INTERNATIONAL STANDARD

ISO 9924-1

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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

Reference number
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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 part of ISO 9924 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 9924-1 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

This second edition cancels and replaces the first edition (ISO 9924-1:1993), which has been technically revised.

ISO 9924 consists of the following parts, under the general title *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*

— *Part 2: Acrylonitrile-butadiene and halobutyl rubbers*

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 part of ISO 9924 should be familiar with normal laboratory practice. This part of ISO 9924 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 part of ISO 9924 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.

1.2 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.

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

1.4 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.

1.5 The method is not suitable for compounds containing mineral fillers, such as carbonates or hydrated aluminium oxides, 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.

1.6 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 normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 9924. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 9924 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 1407:1992, *Rubber — Determination of solvent extract.*

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards.*

3 Principle

3.1 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.

3.2 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 in accordance with ISO 1407, from the total organic content, provided that all non-rubber ingredients can be extracted.

3.3 The oven temperature is raised from 550 °C to 650 °C in a stream of nitrogen, then the gas is changed from nitrogen to air or oxygen, or a mixture of air or oxygen, and the temperature is maintained at 650 °C 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. A balanced flow of gas is maintained throughout the changeover to avoid buoyancy effects.

3.4 The mass of the residue at 650 °C represents the ash.

4 Reagents

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

4.2 Dry air or oxygen.

5 Apparatus

5.1 Thermogravimetric analyser.

There are many types of analyser commercially available. All should be suitable for use with this part of ISO 9924, but their suitability should be checked using the procedure in clause 6. Calibrate and operate the thermogravimetric analyser in accordance with the manufacturer's instructions.

The basic components of an analyser are as follows:

5.1.1 Thermogravimetric balance.

5.1.2 Electrically heated, thermo-regulated oven.

5.1.3 Temperature programmer, for the oven.

5.1.4 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.

5.1.5 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.

5.1.6 Auxiliary equipment for producing differential curves (useful but not mandatory for this part of ISO 9924).

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

6 Thermogravimetric analyser checks

6.1 Measurement of purge time t_p

6.1.1 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.

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

6.1.3 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.

6.1.4 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.

6.1.5 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.

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

NOTE 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.

6.1.7 The purge time t_p, which is the time required to purge all oxygen from the system, is given by the following equation:

$$t_p = t_2 - t_1$$

6.2 Discrimination between carbon black and calcium carbonate

6.2.1 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.

6.2.2 Provided that nitrogen having a low enough concentration of oxygen is used, that purging is carried out for a time greater than the purge time determined in 6.1, 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, there should be no problem in distinguishing between, and measuring separately, black and whiting (calcium carbonate). To check the operation of the thermogravimetric analyser, carry out the following procedure:

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

6.2.4 Purge the apparatus with nitrogen for 10 min beyond the purge time t_p.

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

6.2.6 Into the thermogravimetric analyser balance pan, introduce a mass of the carbon black/calcium carbonate mixture (see 6.2.3) as specified in the manufacturer's instructions.

6.2.7 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 6.1).

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

6.2.9 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.

6.2.10 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.

6.2.11 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.

6.2.12 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.

6.2.13 Determine the ratio K of the mass changes in the two different atmospheres using the following equation:

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

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.

6.2.14 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.

7 Procedure

NOTE Because of the slightly different behaviour of some rubbers and vulcanizates upon heating and ashing, the analyst will need 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 infra-red spectra will provide the necessary information to allow the analyst to proceed with the method or to make appropriate modifications.

7.1 Preliminary operations

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

7.1.2 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 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.

7.1.3 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 6.1).

NOTE 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.

7.2 Test procedure

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

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

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

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

7.2.5 Raise the temperature to 650 °C 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.

7.2.6 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.

7.2.7 Raise the oven temperature to 650 °C 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.

7.2.8 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.

