INTERNATIONAL STANDARD

ISO 7270-1

First edition
2003-04-15

Rubber — Analysis by pyrolytic gas-chromatographic methods —

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

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

Partie 1: Identification des polymères (un seul polymère ou un mélange de polymères)

Reference number
ISO 7270-1:2003(E)

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Published in Switzerland

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Foreword

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

This part of ISO 7270 cancels and replaces ISO 7270:1987, 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*

At the time of publication of this part of ISO 7270, Part 2 was in preparation.

Rubber — Analysis by pyrolytic gas-chromatographic methods —

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

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 a method for the identification of polymers, or blends of polymers, in raw rubbers and in vulcanized or unvulcanized compounds from pyrograms (pyrolysis-gas chromatographic patterns) obtained under the same conditions. This allows qualitative identification of single rubbers or blends, with exceptions discussed below. This part of ISO 7270 is not intended for quantitative analysis.

The method applies first and foremost to single polymers. When the pyrogram indicates a characteristic hydrocarbon, the method is also applicable to blends. For details, see Clause 4. The method may be also applicable to other types of polymer, but this must be verified by the analyst in each particular case.

NOTE The use of this part of ISO 7270 pre-supposes sufficient working knowledge of the principles and techniques of gas chromatography to enable the analyst to carry out the operations described and to 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 1407:1992, *Rubber — Determination of solvent extract*

ISO 1629:1995, *Rubber and latices — Nomenclature*

3 Principle

3.1 Raw or vulcanized rubbers and/or their blends are pyrolysed and the pyrolysis products are subjected to gas-chromatographic analysis under predefined conditions. The chromatograms produced are referred to as pyrograms.

3.2 Pyrograms are interpreted by comparison with reference pyrograms produced from the same rubbers and/or blends, prepared and analysed under the same conditions.

4 Single polymers and blends

4.1 General

The rubbers in the following listing are grouped in accordance with ISO 1629.

4.2 Group M

a) Chlorinated polyethylene (CM) and chlorosulfonated polyethylene (CSM).

NOTE 1 The pyrogram will not differentiate between these chlorinated polyethylenes.

b) Ethylene-propylene copolymers (EPMs) and ethylene-propylene-diene terpolymers (EPDMs).

NOTE 2 The pyrogram can differentiate terpolymers from copolymers when the pyrogram indicates characteristic “diene” monomer pyrolysis products.

c) Acrylic rubbers (ACMs).

4.3 Group O

Epichlorohydrin rubbers [homopolymer (CO), copolymer (ECO) and terpolymers].

NOTE The pyrogram will not differentiate betwen these various types of epichlorohydrin polymer.

4.4 Group Q

Polysiloxanes.

4.5 Group R

a) Polybutadiene (BR).

NOTE 1 The pyrogram will not differentiate between polymers containing different proportions of isomers.

b) Polychloroprene (CR).

NOTE 2 The pyrogram will not differentiate between the various types of polychloroprene rubber, or polychloroprene rubber from other types of chlorinated rubber.

c) Isobutene-isoprene copolymer (IIR).

NOTE 3 The pyrogram will not differentiate butyl rubber from its halogenated forms or from isobutene.

d) Polyisoprene (NR or IR).

NOTE 4 The pyrogram will not differentiate natural from synthetic polyisoprenes.

e) Acrylonitrile-butadiene copolymer (NBR).

NOTE 5 In some cases, NBR can be differentiated from hydrogenated acrylonitrile-butadiene copolymer (HNBR). The pyrogram will not differentiate a single NBR from an NBR/BR blend or a blend of various types of NBR.

f) Styrene-butadiene copolymer (SBR).

NOTE 6 In some cases, block polymers can be differentiated from random polymers. The pyrogram will not differentiate a single SBR from an SBR/BR blend or a blend of various types of SBR.

4.6 Blends

With the exception of blends containing both styrene-butadiene copolymer and polybutadiene, the method enables blends of the following polymers to be identified:

a) polyisoprene (NR or IR);

b) polybutadiene (BR);

c) isobutene-isoprene copolymers (IIRs);

d) styrene-butadiene copolymers (SBRs).

5 Reagents

All reagents shall be of analytical grade.

5.1 Solvents for extraction purposes

The following solvents are suitable (see 7.2):

5.1.1 Acetone.

5.1.2 Methanol.

5.1.3 Methyl ethyl ketone.

5.2 Carrier gas

5.2.1 Nitrogen.

5.2.2 Helium.

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

6 Apparatus

6.1 Extraction apparatus

As specified in ISO 1407.

6.2 Pyrolysis/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 electrically heated pyrolysis device are suitable:

6.2.1.1 Micro-furnace, with quartz tubes in which the test portion is pyrolysed.

6.2.1.2 Curie-point pyrolyser, with a holder (pyrolysis probe) containing ferromagnetic material which surrounds the test portion and is heated to the Curie-point temperature to pyrolyse the test portion.

6.2.1.3 Platinum-filament pyrolyser, with a holder (pyrolysis probe) containing a platinum filament which surrounds the test portion and is heated to pyrolyse the test portion.

6.2.3 Gas chromatograph

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

Selective detectors such as ECD (electron capture detector), FPD (flame photometric detector), FTD (flame thermionic detector), AED (atomic emission detector) can give useful information. For identification of pyrolysis products, a mass spectrometer detector can be utilized.

6.2.4 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.

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.

NOTE 3 Usually, capillary columns require little evaluation, while it often is necessary to evaluate many conditions for polar and non-polar packed columns.

The conditions chosen will depend on the column used. Typical operating conditions for the gas chromatograph with both polar and non-polar columns can be found in Tables 1 to 5. Typical pyrograms obtained can be found in Figures 1 to 44.

6.2.5 Data-handling equipment

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

7 Procedure

7.1 Accurate comparison of the pyrogram of an unknown polymer with the reference is only possible under the same conditions.

7.2 Extraction of test samples is recommended to remove additives which may interfere with the chromatographic separation. For oil-extended materials, extraction of the extender oil is essential otherwise this oil may cause serious interference in the pyrogram. Carry out the extraction following the general principles of either method A or method B in ISO 1407:1992. The chosen solvent shall not affect the polymer and shall remove as much of the additives as possible. After extraction, dry the test sample, as residual solvent may cause interference with the pyrolysis products (see 8.4).

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

7.4 Place the test portion in the pyrolysis device and pyrolyse. An appropriate pyrolysis temperature is 400 °C to 800 °C for a micro-furnace or Curie-point pyrolyser, and 800 °C to 1 200 °C for a platinum-filament pyrolyser.

7.5 Record the pyrogram for comparison with the pyrogram of a known polymer or polymer blend obtained under the same conditions.

8 Interpretation of results

8.1 Each polymer will be characterized by the retention times of its main peaks. Some polymers produce characteristic hydrocarbons and their identification is relatively easy. Examples of this type are as follows:

a) polyisoprene, which yields mainly isoprene and dipentene (isoprene dimer);

b) styrene-butadiene copolymers, which yield mainly butadiene, 4-vinyl-1-cyclohexene (butadiene dimer) and styrene;

c) polybutadiene, which yields mainly butadiene and 4-vinyl-1-cyclohexene (butadiene dimer);

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

8.2 Some polymers do not yield 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.

8.3 The characteristic hydrocarbons in the unknown polymer are identified by comparison of retention times for a known blend of polymer, or by direct injection of the pure hydrocarbon into the chromatograph. Results may be tabulated for ready reference.

8.4 The analyst should be aware of additives which may not be extractable and which may or may not affect the chromatographic pattern.

9 Test report

The test report shall contain the following information:

a) all details necessary for full identification of the sample analysed;

b) the type of pyrolysis device used;

c) the pyrolysis temperature;

d) the gas-chromatographic conditions used;

e) the data-handling equipment used;

