INTERNATIONAL STANDARD

ISO 1408

Third edition
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Rubber — Determination of carbon black content — Pyrolytic and chemical degradation methods

Caoutchouc — Dosage du noir de carbone — Méthode pyrolytique et méthodes par dégradation chimique

Reference number
ISO 1408:1995(E)

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.

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 1408 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This third edition cancels and replaces the second edition (ISO 1408:1987), of which it constitutes a minor revision.

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Rubber — Determination of carbon black content — Pyrolytic and chemical degradation methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard 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 International Standard specifies a pyrolytic method (A) and two chemical degradation methods (B and C) for the determination of the carbon black content of rubber.

1.2 Method A is preferred and should be used for the following polymers, except when certain compounding materials such as lead and cobalt salts, graphitic carbon blacks, phenolic and other resins, bitumen, or cellulose, etc., which cause the formation of a carbonaceous residue during pyrolysis, are present:

— polyisoprene, natural or synthetic;

— polybutadiene;

— styrene-butadiene copolymers;

— butyl rubber;

— acrylate rubber;

— ethylene-propylene copolymer;

— ethylene-propylene terpolymer;

— polyethers;

— polyethylene-derived polymers;

— silicone rubbers;

— fluorosilicone rubbers;

— chlorosulfonated polyethylenes containing less than 30 % (*m/m*) of chlorine.

The precision of this method may be affected if mineral fillers, e.g. alumina or calcium carbonate, are present which decompose or dehydrate, or form volatile halides in the case of halogenated polymers, at the pyrolysis temperature.

The method cannot be used for either chloroprene rubbers or butadiene-nitrile rubbers having an acrylic acid nitrile content greater than 30 % (*m/m*).

1.3 Method B is chiefly intended to be used with samples not amenable to the pyrolytic method A, although it can be used for all samples based on unsaturated rubbers except for isobutylene-isoprene copolymers.

1.4 Method C is relatively hazardous and should be used only for the analysis of samples based on isobutylene-isoprene copolymers and ethylene-propylene copolymers and related terpolymers when methods A and B fail.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged

to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 383:1976, *Laboratory glassware — Interchangeable conical ground joints.*

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

3 Principle

3.1 Method A

A weighed test piece of the rubber is extracted with acetone and, if bitumen is present, with dichloromethane. The extracted rubber is pyrolized in a combustion boat at 850 °C in a stream of nitrogen. The boat containing the non-volatile residue is cooled and weighed.

The carbon black is then burnt off in air or oxygen in a furnace at the same temperature. The boat and its contents are cooled and reweighed. The loss in mass represents the carbon black.

3.2 Method B

A weighed test piece of the rubber is extracted with acetone. The organic components are destroyed by oxidation with nitric acid, the acid-soluble inorganic components dissolving simultaneously in the nitric acid. The residue, which consists of carbon black and acid-insoluble mineral fillers is filtered, washed and then dried to constant mass at 850 °C in a nitrogen atmosphere to avoid oxidation of the carbon black.

The weighed residue is reheated at the same temperature (850 °C) (to avoid further change in mass of the inorganic matter) but this time in air so as to cause oxidation of the carbon black to carbon dioxide. The residue is cooled and reweighed. The loss in mass represents the carbon black.

3.3 Method C

After swelling of a test piece by hot *p*-dichlorobenzene, the organic matter is oxidized by *tert*-butyl hydroperoxide. The undissolved carbon black and mineral fillers are filtered, washed and then dried to constant mass at 850 °C in a nitrogen atmosphere to avoid oxidation of the carbon black.

The weighed residue is reheated at the same temperature (850 °C) (to avoid further change in mass of the inorganic matter) but this time in air so as to cause oxidation of the carbon black to carbon dioxide. The residue is cooled and reweighed. The loss in mass represents the carbon black.

4 Method A

WARNING — All recognized health and safety precautions shall be in effect when carrying out this method. All evaporations shall be carried out in a fume cupboard (hood).

