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## Rubber — Identification of polymers (single polymers and blends) — Pyrolytic gas chromatographic method

**iTeh STANDARD PREVIEW**

*Caoutchouc — Identification des polymères (un seul polymère ou mélanges de polymères) —  
Méthode par pyrolyse et chromatographie en phase gazeuse*

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## Foreword

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International Standard ISO 7270 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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# Rubber — Identification of polymers (single polymers and blends) — Pyrolytic gas chromatographic method

## 1 Scope

This International Standard describes methods for the identification of the polymer or the blend of polymers in raw rubbers and in vulcanized or unvulcanized compounds from the gas chromatographic patterns of their pyrolysis products (pyrograms).

Three methods are described, as follows:

- a) method A, which may be used for all rubbers to determine the nature of the polymer or polymers present; the method will be easiest to apply in the case of single polymers;
- b) method B, which is particularly useful for determining the nature of the polymers present in blends, and is recommended for use when method A is not successful;
- c) method C, which is used only if method A indicates the presence of styrene-butadiene copolymers or if method B indicates the presence of 2-vinylcyclohexene and styrene peaks in the pyrogram, and it is required to determine whether polybutadiene is present as well as styrene-butadiene copolymers.

The use of the methods described in this International Standard presupposes sufficient working knowledge of the principles and techniques of gas chromatography to be able to carry out the operations described and to interpret the results correctly.

## 2 Field of application

2.1 Methods A and B enable the following types of polymers to be identified:

- a) polyisoprene, of natural or synthetic origin;
- b) styrene-butadiene copolymers;
- c) polybutadiene;
- d) polychloroprene;
- e) acrylonitrile-butadiene copolymers;
- f) ethylene-propylene copolymers and related terpolymers;
- g) isobutene-isoprene copolymers.

The methods may also be applicable to other types of polymer, but this must be verified by the analyst in each particular case.

With the exception of blends containing both styrene-butadiene copolymers and polybutadiene, methods A and B also enable blends of the following polymers to be identified:

- a) polyisoprene of natural or synthetic origin;
- b) polybutadiene;
- c) isobutene-isoprene or halogenated isobutene-isoprene copolymers;
- d) styrene-butadiene copolymers.

2.2 Method C is to be used only when the presence of a styrene-butadiene copolymer is indicated by the presence of both styrene and 2-vinylcyclohexene peaks in the pyrogram, and it is required to determine whether polybutadiene is also present. The method is not applicable if other styrene polymers or copolymers, or unextractable styrene-containing resins, are present, or if styrene-butadiene block copolymers are present.

The method is also not applicable if the microstructure of the styrene-butadiene copolymers is not known.

2.3 Methods A and B will not differentiate the following single polymers or blends:

- a) natural polyisoprene from synthetic polyisoprene;
- b) styrene-butadiene copolymers produced by solution polymerization from those produced by emulsion polymerization or styrene-butadiene copolymers having different monomer ratios or different microstructures; it is sometimes possible to distinguish styrene-butadiene copolymers containing different amounts of styrene as well as random polymers from block polymers;
- c) polybutadienes with different microstructures;
- d) different types of polychloroprene;
- e) acrylonitrile-butadiene copolymers with different monomer ratios, except when the monomer ratios are widely different;
- f) ethylene-propylene copolymers with different monomer ratios, or the copolymers from the related terpolymers;

g) isobutene-isoprene copolymers (butyl rubbers) from halogenated butyl rubbers;

h) polyisoprene containing different amounts of *cis-trans* isomers.

2.4 None of the methods (A, B or C) will enable ebonite (hard rubber) to be identified.

### 3 Reference

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

### 4 Principle

#### 4.1 General

Pyrolysis of a small test portion at an elevated temperature in an enclosed system and analysis of the pyrolysis products by gas chromatography.

#### NOTES

1 The qualitative composition of the pyrolysis product depends upon the type of rubber being studied.

2 The quantitative composition of the pyrolysis products may be affected by the degree of cure, the recipe used, etc., but the most important factors are the pyrolysis conditions.

3 The success of methods A, B or C depends upon examining the unknown rubber under exactly the same gas pyrolysis and chromatographic conditions as were used for preparation of the reference pyrograms or the calibration tables. Constancy of the pyrolysis temperature, in particular, is essential for method C.

#### 4.2 Method A

Comparison of the pyrogram obtained with that of a known rubber.

NOTE — The success of the method depends upon examining known and unknown rubbers of approximately the same test recipe and state of cure under exactly the same experimental conditions.

#### 4.3 Method B

Identification of the characteristic hydrocarbons in the unknown rubber by comparison of retention times under the same chromatographic conditions for a known blend of rubber. These retention times are obtained from pyrograms of a known rubber or by direct injection of the pure hydrocarbon into the chromatograph.

#### 4.4 Method C

Calculation of the relative sizes of peaks due to styrene and vinylcyclohexene, identified in method A.

