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Rubber — Identification of polymers — Pyrolytic gas-chromatographic method using mass-spectrometric detection

Caoutchouc — Identification des polymères — Méthode par pyrolyse et chromatographie en phase gazeuse avec détection par spectrométrie de masse

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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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 documents 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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This document 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 17257:2013), of which it consists a minor revision to correct a grammatical error in the Scope.

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 — Identification of polymers — Pyrolytic gas-chromatographic method using mass-spectrometric detection

1 Scope

This document provides a qualitative method for the identification of rubbers by their pyrolysis products using tandem gas-chromatography/mass spectrometry.

The method applies to rubbers in the raw state and to unvulcanized and vulcanized compounds. Compounds can be based on a single rubber or a blend of two or more rubbers. Where the level of a particular rubber in a blend is <10 %, detection and identification can be difficult.

A non-restrictive list of rubbers is given in Clause 4.

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, *Rubber — Determination of solvent extract*

ISO 1629, *Rubber and latices — Nomenclature*

3 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 List of rubbers

The following list is not restrictive.

Rubbers are presented according to ISO 1629.

4.1 Group M

4.1.1 Chloropolyethylene (CM)

4.1.2 Chlorosulfonylpolyethylene (CSM)

4.1.3 Ethylene-propylene copolymer (EPM) and Ethylene-propylene-diene terpolymer (EPDM)

The method cannot distinguish between them.

4.1.4 Fluorocarbon rubber having substituent fluoro, perfluoroalkyl, or perfluoroalkoxy groups on the polymer chain (FKM)

The method cannot distinguish between them.

4.2 Group O

4.2.1 Homopolymer of epichlorhydrin (CO), copolymer of epichlorhydrin-ethylene oxide (ECO), terpolymer of epichlorhydrin-ethylene oxide-allyl glycidyl ether (GECO)

The method cannot distinguish among them.

4.3 Group Q

4.3.1 Polysiloxanes (MQ, VMQ, PVMQ)

The method cannot distinguish MQ and VMQ, but can distinguish PVMQ from the two other polymers.

4.4 Group R

4.4.1 Butadiene rubber (BR)

4.4.2 Chloroprene rubber (CR)

4.4.3 Isobutene-isoprene rubber (IIR), chlorinated IIR (CIIR) and brominated IIR (BIIR)

The method cannot distinguish among them.

4.4.4 Natural rubber (NR) and synthetic isoprene rubber (IR)

The method cannot distinguish between them.

4.4.5 Acrylonitrile-butadiene rubber (NBR), hydrogenated NBR (HNBR) and carboxylated NBR (XNBR)

The method can only distinguish HNBR from the two other polymers (NBR and XNBR).

4.4.6 Styrene-butadiene rubber (SBR)

The method allows butadiene-α-methylstyrene rubber to be distinguished from styrene-butadiene rubber.

4.5 Rubber blends

In copolymer-homopolymer blends having one common monomer (e.g. SBR/BR, NBR/BR), the technique does not allow the homopolymer to be distinguished.

This is also valid for blends with terpolymers.

5 Principle

5.1 Raw rubbers, or vulcanized or unvulcanized compounds which previously have been solvent extracted, are pyrolysed and the pyrolysate analysed by gas chromatography with mass spectrometric detection.

5.2 The results are interpreted by examining the mass spectra of the specific chromatographic peaks.

6 Reagents

All reagents shall be of an analytical grade.

6.1 **Solvents**, for the extraction according to ISO 1407.

6.2 **Inert carrier gas**.

7 Equipment

7.1 Extraction devices according to ISO 1407.

7.2 The chromatographic equipment consists of three associated parts:

a) pyrolysis system;

b) gas chromatograph equipped with chromatographic columns;

c) mass detector in electronic impact mode.

These elements are connected with an acquisition and data processing system.

A schematic diagram of the equipment is given in Annex A.

7.2.1 Pyrolysis system

Non-volatile polymers are decomposed at elevated temperature to generate volatile products able to be analysed by chromatography. In order to obtain reproducible results of decomposition, the pyrolysis parameters (temperature, time) shall be established separately.

Different types of equipment that give a rapid and reproducible pyrolysis are available. The three most common types are the following:

— platinum filament pyrolyser;

— Curie point pyrolyser;

— micro furnace pyrolyser.

