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

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

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

Partie 2: Caoutchoucs acrylonitrile-butadiène et butyl halogéné



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Printed in Switzerland

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

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 2:

Acrylonitrile-butadiene and halobutyl 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 determining the total organic content, carbon black content, carbonaceous residue and ash in vulcanizates and uncured compounds containing polymers which form a carbonaceous residue on pyrolysis (see 1.2). The loss in mass at around 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 hydrocarbon polymers covered by part 1 of this International Standard plus the following copolymers with polar groups which form a carbonaceous residue on pyrolysis:

- a) acrylonitrile-butadiene copolymers (NBRs);
- b) carboxylated acrylonitrile-butadiene copolymers (XNBRs);
- c) hydrogenated acrylonitrile-butadiene copolymers (HNBRs);
- d) chlorinated isobutylene-isoprene copolymers (CIIRs);
- e) brominated isobutylene-isoprene copolymers (BIIRs).

NOTE 1 The field of application of the method may be extended to include the analysis of compounds containing rubbers different from those given in this clause provided that the applicability of the method is tested beforehand using known compounds or vulcanizates having similar composition.

NOTE 2 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 800 °C, unless suitable corrections based on prior knowledge of filler behaviour can be made.

NOTE 3 The method is not suitable for the determination of the total polymer content of compounds containing non-rubber organic ingredients that cannot be completely removed by solvent extraction carried out in accordance with ISO 1407.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this part of ISO 9924. For dated references, subsequent amendments to, or revisions of, this publication 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 edition of the normative document 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*.

3 Principle

3.1 A weighed test portion is heated, following a pre-set programme, from 40 °C to 600 °C in a stream of nitrogen until all the organic material is pyrolysed. If nitrile-butadiene copolymers are present, a small amount of the polymer will be pyrolysed to form a carbonaceous residue that has to be determined in order to obtain the correct total organic content.

3.2 For this purpose, the oven temperature is decreased to 400 °C in a stream of nitrogen and maintained at 400 °C for 5 min. The gas stream is then changed from nitrogen to air or oxygen and the oven temperature raised slowly to 800 °C. During this heating in an oxidizing atmosphere, two distinct losses in mass occur due to combustion. The first is due to the combustion of the carbonaceous residue, and the amount is determined and added to the previously determined loss in nitrogen at 600 °C to obtain the correct value of the total organic content. The second is due to the normal combustion of the carbon black.

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 mass of the residue at 800 °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 either a stream of nitrogen or, alternatively, a stream of 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. Digital data acquisition stations with related software for drawing the temperature/mass and/or time/mass curves are also suitable: in this case better accuracy in the calculation of the mass losses can be achieved.

5.1.6 Auxiliary equipment for producing differential curves (mandatory for this part of ISO 9924).

5.1.7 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, set the oven temperature to increase to 650 °C at a rate of 10 °C/min and then hold the temperature 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 an 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 agreement 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.

6.2.10 Switch from the stream of nitrogen to 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 procedure corrects for changes in buoyancy of the balance pan and test portion in gases of different density.

6.2.11 Maintain the oven temperature 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 R of the mass changes in the two different atmospheres using the following equation:

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

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 R should be $0,44 \pm 0,022$. If this condition is satisfied, the apparatus is functioning satisfactorily.

7 Procedure

7.1 Switch on the balance and the recorder and set the oven to 40 °C.

7.2 Weigh a test portion of thinly sheeted test sample to the nearest 0,1 mg into the thermobalance. The mass taken should preferably be in agreement with the manufacturer's instructions, but 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, accurate preweighing is unnecessary.

7.3 Close the apparatus and purge with a stream of nitrogen at a constant and pre-determined flow rate which is in agreement 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 600 °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.

7.4 Raise the oven temperature to 600 °C at a rate of 20 °C/min with a nitrogen atmosphere. When the temperature of 600 °C is reached, the polymer should be completely pyrolysed and the mass indicated on the mass/temperature plot should be constant. If not, maintain the temperature at 600 °C until the mass indicated is constant.

