International Standard 5945

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Rubber — Determination of polyisoprene content

Caoutchouc — Détermination de la teneur en polyisoprène

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Foreword

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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.

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It has been approved by the member bodies of the following countries:

Australia	Germany, F. R.	South Africa, Rep. of
Austria	Hungary	Spain
Belgium	India	Sweden
Brazil	Ireland	Switzerland
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Czechoslovakia	Mexico	USA
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No member body expressed disapproval of the document.

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Rubber — Determination of polyisoprene content

1 Scope and field of application

1.1 This International Standard specifies a method for the determination of polyisoprene occurring as natural isoprene rubber (NR)[1], synthetic isoprene rubber (IR), balata and gutta percha, in the total solids from NR or IR latices, in solid raw rubbers, or in cured or uncured compounds.

The method is applicable to these isoprene rubbers alone or in blends. It cannot be used for hard rubber (ebonite) without modification.

1.2 Compounding ingredients, such as carbon black, mineral oil and sulphur, in soft rubbers do not interfere (see table 1) (but see also 8.2). If vinyl acetate polymers are present, the method should not be used.

1.3 The method is applicable to blends of the rubbers mentioned in 1.1 with SBR, BR and NBR.

If halogenated rubbers are present, a slightly modified procedure, described in 7.7.3, should be used. Some interference may be expected, because these rubbers react with chromic acid in a manner similar to polyisoprene. If these interfering rubbers are the major part of the blend, they may impede the reaction of the polyisoprene with the chromic acid. The digestion should then be checked for completeness on known mixtures of these interfering rubbers.

Milling of the test portion as finely as possible is advisable.

1.4 The method may be used for the determination of polyisoprene in reclaimed rubbers, but it has been found to give consistently lower values than the previously accepted estimates for the polyisoprene content.

1.5 If rubbers other than those mentioned in 1.3 are present (CSM, EPDM, IIR, CIIR and BIIR), the digestion time should be modified. The estimates should be corrected by comparison with results from similar rubber blends. If these interfering rubbers are present in the blend, they may impede the reaction of the polyisoprene with the chromic acid and the method is not applicable. Greatest deviations are found if polysulphide rubbers are present as part of the mixture. (See table 2.)

2 References

ISO 123, *Rubber latex — Sampling.*

ISO 124, *Rubber latices — Determination of total solids content.*

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

ISO 1795, *Raw rubber in bales — Sampling.*

ISO 1796, *Rubber, raw — Sample preparation.*

3 Principle

Quantitative oxidation of the polyisoprene present in a test portion with a hot digestion mixture of sulphuric and chromic acids; distillation of the acetic acid formed, aeration of the distillate to remove carbon dioxide and titration of the acetic acid with sodium hydroxide solution.

The calculation is based on the observation that a 75 % yield of acetic acid is always obtained in oxidation of the isoprene unit under the specified test conditions.

4 Reagents

All recognized health and safety precautions shall be exercised when performing this method of analysis.

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Phenolphthalein, 2 g/dm^3 alcoholic indicator solution.

Dissolve 0,2 g of phenolphthalein in 50 cm^3 of 95 % (*V*/*V*) ethanol. Dilute to 100 cm^3 with the same ethanol.

4.2 Chromic acid digestion mixture.

Dissolve 200 g of chromium trioxide (CrO_3) in 500 cm^3 of water. Carefully add, while stirring, 150 cm^3 of sulphuric acid (H_2SO_4), ϱ_{20} = 1,84 Mg/m^3.

1) For the meanings of the abbreviations, see ISO 1629, *Rubbers and latices — Nomenclature.*

4.3 Sodium hydroxide, standard volumetric solution, of concentration, $c(NaOH) = 0,1$ mol/dm³* or 0,05 mol/dm³**.

The choice of concentration depends upon the size of the test portion, the amount of polyisoprene and the test assembly used.

4.4 Extraction solvents : acetone, chloroform (used in a closed extraction system) or dichloromethane.

4.5 Potassium iodide solution.

Dissolve 84 g of potassium iodide in water and dilute to 1 000 cm³.

4.6 Sodium thiosulphate solution.

Dissolve 79 g of sodium thiosulphate ($Na_2S_2O_3$) in water and dilute to 1 000 cm³.

5 Apparatus

5.1 Balance, accurate to 0,000 1 g.

5.2 Extraction apparatus, as described in ISO 1407.

5.3 Digestion and distillation assembly.

A suitable assembly for the digestion and distillation apparatus is shown in figure 1. Heating is carried out by heating mantles. Any apparatus which will perform the same functions, in the same sequence, as the items shown, may be substituted.