4.1 Reagents

During the analysis, unless otherwise stated, use only reagents of analytical reagent grade (or equivalent) and only distilled water or water of equivalent purity.

4.1.1 Nitrogen, dry and free from oxygen.

NOTE 1 Commercial "oxygen-free" nitrogen may require further purification.

4.1.2 Oxygen or **air**, gaseous, dry.

4.1.3 Xylene, general laboratory grade.

4.1.4 Acetone.

4.1.5 Dichloromethane.

4.1.6 Ethanol-toluene azeotrope (ETA).

Mix 7 volumes of absolute ethanol with 3 volumes of toluene. Alternatively, mix 7 volumes of commercial-grade ethanol with 3 volumes of toluene and boil the mixture with anhydrous calcium oxide (quicklime) under reflux for 4 h. Then distil the azeotrope and collect the fraction with a boiling range not exceeding 1 °C, for use in the test.

4.2 Apparatus

Ordinary laboratory apparatus, plus the following:

4.2.1 Combustion boat, made of silica, of length 50 mm to 60 mm, with handle.

4.2.2 Tube furnace assembly see figure 1, comprised of the following component parts:

4.2.2.1 Combustion tube, made of quartz or of impervious aluminous porcelain, and fitted with means for advancing and withdrawing the combustion boat (4.2.1). The inside diameter shall be sufficient to allow the combustion boat to enter the tube and move easily through it. The tube shall be 30 cm longer than the tube furnace (4.2.2.2). One end of the tube

shall be provided with a gas-inlet system for nitrogen, the opposite end with a suitable outlet system for the vapours produced during the pyrolysis.

4.2.2.2 Horizontal-tube furnace, having an inside diameter sufficiently large to allow the combustion tube (4.2.2.1) to enter the heated section of the furnace. The furnace shall be electrically heated, thermostatically maintained at 850 °C ± 25 °C and fitted with a temperature-indicating device.

4.2.2.3 Silica glass rod with hook, of length sufficient to reach through the combustion tube (4.2.2.1) and inlet tube (4.2.2.4), and of diameter sufficient to make tight contact with the rubber tube in the inlet tube.

4.2.2.4 Inlet tube, with side tube for nitrogen supply and with a short length of rubber tubing in which the silica glass rod (4.2.2.3) is held by an airtight joint but can slide in and out of the combustion tube (4.2.2.1). The tubing used for the gas-inlet system shall be made of plasticized PVC or other material having a low permeability to oxygen and water vapour.

4.2.2.5 Vapour absorption equipment, consisting of rubber tubing for the connection of the outlet system of the combustion tube (4.2.2.1) with a trap for readily condensable vapours, two gas-washing bottles containing xylene (4.1.3), and flowmeters and flow-controllers for nitrogen or oxygen or air supplies.

4.2.3 Suitable extraction apparatus, as specified in ISO 1407.

4.2.4 Desiccator.

4.2.5 Muffle furnace, electrically heated, thermostatically controllable at 850 °C ± 25 °C.

4.3 Sampling

Cut a test sample of at least 1,5 g from the laboratory sample, preferably from more than one place, so that proper representation of the whole sample is achieved.

4.4 Procedure

4.4.1 Prepare the test sample by passing the rubber six times between the rolls of a laboratory mill set to a nip not exceeding 0,5 mm. Cut from the sheet a test piece having a mass of approximately 0,1 g to 0,5 g. If it is not possible to pass the sample through the mill, the sample may be cut into pieces less than 1 mm per side.

4.4.2 Weigh the test piece to the nearest 0,1 mg (mass m_0). Record this mass. Wrap the test piece in filter paper and extract with acetone (4.1.4) for 4 h or until the solvent in contact with the test piece is colourless. If bitumen is present in the compound, extract with dichloromethane (4.1.5) for 4 h or until the solvent in contact with the test piece appears colourless.