7.2.2 Chromatographic columns

7.2.2.1 General

There are several categories of chromatographic columns available in the market. They are characterized by

— the nature of the material constituting the tube (generally silica covered with a polymer, aluminium or deactivated stainless steel, etc.);

— the column length;

— the column diameter;

— the nature, thickness, and polarity of the stationary phase placed on the internal surface of the capillary tube.

The column shall be chosen by taking into account its efficiency of separation (number of theoretical plates) and the relative polarity of the various compounds generated during rubber pyrolysis.

7.2.2.2 Examples of useful capillary columns

a) Capillary column in fused silica of 0,32 mm diameter and 30 m, of apolar type. Stationary phase — film of dimethyl polysiloxane, 1 µm thick;

b) Capillary column in fused silica of 0,32 mm diameter and 30 m, of polar type. Stationary phase — film of polyethylene glycol, 0,5 µm thick.

8 Operating conditions

8.1 General

The reproducibility is guaranteed by checking the conformity of the device and by respecting the procedure.

8.2 Gas chromatograph adjustment

Adjust the various controls of the gas chromatograph according to the retained operating conditions.

For information, typical operating conditions are given in Annex B.

8.3 Extraction

Carry out the extraction according to ISO 1407. The rubber residue is dried until constant mass is achieved.

NOTE This preliminary extraction is not mandatory but allows the elimination of compound constituents which could interfere with the pyrolysis product.

8.4 Test portion

Take a test portion of mass appropriate to the apparatus used, usually about 0,1 mg.

8.5 Pyrolysis

Place the test portion in the pyrolysis device and purge for the necessary time.

Pyrolyse at a temperature between 400 °C and 800 °C; usually the pyrolysis temperature is about 600 °C.

Record the experimental data.

9 Interpretation of results

9.1 General

The identification of rubbers is achieved by noting the presence of certain characteristic decomposition products and by consulting the mass spectra database.

Two examples of chromatograms are presented in Annex C.

The following clauses summarize all the characteristic products by family of polymer. For the interpretation of the results, refer to Annex D according to the type of column used.

9.2 Group M

9.2.1 Chloropolyethylene (CM) and chlorosulfonylpolyethylene (CSM)

— Hydrochloric acid (CAS 7647-01-0)

— Benzene (CAS 71-43-2)

It is possible, in certain case, to differentiate these two polymers by the presence of sulfur dioxide (CAS 7446-09-5).

9.2.2 Ethylene-propylene copolymer (EPM) and Ethylene-propylene-diene terpolymer (EPDM)

— Propene (CAS 115-07-1)

— 1-Hexene (CAS 592-41-6) or 2-Methyl-1-pentene (CAS 763-29-1)

— 1-Heptene (CAS 592-76-7) or 5-Methyl-1-hexene (CAS 3524-73-0)

— 2-Methyl-1-heptene (CAS 15870-10-7)

— 1,3,5-Cycloheptatriene (CAS 544-25-2)

9.2.3 Fluorocarbon rubber having substituent fluoro, perfluoroalkyl, or perfluoroalkoxy groups on the polymer chain (FKM)

— 1,1-Difluoroethene (CAS 75-38-7)

9.3 Group O

9.3.1 Homopolymer of epichlorhydrin (CO), copolymer of epichlorhydrin-ethylene oxide (ECO), terpolymer of epichlorhydrin-ethylene oxide-allyl glycidyl ether (GECO)

— Hydrochloric acid (CAS 7647-01-0)

— 1-Chloro-1-propene (CAS 590-21-6)

9.4 Group Q

9.4.1 Polysiloxanes (MQ, VMQ, PVMQ)

— Hexamethylcyclotrisiloxane (CAS 541-05-9)

— Octamethylcyclotetrasiloxane (CAS 556-67-2)

— Decamethylcyclopentasiloxane (CAS 541-02-6)

— Dodecamethylcyclohexasiloxane (CAS 540-97-6)

The presence of benzene allows the polymers PVMQ of the VMQ and MQ to be distinguished.

