (CAS 132259-10-0).

6 Apparatus

6.1 Extraction apparatus

As specified in ISO 1407.

6.2 Pyrolysis/gas chromatography system

6.2.1 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.

6.2.2 Pyrolysis device

The following types of pyrolysis device are suitable:

- micro-furnace pyrolyser;
- Curie-point pyrolyser;
- platinum-filament pyrolyser.

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[1] CAS Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6.2.3 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 document. An FID is preferable for use with capillary columns.

6.2.4 Chromatographic columns

A variety of column materials, column lengths, column diameters and stationary and liquid phases are suitable for use in this document, 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 (CAS 107-51-7) and partially modified [diphenyl- (CAS 68951-93-9), cyanopropylphenyl- (CAS 25561-30-2) or other] semi-polar silicones (CAS 7440-21-3) are suitable.

NOTE 3 When using an ordinary (30 m) capillary column, it is difficult to separate isobutene (CAS 115-11-7) 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.

6.2.5 Data-handling equipment

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

7 Procedure

7.1 Preparation of test samples from calibration samples and unknown sample

7.1.1 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.

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

7.1.3 Process or extender oil and additives in both the calibration samples and the unknown sample shall be extracted in accordance with ISO 1407:2023, 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 ISO 1407:2023, method B.

NOTE Process and extender oils can cause serious interference.

7.1.4 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.

7.2 Test conditions

7.2.1 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.

7.2.2 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.

7.2.3 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

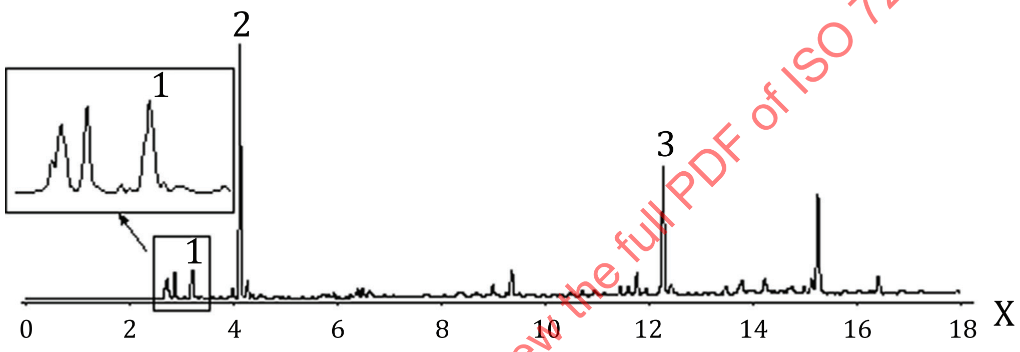
Pyrolysis	
Device	Micro-furnace
Pyrolysis temperature	550 °C
Gas-chromatographic column	
Liquid phase	5 % diphenyldimethylpolysiloxane (CAS 68083-14-7)
Film thickness	1,0 μm
Column diameter/material	0,25 mm ID/stainless steel (deactivated)
Column length	30 m
Chromatographic conditions	
Carrier gas and 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

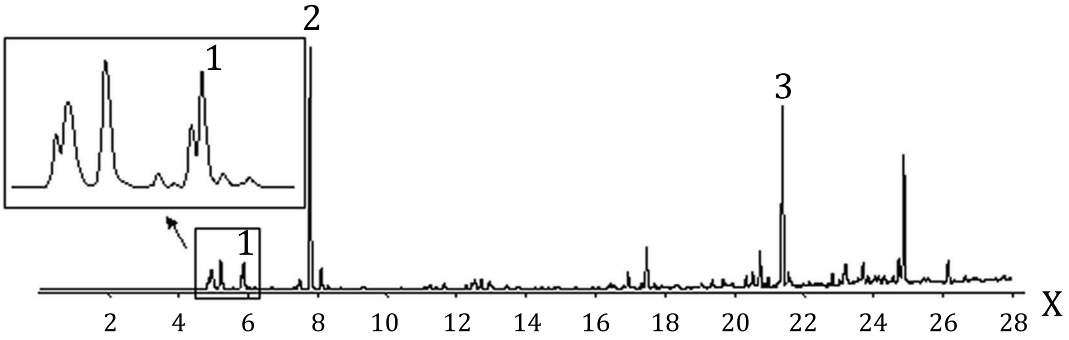
Pyrolysis	
Device	Curie-point pyrolyser
Pyrolysis temperature/time	590 °C/3 s
Gas-chromatographic column	
Liquid phase	20 % silicone 710/Chromosorb W (60 to 80 mesh)
Column diameter/material	3 mm ID/stainless steel
Column length	3 m
Chromatographic conditions	
Carrier gas	Helium
Type of detector	FID
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