Uncured coumpounds cannot be extracted with dichloromethane. ETA (4.1.6) may be used instead of acetone or dichloromethane.

NOTE 2 Extraction with dichloromethane is only necessary if materials not completely soluble in acetone, such as bitumen, are present.

Extraction can be facilitated by comminuting the test piece before weighing. To do this, pass it through a mill with minimum clearance between the rolls.

4.4.3 Remove the extracted test piece from the filter paper and dry in an oven maintained at 100 °C ± 3 °C until the solvent is completely removed.

4.4.4 Quantitatively transfer the dried test piece to the combustion boat (4.2.1) and place the boat in the combustion tube (4.2.2.1) near the nitrogen inlet system.

4.4.5 Close the tube with the entry fitting and connect to the nitrogen supply (4.1.1). Introduce the combustion tube into the furnace (4.2.2.2) heated to 850 °C ± 25 °C but keep the boat in the cool part of the combustion tube. Connect the opposite end of the tube to the vapour absorption equipment (4.2.2.5).

4.4.6 Pass nitrogen through the tube at about 200 cm^3/min for 5 min or more to eliminate the air contained in the combustion tube.

4.4.7 Reduce the rate of nitrogen flow to about 100 cm^3/min and move the boat slowly into the heated zone of the combustion tube over a period of about 5 min.

4.4.8 Leave the boat in the hot zone for a further 5 min in order to complete the pyrolysis.

4.4.9 Withdraw the boat to the cold part of the tube and allow to cool for 10 min, while still maintaining the flow of nitrogen.

4.4.10 Transfer the boat to the desiccator (4.2.4), complete the cooling and weigh to the nearest 0,1 mg (mass m_1). Record this mass.

4.4.11 Place the boat in the combustion tube again and close the tube; connect the inlet system of the tube to the oxygen or air supply (4.1.2) and pass the gas through the tube at about 100 cm^3/min. Move the boat to the heated zone and keep it there until all traces of carbon black have been removed.

4.4.12 As an alternative to 4.4.11, heat the boat in the muffle furnace (4.2.5) at 850 °C ± 25 °C until all traces of carbon black have been removed.

4.4.13 Transfer the boat to the desiccator and allow to cool to room temperature.

4.4.14 Weigh the boat to the nearest 0,1 mg (mass m_2). Record this mass.

4.4.15 Carry out the determination in duplicate.

4.5 Expression of results

Calculate the carbon black content, as a percentage by mass, from the formula

$$\frac{m_1 - m_2}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test piece (see 4.4.2);

m_1 is the mass, in grams, of the combustion boat and its contents after heating in nitrogen (see 4.4.10);

m_2 is the mass, in grams, of the combustion boat and its contents after combustion of the carbon black in oxygen or air (see 4.4.14).

NOTES

3 The test piece may be taken from previously extracted material. In this case, a correction for solvent extract level would normally be made to obtain m_0.

4 Any matter volatile at 850 °C in the carbon black (as purchased) will be lost during the pyrolysis in nitrogen. The final result for the mass percentage of carbon black will therefore be low by this amount. In cases where the carbon black type and origin are known, a suitable correction can be made.

5 Method B

WARNING — Because of possible health and safety hazards inherent in this method, recognized health and safety precautions shall be observed with the use of acids and solvents. All operations shall be carried out in a properly ventilated fume hood, and safety glasses shall be worn during digestions, extractions and washings.

5.1 Reagents

Reagents specified in 4.1, plus the following:

5.1.1 Nitric acid (ρ = 1,42 Mg/m^3).

5.1.2 Hydrochloric acid solution.

Add 2 parts by volume of concentrated hydrochloric acid (ρ = 1,18 Mg/m^3) to 98 parts by volume of water.

5.1.3 Chloroform.

5.1.4 Acetone-chloroform mixture, 1 + 1 (V/V).

5.1.5 Sodium hydroxide solution, 250 g/dm^3.

5.1.6 Sodium hydroxide solution, 150 g/dm^3.

5.2 Apparatus

Apparatus specified in 4.2, plus the following:

5.2.1 Gooch crucible with a filtering layer of suitable inert, thermally stable filter material in the bottom, prepared as follows.