5.4 Aeration assembly (see figure 2), containing a capillary tube, which, when connected to a reduced pressure line, will maintain, through the receiving flask, an air flow of approximately 33 cm³/s. If the absolute pressure is less than 4 kPa (30 mmHg), a capillary tube of length approximately 100 mm and of 1 mm bore will maintain the required air flow.

Since it is essential to maintain the aeration at a rate within 20 % of 33 cm³/s, each capillary tube shall be tested before use. The following method may be used.

Invert a graduated tube over a beaker filled with water and evacuate the air through the capillary by means of a tube extending up into the graduated tube. The rate of air flow will be the same as the rate at which water fills the graduated tube.

5.5 Absorption device, to prevent carbon dioxide from entering the aeration assembly.

6 Sampling

Sample raw rubber in accordance with ISO 1795, or use any other method that provides a representative sample of the product to be analysed in the case of cured or uncured compounds.

Sample latex in accordance with ISO 123.

7 Procedure

7.1 Preparation of test sample

Mill the test sample to as thin a sheet as possible, not exceeding 0,5 mm.

For a finished product, if milling to thicknesses of 0,5 mm or less is not practicable, cut the sample into the smallest possible pieces.

The thickness limit of 0,5 mm shall not be exceeded; otherwise samples of some uncured NR or IR rubbers, or blends of CSM, EPDM, IIR, BIIR or CIIR compounds, cured or uncured, may not be sufficiently thin to allow complete oxidation by the chromic acid.

For latex, prepare a film in accordance with ISO 124.

7.2 Test portion

Weigh, to the nearest 0,000 1 g, a mass of test portion appropriate for the apparatus to be used and the expected polyisoprene content of the sample. For the apparatus shown in figure 1, a test portion of 0,15 to 0,25 g is normally satisfactory; if the expected polyisoprene content is particularly low, a larger test portion will be necessary.

7.3 Extraction

If the sheeted test portion is coherent, place it in the extraction cup (see ISO 1407). If it is unmanageable, or sticky, wrap it in filter paper before placing in the cup.

Extract the test portion for 16 h, or overnight, with the acetone (4.4). Alternatively place the unwrapped test portion in the required solvent and reflux directly for 4 h as for the rapid reflux extraction in accordance with ISO 1407.

If the presence of bituminous material (mineral rubber) or factice is suspected, carry out a further extraction for 4 h with the chloroform, in a closed system, or the dichloromethane (4.4).

WARNING — Do not mix acetone and chloroform. In the presence of bases, they may form explosive mixtures.

* Hitherto expressed as "0,1 N or 0,1 M standard volumetric solution".

** Hitherto expressed as "0,05 N or 0,05 M standard volumetric solution".

Raw rubbers which are not oil extended, may be digested without prior extraction.

All test portions shall be thoroughly dried before proceeding to the digestion (7.4).

7.4 Digestion

If necessary, unwrap the test portion; bits of paper adhering to the test portion need not be completely removed; small amounts of cellulose do not interfere with the determination.

Place the test portion in the digestion flask (see 5.3) and add an appropriate volume of the digestion mixture (4.2). For the apparatus shown in figure 1, 25 cm^3 should be used. Greater volumes may be used according to the type of apparatus.

Place the receiver flask, containing 100 cm^3 of water, under the condenser and adapter of the distillation assembly.

Heat the digestion mixture to 100 ± 5 °C for a period sufficient to ensure complete digestion of the polyisoprene. Determine the correct heating mantle setting by heating the digestion mixture, without the sample, measuring the temperature of the digestion mixture with a thermometer. For the apparatus shown in figure 1, a digestion time of 30 min is sufficient. Other types of apparatus may need longer digestion times — up to 1 h, for example.

If the test portion is a mixture of NR and/or IR with the rubbers specified in 1.5, complete digestion of these rubbers is not possible, but the polyisoprene will be digested. Although each apparatus may require different digestion times, the time should be maintained consistent for each type of apparatus.

7.5 Distillation

7.5.1 During the digestion step, the steam generation flask should be heated with the stopper removed, so that steam is available at the end of the digestion period. If the laboratory is equipped with a steam line, this is unnecessary.

