
**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 en 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 et butadiène-styrène*



Foreword

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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.

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

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, halobutyl, polyurethane, silicone and sulfide rubbers*

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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

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1 Scope

1.1 This part of ISO 9924 specifies a thermogravimetric method for the determination of total organic components, carbon black and ash in vulcanizates and uncured compounds. The loss of mass at 300 °C is an approximate guide to the volatile-matter content of the compound.

1.2 The method is suitable for rubber compounds or 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 1 The field of application of the method may be extended to the analysis of compounds containing rubbers different from those reported in this subclause, provided that its applicability is tested beforehand using known compounds or vulcanizates having similar compositions. Other compounds will be 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 ranges of 25 °C to 650 °C or 850 °C. When these final temperatures must be used, suitable corrections based on prior knowledge of filler behaviour at elevated temperatures shall be employed.

1.6 The method is not suitable for the determination of the total polymer content in compounds or vulcanizates from which all non-rubber organic matter cannot be removed by solvent extraction carried out in accordance with ISO 1407.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 9924. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 9924 are encouraged to investigate the possibility of applying the most recent edition of the

standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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

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 amount 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 furnace temperature is then raised to 550 °C in a stream of nitrogen and maintained at 550 °C for 15 min. The organic matter undistilled at 300 °C and the polymer distill off and the loss in mass between 70 °C and 550 °C represents the total amount of organic matter.

NOTE 2 The total amount of rubber is calculated by subtracting the value of the solvent extract, determined in accordance with ISO 1407, from the total amount of organic matter, provided that all non-rubber organic matter can be extracted.

3.3 The furnace temperature is raised from 550 °C to 650 °C (or 850 °C — see note 3) in a stream of nitrogen, then the gas is changed from nitrogen to air or oxygen, or a mixture of nitrogen and air or oxygen, and the temperature is maintained at 650 °C (or 850 °C) for 15 min or until no further mass loss is observed. The carbon black is burnt off, and the loss in mass in the oxidizing atmosphere at 650 °C (or 850 °C) thus represents the amount of carbon black present. Care shall be taken to maintain a balanced flow of gas throughout the changeover to avoid buoyancy effects.

NOTE 3 If graphitic black is present, the temperature is raised to 850 °C in order to burn off the black completely.

3.4 The residual mass at 650 °C (or 850 °C if graphitic black is present) represents the ash.

4 Reagents

WARNING — All recognized health and safety precautions shall be observed when carrying out the operations specified in this part of ISO 9924, especially when using compressed gases.

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

4.2 Dry air or dry oxygen.

5 Apparatus

5.1 Thermogravimetric analyser.

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

The basic components of such an analyser are as follows:

5.1.1 Thermogravimetric balance.

5.1.2 Electrically heated, thermo-regulated furnace.

5.1.3 Temperature programmer for the furnace.

5.1.4 Flow-control device, designed to allow either a stream of nitrogen or, alternatively, air or oxygen to flow through the apparatus 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 differentiation, etc., is useful but not mandatory.

5.2 Analytical balance, with 0,1 mg accuracy.

6 Thermogravimetric analyser checks

6.1 Measurement of purge time (t_p)

6.1.1 Place a sample of carbon black or black-filled rubber of mass in accordance with the manufacturer's instructions in the sample pan of the thermogravimetric balance (5.1.1) and heat to 650 °C in the furnace (5.1.2) in an atmosphere of nitrogen (4.1).

6.1.2 Maintain the temperature at 650 °C, introduce air or oxygen (4.2), and allow the sample to combust completely.

6.1.3 When there is no further mass change, switch off the furnace heater and allow the apparatus to cool to room temperature, but maintain the air or oxygen flow.

6.1.4 When the temperature of the furnace is back to 25 °C \pm 5 °C, introduce a sample of carbon black of mass in accordance with the manufacturer's instructions into the balance pan of the preconditioned thermogravimetric analyser and close the apparatus.

6.1.5 Record the time (t_1), switch to a pure-nitrogen gas flow, and set the furnace 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).

Visually check the sample pan to make sure the carbon black is still present since, with some analysers, the mass loss may be constant even though all the carbon black has been 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 equation:

$$t_p = t_2 - t_1$$

6.2 Discrimination between carbon black and calcium carbonate

6.2.1 Provided that

nitrogen having an adequately low oxygen concentration is used,

purging is carried out for a time greater than the purge time determined as in 6.1,

there are no leaks in the apparatus and

the furnace 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 calcium carbonate. To verify the operation of the thermogravimetric analyser, carry out the following check.

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

6.2.3 Purge the apparatus with nitrogen for a time greater than the purge time (t_p) (see 6.1).

6.2.4 Switch on the recorder (5.1.5) and set the furnace temperature to 25 °C \pm 5 °C.

6.2.5 Introduce into the thermogravimetric-analyser balance pan a mass of the black/calcium carbonate mixture which is in accordance with the manufacturer's instructions.

6.2.6 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).

6.2.7 Raise the furnace temperature to 800 °C at a rate of 10 °C/min.

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

6.2.9 Switch from the stream of nitrogen to a stream of air or oxygen, or partially replace the nitrogen by a stream of 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 operation corrects for changes in buoyancy of the balance pan and sample in gases of different density.