Make a dispersion of the filter material in water, pour some of the dispersion into the Gooch crucible, and apply a moderate vacuum. When a thick layer covers the bottom of the crucible, press a ceramic disc having small holes on to the fibrous layer. Pour more dispersion into the crucible until the disc is covered with a homogeneous layer of fibres, and apply a moderate vacuum. Before use, treat the crucible in accordance with the procedures described in 5.3.5 to 5.3.16 and then heat at 850 °C ± 25 °C for 2 h.

The tube furnace and associated systems (4.2.2) have to be capable of accepting the Gooch crucible.

5.3 Procedure

5.3.1 Weigh a test piece of about 0,3 g to 0,5 g of thinly sheeted sample to the nearest 0,1 mg (mass m_0). Record this mass. Extract and dry the test piece in accordance with 4.4.2 and 4.4.3.

5.3.2 Quantitatively transfer the dried test piece to a 100 cm^3 beaker containing about 10 cm^3 of nitric acid (5.1.1); cover with a watch-glass.

5.3.3 The oxidation reaction usually starts after a few minutes at room temperature. If it does not, warm the beaker gently on a boiling water bath until the reaction starts. Complete the first step of the reaction at room temperature with occasional heating on the boiling water bath, if necessary.

5.3.4 Make up to 50 cm^3 by washing the walls of the beaker with nitric acid (5.1.1) and complete the oxidative reaction by heating the beaker on the boiling water bath for 2 h with occasional stirring. The oxidation is complete when no bubbling or foam is observed on the surface of the liquid.

NOTE 5 Heating times and conditions mentioned in 5.3.3 and 5.3.4 must be adhered to strictly. Insufficient oxidation will cause the carbon black to be overestimated, owing to the presence of unoxidized polymer. Prolonged heating, on the other hand, will cause loss of carbon black by oxidation to carbon dioxide, as in the determination of styrene content by nitration (ISO 5478:1990, *Rubber — Determination of styrene content — Nitration method*), where more vigorous heating conditions are used to partially or completely remove carbon black. Such loss of carbon black is particularly likely to occur with carbon blacks of fine particle size.

5.3.5 Filter the warm solution through the Gooch crucible (5.2.1) with the aid of a moderate vacuum, maintaining the greater part of the insoluble residue in the beaker.

5.3.6 Wash the residue in the beaker three times with three portions of 10 cm^3 of warm nitric acid (5.1.1), filtering the washings through the Gooch crucible and maintaining the greatest part of the insoluble matter in the beaker.

5.3.7 Discard the filtrate and wash the filter flask thoroughly with water to remove all traces of nitric acid.

WARNING — Nitric acid and acetone may react and cause an explosion

5.3.8 Wash the insoluble matter in the beaker three times with three portions of 10 cm^3 of acetone (4.1.4), filtering the washings through the Gooch crucible and maintaining the greater part of the insoluble matter in the beaker.

5.3.9 Wash the insoluble matter in the beaker three times with three portions of 10 cm^3 of acetone-chloroform mixture (5.1.4), filtering the washings through the Gooch crucible and maintaining the greater part of the insoluble matter in the beaker.

5.3.10 Wash the insoluble matter in the beaker with three portions of 10 cm^3 of chloroform (5.1.3), filtering the washings through the Gooch crucible and maintaining the greater part of the insoluble matter in the beaker.

WARNING — Under basic conditions, mixtures of chloroform and acetone may explode. Thoroughly wash out the filter flask with acetone and then water before proceeding to 5.3.11.

5.3.11 Add to the beaker 25 cm^3 of 250 g/dm^3 sodium hydroxide solution (5.1.5) and heat on a boiling water bath for 30 min with occasional stirring.

