TC45

INTERNATIONAL STANDARD 5475

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Rubber — Identification of polymers — Pyrolytic/gas chromatographic method — Single polymers

Caoutchouc — Identification des polymères — Méthode par pyrolyse et chromatographie en phase gazeuse — Caoutchouc à base d'un seul polymère

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5475 was developed by Technical Committee ISO/TC 45, *Rubber and rubber products*, and was circulated to the member bodies in June 1977.

It has been approved by the member bodies of the following countries :

Australia	Greece	Romania
Austria	Hungary	South Africa, Rep. of
Belgium	India	Spain
Brazil	Ireland	Sweden
Bulgaria	Italy	Switzerland
Canada	Korea, Rep. of	Turkey
Czechoslovakia	Malaysia	United Kingdom
Egypt, Arab Rep. of	Mexico	U.S.A.
France	Netherlands	U.S.S.R.
Germany, F.R.	Poland	Yugoslavia

No member body expressed disapproval of the document.

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Rubber — Identification of polymers — Pyrolytic/gas chromatographic method — Single polymers

1 SCOPE AND FIELD OF APPLICATION

This International Standard is a guide to the identification of the polymer in raw rubbers or in vulcanized and unvulcanized compounds, based on a single rubber, by the gas chromatographic patterns of their pyrolysis products (pyrograms). Implementation of this International Standard presupposes a working knowledge of the principles and techniques of gas chromatography, sufficient to carry out this recommended practice and to interpret the results correctly. The layout adopted takes account of ISO 2718, *Standard layout for a method of chemical analysis by gas chromatography.*

An enlarged International Standard, which will also cover the identification of blends of polymers, is in course of preparation.

1.1 The method enables the following types of polymer to be identified :

1.1.1 Polyisoprene of natural or synthetic origin.

1.1.2 Butadiene-styrene copolymers.

1.1.3 Polybutadiene.

1.1.4 Polychloroprene.

1.1.5 Butadiene-acrylonitrile copolymers.

1.1.6 Ethylene-propylene copolymers and related terpolymers.

1.1.7 Isobutene-isoprene copolymers.

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

1.3 The method will not differentiate the following polymers :

1.3.1 Natural polyisoprene from synthetic polyisoprene.

1.3.2 Butadiene-styrene copolymers produced by solution polymerization from those produced by emulsion polymerization. It is sometimes possible to distinguish butadiene-styrene copolymers containing different amounts of styrene as well as random polymers from block polymers.

1.3.3 Polybutadienes with different micro-structures.

1.3.4 Different types of polychloroprene.

1.3.5 Butadiene-acrylonitrile copolymers with different monomer ratios.

1.3.6 Ethylene-propylene copolymers with different monomer ratios, or the copolymers from the related terpolymers.

1.3.7 Isobutene-isoprene copolymers (butyl rubbers) from halogenated butyl rubbers.

1.3.8 Polyisoprene containing different amounts of *cis-trans* isomers.

1.4 The method does not identify ebonite or hard rubbers.

2 REFERENCE

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

3 PRINCIPLE

3.1 The method is based upon comparison of the gas chromatographic pattern of the pyrolysis products of a known rubber with that of an unknown rubber. The results of this separation will hereafter be referred to as the pyrogram.

3.2 The pyrogram of the known rubber is filed for future reference. The pyrogram of the unknown rubber is compared with this for identification.

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

3.4 The qualitative composition of the pyrolysis products depends upon the type of rubber being studied.

3.5 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.

4 APPARATUS AND MATERIALS

4.1 Pyrolysis devices

The applicability of this International Standard has been checked on the following types :

4.1.1 Silica tubes, electrically heated, at a pre-fixed temperature.

The volatile products, entrained by the carrier gas, enter the chromatograph through heated tubing.

4.1.2 Platinum filaments, electrically heated.

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

4.1.3 Small sample holders of ferromagnetic material heated to the Curie point temperature.

The volatile products, entrained by the carrier gas, enter the gas chromatograph through heated tubing.

4.2 Gas chromatograph

The application of this International Standard has been checked on a wide variety of gas chromatographs employing both flame ionization and thermal conductivity detectors. Any commercially available instrument capable of complying with the requirements of 4.3 is satisfactory. Dual-column operation and temperature programming is strongly recommended, but not mandatory.

