



JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS K 6231 : 2004

(ISO 7270-1 : 2003)

(JRMA/JSA)

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

ICS 83.060

Reference number : JIS K 6231 : 2004 (E)

PROTECTED BY COPYRIGHT

Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by The Japan Rubber Manufacturers Association (JRMA)/Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14. Consequently **JIS K 6231:1998** is replaced with this Standard.

This Standard has been made based on **ISO 7270-1:2003 Rubber — Analysis by pyrolytic gas-chromatographic methods — Part 1: Identification of polymers (single polymers and polymer blends)** for the purpose of making it easier to compare this Standard with International Standard; to prepare Japanese Industrial Standard conforming with International Standard; and to propose a draft of an International Standard which is based on Japanese Industrial Standard. Attention is drawn to the possibility that some parts of this Standard may conflict with a patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have technical properties. The relevant Minister and Japanese Industrial Standards Committee are not responsible for identifying the patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have the said technical properties.

Date of Establishment: 1998-03-20

Date of Revision: 2004-03-20

Date of Public Notice in Official Gazette: 2004-03-22

Investigated by: Japanese Industrial Standards Committee
Standards Board

Technical Committee on Chemical
Products

JIS K 6231 : 2004, First English edition published in 2005-03

Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

© JSA 2005

All rights reserved. No part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

Printed in Japan

Contents

	Page
Introduction	1
1 Scope	1
2 Normative references	1
3 Principle	2
4 Applicable single polymers and blends	2
4.1 Group M	2
4.2 Group O	2
4.3 Group Q	2
4.4 Group R	2
4.5 Blends	3
5 Reagents	3
5.1 Solvents for extraction purposes	3
5.2 Carrier gas	3
5.3 Gas for flame-ionization detector (FID)	3
6 Apparatus	4
6.1 Extraction apparatus	4
6.2 Pyrolysis/chromatography system	4
7 Procedure	5
8 Interpretation of results	5
9 Test report	6

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

Introduction This Japanese Industrial Standard has been prepared based on the first edition of **ISO 7270-1 Rubber — Analysis by pyrolytic gas-chromatographic methods — Part 1: Identification of polymers (single polymers and polymer blends)** published in 2003 without modifying the technical contents.

WARNING Persons using this Standard should be familiar with normal laboratory practice. This Standard 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

1.1 This Standard 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.

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 polymers, but this must be verified by the analyst in each particular case.

1.2 The use of this Standard 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.

NOTE : The International Standard corresponding to this Standard is as follows.

In addition, symbols which denote the degree of correspondence in the contents between the relevant International Standard and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21**.

ISO 7270-1 : 2003 *Rubber — Analysis by pyrolytic gas-chromatographic methods — Part 1: Identification of polymers (single polymers and polymer blends)* (IDT)

2 Normative references The following standards contain provisions which, through reference in this Standard, constitute provisions of this Standard. If the indication of the year of coming into effect or the year of publication is given to these referred standards, only the edition of the indicated year constitutes the provision of this Standard but the revision and amendment made thereafter do not apply.

JIS K 6229:1998 *Rubber — Determination of solvent extract*

NOTE : **ISO 1407**:1992 *Rubber — Determination of solvent extract* is equivalent to the said standard.

JIS K 6397:1997 *Rubbers and latices — Nomenclature*

NOTE : **ISO 1629**:1995 *Rubber and latices — Nomenclature* is equivalent to the said standard.

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 Applicable single polymers and blends

NOTE : The rubbers in the following listing are grouped in accordance with **JIS K 6397**.

4.1 Group M

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

NOTE : The pyrogram will not differentiate between CM and CSM.

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

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

4.1.3 Acrylic rubbers (ACMs).

4.2 Group O

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

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

4.3 Group Q

4.3.1 Polysiloxanes.

4.4 Group R

4.4.1 Polybutadiene (BR).

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

4.4.2 Polychloroprene (CR).

NOTE : The pyrogram will not differentiate between the various types of CR.

4.4.3 Isobutene-isoprene copolymer (IIR).

NOTE : The pyrogram will not differentiate IIR from halogenated IIR.

4.4.4 Polyisoprene [natural rubbers (NR) or synthetic polyisoprene rubbers (IR)].

NOTE : The pyrogram will not differentiate NR from IR.

4.4.5 Acrylonitrile-butadiene copolymer (NBR).

NOTE : 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.

4.4.6 Styrene-butadiene copolymer (SBR).

NOTE : 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.

4.5 Blends With the exception of blends containing both SBR and BR, the method enables blends of the following polymers to be identified:

- a) polyisoprene (NR or IR);**
- b) polybutadiene (BR);**
- c) isobutene-isoprene copolymers (IIR);**
- 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:

5.1.1 Acetone.

5.1.2 Methanol.

5.1.3 Methyl ethyl ketone.

5.2 Carrier gas Nitrogen or helium.

5.3 Gas for flame-ionization detector (FID)

5.3.1 Hydrogen.

5.3.2 Purified compressed air to burn hydrogen

6 Apparatus

6.1 Extraction apparatus As specified in clause 4 of JIS K 6229.

6.2 Pyrolysis/chromatography system 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.

6.2.1 Pyrolysis device The following types of electrically heated pyrolysis device are suitable:

6.2.1.1 Micro-furnace, with quartz tubes heated at a prefixed temperature into which the test portion is dropped or conveyed in a sample boat to be 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.

6.2.2 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 Standard.

NOTE : 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.

6.2.3 Chromatographic columns A variety of column lengths and diameters and stationary and liquid phases are suitable for use in this Standard, 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 2 to 5. The list of typical pyrograms obtained (figures 1 to 44) is given in table 1.

6.2.4 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 method in **JIS K 6229**. 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 (**7.3**) 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-cyclohexane (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

Group	Rubber (example)	Number of figure			
		Capillary column		Packed column	
		Semi-polar	Semi-polar	Polar	Non-polar
		Micro-furnace	Curie point	Micro-furnace	Curie point
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 (Figures 1 to 15)

Pyrolysis Device Pyrolysis temperature	Micro-furnace 600 °C
Gas-chromatographic column Liquid phase Film thickness Column inside diameter Column length	5 % diphenylpolysiloxane Ultra ALLOY-5 1.0 µm 0.25 mm 30 m
Chromatographic conditions Carrier gas Injector temperature Type of detector Detector temperature	Helium 320 °C FID 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

Table 3 (Figures 16 to 27)

Pyrolysis Device Pyrolysis temperature	Curie-point pyrolyser 590 °C (5 s)
Column Liquid phase Film thickness Column inside diameter Column length	5 % diphenylpolysiloxane-DB-5ms 0.25 µm 0.25 mm 30 m
Chromatographic conditions Carrier gas Injector temperature Type of detector Detector temperature	Helium 280 °C FID 280 °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