5.3.12 Dilute with 35 cm^3 of warm water and filter the mixture through the Gooch crucible, quantitatively transferring the insoluble matter into the crucible.

5.3.13 Wash the beaker and the Gooch crucible with three portions of 10 cm^3 of 150 g/dm^3 sodium hydroxide solution (5.1.6).

5.3.14 Complete the quantitative transfer of the insoluble matter into the Gooch crucible by washing the beaker and the crucible with hydrochloric acid solution (5.1.2).

5.3.15 Wash the Gooch crucible with 10 cm^3 of acetone (4.1.4).

5.3.16 Dry the Gooch crucible at 850 °C ± 25 °C in a nitrogen atmosphere using the tube furnace and associated apparatus (4.2.2). Cool in the desiccator (4.2.4) and weigh to the nearest 0,1 mg (mass m_1). Record this mass.

5.3.17 Disconnect the nitrogen flow to the tube furnace and replace it with air or oxygen (4.1.2). Heat the Gooch crucible again at 850 °C ± 25 °C until all traces of carbon black have disappeared. Cool the Gooch crucible in the desiccator and weigh to the nearest 0,1 mg (mass m_2). Record this mass.

5.3.18 It is essential to check the experimental procedure by first carrying out the complete procedure on a sample containing a known amount of a similar grade of carbon black.

5.3.19 Carry out the determination in duplicate.

5.4 Expression of results

Calculate the carbon black content, as a percentage by mass, from the formula

$$\frac{m_1 - m_2}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test piece (see 5.3.1);

m_1 is the mass, in grams, of the Gooch crucible and its contents after drying at 850 °C in nitrogen (see 5.3.16);

m_2 is the mass, in grams, of the Gooch crucible and its contents after heating at 850 °C in air or oxygen (see 5.3.17).

NOTE 6 Any matter volatile at 850 °C in the carbon black (as purchased) will be lost during the pyrolysis in nitrogen. The final result for the mass percentage of carbon black will therefore be low by this amount. In cases where the carbon black type and origin are known, a suitable correction can be made.

6 Method C

WARNING — Because of possible health and safety hazards inherent in this method, recognized health and safety precautions shall be observed with the use of peroxides and solvents. All operations shall be carried out in a properly ventilated fume hood, and safety glasses shall be worn during digestions, extractions and washings.

6.1 Reagents

Reagents specified in 4.1 and 5.1, plus the following:

6.1.1 1,4-Dichlorobenzene (*p*-dichlorobenzene) or **1,2-dichlorobenzene** (*o*-dichlorobenzene).

6.1.2 ***tert*-Butyl hydroperoxide solution**, 60 % minimum purity. The remaining 40 % is commonly water or di-*tert*-butyl peroxide or *tert*-butanol.

This solution is stable for several months, if stored in a cool place.

6.1.3 Toluene.

6.2 Apparatus

Apparatus specified in 4.2 and 5.2, plus the following:

6.2.1 Flat-bottomed flask, capacity 150 cm^3, with conical ground-glass joint, 34/35, female, complying with the requirements of ISO 383.

6.2.2 Air condenser, with conical ground-glass joint, 34/35, female, complying with the requirements of ISO 383.

6.2.3 Water-cooled condenser, length 250 mm, with conical ground-glass joint, 34/35, male, complying with the requirements of ISO 383.

6.2.4 Hotplate, capable of being maintained at 200 °C.

6.2.5 Gooch crucible with a filtering layer, prepared as specified in 5.2 but treated in accordance with the procedures described in 6.3.7 to 6.3.15 and then heated at 850 °C ± 25 °C for 2 h.

6.3 Procedure

6.3.1 Weigh a test piece of about 0,3 g to 0,5 g of thinly sheeted sample to the nearest 0,1 mg (mass m_0). Record this mass. Place the test piece in a flask containing 20 g of dichlorobenzene (6.1.1).

6.3.2 Reflux the mixture gently (to avoid charring) in an efficient fume cupboard (hood) using the air condenser (6.2.2) for 30 min to 60 min.