9.5 Group R

9.5.1 Butadiene rubber (BR)

— 1,3-Butadiene (CAS 106-99-0)

— 4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene (CAS 100-40-3)

9.5.2 Chloroprene rubber (CR)

— Hydrochloric acid (CAS 7647-01-0)

— 2-Chloro-1,3-butadiene (CAS 126-99-8)

— 1-Chloro-5-(1-chloroethenyl)-cyclohexene (CAS 13547-07-4)

— 1-Chloro-4-(1-chloroethenyl)-cyclohexene (CAS 13547-06-3)

9.5.3 Isobutene-isoprene rubber (IIR), chlorinated IIR (CIIR) and brominated IIR (BIIR)

— Isobutylene or 2-methylpropene (CAS 115-11-7)

— Diisobutylene or 2,4,4-trimethyl-1-pentene (CAS 107-39-1)

— Triisobutylene (CAS 7756-94-7)

9.5.4 Natural rubber (NR) or synthetic isoprene rubber (IR)

— Isoprene (CAS 78-79-5)

Isomers of the limonene:

— 1-Methyl-5-(1-methylethenyl)-cyclohexene (CAS 13898-73-2)

— 1-Methyl-4-(1-methylethenyl)-cyclohexene (CAS 138-86-3)

9.5.5 Acrylonitrile-butadiene rubber (NBR), hydrogenated NBR (HNBR) and carboxylated NBR (XNBR)

9.5.5.1 NBR and XNBR

— 1,3-Butadiene (CAS 106-99-0)

— 4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene (CAS 100-40-3)

— 2-Propenenitrile or Acrylonitrile (CAS 107-13-1)

9.5.5.2 HNBR

— 2-Propenenitrile or Acrylonitrile (CAS 107-13-1)

— Hexanenitrile or Capronitrile (CAS 628-73-9)

9.5.6 Styrene-butadiene rubber (SBR)

— 1,3-Butadiene (CAS 106-99-0)

— 4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene (CAS 100-40-3)

— Ethenylbenzene or Styrene (CAS 100-42-5)

In case of butadiene-alpha-methylstyrene copolymers, there is a strong peak of alpha-methylstyrene or isopropenylbenzene (CAS 98-83-9).

10 Test report

The test report shall include the following particulars:

a) sample details: a full description of the sample;

b) test method:

— a reference to this document, i.e. ISO 17257:2020;

— characteristics of the column, if necessary thermal program and spectral condition;

— identification of the pyrolyser GC-MS equipment used;

c) test details: details of any procedures not specified in this document, if any;

d) test results:

— chromatogram of sample;

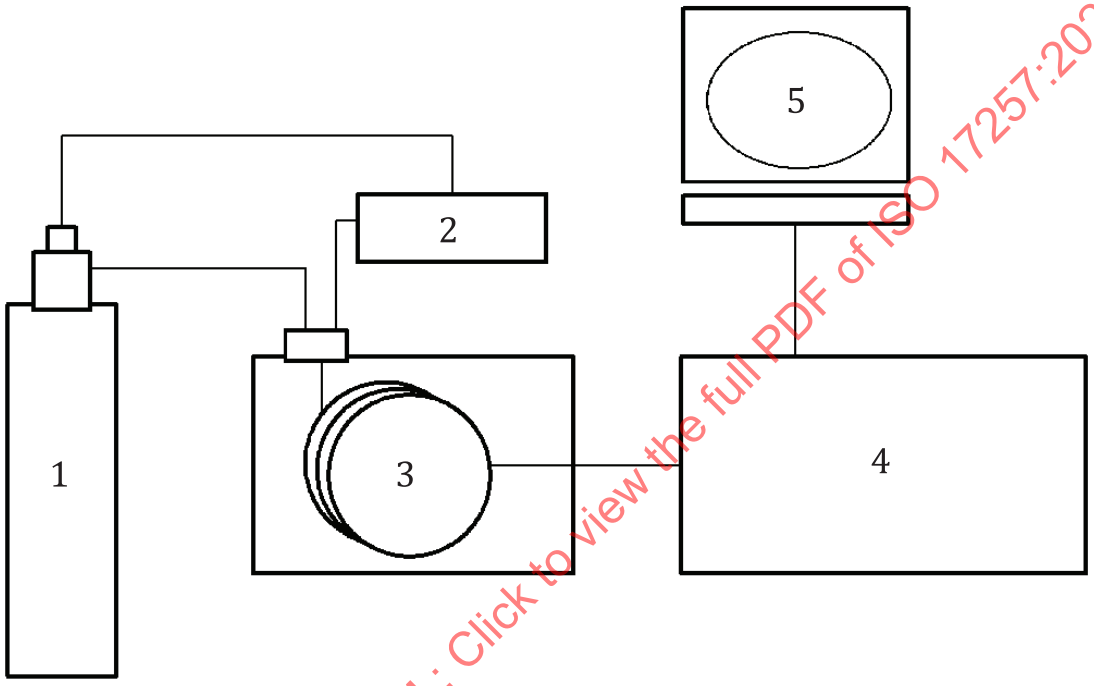
— identification of the rubber(s) in the sample;

e) date of test.