6.2.10 Raise the furnace temperature to 800 °C as rapidly as possible and maintain the furnace temperature at 800 °C for 15 min or until the mass indicated on the temperature/mass (or mass/time) plot is constant.

6.2.11 Switch off the furnace heater and replace the gas stream by a stream of pure nitrogen (4.1). Switch off the recorder and empty the residual ash from the sample holder. The apparatus is now ready for the next test portion.

6.2.12 Determine the ratio R , using the expression:

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

where

Δm_1 is the loss in mass (or the chart step), in milligrams, in the nitrogen atmosphere;

Δm_2 is the loss in mass (or the chart step), in milligrams, in the air or oxygen atmosphere.

6.2.13 The value of the ratio R should be $0,44 \pm 0,022$. If this condition is satisfied, the apparatus is considered to be functioning satisfactorily.

7 Procedure

NOTE 4 Because of the slightly different behaviour of some rubbers or 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 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 (5.1.1) and the recorder (5.1.5) and set the furnace temperature 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 accordance with the manufacturer's instructions, and will commonly be in the range 4 mg to 10 mg.

NOTE 5 In some types of apparatus, it is possible to adjust the recorder to 100 % after sample insertion. 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 (4.1) at a constant and predetermined 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 6 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 samples at 650 °C. To minimize the purging 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 (4.2). The additional oxygen or air should be bled into the apparatus at a point as close as practicable to the furnace chamber.

7.2 Standard procedure

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

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

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

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

7.2.5 Raise the furnace temperature to 650 °C as rapidly as possible and maintain the furnace temperature at 650 °C for 15 min or until the mass indicated on the temperature/mass (or mass/time) plot is constant.

7.2.6 Lower the furnace temperature to 300 °C and switch from the stream of nitrogen to a stream of air or oxygen, or partially replace the nitrogen by a stream of 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 furnace temperature to 650 °C as rapidly as possible and maintain at this temperature until the mass indicated on the temperature/mass (or mass/time) plot is constant. Usually 15 min is a sufficient time.

7.2.8 Switch off the furnace heater and replace the gas stream by a stream of pure nitrogen (4.1). Switch off the recorder and empty the residual ash from the sample holder.

7.2.9 Check the colour of the residue in the sample holder. If it is still black, graphitic black, which is combustible only with difficulty, was originally present. In this case, take a fresh test portion and treat it in accordance with the procedure specified in 7.3. If the colour is not black or grey, go to clause 8.

7.3 Procedure if graphitic black is present

7.3.1 Proceed in accordance with 7.2.1 to 7.2.4.

7.3.2 Raise the furnace temperature to 850 °C at the rate of 20 °C/min, and maintain at this temperature until the mass indicated on the mass/temperature (or mass/time) plot is constant.

7.3.3 Lower the furnace temperature to 300 °C and switch from the stream of nitrogen to a stream of air or oxygen or partially replace the nitrogen by a stream of 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.

7.3.4 Raise the furnace temperature to 850 °C as rapidly as possible and maintain at 850 °C for 15 min or until the mass indicated on the mass/temperature (or mass/time) plot is constant.

7.3.5 Switch off the furnace heater and replace the gas stream by a stream of pure nitrogen (4.1). Switch off the recorder and empty the residual ash from the sample holder. The apparatus is now ready for the next test portion.

8 Expression of results

8.1 For instruments indicating the mass in milligrams

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

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

where

m_0 is the mass, in milligrams, of the test portion (see note 5);

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 of total organic matter is given by the 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 5);

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

8.1.3 The percentage of carbon black or graphitic black is given by the equation:

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

where

m_0 is the mass, in milligrams, of the test portion (see note 5);

m_2 is the mass, in milligrams, indicated at the end of the heating period at 550 °C (see 7.2.4) or 850 °C (see 7.3.2);

m_3 is the mass, in milligrams, indicated at the end of the heating period at 650 °C for carbon black or 850 °C for graphitic black in air or oxygen or in a mixture of nitrogen with air or oxygen.

8.1.4 The percentage of ash is given by the equation:

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

where

m_0 is the mass, in milligrams, of the test portion (see note 5);

m_3 is the mass, in milligrams, indicated at the end of the heating period at 650 °C for carbon black or 850 °C for graphitic black in air or oxygen or in a mixture of nitrogen with air or oxygen.

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

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

8.2.2 The percentage 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 of carbon black or graphitic black is the percentage change in mass from 550 °C to 650 °C or 850 °C in air or oxygen or in a mixture of nitrogen with air or oxygen, respectively.

8.2.4 The percentage of ash is the percentage mass remaining at the end of the heating period at 650 °C for carbon black or 850 °C for graphitic black 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 of total polymer is given by the equation:

$$\% \text{ approximate total polymer} = \% \text{ total organic matter} - \% \text{ extract}$$

where

% total organic matter is as calculated in 8.1.2;

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

9 Test report

The test report shall include the following information:

- a reference to this part of ISO 9924;
- all details necessary for the identification of the test sample;
- the type of apparatus used;
- the final temperature reached;
- the results obtained;
- any unusual features noted during the determination;
- any operation not included in this part of ISO 9924, or in the International Standard to which reference is made, which might have affected the results.

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