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

*Caoutchouc — Détermination de la teneur en noir de carbone — Méthode pyrolytique et
méthodes par dégradation chimique*

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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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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

This second edition cancels and replaces the first edition (ISO 1408 : 1976), of which it constitutes a technical revision, two chemical degradation methods having been added.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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

1 Scope and field of application

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, corresponding to ISO 1408 : 1976, 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) 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 References

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

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

3 Principle

3.1 Method A (section one)

Extraction of a weighed test portion of the rubber with acetone and, if bitumen is present, with dichloromethane. Pyrolysis of the extracted rubber in a combustion boat at 850 °C in a stream of nitrogen. Cooling and weighing of the boat containing the non-volatile residue.

Burning off the carbon black in air or oxygen in a furnace at the same temperature. Cooling and reweighing of the boat and its contents. The loss in mass represents the carbon black.

3.2 Method B (section two)

Extraction of a weighed test portion of the rubber with acetone. Destruction of the organic components by oxidation with nitric

acid, with simultaneous dissolution of acid-soluble inorganic components in the nitric acid. Filtration of the residue, which consists of carbon black and acid-insoluble mineral fillers. Washing and drying to constant mass at 850 °C in a nitrogen atmosphere to avoid oxidation of the carbon black.

Reheating the weighed residue 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. Cooling and reweighing of the residue. The loss in mass represents the carbon black.

3.3 Method C (section three)

After swelling of the test portion by hot *p*-dichlorobenzene, oxidation of the organic matter by *tert*-butyl hydroperoxide. Filtration of the undissolved carbon black and mineral fillers. Washing and drying to constant mass at 850 °C in a nitrogen atmosphere to avoid oxidation of the carbon black.

Reheating of the weighed residue 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. Cooling and reweighing of the residue. The loss in mass represents the carbon black.

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Section one : Method A

4 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.

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

4.1 Nitrogen, dry and free from oxygen.

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

4.2 Oxygen or air, gaseous, dry.

4.3 Xylene, general laboratory grade.

4.4 Acetone.

4.5 Dichloromethane.

4.6 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 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.

5 Apparatus

Ordinary laboratory apparatus, and

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

5.2 Tube furnace assembly (see figure), comprised of the following component parts.

5.2.1 Combustion tube, made of quartz or of impervious aluminous porcelain, and fitted with means for advancing and withdrawing the combustion boat (5.1). The inside diameter shall be suitable to allow the combustion boat to enter the tube and move easily through it. The tube shall be 30 cm longer than the electric tube furnace (5.2.2). One end of the tube is provided with a gas-inlet system for nitrogen, the opposite end with a suitable outlet system for the vapours produced during the pyrolysis.

5.2.2 Horizontal tube furnace having suitable inside diameter to allow the combustion tube (5.2.1) to enter the heated section of the furnace. The furnace is electrically heated and thermostatically maintained at 850 ± 25 °C, with a temperature-indicating meter.

5.2.3 Silica glass rod with hook, of length sufficient to reach through the combustion tube (5.2.1) and inlet tube (5.2.4), and of diameter sufficient to make tight contact with the rubber tube in the inlet tube.

5.2.4 Inlet tube with side tube for nitrogen supply and with a short length of rubber tubing in which the silica glass rod (5.2.3) is held by an air-tight joint but can slide in and out of the combustion tube (5.2.1). 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.

5.2.5 Vapour absorption equipment consisting of rubber tubing for the connection of the outlet system of the combustion tube (5.2.1) with a trap for readily condensable vapours, two gas-washing bottles containing xylene (4.3), and flow-meters and flow-controllers for nitrogen or oxygen or air supplies.

5.3 Suitable extraction apparatus, as specified in ISO 1407.

5.4 Desiccator.

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

6 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.

7 Procedure

7.1 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 portion having a mass of approximately 0,1 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.

7.2 Weigh the test portion to the nearest 0,1 mg (mass m_0). Record this mass. Wrap the test portion in filter paper and extract with acetone (4.4) for 4 h or until the solvent in contact with the test portion is colourless. If bitumen is present in the compound, extract with dichloromethane (4.5) for 4 h or until the solvent in contact with the test portion appears colourless.

Uncured compounds cannot be extracted with dichloromethane. ETA (4.6) may be used instead of the acetone and dichloromethane.

NOTE — 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 portion before weighing. To do this, pass it through a mill with minimum clearance between the rolls.

7.3 Remove the extracted test portion from the paper and dry in an oven controlled at 100 ± 3 °C until the solvent is completely removed.