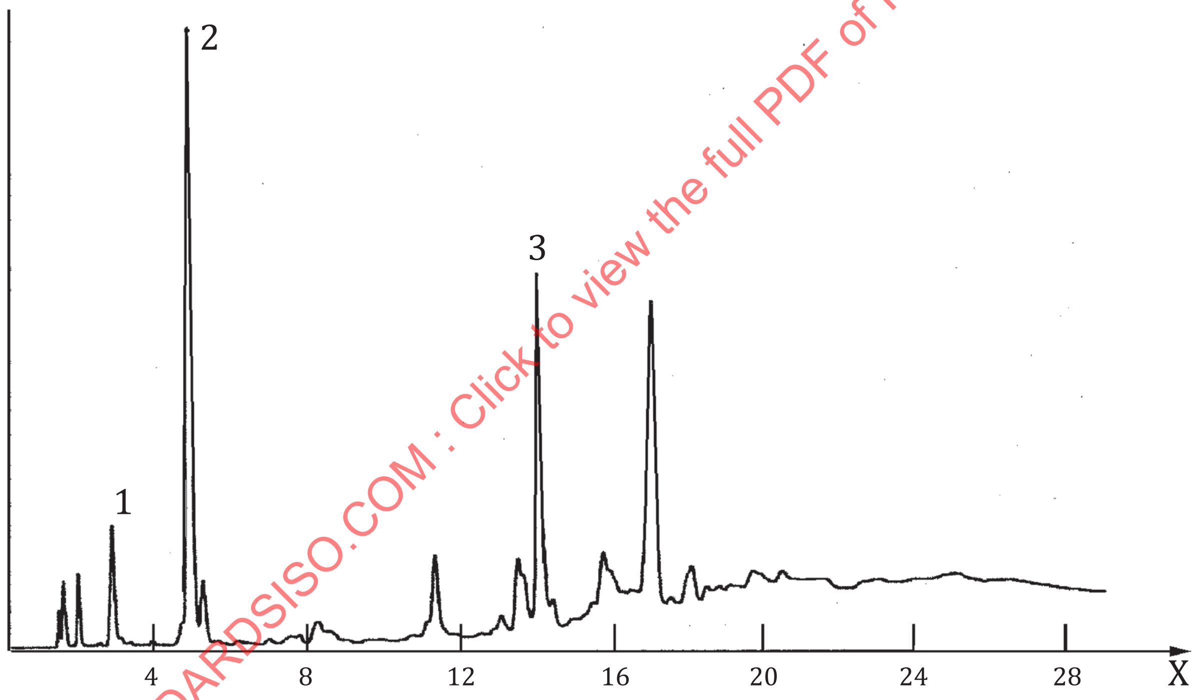
Figure 1 — Example of chromatogram obtained with 30 m capillary column



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

7.3 Preparation of calibration curves

7.3.1 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.

7.3.2 Record the peak areas P_{ST}, P_{BD} and P_{IP} for styrene, butadiene and isoprene, respectively, obtained from the data-handling equipment (6.2.5). Calculate the percentage peak area for each of these components, A_{ST}, A_{BD} and A_{IP}, relative to their total, as follows:

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

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

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

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.

7.3.3 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*).

7.4 Analysis of the unknown sample

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

7.4.2 Record the peak areas Q_{ST}, Q_{BD} and Q_{IP} for styrene, butadiene and isoprene, respectively, obtained from the data-handling equipment (6.2.5).

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

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

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

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

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.

8 Expression of results

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

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

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

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

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 7.3.3;
C_{ST}, C_{BD} and C_{IP}	are as defined in 7.4.2.

9 Precision

See Annex A.

10 Test report

The test report shall include the following information:

a) sample details:

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

   2) the extraction solvent;

b) test method:

   1) a full reference to the test method used, i.e. a reference to this document (ISO 7270-2:2024);

  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 document;

d) test results:

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

  2) the date of the test.

Annex A
(informative)

Precision

A.1 General

An interlaboratory test programme (ITP) to determine the precision of the test method for vulcanized compounds was conducted in 2001 in accordance with ISO/TR 9272:1986[2], using the apparatus and conditions given in Table 2. The precision was evaluated as a type 1 precision as defined in ISO/TR 9272.

Six laboratories participated in the programme.

Three vulcanized compounds, designated A, B and C, with different blend ratios of styrene-butadiene rubber (SBR) and isoprene rubber (IR) were used as the unknown samples. Four vulcanized compounds with different blend ratios of SBR/IR were delivered as calibration samples for the determination of the calibration curves, along with information on the component ratio in each. The SBR used in the ITP was made up of 50 % styrene monomer units and 50 % butadiene monomer units.

A "test result" was taken as the mean value from two tests carried out on the same day on each unknown sample. Test results were obtained on two different days seven days apart.

The precision results as determined by this ITP should not be applied to acceptance or rejection testing of any group of materials or products without documentation showing that the results of this ITP actually apply to the products or materials being tested.

A.2 Results

The precision results are given in Tables A.1, A.2 and A.3.

The actual blend ratio of SBR/IR in the three unknown samples A, B and C is given in Table A.4 for comparison with the ITP results.

Repeatability: The repeatability r of the test method has been established as the appropriate value tabulated in Tables A.1, A.2 and A.3 for each material. Two single test results that differ by more than the tabulated value should be considered suspect and suggest that some appropriate investigative action be taken.

Reproducibility: The reproducibility R of the test method has been established as the appropriate value tabulated in Tables A.1, A.2 and A.3 for each material. Two single test results that differ by more than the tabulated value should be considered suspect and suggest that some appropriate investigative action be taken.

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[2] Withdrawn. Replaced by ISO 19983.