ISO/~~DIS~~ FDIS 9924-3~~:2023(E)~~

ISO/TC 45/SC 2~~/WG 5~~

Secretariat: JISC

Date: 2023-~~02-14~~10-23

Rubber and rubber products — Determination of the composition of vulcanizates and uncured compounds by thermogravimetry

Part 3: Hydrocarbon rubbers, halogenated rubbers and polysiloxane rubbers

Caoutchouc et produits à base de caoutchouc — Détermination de la composition des vulcanisats et des mélanges non vulcanisés par thermogravimétrie~~— Partie 3: Caoutchoucs hydrocarbonés, caoutchoucs halogénés et caoutchoucs polysiloxanes~~

Partie 3: Caoutchoucs hydrocarbonés, caoutchoucs halogénés et caoutchoucs polysiloxanes

FDIS stage

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

Published in Switzerland

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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 9924-3:2009), which has been technically revised.

The main changes are as follows:

— ~~—~~extension of the scope by deleting the mandatory preliminary extraction;

— ~~—~~the result of 2006 ITP has been deleted, the result of 2022 ITP has been added in Annex C~~Annex G~~.

A list of all parts in the ISO 9924 series can be found on the ISO website.

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 and rubber products — Determination of the composition of vulcanizates and uncured compounds by thermogravimetry — —

Part 3: Hydrocarbon rubbers, halogenated rubbers and polysiloxane rubbers

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document 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 determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies a thermogravimetric method for the determination of the main constituents of rubber compounds such as elastomer(s), carbon black and mineral filler.

It establishes the “fingerprint” of the tested material. However, the result does not always correspond exactly to the theoretical formula of the rubber.

This method applies to raw or compounded rubbers, vulcanized and unvulcanised, with or without extraction.

This method applies to rubbers with hydrocarbon backbones (NR, BR, SBR, IIR, EPDM, ACM, AEM, etc.) used alone or as mixtures. For the mixtures, the polymer content corresponds to the total rubber and it is not usually possible to identify individual polymers.

This method applies to rubbers with halogenated hydrocarbon backbones (CR, CSM, FKM, CM, CO, ECO, etc.) or containing nitrogen (NBR, HNBR, NBR/PVC, etc.), as well as to their mixtures. However, these rubbers often form carbonaceous residues which interfere with the analysis. Application of an appropriate procedure minimizes these interferences.

This method also applies to rubbers with a polysiloxane backbone (VMQ, etc.) and to rubbers not listed above.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

A weighed test portion is heated following a pre-set programme in a known atmosphere.

Initial pyrolysis in an inert atmosphere (nitrogen) is followed by combustion in an oxidizing atmosphere.

Generally, the reactions that generate mass variations are decompositions, oxidations or reactions volatilizing a constituent.

The loss in mass as a function of temperature indicates a quantitatively usable thermogram which is characteristic of the material.

5 Reagents

5.1 Nitrogen of minimal purity 99,995 % mass fraction, with an oxygen content of less than 10 mg/kg (ppm) and hydrocarbon content less than 1,5 mg/kg (ppm).

5.2 Dry air, with no detectable trace of oil.

The air used may be reconstituted nitrogen and oxygen of purity minimum 99,5 % mass fraction. In some cases, pure oxygen may be used.

6 Apparatus

6.1 Thermogravimetric analyser (TGA).

6.1.1 General. Various types of analyser are commercially available. The basic components of an analyser are listed in 6.1.2~~6.1.2~~ to 6.1.8~~6.1.8.~~

6.1.2 Thermogravimetric balance, comprising a microbalance provided with a pan made from a nonoxidizable material that can weigh up to 50 mg, is readable to the nearest 1 µg and equipped with an oven capable of being maintained at temperatures from room temperature to approximately 1 000 °C.

6.1.3 Appropriate enclosure, allowing the sample to be kept under a specified atmosphere.

6.1.4 Pan or **crucible,** of size suitable to accommodate the sample and small enough to reduce the influence of buoyancy.

6.1.5 Temperature-control system, allowing heating rates to be controlled from 10 °C/min to 50 °C/min.

6.1.6 Gas selector, allowing successive introduction of the inert gas and oxidizing gas while controlling the flow rate.

6.1.7 Measurement equipment, for gas flow rate in the range 10 cm^3/min to 250 cm^3/min.

6.1.8 Data acquisition and processing system.

7 Preparation of samples

7.1 Conditioning of samples

Test samples should be conditioned in standardized laboratory conditions of temperature and humidity in accordance with ISO 23529. These conditions are preferred, but are not mandatory.

In order to refine the centesimal composition, prior extraction of plasticizers and additives with an appropriate solvent might be useful. In this case, the method described in ISO 1407 can be applied. The thermogravimetric analysis shall then be carried out on the non-extractable part previously dried until constant weight.

7.2 Test portion

Prepare a test portion of 8 mg ± 3 mg cut into a single piece.

NOTE The preparation of the test portion can influence the kinetics of the phenomena.

8 Procedure

8.1 General

Considering the variety of the decomposition modes linked to the nature of polymers, two procedures are defined:

a) ~~a)~~ procedure A for carbon rubbers;

b) ~~b)~~ procedure B for polysiloxane and fluorocarbon rubbers.