8 Expression of results

8.1 For instruments indicating the mass in milligrams

8.1.1 The percentage content of matter volatile at 300 °C is given by the following equation:

$$\text{\% matter volatile at 300 °C} = \frac{m_0 - m_1}{m_0} \times 100$$

where

m_0 is the mass, in milligrams, of the test portion (see note to 7.1.2);

m_1 is the mass, in milligrams, indicated at the end of the heating period at 300 °C (see 7.2.2).

8.1.2 The percentage content of total organic matter is given by the following equation:

$$\text{\% total organic matter} = \frac{m_0 - m_2}{m_0} \times 100$$

where

m_0 is the mass, in milligrams, of the test portion (see note to 7.1.2);

m_2 is the mass, in milligrams, indicated at the end of the heating period at 550 °C (see 7.2.4).

8.1.3 The percentage content of carbon black is given by the following equation:

$$\% \text{ carbon black} = \frac{m_2 - m_3}{m_0} \times 100$$

where

m_0 is the mass, in milligrams, of the test portion (see note to 7.1.2);

m_2 is the mass, in milligrams, indicated at the end of the heating period at 550 °C (see 7.2.4);

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.

8.1.4 The percentage of ash is given by the following equation:

$$\% \text{ ash} = \frac{m_3}{m_0} \times 100$$

where

m_0 is the mass, in milligrams, of the test portion (see note to 7.1.2);

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.

8.2 For instruments adjustable to give an initial reading of 100 %

8.2.1 The percentage content of matter volatile at 300 °C is the percentage change in mass up to the end of the 300 °C heating period.

8.2.2 The percentage content of total organic matter is the percentage change in mass up to the end of the 550 °C heating period.

8.2.3 The percentage content of carbon black is the percentage change in mass from 550 °C to 650 °C in air or oxygen or in a mixture of nitrogen with air or oxygen.

8.2.4 The percentage of ash is the percentage mass remaining at the end of the heating period at 650 °C in air or oxygen or in a mixture of nitrogen with air or oxygen (see 8.1.4), and may be read directly from the mass/temperature (or mass/time) plot.

8.3 Total polymer content

The approximate percentage content of total polymer is given by the following equation:

% approximate total polymer = % total organic matter minus % extract

where

the % total organic matter is as calculated in 8.1.2;

the % extract is the percentage of solvent extract determined in accordance with ISO 1407.

9 Precision

9.1 The precision of this method was determined in accordance with ISO/TR 9272. The results are given in Tables 1 and 2. The precision parameters should not be used for acceptance or rejection of any group of materials without documentation that the parameters are applicable to the particular group of materials and the specific test protocols of the test method.

9.2 The results contained in Table 1 are averaged values and give an estimate of the precision of this test method as determined in an interlaboratory round robin consisting of four laboratories performing duplicate analyses on two different NBR compounds with different levels and/or types of plasticizer (oil) and carbon black. A test result is described as a single measurement of all four test parameters.

9.3 The results contained in Table 2 give an estimate of the precision of this test method as determined in an interlaboratory round robin consisting of four laboratories performing single analyses on three different days in the same week on each of two rubber compounds, one containing equal levels of BR, NR and SBR together with plasticizer (oil) and carbon black, the other containing EPDM and carbon black. A test result is described as a single measurement of all four test parameters.

9.4 **Repeatability:** The repeatability r (in measurement units) of the test method has been established as the appropriate value tabulated in Tables 1 and 2. Two single test results, obtained under normal test method procedures, that differ by more than the tabulated r (for any given level) must be considered to have come from different or non-identical sample populations.

9.5 **Reproducibility:** The reproducibility R (in measurement units) of this test method has been established as the appropriate value tabulated in Tables 1 and 2. Two single test results, obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated R (for any given level) must be considered to have come from different or non-identical sample populations.

Table 1 — Estimate of precision for NBR

Parameter	r	R
Mass loss at 300 °C	0,94	2,89
Total organic content	1,18	2,92
Carbon black	0,61	1,90
Ash	1,00	2,70

where

r is the repeatability, in measurements units;

R is the reproducibility, in measurements units.