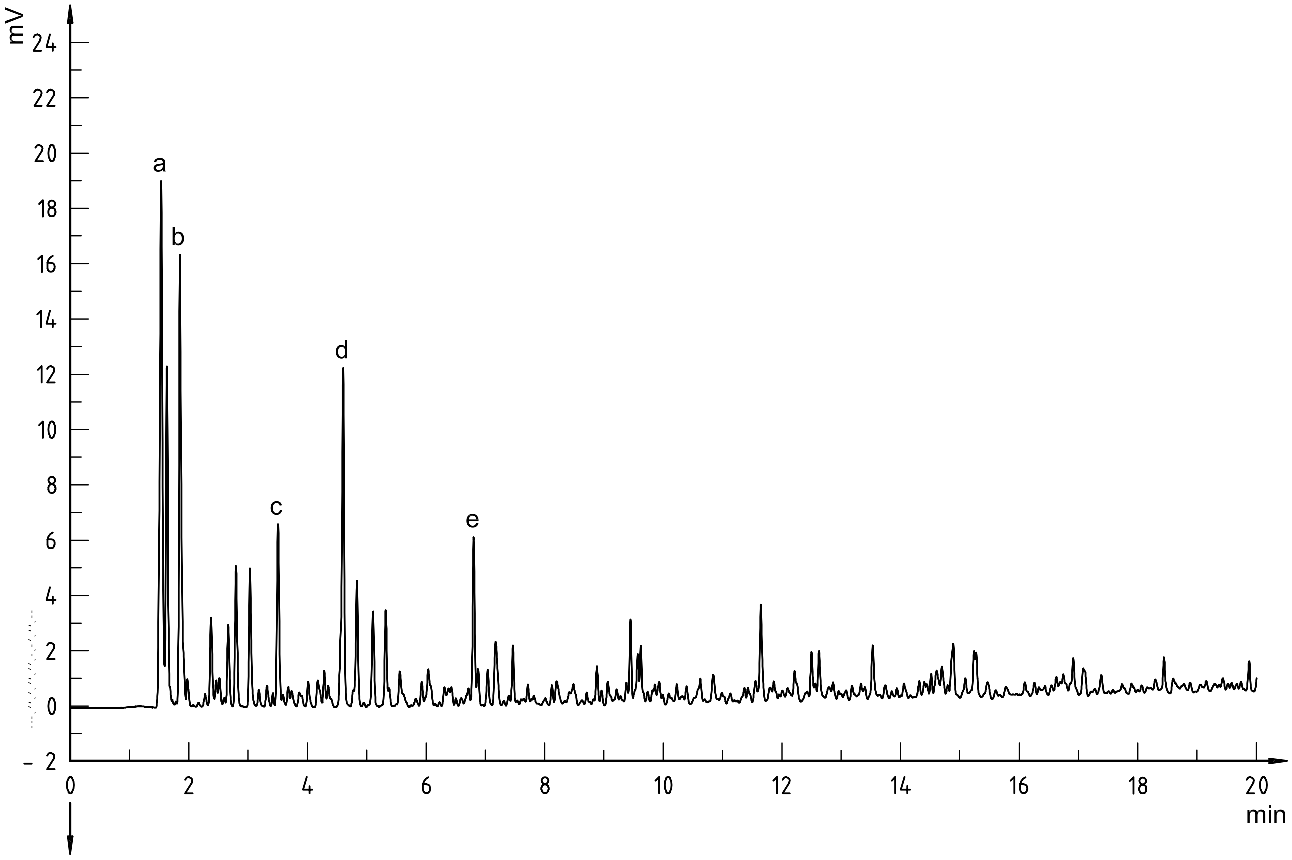
f) the polymer or polymer blend found in the sample.

Table 1 — List of pyrograms contained in this part of ISO 7270

Group	Rubber (example)	Number of figure			
		Micro-furnace	Curie point	Micro-furnace	Curie point
		Semi-polar capillary column	Semi-polar capillary column	Polar packed column	Non-polar packed column
Group M					
CM	Chlorinated polyethylene	1	—	—	—
CSM	Chlorosulfonated polyethylene	2	16	—	33
EPM	Ethylene-propylene copolymer	3	—	—	—
EPDM	Ethylene-propylene-diene terpolymer	4	17	—	34
ACM	Acrylic rubber	5	18	28	35
Group O					
CO	Epichlorohydrin rubber	6	19	—	36
Group Q					
	Polysiloxanes	7	20	—	37
Group R					
BR	Polybutadiene	8	21	—	38
CR	Polychloroprene	9	22	29	39
IIR	Isobutene-isoprene copolymer	10	23	—	40
	Halogenated isobutene-isoprene copolymer	11	—	—	—
NR or IR	Polyisoprene	12	24	30	41
NBR	Acrylonitrile-butadiene copolymer	13	25	31	42
HNBR	Hydrogenated acrylonitrile-butadiene copolymer	14	26	—	43
SBR	Styrene-butadiene copolymer	15	27	32	44

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

Pyrolysis	
Device	Micro-furnace
Pyrolysis temperature	600 °C
Gas-chromatographic column	
Liquid phase	5 % diphenylpolysiloxane Ultra ALLOY-5
Film thickness	1,0 µm
Column diameter	0,25 mm ID
Column length	30 m
Chromatographic conditions	
Carrier gas	Helium
Injector temperature	320 °C
Type of detector	FID
Detector temperature	350 °C
Temperature programme	Isothermal for 2 min at 50 °C then 10 °C/min from 50 °C to 280 °C then isothermal for 10 min at 280 °C



Retention times

a 1,53

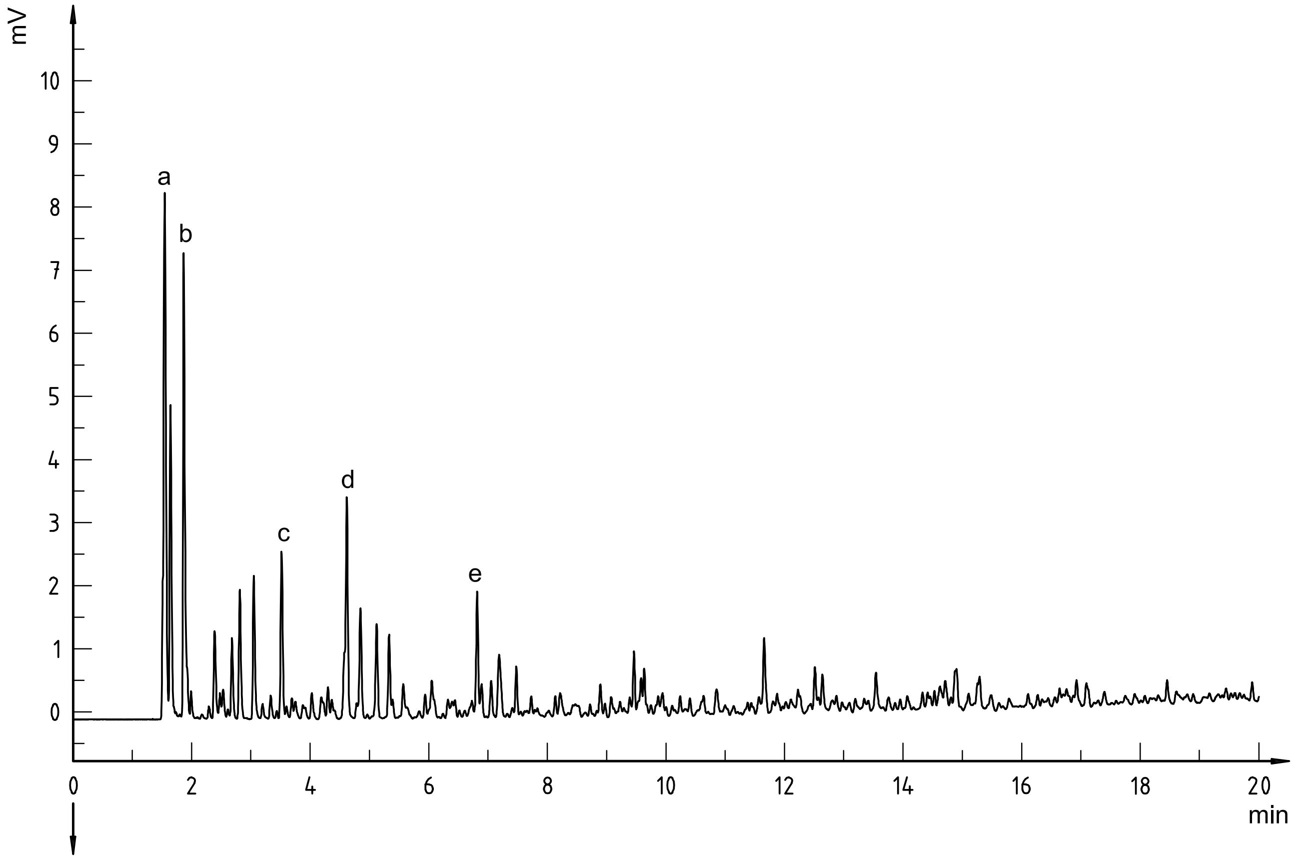
b 1,85

c 3,50

d 4,60 (benzene)

e 6,80 (toluene)

Figure 1 — Chlorinated polyethylene (CM)