7.5 Cool the oven from 600 °C to 400 °C with a nitrogen atmosphere and allow the oven to equilibrate at 400 °C for 5 min.

7.6 Switch from the stream of nitrogen to 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.

7.7 Raise the oven temperature from 400 °C to 800 °C at a rate of 10 °C/min.

7.8 Maintain the oven temperature at 800 °C for 5 min or until the mass is constant.

7.9 Switch off the oven heater and replace the stream of air or oxygen 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 Recordings

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

a) a plot of the percentage loss in mass (mass %) vs. temperature (curve 1 in Figure 1);

b) a derivative plot $\frac{d(\text{mass}\%)}{dT}$ (curve 2 in Figure 1).

These will be used to obtain the contents of the various compounding ingredients.

NOTE Figure 1 was obtained from the analysis of an acrylonitrile-butadiene copolymer containing 33 % by mass of acrylonitrile. A carbonaceous residue due to pyrolysis of the NBR in nitrogen is revealed at the beginning of pyrolysis in an oxidative atmosphere.

8.2 Approximate determination of plasticizers and non-rubber organic compounds

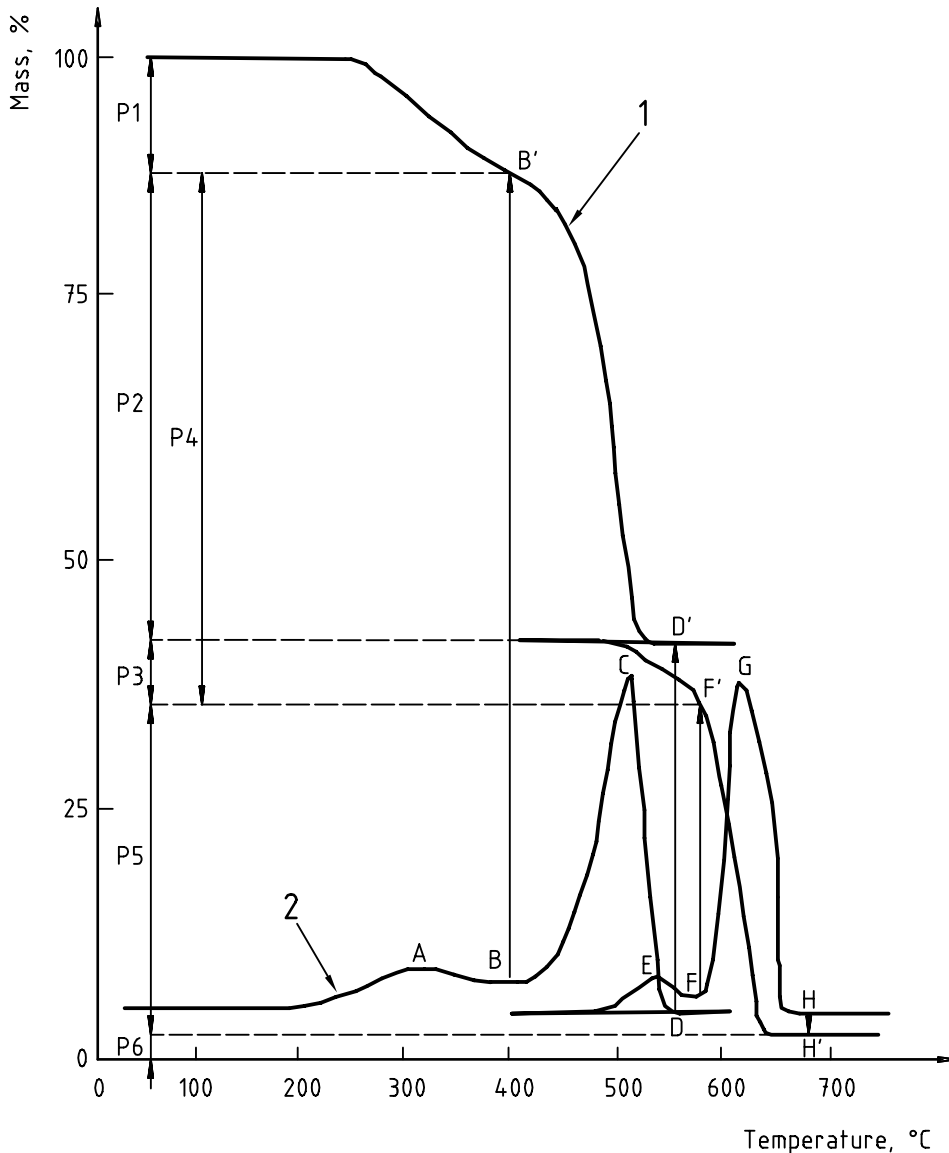
8.2.1 The first peak in the derivative curve (point A in Figure 1) corresponds to the maximum rate of pyrolysis and volatilization of the volatile ingredients, mainly plasticizers and non-rubber organic compounds, in nitrogen. When the trough following this peak is reached (point B), pyrolysis of these ingredients is complete.