Annex A
(informative)

Schematic diagram of the chromatographic equipment

Figure A.1 shows a schematic diagram of equipment specified in 6.2.



Key

1 carrier gas
2 pyrolyser
3 gas chromatograph
4 mass spectrometer
5 acquisition and data processing system

Figure A.1 — Schematic diagram of a gas-chromatograph equipped with a pyrolyser coupled with a mass spectrometer

Annex B
(informative)

Examples of operating conditions

Examples of operating conditions are given in Table B.1.

Table B.1 — Examples of operating conditions

Apolar column	Polar column
— Initial temperature at 40 °C — Isothermal for 2 min at 40 °C — Increase to 140 °C (10 °C/min) — Increase to 290 °C (20 °C/min) — Isothermal for 5 min at 290 °C	— Initial temperature at 30 °C — Isothermal for 2 min at 30 °C — Increase to 200 °C (5 °C/min) — Isothermal for 10 min in 200 °C
Injector temperature: 250 °C Carrier gas: Helium The flow rate output of the carrier gas in the column is adjusted between 1 ml/min and 2 ml/min. Calibration of the mass spectrometer: Interface temperature: 250 °C to 290 °C Ionization mode: electronic impact mode (70 eV) Track of acquisition covering at least the range m/z: 29 to 500	

Annex C
(informative)

Chromatogram examples

Chromatogram examples, obtained under operation conditions stated in Table B.1 with an apolar column, are given in Figures C.1 and C.2.

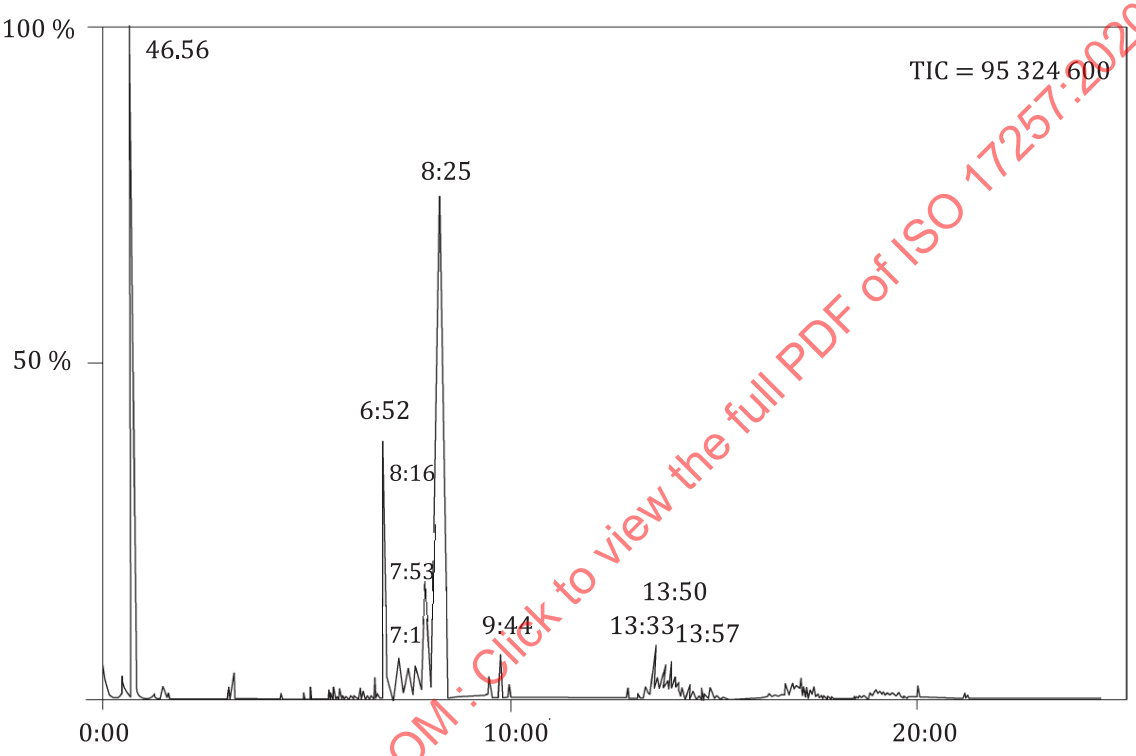


Figure C.1 — Chromatogram of a natural rubber (NR)