4.3 Gas chromatographic columns

The applicability of this International Standard has been checked on a wide variety of column lengths, diameters, supports and liquid phases. The only requisite is that there shall be sharp separation between the following : isobutene, butadiene, isoprene, vinylcyclohexene, styrene and dipentene.

4.4 Carrier gas

The applicability of this International Standard has been checked with both helium and nitrogen as the carrier gas. Both are satisfactory.

5 PROCEDURE

5.1 Test portion

A test portion of mass up to 0,003 g is normally required. The actual mass required depends on the apparatus used.

5.2 Extraction

Although not mandatory, some benefits may be obtained from extraction according to ISO 1407. If the test portion has been extracted prior to obtaining the pyrogram, the known rubber must also be extracted.

5.3 Pyrolysis

The following conditions apply to the three types of pyrolysis device of 4.1.

5.3.1 *Silica tubes* (4.1.1)

Place 0,001 to 0,005 g of rubber in a small silica or porcelain boat in the cold part of the pyrolysis tube. Stopper the tube and flush with the carrier gas (4.4). Transfer the boat to the hot part of the tube, maintained at a temperature between 500 and 800 °C and preferably between 550 and 650 °C. The length of time depends upon the pyrolysis device; however, time and temperature shall be kept constant. Convey the volatile pyrolysis products into the gas chromatograph (4.2) 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.

5.3.2 *Electrically heated platinum filaments* (4.1.2)

Place the test portion (5.1) in the pyrolysis probe. Insert in the injection port of the gas chromatograph (4.2) 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. Record the pyrogram.

5.3.3 *Curie point apparatus* (4.1.3)

Place the test portion (5.1) in the coils of ferromagnetic wire or wrap the wire securely around the test portion and pyrolyse according to the manufacturer's directions for use 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 (4.2). Record the pyrogram.

5.4 Separation of the volatile pyrolysis components

5.4.1 *Columns*

As stated in 4.3, a wide variety of columns may be used. As an example, the following describes the separation of volatile pyrolysis components of polyisoprene. Equivalent materials may be used.

5.4.2 *Polar liquid phase*

Stainless steel tubing, 4 to 6 m long, of outside diameter less than 4 mm, packed with 10 to 20 % di(2-ethylhexyl) sebacate on a 150 to 180 µm diatomaceous silica support.

Carrier gas flow of 0,2 to 0,3 cm^3/s.

Inlet temperature of 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.

5.4.3 *Non-polar liquid phase*

Stainless steel tubing, 3 m long, of outside diameter 3,2 mm, packed with 10 % high vacuum hydrocarbon grease on a 150 to 180 µm diatomaceous silica support.

Carrier gas flow of 0,1 to 0,8 cm^3/s.

Inlet temperature of 170 to 200 °C.

Maintain the temperature of the oven at 50 °C for 3 min, during which isoprene is 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.

6 POLYMER IDENTIFICATION (INTERPRETATION OF THE PYROGRAM)

6.1 Each polymer type shows a distinctive pyrogram, under the same pyrolysis and gas chromatographic conditions.

6.2 Identification is achieved by comparing the pyrogram of the unknown rubber with the pyrogram of a known rubber, under exactly the same operating conditions.

6.3 It is recommended that, in addition to maintaining a library of pyrograms, the analyst should compare the unknown with a known, which appears most like his unknown, at the time of analysis. In this manner, slight variations in operating parameters, which might influence the pyrogram, may be avoided.

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

6.4.1 Polyisoprene rubbers, which yield mainly isoprene and dipentene.

6.4.2 Butadiene-styrene copolymers, which yield mainly butadiene, vinylcyclohexene and styrene.

6.4.3 Polybutadiene rubbers, which yield mainly butadiene and vinylcyclohexene.

6.4.4 Isobutene-isoprene copolymers, which yield mainly isobutene.

6.5 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 TEST REPORT

The test report shall include the following particulars :

a) reference to this International Standard;

b) all details required for full sample identification;

c) identification of the rubber(s) in the sample;

d) date of test.