8.2.2 Transfer from point B on the derivative curve (curve 2) to point B' vertically above it on the main curve (curve 1). When necessary, allow for any shift in origin between the two curves. Read off the percentage loss in mass corresponding to that point. The difference between this reading and 100 % (P1) corresponds to the volatile-matter content, plasticizer included, expressed as a percentage by mass. Since, in this region, overlap with low-molecular-mass fractions of the polymer is possible, the value obtained can only be considered as an approximate guide to the content of plasticizers and non-rubber ingredients in the compound.

8.3 Total organic content

8.3.1 Hydrocarbons

8.3.1.1 The second peak in the derivative curve (point C) corresponds to the maximum rate of pyrolysis in nitrogen of the hydrocarbons. Applying the same approach as for non-rubber organic materials, consider the trough following this peak (point D) as the point where rubber pyrolysis in nitrogen at 600 °C has reached completion.



Key

- 1 Main curve (mass vs temperature)
- 2 Derivative curve

Determination of plasticizers and non-rubber organic compounds (see 8.2)

- A First peak in derivative curve
- B First trough in derivative curve following point A
- B' Point on main curve corresponding to point B on derivative curve
- P1 Volatile-matter content (mass %)

Determination of hydrocarbons (see 8.3.1)

- C Second peak in derivative curve
- D Second trough in derivative curve
- D' Point on main curve corresponding to point D on derivative curve
- P2 hydrocarbon content in mass %
- P3 carbonaceous-residue content in mass %

Determination of NBR, CIIR and BIIR (see 8.3.2)

- E Third peak in derivative curve
- F Third trough in derivative curve
- F' Point on main curve corresponding to point F on derivative curve
- P4 NBR, CIIR and BIIR content in mass %

Determination of carbon black (see 8.4)

- G Fourth peak in derivative curve
- H Fourth trough in derivative curve
- H' Point on main curve corresponding to point H on derivative curve
- P5 Carbon black content in mass %

Determination of inorganic fillers and ash (see 8.5)

- P6 Inorganic-filler and ash content in mass %

Figure 1 — Mass/temperature plot

8.3.1.2 Transfer from point D on the derivative curve to point D' vertically above it on the main curve. Read off the percentage loss in mass corresponding to that point. The difference between this reading and 100 % (P1 + P2) corresponds to the total organic hydrocarbon content, expressed as a percentage by mass.

8.3.1.3 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 of the non-rubber organic ingredients can be extracted.

8.3.2 Acrylonitrile-butadiene and halobutyl rubbers

8.3.2.1 Rubbers containing acrylonitrile or halogen entities will not pyrolyse completely in nitrogen. They will leave a small amount of carbonaceous residue. To burn off the carbonaceous residue, cool the oven to 400 °C and switch the gas from nitrogen to air (or oxygen). Then raise the oven to 800 °C and maintain at this temperature until constant mass is reached. The additional percentage mass loss corresponds to the pyrolysis of the carbonaceous residue.