Retention times

a 1,55

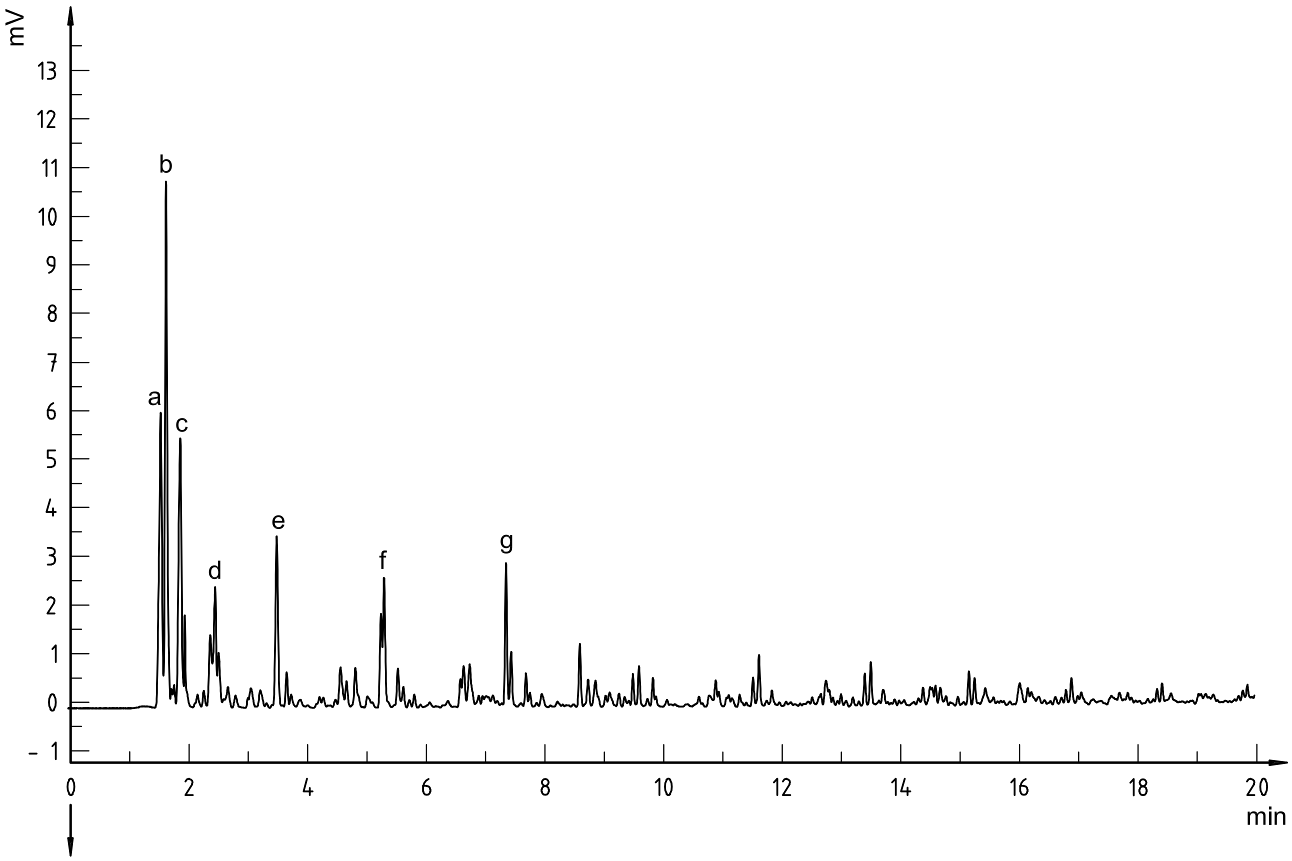
b 1,87

c 3,52

d 4,62 (benzene)

e 6,82 (toluene)

Figure 2 — Chlorosulfonated polyethylene (CSM)



Retention times

a 1,56

b 1,65

c 1,89 (C_4)

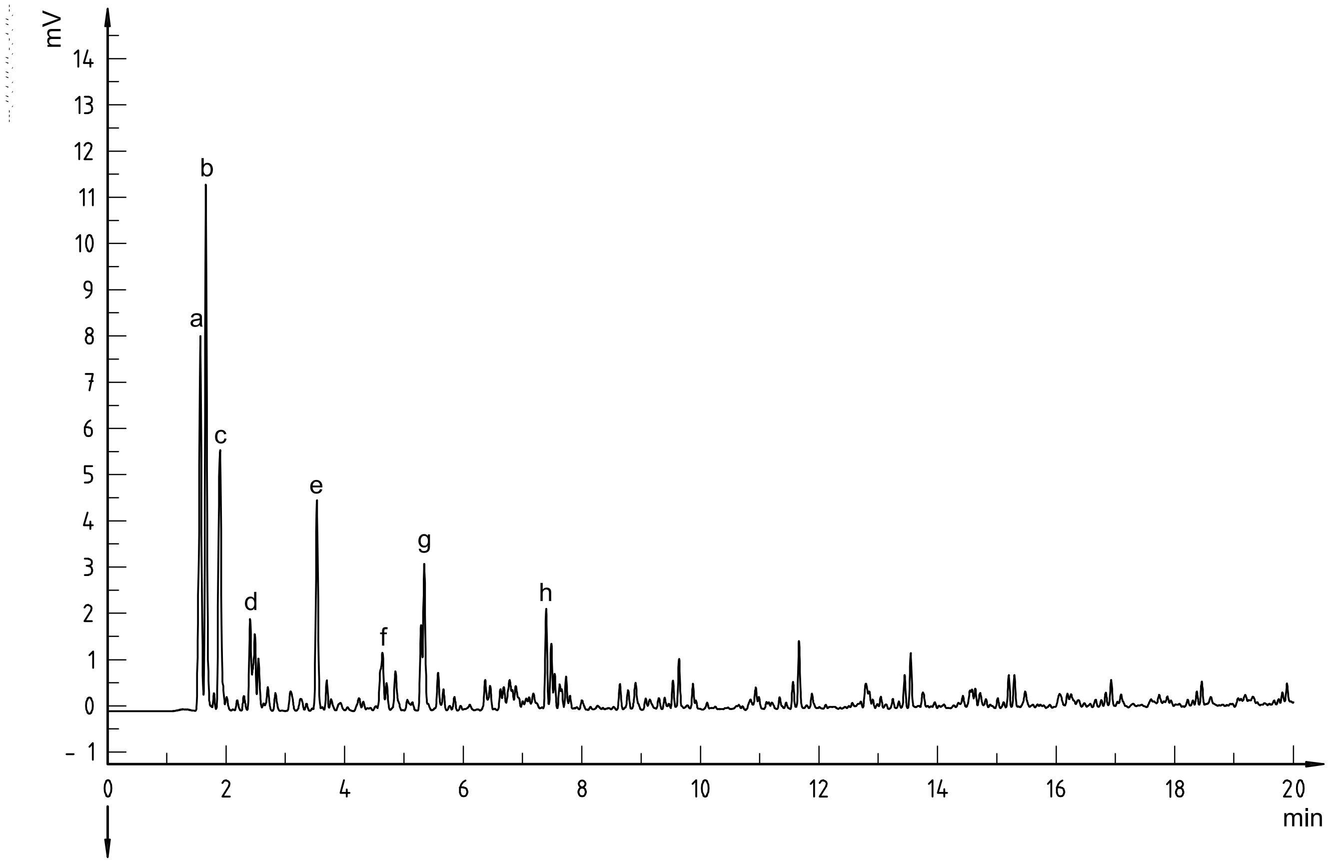
d 2,40 (C_5)

e 3,52 (C_6)

f 5,33 (C_7)

g 7,38 (C_8)

Figure 3 — Ethylene-propylene copolymer (EPM)



Retention times

a 1,57

b 1,66

c 1,90 (C_4)

d 2,40 (C_5)

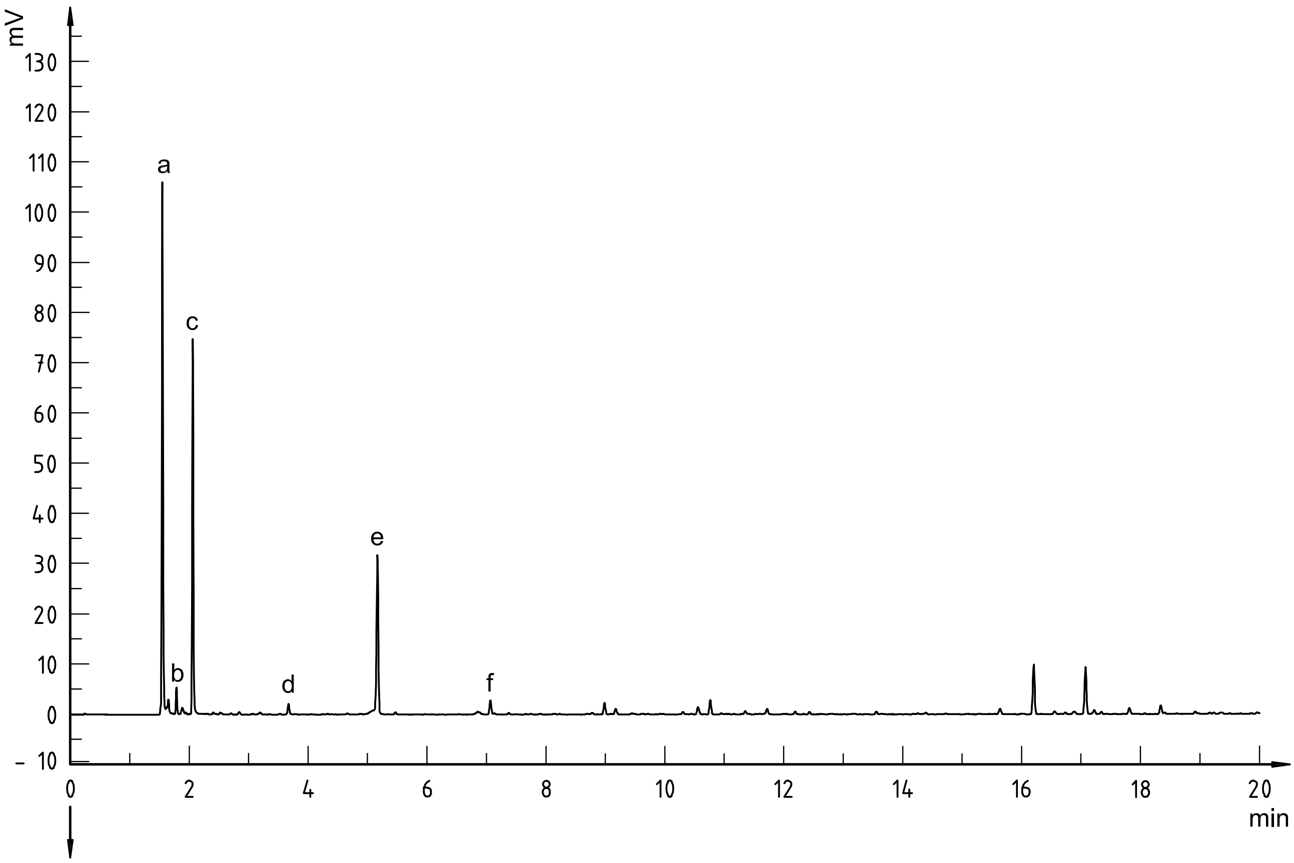
e 3,53 (C_6)

f 4,64

g 5,34 (C_7)

h 7,40 (C_8)