A relative excess of 2-vinylcyclohexene over that given by styrene-butadiene copolymers indicates the additional presence of polybutadiene. An approximate indication of the relative amounts of the two polymers is obtained.

## 5 Apparatus and materials

### 5.1 Pyrolysis devices

The following types of pyrolysis device are suitable.

#### 5.1.1 Silica tubes

These are electrically heated at a pre-fixed temperature. The volatile products, entrained by the carrier gas, are conveyed to the chromatograph through heated tubing.

#### 5.1.2 Electrically heated platinum filaments

Pyrolysis is carried out within the chromatograph inlet and the volatile products are immediately swept into the column by the carrier gas.

#### 5.1.3 Curie point device

This comprises small sample holders of ferromagnetic material heated to the Curie temperature. This device is particularly recommended if method C is to be used.

### 5.2 Gas chromatograph

Gas chromatographs employing either flame ionization or thermal conductivity detectors can be used. See however the last sentence of 5.4. Dual-column operation and temperature programming are strongly recommended, especially when method C is to be used, but are not essential.

### 5.3 Gas chromatographic columns

A wide variety of column lengths, diameters, supports and liquid phases has been found suitable for the methods described in this International Standard. The main requirement is that there shall be sharp separation between isobutene, butadiene, isoprene, 2-vinylcyclohexene, styrene and dipentene. In addition, the liquid phase shall not be significantly volatile at the chosen column temperature.

NOTE — For the selection of columns, reference should be made to the recommendations in Preferred stationary liquids for gas chromatography, *Journal of Chromatographic Science*, **13**, (March 1975), p. 115.

### 5.4 Carrier gas

Either helium or nitrogen shall be used as the carrier gas. Both are satisfactory, but have to be free from oxygen in order to prevent combustion.

Nitrogen is the preferred carrier gas when the Curie point device (5.1.3) is used. A thermal conductivity detector should not be used, however, when the carrier gas is nitrogen.

### 5.5 Integrator

Measurement of peak areas by means of a suitable integrator or computer is strongly recommended, but is not essential.

## 6 Procedure

### 6.1 Extraction of test sample

Although it is not essential, some benefits may be obtained by carrying out an extraction in accordance with ISO 1407. If the test sample is extracted prior to obtaining the pyrogram, any known rubber, used for identification, shall also be extracted.

### 6.2 Test portion

Take a test portion of mass appropriate to the apparatus used.

NOTE — Greater reproducibility of results will be obtained by using small test portions, normally less than 1 mg.

### 6.3 Pyrolysis

#### 6.3.1 Pyrolysis using silica tubes (5.1.1)

Place the test portion (6.1) in a small silica or porcelain boat in the cold part of the silica tube (5.1.1). Stopper the tube and flush with the carrier gas (5.4). Transfer the boat to the hot part of the tube, maintained at a temperature between 500 and 800 °C, preferably between 550 and 650°C. The period of pyrolysis depends upon the pyrolysis device but both the period and the temperature shall be kept constant once established. Convey the volatile pyrolysis products into the gas chromatograph (5.2) through tubing heated to a known, fixed temperature, which shall be higher than that at the gas chromatograph inlet to minimize condensation. Record the pyrogram.

#### 6.3.2 Pyrolysis using electrically heated platinum filaments (5.1.2)

Place the test portion (6.1) into the pyrolysis probe. Insert in the injection port of the gas chromatograph (5.2) and allow the base line to stabilize. Energize the probe, using the procedure recommended by the manufacturer of the unit, to attain temperatures of 800 to 1 200 °C. It is essential that the temperature remains constant once established if the method is to be used for comparison purposes. Record the pyrogram.

#### 6.3.3 Pyrolysis using Curie point device (5.1.3)

Place the test portion (6.1) in the coils of ferromagnetic wire, or wrap the wire securely around the test portion, and pyrolyse using the procedure recommended by the manufacturer of the unit. Energize the apparatus to obtain temperatures of 550 to 650 °C (depending on the composition of the alloy used for the wire) and introduce the pyrolysis products into the gas chromatograph (5.2). It is essential that the temperature remains constant once established if the method is to be used for comparison purposes. Record the pyrogram.

## 6.4 Separation of volatile pyrolysis components

### 6.4.1 General

The procedure to be used will depend on the columns used. As an example, the separation of volatile pyrolysis components of polyisoprene is described (6.4.2 and 6.4.3). Equivalent materials may be used.

### 6.4.2 Polar liquid phase

Column: stainless steel tubing, of length 4 to 6 m with an inside diameter of 1 mm minimum, packed with 10 % to 20 % di(2-ethylhexyl) sebacate on a diatomaceous silica support of particle size 150 to 180 µm.

Carrier gas flow rate: 0,2 to 0,3 cm<sup>3</sup>/s.

Inlet temperature: 170 °C.

Maintain the temperature of the oven at 50 °C until isoprene is completely eluted, then raise the temperature to 150 °C at a rate of 20 to 40 °C/min, and maintain at this temperature until dipentene is eluted.