NOTE 7 It may be beneficial to stir the mixture, while refluxing, to minimize the possibility of charring. This can conveniently be done by using a PTFE-coated stirring bar and a magnetic stirrer.

6.3.3 After allowing the mixture produced in 6.3.2 to cool to 80 °C to 90 °C, replace the air condenser with the water-cooled condenser (6.2.3) and add 5 cm^3 of *tert*-butyl hydroperoxide solution (6.1.2).

6.3.4 Reflux the mixture gently in the fume cupboard (hood) for 30 min to 60 min, then cool to 50 °C to 60 °C.

6.3.5 Add, through the condenser, 100 cm^3 to 150 cm^3 of toluene (6.1.3).

6.3.6 Allow the solution to stand for 1 h to 2 h. At the end of this period, the insoluble matter has to be settled on the bottom of the flask and the solution has to be clear. If the solution is not clear after standing for 2 h, repeat the determination, increasing the times specified in 6.3.2 and 6.3.4.

6.3.7 Filter through the Gooch crucible (6.2.5) under moderate vacuum, and wash the flask three times with three portions of 10 cm^3 of toluene (6.1.3), filtering the washings through the Gooch crucible. If any problem occurs with the filtration, repeat the determination, but use acetone (4.1.4) instead of toluene (6.1.3) in 6.3.5 and 6.3.7. Check that the filtrate is free from carbon black, then discard the filtrate.

6.3.8 Wash the flask three times with three portions of 10 cm^3 of acetone (4.1.4), filtering the washings through the Gooch crucible.

6.3.9 Discard the filtrate and wash the filter flask with water.

WARNING — Nitric acid and acetone may react and cause an explosion

6.3.10 Wash the flask and the Gooch crucible three times with three portions of 10 cm^3 of warm nitric acid (5.1.1).

6.3.11 Wash the flask and the Gooch crucible with the hydrochloric acid solution (5.1.2) and complete the quantitative transfer of the insoluble matter to the Gooch crucible.

6.3.12 Discard the filtrate and wash the filter flask with water.

6.3.13 Wash the Gooch crucible with 10 cm^3 of acetone (4.1.4).

6.3.14 Dry the Gooch crucible at 850 °C ± 25 °C in a nitrogen atmosphere, using the tube furnace and associated apparatus (4.2.2). Allow to cool in the desiccator (4.2.4) and weigh to the nearest 0,1 mg (mass m_1). Record this mass.

6.3.15 Disconnect the nitrogen flow to the tube furnace and replace it with air or oxygen (4.1.2). Heat the Gooch crucible again at 850 °C ± 25 °C until all traces of carbon black have disappeared. Allow the Gooch crucible to cool in the desiccator and weigh to the nearest 0,1 mg (mass m_2).

6.3.16 It is essential to check the experimental procedure by first carrying out the complete procedure on a sample containing a known amount of a similar grade of carbon black.

6.3.17 Carry out the determination in duplicate.

6.4 Expression of results

Calculate the carbon black content, as a percentage by mass, from the formula

$$\frac{m_1 - m_2}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test piece (see 6.3.1);

m_1 is the mass, in grams, of the Gooch crucible and its contents after drying at 850 °C in nitrogen (see 6.3.14);

m_2 is the mass, in grams, of the Gooch crucible and its contents after heating at 850 °C in air or oxygen (see 6.3.15).

NOTE 8 Any matter volatile at 850 °C in the carbon black (as purchased) will be lost during the pyrolysis in nitrogen. The final result for the mass percentage of carbon black will therefore be low by this amount. In cases where the carbon black type and origin are known, a suitable correction can be made.

7 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the method used (method A, B or C);

d) the mean of the two results and the units in which they are expressed;

e) any unusual features noted during the determination;

f) any operation not included in this International Standard or in the International Standards to which reference is made, as well as any operation regarded as optional;

g) the date of the test.