Figure 4 — Ethylene-propylene-diene terpolymer (EPDM)



Retention times

a 1,55

b 1,79

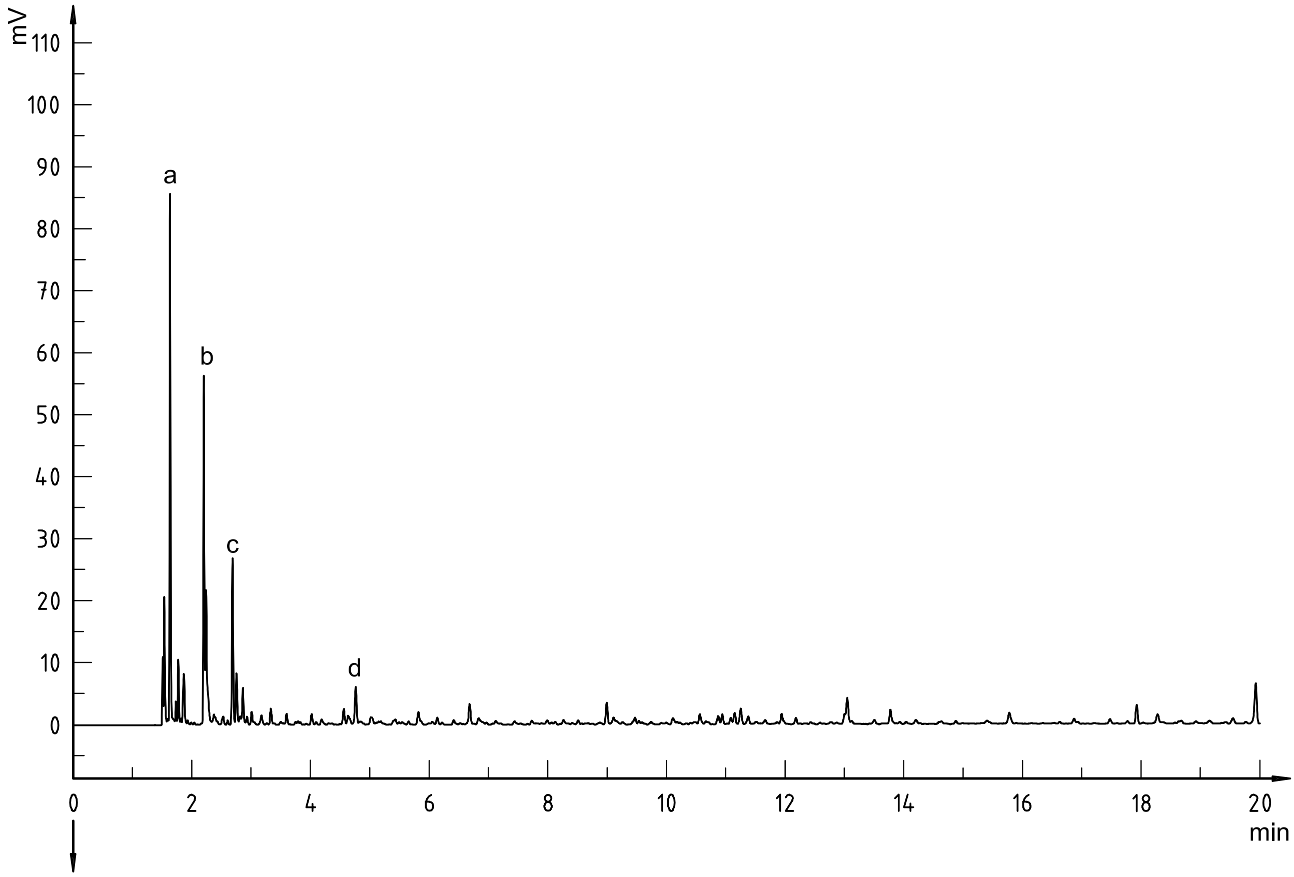
c 2,06 (ethanol)

d 3,67

e 5,17 (ethyl acrylate)

f 7,07

Figure 5 — Acrylic rubber (ACM)



Retention times

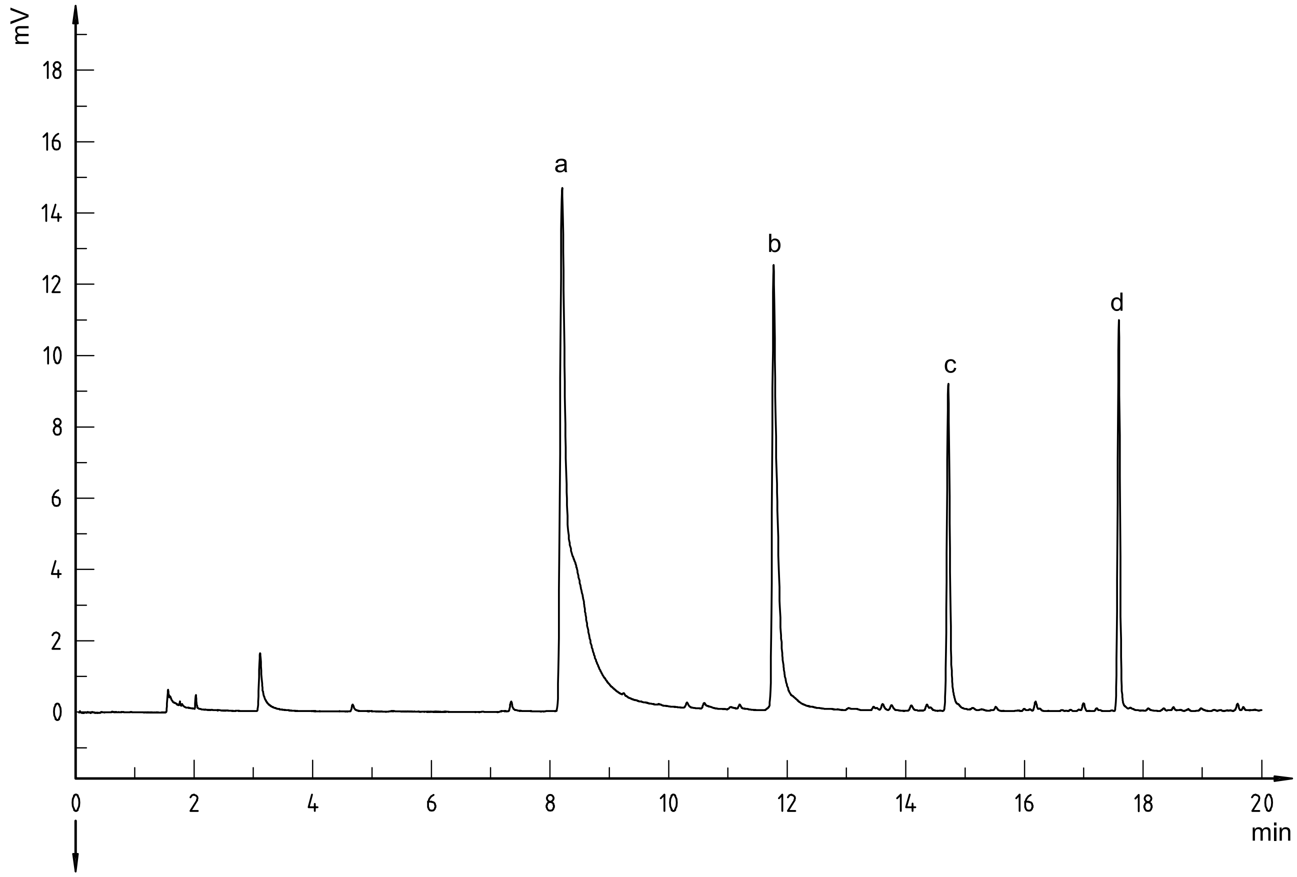
a 1,63

b 2,20

c 2,69 (3-chloroprene)

d 4,67

Figure 6 — Epichlorohydrin rubber (CO)