7.4 Quantitatively transfer the dried test portion to the combustion boat (5.1) and place the boat in the combustion tube (5.2.1) near the nitrogen inlet system.

7.5 Close the tube with the entry fitting and connect to the nitrogen (4.1) supply. Introduce the combustion tube into the furnace (5.2.2) heated to 850 ± 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 (5.2.5).

7.6 Pass the nitrogen through the tube at about 200 cm³/min for 5 min or more to eliminate the air contained in the combustion tube.

7.7 Reduce the rate of nitrogen flow to about 100 cm³/min and move the boat slowly into the heated zone of the combustion tube over a period of about 5 min.

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

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

7.10 Transfer the boat to the desiccator (5.4), complete the cooling and weigh to the nearest 0,1 mg (mass m_1). Record this mass.

7.11 Place the boat in the combustion tube again and close the tube; connect the inlet system of the tube to the oxygen or air (4.2) supply and pass the gas through the tube at about 100 cm³/min. Move the boat to the heated zone and keep it there until all traces of carbon black have been removed.

7.12 As an alternative to 7.11, heat the boat in the muffle furnace (5.5) at 850 ± 25 °C until all traces of carbon black have been removed.

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

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

7.15 Carry out the determination in duplicate.

8 Expression of results

The carbon black content is given, as a percentage by mass, by the formula

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

where

m_0 is the mass, in grams, of the test portion (7.2);

m_1 is the mass, in grams, of the combustion boat and its contents after heating in nitrogen (7.10);

m_2 is the mass, in grams, of the combustion boat and its contents after the combustion of the carbon black in oxygen or air (7.14).

NOTES

1 The test portion may be taken from previously extracted material. In this case a correction for solvent extract level may be made to obtain m_0 .

2 Any matter volatile at 850 °C inherent 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.

9 Test report

The test report shall include the following particulars :

- complete identification of the sample;
- reference to this International Standard;
- the method used (method A);
- the mean of the two results;
- any unusual features noted during the determination;
- any operation not included in this International Standard or in the International Standards to which reference is made, or any operation regarded as optional.

Section two : Method B

10 Reagents

WARNING — Because of possible health and safety hazards inherent in following this procedure, 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.

Reagents specified in clause 4, and

10.1 Nitric acid ($\rho = 1,42 \text{ Mg/m}^3$).

10.2 Hydrochloric acid solution.

Dilute 2 parts by volume of hydrochloric acid ($\rho = 1,18 \text{ Mg/m}^3$) with 98 parts by volume of water.

10.3 Chloroform.

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

10.5 Sodium hydroxide solution, 250 g/l.

10.6 Sodium hydroxide solution, 150 g/l.

11 Apparatus

Apparatus specified in clause 5, and

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

Make a dispersion of the filter aid in water, pour 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 onto 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 according to the procedures described in 12.5 to 12.16 and then heat at $850 \pm 25 \text{ }^\circ\text{C}$ for 2 h.

The tube furnace and associated systems (5.2) have to be capable of accepting the Gooch crucible.

12 Procedure

12.1 Weigh a test portion of about 0,3 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 portion according to 7.2 and 7.3.

12.2 Quantitatively transfer the dried test portion to a 100 cm^3 beaker containing about 10 cm^3 of nitric acid (10.1); cover with a watch-glass.

12.3 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.

12.4 Make up to 50 cm^3 by washing the walls of the beaker with nitric acid (10.1) 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 — Heating times and conditions mentioned in 12.3 and 12.4 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), 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.

12.5 Filter the warm solution through the Gooch crucible (clause 11) with the aid of a moderate vacuum, maintaining the greater part of the insoluble residue in the beaker.

12.6 Wash the residue in the beaker three times with three portions of 10 cm^3 of warm nitric acid (10.1), filtering the washings through the Gooch crucible and maintaining the greatest part of the insoluble matter in the beaker.

12.7 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.

12.8 Wash the insoluble matter in the beaker three times with three portions of 10 cm^3 of acetone (4.4), filtering the washings through the Gooch crucible and maintaining the greater part of the insoluble matter in the beaker.

12.9 Wash the insoluble matter in the beaker three times with three portions of 10 cm^3 of acetone-chloroform mixture (10.4), filtering the washings through the Gooch crucible and maintaining the greater part of the insoluble matter in the beaker.

12.10 Wash the insoluble matter in the beaker with three portions of 10 cm^3 of chloroform (10.3), 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 12.11.

12.11 Add to the beaker 25 cm³ of the sodium hydroxide solution (10.5) and heat on a boiling water bath for 30 min with occasional stirring.

