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

Part 1: **Butadiene, ethylene-propylene copolymer and terpolymer, isobutene-isoprene, isoprene and styrene-butadiene rubbers**

Caoutchouc et produits à base de caoutchouc — Détermination de la composition des vulcanisats et des mélanges non vulcanisés par thermogravimétrie —

Partie 1: Caoutchoucs butadiène, copolymères et terpolymères éthylène-propylène, isobutène-isoprène, isoprène et butadiène-styrène

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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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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

This document was prepared by ISO/TC 45, *Rubber and rubber products*, SC 2, *Testing and analysis*.

This fourth edition cancels and replaces the third edition (ISO 9924-1:2016), which has been technically revised:

The main changes are as follows:

— Clause 3 is added;

— Added "If graphite is present" (see 4.3, 4.4). to make the document more comprehensive;

— Modified the steps of heating rate (see 8.2.5 and 8.2.7) to make the decomposition process of the sample more uniform;

— Modified the carbon black content part (see 9.2.3). The modified expression is more reasonable and consistent with the "test procedure" clause;

— Modified the variables of formulae (see 9.1 and 9.3) to be written using symbols instead of text.

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 1:
Butadiene, ethylene-propylene copolymer and terpolymer, isobutene-isoprene, isoprene and styrene-butadiene rubbers

WARNING — 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 ensure compliance with any national regulatory conditions.

1 Scope

This document specifies a thermogravimetric method for the determination of the total organic content, carbon black content and ash in vulcanizates and uncured compounds. The loss in mass at 300 °C is an approximate guide to the volatile-matter content of the compound.

The method is suitable for the analysis of rubber compounds and vulcanizates containing the following rubbers occurring alone or as mixtures:

a) polyisoprene of natural or synthetic origin;

b) polybutadiene;

c) styrene-butadiene copolymers;

d) isobutylene-isoprene copolymers;

e) ethylene-propylene copolymers and related terpolymers.

NOTE The field of application of the method may be extended to the analysis of compounds containing rubbers different from those given in this subclause, provided that the applicability of the method is tested beforehand using known compounds or vulcanizates having a similar composition. Other compounds are covered in ISO 9924-2.

The method is not suitable for rubbers containing polymers which form a carbonaceous residue during pyrolysis, such as many chlorine- or nitrogen-containing rubbers.

The method is also not suitable for materials containing additives which cause the formation of carbonaceous residues during pyrolysis, such as cobalt and lead salts or phenolic resins.

The method is not suitable for compounds containing blowing agents and mineral fillers, such as carbonates, hydrated aluminium oxides, hydrated silicon oxides or silicates which decompose in the temperature range from 25 °C to 650 °C, unless suitable corrections based on prior knowledge of filler behaviour can be made.

The method is not suitable for the determination of the total polymer content of compounds or vulcanizates containing non-rubber organic ingredients that cannot be completely removed by solvent extraction carried out in accordance with ISO 1407.

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*

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

4.1 A weighed test portion is heated, following a pre-set programme, from 70 °C to 300 °C in a stream of nitrogen and is maintained at 300 °C for 10 min. The loss in mass indicates, approximately, the total content of non-rubber organic matter volatile at 300 °C. In general, this value is not equivalent to the value of the solvent extract.

4.2 The oven temperature is then raised to 550 °C, still in a stream of nitrogen, and maintained at 550 °C for 15 min. The organic matter which was undistilled at 300 °C and the polymer distill off, and the loss in mass between 70 °C and 550 °C represents the total organic matter content.

NOTE The total rubber content is calculated by subtracting the value of the solvent extract, determined according to ISO 1407, from the total organic content, provided that all non-rubber ingredients can be extracted.

4.3 Reduce the oven temperature to 300 °C in a stream of nitrogen, then the gas is changed from nitrogen to air or oxygen, or a mixture of air or oxygen. Then, raise the oven temperature to 650 °C and maintain at this temperature for 15 min or until no further loss in mass is observed. The carbon black is burnt off, and the loss in mass in the oxidizing atmosphere at 650 °C, thus represents the carbon black content. If graphite is present at 850 °C, a balanced flow of gas is maintained throughout the changeover to avoid buoyancy effects.

4.4 The mass of the residue at 650 °C represents the ash (if graphite is present, at 850 °C).

5 Reagents

5.1 **Dry nitrogen**, with an oxygen content of less than 10 mg/kg (ppm).

5.2 **Dry air or oxygen**.

6 Apparatus

6.1 **Thermogravimetric analyser**. There are many types of analysers commercially available. All should be suitable for use with this document, but their suitability should be checked using the procedure in Clause 7. Calibrate and operate the thermogravimetric analyser in accordance with the manufacturer's instructions.

The basic components of an analyser are as follows.