Retention times

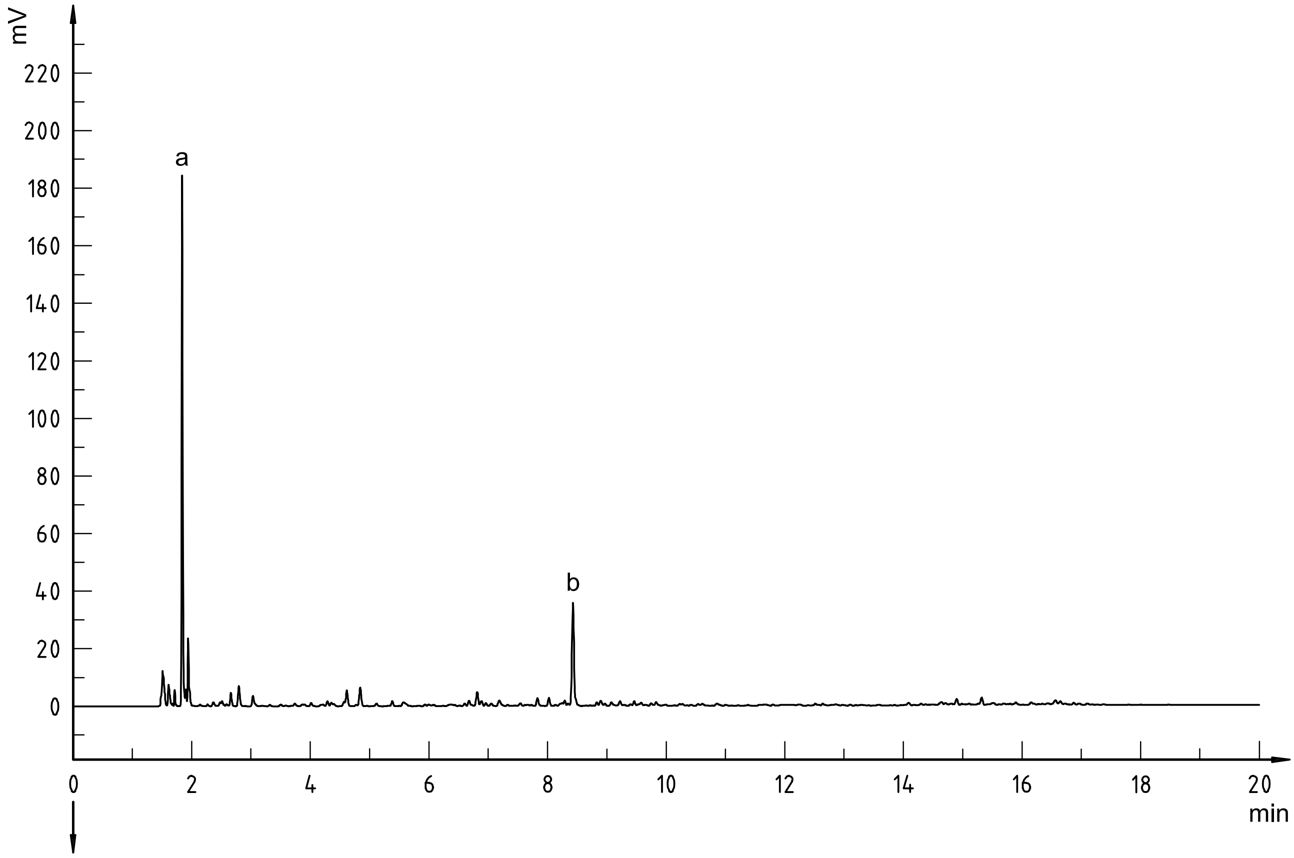
a 8,17 (n = 3)

b 11,75 (n = 4)

c 14,70 (n = 5)

d 17,59 (n = 6)

Figure 7 — Polysiloxane: $[Si(CH_3)_2O]_n$

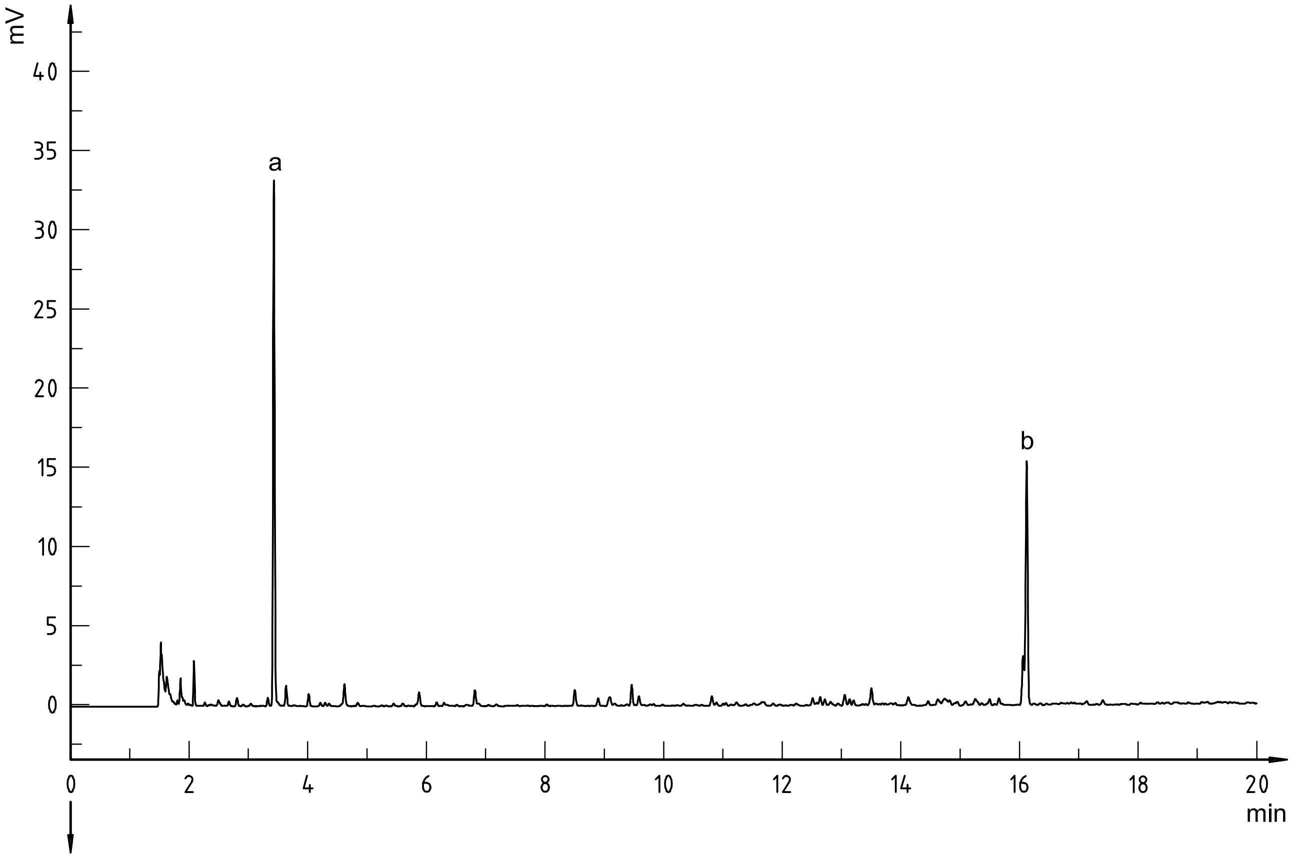


Retention times

a 1,84

b 8,43 (4-vinyl-1-cyclohexene) (dimer)

Figure 8 — Polybutadiene (BR)

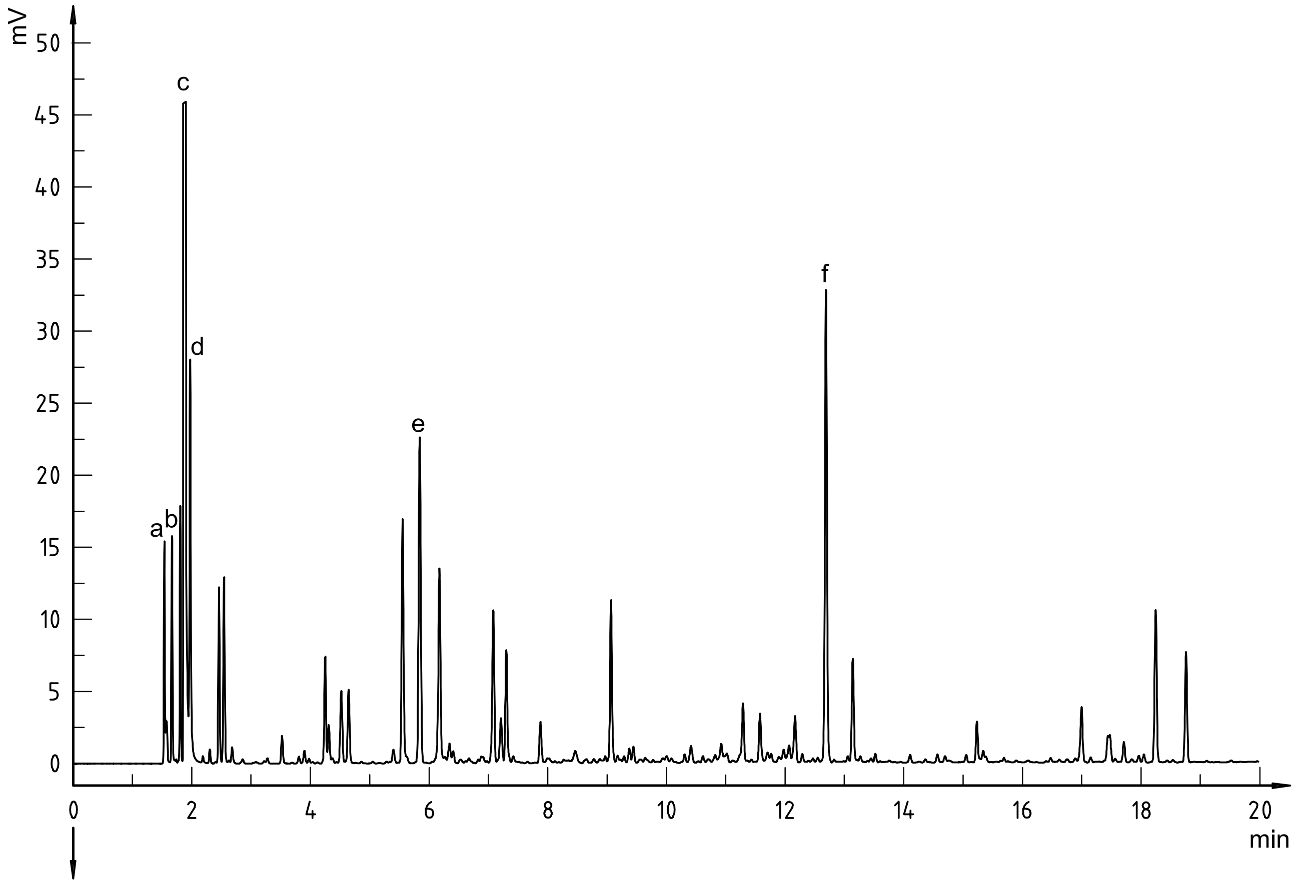


Retention times

a 3,43 (chloroprene)

b 16,13 (dimer)