### 6.4.3 Non-polar liquid phase

Column: stainless steel tubing of length 3 m with an inside diameter of 1 mm minimum, packed with 10 % high vacuum hydrocarbon grease on a diatomaceous silica support of particle size 150 to 180 µm.

Carrier gas flow rate: 0,1 to 0,8 cm<sup>3</sup>/s.

Inlet temperature: 170 to 200 °C.

Maintain the temperature of the oven at 50 °C until isoprene is completely eluted, then raise the temperature at a rate of 4 to 6 °C/min to 130 to 150 °C, and maintain at this temperature until dipentene is eluted.

## 7 Identification of polymers (interpretation of the pyrogram)

### 7.1 General

Each type of polymer produces a distinctive pyrogram under specified pyrolysis- and gas-chromatographic conditions.

### 7.2 Method A

Compare the pyrogram from the test portion with the pyrogram of a known rubber or blend, obtained under exactly the same operating conditions.

#### NOTES

1 It is recommended that, in addition to maintaining a library of pyrograms, the analyst should obtain a pyrogram of the known which appears most like the unknown, at the time of the analysis of the unknown. Thus slight variations in operating parameters, which might influence the pyrogram, may be avoided.

2 Some rubbers produce very characteristic hydrocarbons and their identification is relatively easy. Examples of this type are as follows:

- a) polyisoprene rubbers, which yield mainly isoprene and dipentene;
- b) styrene-butadiene copolymers, which yield mainly butadiene, 2-vinylcyclohexene and styrene;

c) polybutadiene rubbers, which yield mainly butadiene and 2-vinylcyclohexene;

d) isobutene-isoprene copolymers, which yield mainly isobutene.

3 Some rubbers do not yield very characteristic hydrocarbons, and careful inspection of the pyrogram is required. Supplementary tests, such as those for halogen and nitrogen, may be an aid to more definite identification.

### 7.3 Method B

Compare the retention times of hydrocarbons emanating from the test portion with those of styrene, butadiene, 2-vinylcyclohexene, isoprene, dipentene and isobutene.

Determine the retention times of these hydrocarbons by injection of each individual hydrocarbon into the chromatograph, or by pyrolysis of rubbers which will yield these hydrocarbons. This information shall be obtained using the same apparatus and operating conditions as used for the analysis of the unknown rubber. Tabulate the data for ready reference.

Pyrolyse the test portion in accordance with 6.3 and measure the retention times of the characteristic hydrocarbons.

Compare the retention times obtained with the tabulated retention times of the known hydrocarbons and identify the constituents of the blend.

See also note 2 of 7.2.

### 7.4 Method C

If method A indicates the presence of styrene-butadiene copolymers, or if method B indicates the presence of 2-vinylcyclohexene and styrene peaks in the pyrogram, and it is required to determine whether polybutadiene is present as well as styrene-butadiene copolymer, proceed as follows.

**7.4.1** Record the pyrogram of a reference vulcanizate prepared with a suitable styrene-butadiene copolymer having the same microstructure and bound styrene content as the test portion and three or more reference vulcanizates based on known blends of the same styrene-butadiene copolymer and polybutadiene in the range from 80 % styrene-butadiene copolymer to 20 % polybutadiene to 20 % styrene-butadiene copolymer to 80 % polybutadiene.

**7.4.2** Measure the areas of the 2-vinylcyclohexene and styrene peaks.

**7.4.3** Calculate the ratio  $R$  of styrene to 2-vinylcyclohexene from the formula

$$R = \frac{A_s}{A_s + 3 A_v}$$

where

$A_s$  is the area of the styrene peak;

$A_v$  is the area of the 2-vinylcyclohexene peak;

3 is an empirical factor.

**7.4.4** Prepare a calibration curve by plotting the ratio  $R$  against the composition of the known blends.

**7.4.5** Pyrolyse the test portion in accordance with 6.3 and measure the retention times of 2-vinylcyclohexene and styrene. Measure the relative areas of the peaks using electronic integrators or computers preferably, or by some other appropriate method. Calculate the ratio  $R$  as defined in 7.4.3.

Determine the ratio of styrene-butadiene copolymer to polybutadiene from the calibration curve (7.4.4).

The ratio determined in this manner will only be approximate.

**7.4.6** If on the calibration curve (7.4.4) less than 20 % polybutadiene is found, polybutadiene may be present, but its presence is questionable. If the polybutadiene content is greater than 20 %, as read from the calibration curve, polybutadiene is definitely present. Quantities of styrene-butadiene of less than 20 % are easily identified provided that the styrene peak can be found in the pyrograms.

**7.4.7** The ratio of styrene-butadiene copolymer to polybutadiene determined in 7.4.5 may be regarded as giving an approximation of the relative quantities of these two polymers in the blend and should be rounded to the nearest 2 %.

## 8 Test report

The test report shall include the following information:

- a reference to this International Standard;
- all details required for the full identification of the sample;
- whether method A, B or C was used;
- identification of the polymer(s) in the sample;
- date of test.

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