If procedure A does not result in a thermogram that achieves constant mass at 600 °C, procedure B shall apply.

A non-exhaustive list of the recommended procedures for each of the various rubber families is given in Table A.1~~Table A.1~~.

8.2 Description of the procedures

Table 1~~Table 1~~ gives details of the operating steps for procedures A and B.

Table 1 — Operating steps

Step	Units	Procedure A	Procedure B
Initial temperature	°C	35 ± 10	35 ± 10
Heating rate under nitrogen	°C/min	20	20
Target temperature under nitrogen	°C	600	800
Maintenance time at target temperature under nitrogen	min	0	5
Cooling under nitrogen	°C	600 to 400	800 to 400
Temperature at the change of atmosphere	°C	400	400
Maintenance time at atmosphere change temperature under air	min	2	2

Step	Units	Procedure A	Procedure B
Heating rate under air	°C/min	20	20
Final temperature under air according to the equipment [a]	°C	800 to 850	800 to 850
Maintenance time at the final temperature under air	min	10 to 20	10 to 20
[a] If procedures do not result in a thermogram that achieves constant mass at final temperature under air, maintain the final temperature condition until constant mass is achieved.			

8.3 Test procedures

8.3.1 Connect the apparatus and adjust (6.1.6~~(6.1.6)~~) the gas flow to a rate between 20 cm^3/min and 250 cm^3/min (6.1.7~~(6.1.7).~~). Set the parameters according to the chosen process.

The recommended flow rate is 100 cm^3/min.

8.3.2 Before the test, ensure that the pan (6.1.4~~(6.1.4)~~) or the crucible is clean and empty.

8.3.3 Close the thermobalance oven (6.1.2~~(6.1.2),~~), purge with a nitrogen (5.1~~(5.1)~~) flow at the preset rate. Wait until stabilization. Adjust the zero to compensate for the mass of the pan or the crucible.

8.3.4 Place the test piece prepared in accordance with 7.2~~7.2~~ in the pan or the crucible and weigh it under the conditions specified in 8.3.3~~8.3.3.~~. Record the mass, m_0.

8.3.5 Conduct the test by following the operating steps specified in Table 1~~Table 1.~~

8.3.6 At the end of the test, allow the oven to cool to room temperature, open it and clean the pan or the crucible.

9 Expression of results

9.1 Recordings

Make two different types of recording to enable the necessary calculations to be made:

a) ~~a)~~ a plot of the percentage variation in mass fraction, w, versus temperature or time;

b) ~~b)~~ a derivative plot, dw/dT.

These will be used to derive the content of the various compound ingredients.

9.2 Calculation of the mass change from curves

An example of a thermogram is given in Figure B.1~~Figure B.1.~~

The derivative plot shall be used to define particular points on the mass variation plot as follows.

Identify on the derivative plot the minima ~~,,,~~A'_0, A'_1, A'_2, and ~~,~~A'_3, corresponding to the closest points to return to zero of the derived function. Note these points on the main curve of mass change. Report A_0, A_1, A_2, and A_3 on the ordinate and read the corresponding masses m_0, m_1, m_2, and m_3,

where

m_0 is the initial mass of the test piece;

m_1 is the mass of the test piece remaining after pyrolysis;

m_2 is the mass of the test piece remaining after pyrolysis and carbon black combustion;

m_3 is the mass of the residue yield.

The percentage mass fraction loss, $w_1 + w_2$, due to pyrolysis is given by Formula (1)~~Formula (1)~~:

~~(1)~~

$$w_1 + w_2 = \frac{m_0 - m_1}{m_0} \times 100 \quad (1)$$

The percentage mass fraction loss, w_5, due to carbon black combustion is given by Formula (2)~~Formula (2)~~:

~~(2)~~

$$w_5 = \frac{m_1 - m_2}{m_0} \times 100 \quad (2)$$

The percentage mass fraction loss, w_7, due to partial or total decomposition of mineral components is given by Formula (3)~~Formula (3)~~:

~~(3)~~

$$w_7 = \frac{m_2 - m_3}{m_0} \times 100 \quad (3)$$

The percentage mass fraction, w_8, corresponding to the residue yield, is given by Formula (4)~~Formula (4)~~:

$$w_8 = \frac{m_3}{m_0} \times 100 \quad (4)$$

The sum of the percentage mass fractions, $w_2 + w_5 + w_7 + w_8$, shall correspond to 100 % (not including the analytical errors).

NOTE These operations can be calculated by computer.

9.3 Interpretation

9.3.1 General

A simple interpretation of the thermogram shall give pyrolysable, non-pyrolysable mass fraction losses and the residue.

9.3.2 Rubbers with hydrocarbon backbones ~~(Figures B.2~~(Figures B.2 and B.3~~B.3)~~)

a) ~~a)~~ Under nitrogen

The first loss in mass fraction, w_1, corresponds to organic compounds of low molecular weight and volatile matter.

The second loss in mass fraction, w_2, corresponds to the pyrolysis of one or several polymers. The end of the polymer decomposition is arbitrarily taken at the end of the heating step under nitrogen.