Figure 9 — Polychloroprene (CR)



Retention times

a 1,51

b 1,78

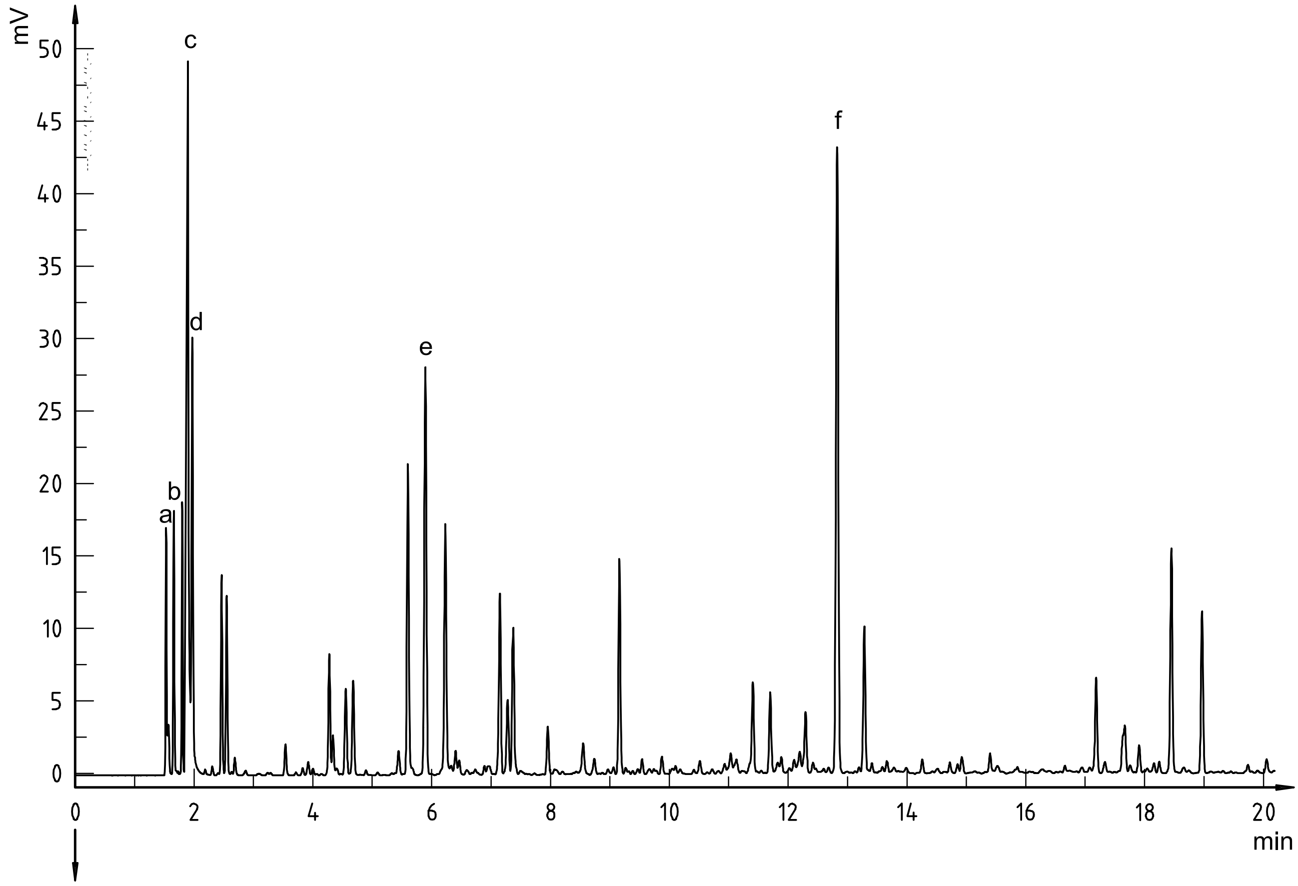
c 1,84 (isobutene)

d 1,95

e 5,83

f 12,69

Figure 10 — Isobutene-isoprene copolymer (IIR)



Retention times

a 1,51

b 1,78

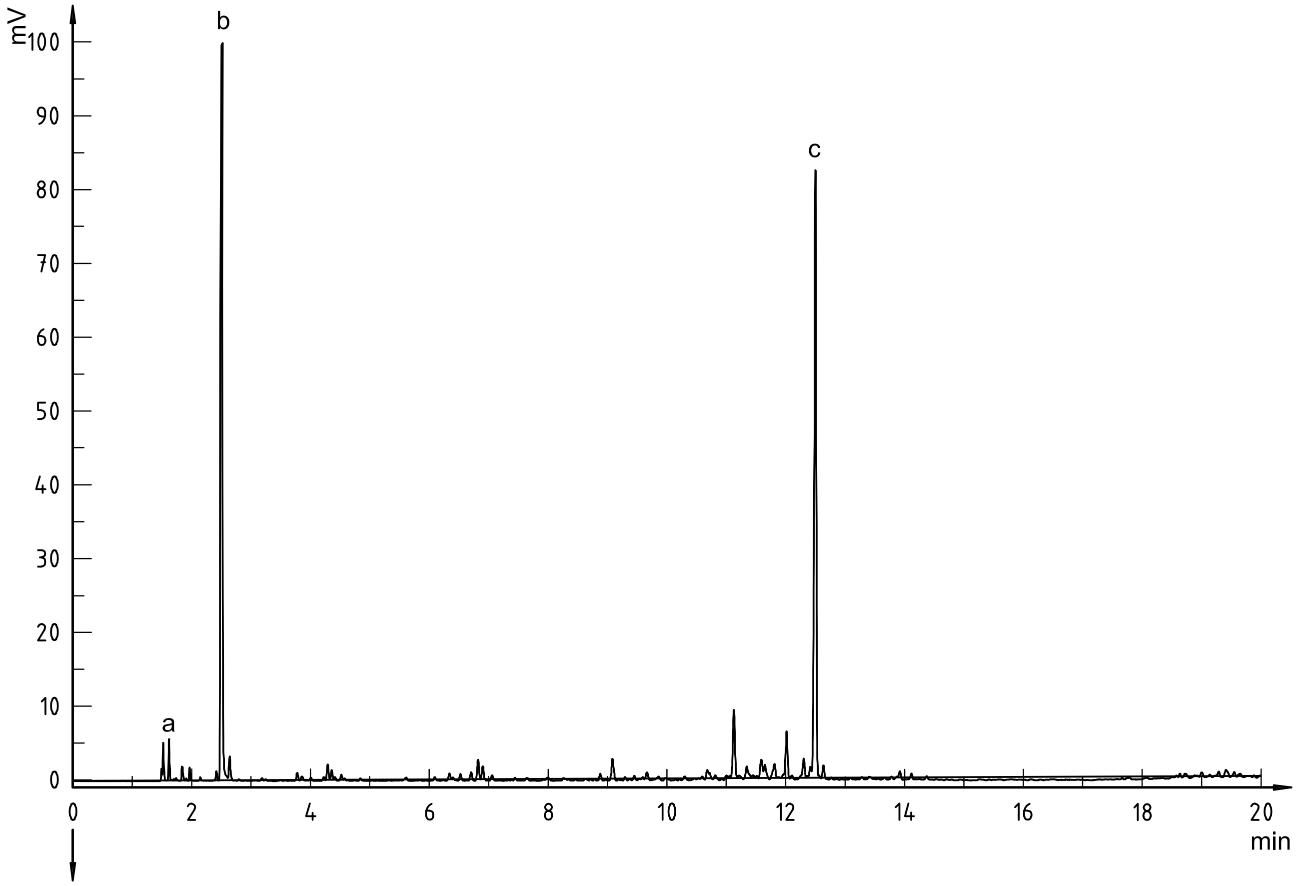
c 1,84 (isobutene)

d 1,95

e 5,84

f 12,71

Figure 11 — Chlorinated isobutene-isoprene copolymer (CIIR)