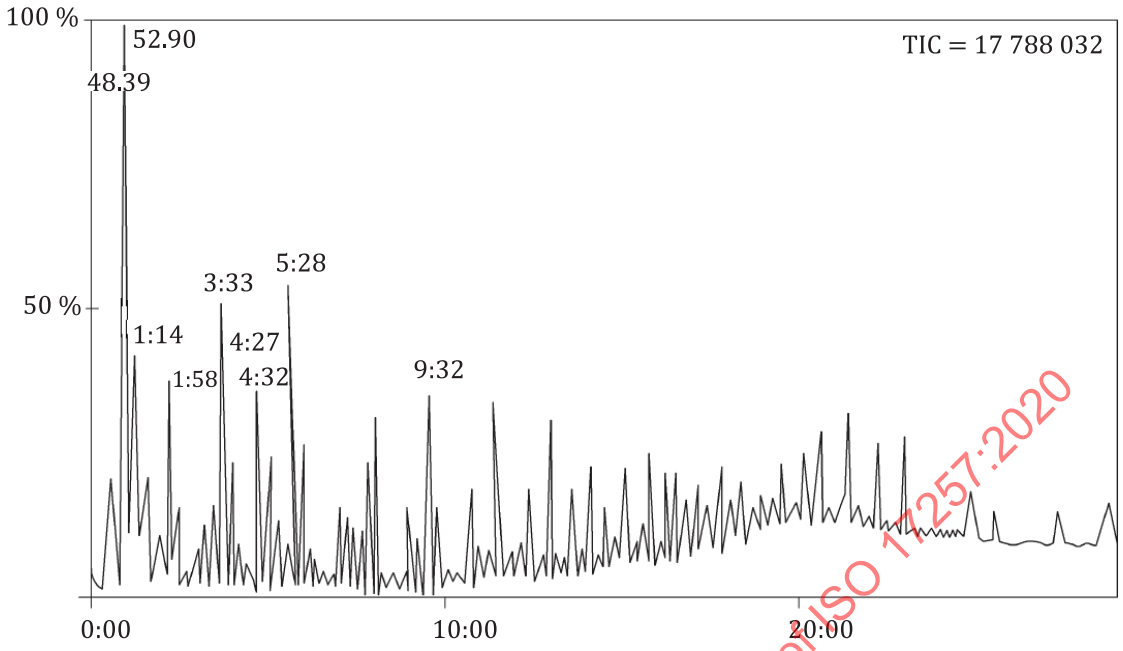


Figure C.2 — Chromatogram of an ethylene-propylene-diene terpolymer (EPDM)

Annex D
(informative)

Chemical compounds identified in rubber pyrolysates

The chemical compounds are given for information in Tables D.1 and D.2 in order of retention time. The black boxes correspond to the characteristic pyrolysis products. Products highlighted by a circle are less characteristic.

Table D.1 — Chemical compounds identified in rubber pyrolysates — Apolar column

MW	Chemical compounds	CAS number	NR/ IR	BR	SBR	αMSBR	IIR/ BIIR/ CIIR	NBR	HNBR	CR	CM	CSM	EPM/ EPDM	VMQ/ MQ	PVMQ	CO/ ECO
36	HCl	7647-01-0								■	■	■				■
64	SO_2	7446-09-5										■				
42	Propene	115-07-1											■			
56	2-Methyl-1-propene or Isobutylene	115-11-7					■									
84	1-Hexene	592-41-6											■			
54	1,3-Butadiene	106-99-0		■	■	■		■			■	■				
88	2-Chloro-1,3-butadiene	126-99-8								■						
53	2-Propenenitrile or Acrylonitrile	107-13-1						■	■							
68	2-Metyl-1,3-butadiene or Isoprene	78-79-5	■													
76	1-Chloro-1-propene-	590-21-6														■
98	1-Heptene	592-76-7											■			
78	Benzene	71-43-2									■	■			■	
94	2-Methyl-1,3,5-hexatriene	19264-50-7											○			
112	2-Methyl-1-heptene	15870-10-7											■			
112	2,4,4-Trimethyl-1-pentene or Diisobutylene	107-39-1					■									
97	Hexanenitrile or Capronitrile	628-73-9							■							
108	4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene	100-40-3		■	■	■		■			○	○				
222	Hexamethylcyclotrisiloxane	541-05-9												○	○	
104	Ethenylbenzene or Styrene	100-42-5			■											
118	Isopropenylbenezene or α-methylstyrene	98-83-9				■										