6.1.1 Thermogravimetric balance.

6.1.2 Thermo-regulated oven, electrically heated.

6.1.3 Temperature programmer, for the oven.

6.1.4 Switching device, allowing a stream of nitrogen or a stream of air or oxygen (or a mixture of nitrogen and air or oxygen) to flow through the oven at a predetermined and constant flow rate.

6.1.5 X/Y recorder, for recording the temperature/mass plot. Alternatively, temperature/time and mass/time plots may be recorded simultaneously using a two-pen Y/T recorder.

6.1.6 Auxiliary equipment for producing differential curves (useful but not mandatory for this document).

6.2 Analytical balance, capable of weighing to 0,1 mg.

7 Thermogravimetric analyser checks

7.1 Measurement of purge time, t_p

7.1.1 Place a test portion of carbon black or black-filled rubber, as specified in the manufacturer's instructions, in the thermobalance sample pan and heat to 650 °C in a stream of nitrogen, at the maximum rate allowed by the temperature programmer.

7.1.2 Maintaining the temperature at 650 °C, introduce air or oxygen and allow the test portion to combust fully.

7.1.3 When there is no further mass change, switch off the oven heater and allow the oven to cool to room temperature, maintaining the air or oxygen flow. At this point, the oven will have been thoroughly purged with air or oxygen. The following operations are designed to determine the time, t_p, required to completely restore the inert atmosphere of nitrogen.

7.1.4 With the oven at 25 °C ± 5 °C, introduce a fresh test portion of carbon black, of mass as specified in the manufacturer's instructions, into the balance pan and close the apparatus.

7.1.5 Record the time, t_1, switch over to nitrogen gas flow, and set the oven temperature to increase to 650 °C at as fast a rate as practicable and then remain constant.

7.1.6 Observe the thermogravimetric analyser mass trace and, when this no longer indicates a mass loss with time, note the time t_2.

As a check, the pan should still contain carbon black since the mass loss should be constant if not all the carbon black has burned off during the heating time.

7.1.7 The purge time, t_p, which is the time required to purge all oxygen from the system, is given by Formula (1):

$$t_p = t_2 - t_1 \quad (1)$$

7.2 Discrimination between carbon black and calcium carbonate

7.2.1 Calcium carbonate will decompose to calcium oxide when heated to 800 °C. Carbon black is thermally stable up to this temperature in a nitrogen atmosphere. In air or oxygen, however, carbon black will be oxidized to carbon dioxide at 800 °C.

7.2.2 There should be no problem in distinguishing between, and measuring separately, black and whiting (calcium carbonate) provided that: nitrogen having a sufficiently low concentration of oxygen is used; that purging is carried out for a time greater than the purge time determined in 7.1; that there are no leaks in the apparatus; and that the oven design and gas flow rate ensure that all carbon dioxide is swept out from the sample chamber.

To check the operation of the thermogravimetric analyser, carry out the following procedure.

a) Grind together equal (to within 1 %) masses of analytical-grade calcium carbonate and the purest grade of carbon black available.

b) Purge the apparatus with nitrogen for 10 min beyond the purge time, t_p.

c) Switch on the recorder and set the oven temperature to 25 °C ± 5 °C.

d) Into the thermogravimetric analyser balance pan, introduce a mass of the carbon black/calcium carbonate mixture (see 7.2.2 a)) as specified in the manufacturer's instructions.

e) Close the apparatus and purge with a stream of nitrogen at a constant and predetermined flow rate which is in accordance with the manufacturer's instructions. Continue purging with nitrogen for a time which is greater than the purge time, t_p (see 7.1).

f) Raise the oven temperature to 800 °C at a rate of 10 °C/min.

g) Maintain the oven temperature at 800 °C until the mass indicated on the mass/temperature (or mass/time) plot is constant, then lower the temperature to 300 °C.

h) Switch from the stream of nitrogen to a stream of air or oxygen, or partly replace the nitrogen by air or oxygen. Adjust the total flow rate of the gas flowing through the apparatus so that there is no discernible change in the apparent mass of the sample. This procedure corrects for changes in buoyancy of the balance pan and test portion in gases of different density.

i) Raise the oven temperature to 800 °C as rapidly as possible and maintain it at 800 °C for 15 min or until the mass indicated on the plot is constant.

j) Switch off the oven heater and replace the stream of air or oxygen by a stream of pure nitrogen. Switch off the recorder and empty the ash residue from the balance pan. The apparatus is now ready for the next test portion.

k) Determine the ratio, K, of the mass changes in the two different atmospheres using Formula (2):

$$K = \frac{\Delta m_1}{\Delta m_2} \tag{2}$$

where

Δm_1 is the loss in mass (or the height of the corresponding chart step) in the atmosphere of nitrogen;

Δm_2 is the loss in mass (or the height of the corresponding chart step) in the atmosphere of air or oxygen.

l) The value of K should be 0,44 ± 0,022 [0,44 = M_r (CO_2)/M_r ($CaCO_3$)]. If this condition is satisfied, the apparatus is functioning satisfactorily.