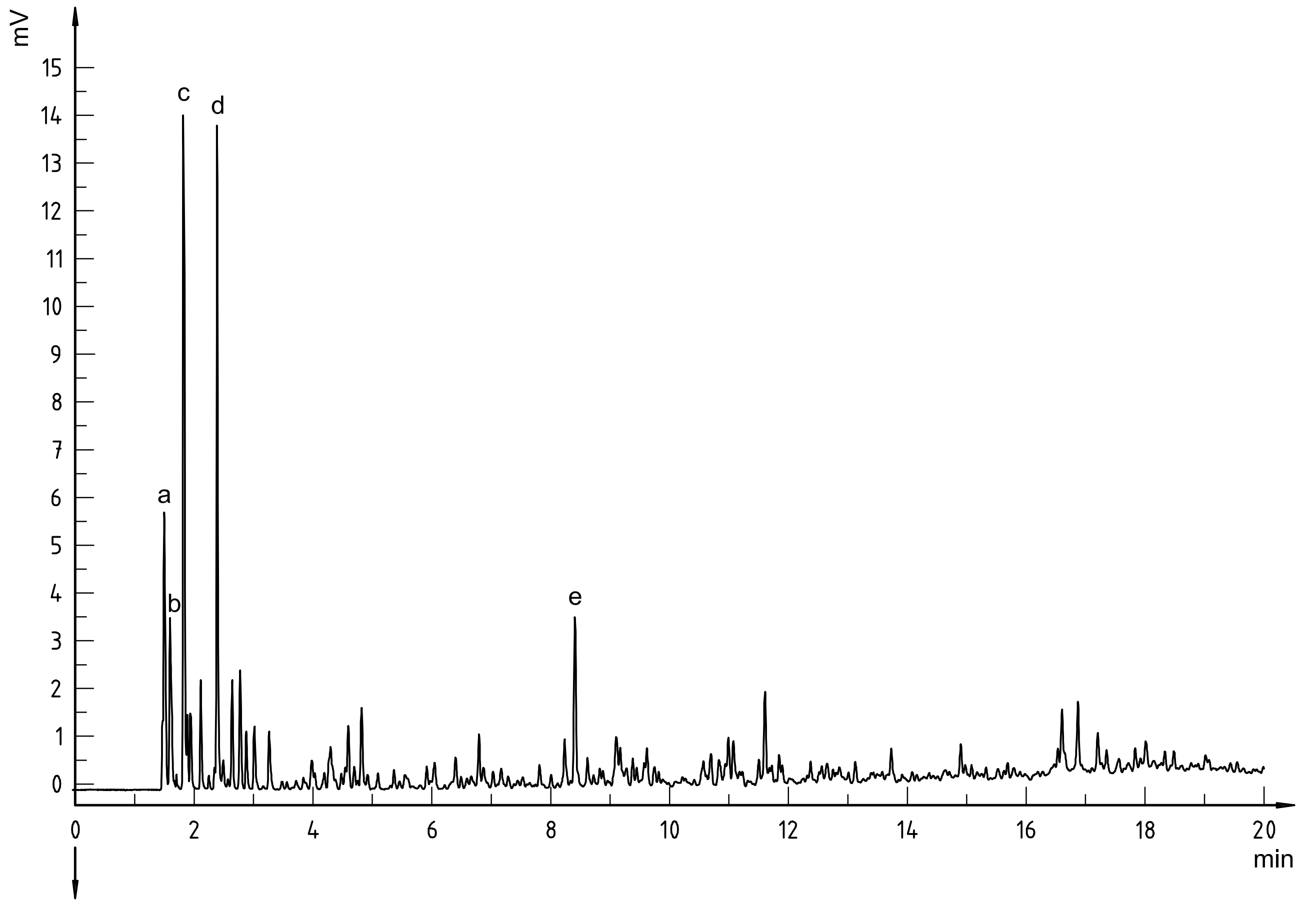
Retention times

a 1,62

b 2,50 (isoprene)

c 12,50 (dipentene) (dimer)

Figure 12 — Polyisoprene (NR)



Retention times

a 1,54

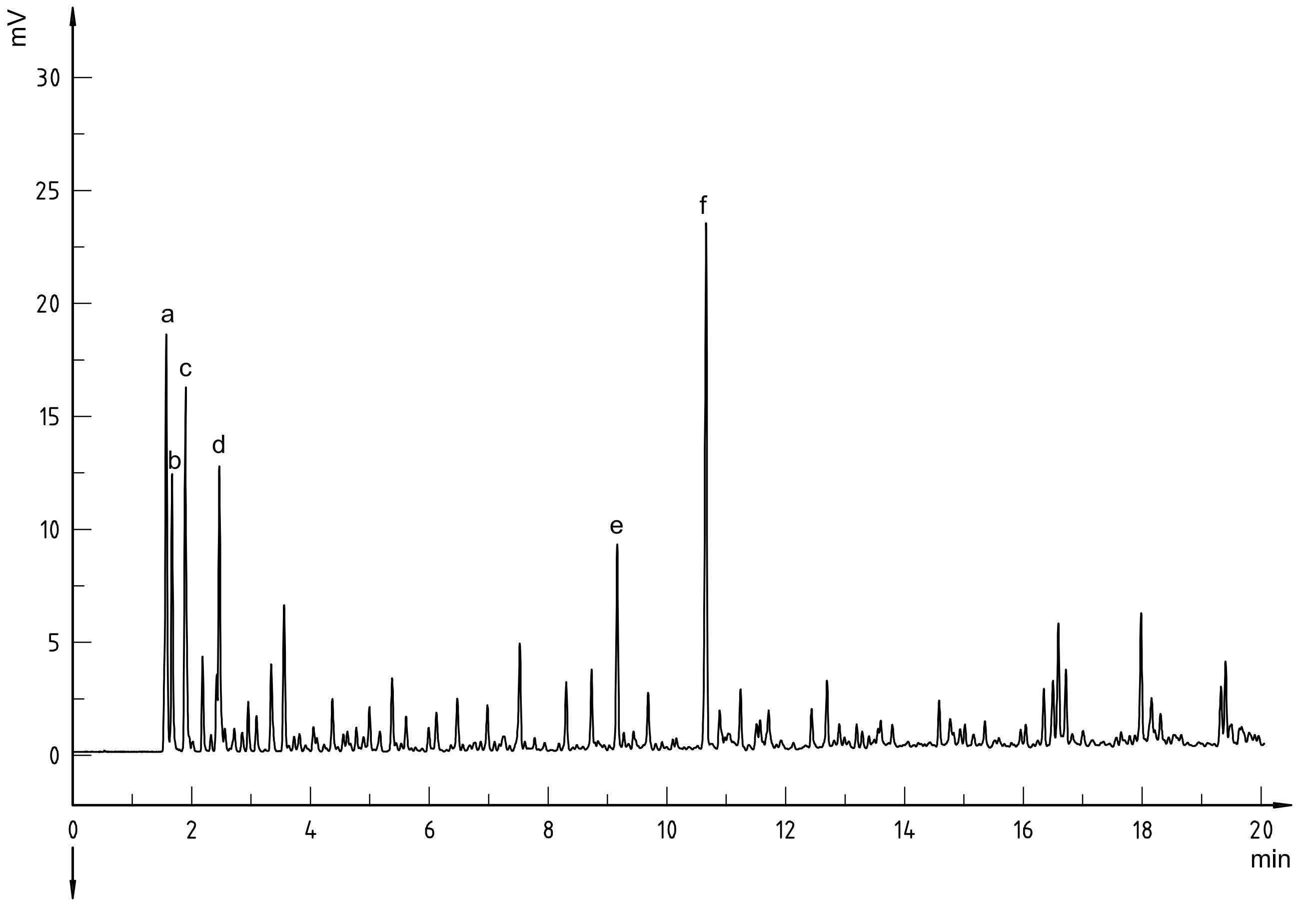
b 1,63

c 1,86 (butadiene)

d 2,43 (acrylonitrile)

e 8,43 (dimer of butadiene)

Figure 13 — Acrylonitrile-butadiene copolymer (NBR)