12.12 Dilute with 35 cm³ of warm water and filter the mixture through the Gooch crucible, quantitatively transferring the insoluble matter into the crucible.

12.13 Wash the beaker and the Gooch crucible with three portions of 10 cm³ of the sodium hydroxide solution (10.6).

12.14 Complete the quantitative transfer of the insoluble matter into the Gooch crucible by washing the beaker and the crucible with the hydrochloric acid solution (10.2).

12.15 Wash the Gooch crucible with 10 cm³ of acetone (4.4).

12.16 Dry the Gooch crucible at 850 ± 25 °C in a nitrogen atmosphere using the tube furnace and associated apparatus (5.2). Cool in the desiccator (5.4) and weigh to the nearest 0,1 mg (mass m_1). Record this mass.

12.17 Disconnect the nitrogen flow to the tube furnace and replace it with air or oxygen (4.2). Heat the Gooch crucible again at 850 ± 25 °C until all trace of carbon black disappears. Cool the Gooch crucible in the desiccator and weigh to the nearest 0,1 mg (mass m_2). Record this mass.

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

12.19 Carry out the determination in duplicate.

13 Expression of results

The carbon black content is given, as a percentage by mass, by the formula

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

where

m_0 is the mass, in grams, of the test portion (12.1);

m_1 is the mass, in grams, of the Gooch crucible and its contents after drying at 850 °C in nitrogen (12.16);

m_2 is the mass, in grams, of the Gooch crucible and its contents after heating at 850 °C in air or oxygen (12.17).

NOTE — Any matter volatile at 850 °C inherent 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.

14 Test report

The test report shall include the following particulars :

- a) complete identification of the sample;
- b) reference to this International Standard;
- c) the method used (method B);
- d) the mean of the two results;
- 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, or any operation regarded as optional.

Section three : Method C

15 Reagents

WARNING — Because of possible health and safety hazards inherent in following this procedure, 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.

Reagents specified in clauses 4 and 10, and

15.1 1,4-Dichlorobenzene [*p*-Dichlorobenzene] or **1,2-Dichlorobenzene** [*o*-Dichlorobenzene].

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

These solutions are stable for several months, if stored in a cool place.

15.3 Toluene.

16 Apparatus

Apparatus specified in clauses 5 and 11, and

16.1 Flat-bottomed flask, capacity 150 cm³, with conical ground glass joint 34/35, female¹⁾.

16.2 Air condenser with conical ground glass joint 34/35, male¹⁾.

16.3 Water-cooled condenser, length 250 mm, with conical ground glass joint 34/35, male¹⁾.

16.4 Hot-plate capable of being controlled at 200 °C.

16.5 Gooch crucible with filtering layer prepared as specified in clause 11 but treated according to the procedures described in 17.7 to 17.15 and then heated at 850 ± 25 °C for 2 h.

17 Procedure

17.1 Weigh a test portion of about 0,3 to 0,5 g of thinly sheeted sample to the nearest 0,1 mg (mass m_0). Record this mass. Place the test portion in a flask containing 20 g of dichlorobenzene (15.1).

17.2 Reflux the mixture gently (to avoid charring) in an efficient fume cupboard (hood) using the air condenser (16.2) for 30 to 60 min.

NOTE — 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.

17.3 After allowing the mixture (17.2) to cool to 80 to 90 °C, replace the air condenser with the water-cooled condenser (16.3) and add 5 cm³ of *tert*-butyl hydroperoxide solution (15.2).

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

17.5 Add, through the condenser, 100 to 150 cm³ of the toluene (15.3).

17.6 Allow the solution to stand for 1 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 17.2 and 17.4.

17.7 Filter through the Gooch crucible (16.5) under moderate vacuum, and wash the flask three times with three portions of 10 cm³ of toluene (15.3), filtering the washings through the Gooch crucible. If any problem occurs with the filtration, repeat the determination, but use acetone (4.4) instead of toluene (15.3) in 17.5 and 17.7. Check that the filtrate is free from carbon black, then discard the filtrate.

17.8 Wash the flask three times with three portions of 10 cm³ of acetone (4.4), filtering the washings through the Gooch crucible.

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

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

17.10 Wash the flask and the Gooch crucible three times with three portions of 10 cm³ of warm nitric acid (10.1).

17.11 Wash the flask and the Gooch crucible with the hydrochloric acid solution (10.2) and complete the quantitative transfer of the insoluble matter to the Gooch crucible.

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

17.13 Wash the Gooch crucible with 10 cm³ of acetone (4.4).

1) Conical ground glass joints complying with the requirements of ISO 383 and designated as recommended in ISO 383.