8.3.2.2 For nitrile and halogenated-butyl rubbers, beyond the pyrolysis peak in nitrogen described above, a rather weak first peak is observed in the derivative curve (point E) at the beginning of pyrolysis in air or oxygen. This corresponds to the maximum rate of pyrolysis in an oxidative atmosphere of the carbonaceous residue produced by the pyrolysis in nitrogen. This contribution must be determined and added to the total organic content (P1 + P2).

8.3.2.3 Transfer from the trough (point F) in the derivative curve following the carbonaceous-residue peak to point F' vertically above it on the main curve. Read off the percentage loss in mass corresponding to that point. The difference between this reading and 100 % (P1 + P4) corresponds to the corrected total organic content of nitrile and halogenated rubbers, expressed as percentage by mass.

NOTE The amount of carbonaceous residue is given by P3 in Figure 1.

8.3.2.4 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 organic ingredients can be extracted.

8.4 Carbon black

8.4.1 The percentage loss in mass on heating in air (or oxygen) to 800 °C after all carbonaceous residue has been volatilized is the amount of carbon black in the sample.

8.4.2 The large peak in the derivative curve (point G) occurring during the oxidation step at a temperature higher than that for the peak assigned to carbonaceous residue from nitrile and halogenated-butyl rubbers corresponds to the maximum rate of combustion of the carbon black.

8.4.3 As above, consider the trough (point H) following this peak as the point where combustion of carbon black has reached completion. Transfer from this point on the derivative curve to point H' vertically below it on the main curve. Read off the corresponding percentage loss in mass. The difference between this value and the previous total organic content obtained at the end of the pyrolysis of the carbonaceous residue (point F') is the carbon black content (P5).

8.5 Inorganic fillers and ash

8.5.1 Only inorganic compounds thermally stable at 800 °C are determined here. This does not include fillers such as carbonates or the water of hydration of inorganic compounds containing water of hydration.

8.5.2 The residue in the balance pan at the end of combustion in air or oxygen (point H') represents dehydrated or modified inorganic fillers plus the ash of the various organic and inorganic ingredients pyrolysed at lower temperatures. It therefore gives the percentage mass content of the dehydrated or modified inorganic fillers (P6).

8.5.3 It is important to remember that, with compounds containing inorganic fillers such as kaolin, calcium carbonate, silica or hydrated alumina, a correction of the content P6 is required to take into account the loss of moisture (in all forms) and the loss of thermal-decomposition products (e.g. carbon dioxide from calcium carbonate). This correction shall be applied after calibration with known compositions analysed by the same procedure.

The loss of absorbed water affects the overall analysis as soon as the temperature exceeds 100 °C. The size of this loss shall be checked over the whole temperature range by performing an analysis on pure filler. Thus, correction of all previously determined plasticizer, elastomer and carbon black contents could be required.

9 Precision

9.1 The precision of this method was determined in an interlaboratory round-robin test (seven laboratories participated) with seven different compounds containing only acrylonitrile-butadiene copolymer (NBR) and different contents and/or types of plasticizer and carbon black. Each material was analysed in duplicate and the following precision data were obtained.

9.2 Repeatability: The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values given in Table 1 only in one case in twenty.

Table 1

Property	Repeatability measurement units
Total organic content, %	1,18
Carbon black, %	0,61
Carbonaceous residue, %	0,94
Ash, %	1,00

9.3 Reproducibility: The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values given in Table 2 only in one case in twenty.

Table 2

Property	Repeatability measurement units
Total organic content, %	2,92
Carbon black, %	1,90
Carbonaceous residue, %	2,89
Ash, %	2,70

10 Test report

The test report shall include the following information:

- a) all details required for complete identification of the sample;
- b) a reference to this part of ISO 9924;
- c) the results obtained;
- d) any deviations from the procedure specified which might have affected the results;
- e) the date of the analysis.