8 Procedure

NOTE Because of the slightly different behaviour of some rubbers and vulcanizates upon heating and ashing, the analyst needs some prior information regarding the composition of the sample to be analysed. This can be obtained by making two or three preliminary analyses with the thermogravimetric analyser and examining the residue in the sample pan at the various stages of heating. In some cases, an examination of the infrared spectra will provide the necessary information to allow the analyst to proceed with the method or to make appropriate modifications.

8.1 Preliminary operations

8.1.1 Switch on the balance and the recorder and set the oven to 70 °C.

8.1.2 Weigh a test portion of thinly sheeted test sample to the nearest 0,1 mg into the thermobalance. The mass taken shall be in agreement with the manufacturer's instructions, and will commonly be in the range of 4 mg to 10 mg.

NOTE In some types of apparatus, it is possible to set the recorder to 100 % after inserting the test portion. In this case, the value of m_0 in 8.1 is equal to 100, and accurate pre-weighing is not necessary.

8.1.3 Close the apparatus and purge with a stream of nitrogen at a constant and pre-determined flow rate, which is in accordance with the manufacturer's instructions. Continue purging with nitrogen for a time greater than the purge time, t_p (see 7.1).

The presence of trace amounts of air or oxygen in the apparatus during heating under nitrogen will lead to erroneous results, and it will not be possible to obtain a constant mass during heating of black-filled materials at 650 °C. To minimize the purge time, it is advisable to maintain a stream of nitrogen through the apparatus even when it is not in use. It is also recommended that the stream of nitrogen be maintained through the apparatus even when heating in air or oxygen. The additional air or oxygen should preferably enter the apparatus at a point as close as practicable to the oven chamber.

8.2 Test procedure

8.2.1 Raise the oven temperature to 300 °C at a rate of 10 °C/min.

8.2.2 Maintain the temperature at 300 °C for 10 min.

8.2.3 Raise the temperature to 550 °C at a rate of 20 °C/min.

8.2.4 Maintain the temperature at 550 °C for 15 min.

8.2.5 Raise the temperature to 650 °C at a rate of 20 °C/min or as rapidly as possible and maintain it at 650 °C for 15 min or until the mass indicated on the mass/temperature (or mass/time) plot is constant.

8.2.6 Lower the temperature to 300 °C and switch from the stream of nitrogen to a stream of air or oxygen, or partly replace the nitrogen by air or oxygen. Adjust the total rate of gas flow through the apparatus so that there is no discernible change in the apparent mass of the sample in order to correct for changes in buoyancy.

8.2.7 Raise the oven temperature to 650 °C at a rate of 20 °C/min or as rapidly as possible and maintain at this temperature until the mass indicated on the mass/temperature (or mass/time) plot is constant. Usually, 15 min is sufficient.

8.2.8 Switch off the oven heater and replace the gas stream by a stream of pure nitrogen. Switch off the recorder and check the colour of the ash in the balance pan.

9 Expression of results

9.1 For instruments indicating the mass in milligrams

9.1.1 The percentage content of matter volatile at 300 °C is given by Formula (3):

$$W_1 = \frac{m_0 - m_1}{m_0} \times 100 \quad (3)$$

where

w_1 is mass fraction of matter volatile at 300 °C, expressed in per cent;

m_0 is the mass, in milligrams, of the test portion (see note to 8.1.2);

m_1 is the mass, in milligrams, indicated at the end of the heating period at 300 °C (see 8.2.2).

9.1.2 The percentage content of total organic matter is given by Formula (4):

$$W_2 = \frac{m_0 - m_2}{m_0} \times 100 \quad (4)$$

where

w_2 is mass fraction of total organic matter, expressed in per cent;

m_0 is the mass, in milligrams, of the test portion (see note to 8.1.2);

m_2 is the mass, in milligrams, indicated at the end of the heating period at 550 °C (see 8.2.4).

9.1.3 The percentage content of carbon black is given by Formula (5):

$$W_3 = \frac{m_2 - m_3}{m_0} \times 100 \quad (5)$$

where

$w_{3,}$ is mass fraction of carbon black, expressed in per cent;

m_0 is the mass, in milligrams, of the test portion (see note to 8.1.2);

m_2 is the mass, in milligrams, indicated at the end of the heating period at 550 °C (see 8.2.4);

m_3 is the mass, in milligrams, indicated at the end of the heating period at 650 °C in air or oxygen or in a mixture of nitrogen and air or oxygen.

9.1.4 The percentage of ash is given by Formula (6):

$$W_4 = \frac{m_3}{m_0} \times 100 \quad (6)$$

where

w_4 is mass fraction of carbon black, expressed in per cent;

m_0 is the mass, in milligrams, of the test portion (see note to 8.1.2);