Retention times

a 1,57

b 1,67

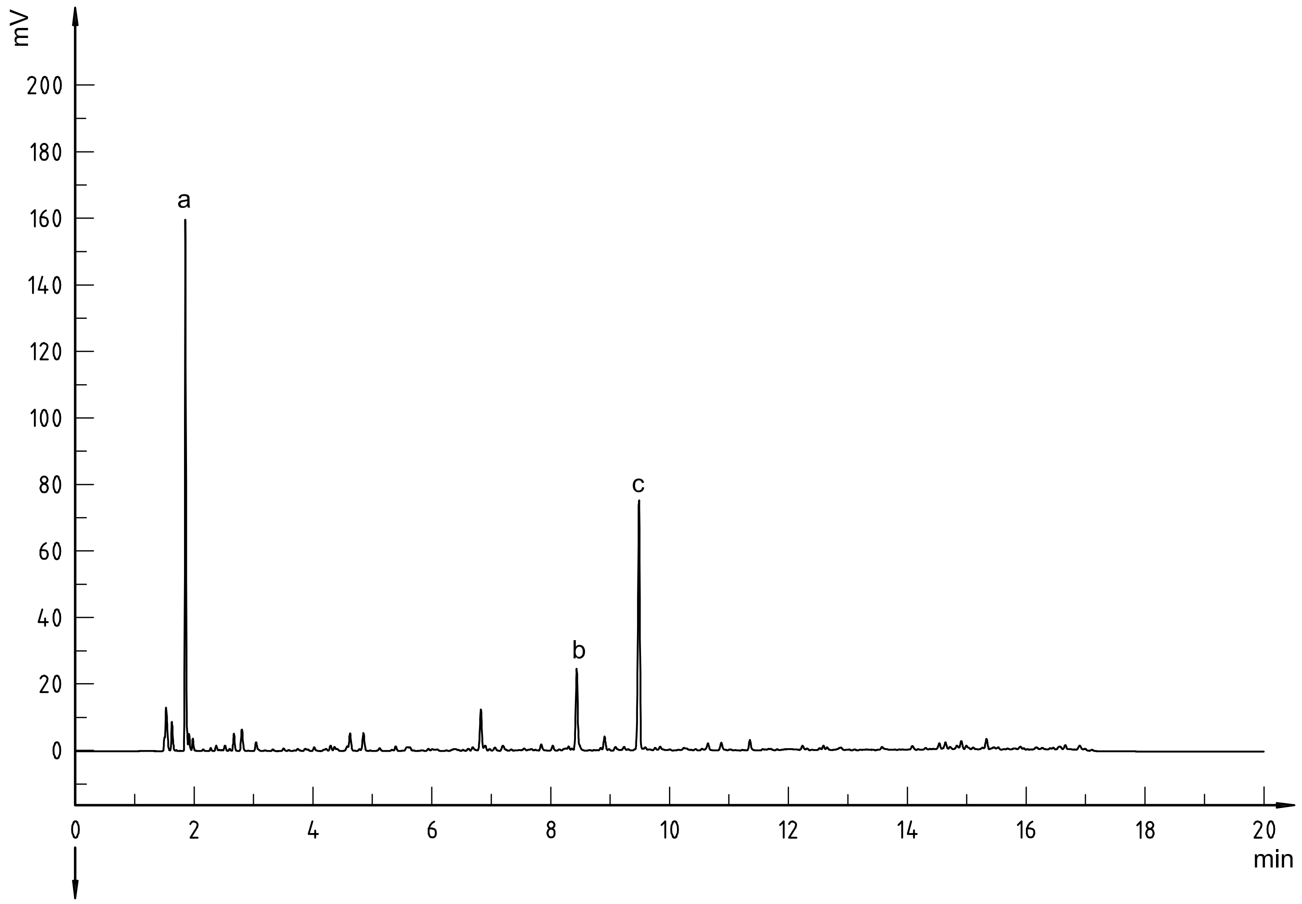
c 1,89 (butadiene)

d 2,46 (acrylonitrile)

e 9,14

f 10,63

Figure 14 — Hydrogenated acrylonitrile-butadiene copolymer (HNBR)



Retention times

a 1,85 (butadiene)

b 8,44 (4-vinyl-1-cyclohexene) (dimer of butadiene)

c 9,49 (styrene)

Figure 15 — Styrene-butadiene copolymer (SBR)

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

Pyrolysis	
Device	Curie-point pyrolyser
Pyrolysis conditions	590 °C (5 s)
Column	
Liquid phase	5 % diphenylpolysiloxane-DB-5ms
Film thickness	0,25 µm
Column diameter	0,25 mm ID
Column length	30 m
Chromatographic conditions	
Carrier gas	Helium
Injector temperature	280 °C
Type of detector	FID
Detector temperature	280 °C
Temperature programme	Isothermal for 2 min at 50 °C then 10 °C/min from 50 °C to 280 °C

Retention times

a 1,486
b 1,886
c 2,460
d 3,360

Figure 16 — Chlorosulfonated polyethylene (CSM)

Retention times

- a 1,500
- b 1,886
- c 2,460
- d 3,510

Figure 17 — Ethylene-propylene-diene terpolymer (EPDM)

Retention times

a 1,47

b 1,58

c 2,52

d 12,13

e 12,92

Figure 18 — Acrylic rubber (ACM)

Retention times

a 1,50

b 1,64

c 1,73

d 7,74

Figure 19 — Epichlorohydrin rubber (CO)

Retention times

a 3,96
b 6,88
c 9,62
d 12,37

Figure 20 — Polysiloxane

Retention times

a 1,51 (butadiene)

b 4,36 (4-vinyl-1-cyclohexene) (dimer)

Figure 21 — Polybutadiene (BR)

Retention times

a 1,91 (chloroprene)

b 11,66 (dimer)

Figure 22 — Polychloroprene (CR)

Retention times

a 1,54

b 2,67

Figure 23 — Isobutene-isoprene copolymer (IIR)

Retention times

a 1,67 (isoprene)

b 7,93 (dipentene) (dimer)

Figure 24 — Polyisoprene (NR)

Retention times

a 1,55 (butadiene)

b 1,66 (acrylonitrile)

c 4,34 (4-vinyl-1-cyclohexene) (dimer of butadiene)

Figure 25 — Acrylonitrile-butadiene copolymer (NBR)

Retention times

a 1,57

b 1,74

c 1,92

d 3,63

Figure 26 — Hydrogenated acrylonitrile-butadiene copolymer (HNBR)

Retention times

a 1,55 (butadiene)

b 4,34 (4-vinyl-1-cyclohexene) (dimer of butadiene)

c 5,34 (styrene)

Figure 27 — Styrene-butadiene copolymer (SBR)

Table 4 — Recommended operating conditions for micro-furnace pyrolysis followed by chromatography with a packed column

Pyrolysis	
Device	Micro-furnace
Pyrolysis temperature	600 °C
Column	
Liquid phase	10 % PEG 20M/Chromosorb W (AW-DMCS) 80/100
Column diameter	2,2 mm ID (stainless steel)
Column length	2 m
Chromatographic conditions	
Carrier gas	Helium
Type of detector	FID
Temperature programme	Isothermal for 2 min at 70 °C then 10 °C/min from 70 °C to 220 °C then isothermal for 30 min at 220 °C

Retention times

a 0,60

b 2,61

c 3,70

Figure 28 — Acrylic rubber (ACM)

Retention times

a 0,59 (2-chloroprene)

b 1,81

c 14,44

Figure 29 — Polychloroprene (CR)

Retention times

a 0,91 (isoprene)

b 7,31 (dipentene) (dimer of isoprene)

Figure 30 — Polyisoprene (NR)

Retention times

a 0,71 (butadiene)

b 0,97 (acrylonitrile)

c 3,67 (4-vinyl-1-cyclohexene) (dimer of butadiene)

Figure 31 — Acrylonitrile-butadiene copolymer (NBR)

Retention times

- a 0,71 (butadiene)
- b 4,63 (4-vinyl-1-cyclohexene) (dimer of butadiene)
- c 8,31 (styrene)

Figure 32 — Styrene-butadiene copolymer (SBR)

Table 5 — Recommended operating conditions for Curie-point pyrolysis followed by chromatography with a packed column

Pyrolysis	
Device	Curie-point pyrolyser
Pyrolysis conditions	590 °C (3 s)
Column	
Liquid phase	20 % Silicone DC-200/Chromosorb W (AW-DMCS) 80/100
Column diameter	3 mm ID (glass)
Column length	3 m
Chromatographic conditions	
Carrier gas	Nitrogen
Type of detector	FID
Temperature programme	Isothermal for 2 min at 50 °C then 10 °C/min from 50 °C to 200 °C then isothermal for 10 min at 220 °C

Retention times

- a 1,506
- b 1,913
- c 2,843
- d 4,710
- e 6,492

Figure 33 — Chlorosulfonated polyethylene (CSM)

Retention times

a 1,432

b 1,546

c 1,960

d 2,886

Figure 34 — Ethylene-propylene-diene terpolymer (EPDM)

Retention times

a 1,542

b 3,666

c 9,975

Figure 35 — Acrylic rubber (ACM)

Retention times

a 1,882

b 4,133

c 5,524

d 9,394

Figure 36 — Epichlorohydrin rubber (CO)

Retention times

a 1,429
b 6,501
c 13,384
d 17,117
e 20,723

Figure 37 — Polysiloxane

Retention times

a 3,25 (butadiene)

b 14,27 (4-vinyl-1-cyclohexene) (dimer of butadiene)

Figure 38 — Polybutadiene (BR)

Retention times

a 7,352 (2-chloroprene)

b 23,703 (dimer)

Figure 39 — Polychloroprene (CR)

Retention times

a 2,71 (isobutene)
b 10,98
c 18,62 (dipentene)

Figure 40 — Isobutene-isoprene copolymer (IIR)

Retention times

a 4,971 (isoprene)

b 18,987 (dipentene) (dimer of isoprene)

Figure 41 — Polyisoprene (NR)

Retention times

a 2,912 (butadiene)

b 4,991 (acrylonitrile)

c 14,114 (4-vinyl-1-cyclohexene) (dimer of butadiene)

Figure 42 — Acrylonitrile-butadiene copolymer (NBR)

Retention times

a 1,542

b 1,976

c 2,897

d 14,73

e 16,316

Figure 43 — Hydrogenated acrylonitrile-butadiene copolymer (HNBR)

Retention times

- [a] 3,25 (butadiene)
- [b] 14,244 (4-vinyl-1-cyclohexene) (dimer of butadiene)
- [c] 15,331 (styrene)

Figure 44 — Styrene-butadiene copolymer (SBR)

ICS 83.060

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