7.5.2 After 30 min, replace the stopper and delivery tube in the mouth of the steam generation flask, and allow steam to enter the digestion flask. Continue heating the digestion flask to maintain the total volume at about 75 cm^3. The rate of distillation and cooling shall be controlled so that the temperature of the condensate is not more than 30 °C.

7.5.3 Collect 150 cm^3 of distillate for the apparatus shown in figure 1, and appropriately larger volumes for larger apparatus.

7.5.4 At the end of distillation (usually 20 min for the apparatus shown in figure 1), remove the delivery tube from the receiver flask, carefully wash the tube with distilled water into the receiver flask and place on the aeration assembly.

7.5.5 Disconnect the steam delivery tube from the digestion flask as soon as the receiver flask is removed from the apparatus. This is to ensure that chromic acid mixture will not be sucked back into the steam generator when the heat source is removed.

7.6 Aeration

Adjust the temperature of the distillate to room temperature and aerate for 30 min for all types of digestion and distillation apparatus.

NOTE — The rates of loss of carbon dioxide and acetic acid during aeration have been investigated for temperature range, type of aeration apparatus and recommended rate of air flow. Variation of any of these factors may lead to erroneous analytical results.

7.7 Titration

7.7.1 Remove the receiver flask from the aeration assembly, washing the delivery tube with distilled water and collecting the washings in the receiver flask. Add 5 drops of the phenolphthalein solution (4.1). Titrate with the 0,05 mol/dm^3 sodium hydroxide solution (4.3), in the case of test portions of 0,15 to 0,25 g, and with the 0,1 mol/dm^3 sodium hydroxide solution (4.3) for larger test portions.

7.7.2 Carry out a blank test of the digestion mixture reagents as often as necessary, or when a new supply of chromic acid is used.

7.7.3 If halogenated rubbers are suspected, add the potassium iodide solution (4.5) to the distillate after aeration and remove any liberated iodine (indicated by a yellow solution) with the sodium thiosulphate solution (4.6). Proceed with the titration as specified in 7.7.1.

8 Expression of results

8.1 Calculate the polyisoprene content, as a percentage by mass, if no combined sulphur is present or if the combined sulphur content is unknown, by the formula

$$\frac{0{,}090\,8 \times (V_1 - V_0) \times c}{m} \times 100$$

where

V_1 is the volume, in cubic centimetres, of the sodium hydroxide solution (4.3) used to titrate the test solution;

V_0 is the volume, in cubic centimetres, of the sodium hydroxide solution (4.3) used to titrate the reagent blank solution (see 7.7.2);

c is the exact concentration, in moles per cubic decimetre, of the sodium hydroxide solution used;

m is the mass, in grams, of the test portion;

0,090 8 is a stoichiometric constant based on the observation that a 75 % yield is always obtained in the oxidation of the isoprene unit under the specified test conditions.

8.2 Calculate the polyisoprene content, as a percentage by mass, if the combined sulphur content is known, by the formula

$$A\ (1 + 0{,}015\ S)$$

where

A is the apparent polyisoprene content, calculated according to 8.1;

S is the combined sulphur content, expressed as a percentage of the apparent polyisoprene content (A).

9 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) identification of the sample;

c) the results obtained and the method of calculation used (8.1 or 8.2);

d) any unusual features which may have affected the results;

e) the date of test.

Table 1 — Degree of interference of rubber compounding ingredients

Compounding ingredient	Interference
Combined sulphur	See 8.2.
Carbon black	None as tested in tread compounds.
Cellulose	Negligible, 2 % or less of its mass reacts as if it were rubber hydrocarbon.
Asphaltic hydrocarbon (mineral rubber)	Removed by acetone and chloroform extraction. If not extracted with chloroform, incorrect results will be obtained.
Factice, brown	Negligible after acetone and chloroform extraction.
Polyisobutylene	Virtually unattacked.
Polyvinyl acetate or polyvinyl acetate copolymers	Interferes by producing acetic acid. Method invalid if these ingredients are present.

Table 2 — Behaviour of rubber-like materials in chromic acid oxidation procedure

Material	Behaviour
Hard NR or IR products	See 8.2.
NR (balata)	Approximately equivalent to isoprene polymer.
Polysulphide rubbers	Approximately 18 % of its mass reacts as if it were isoprene polymer.
NBR	Approximately 1,5 to 2 % of its mass reacts as if it were isoprene polymer.
SBR	Approximately 3 % of its mass reacts as if it were isoprene polymer.
CR	Approximately 3 % of its mass reacts as if it were isoprene polymer, if a modification of the procedure is used to avoid the interference of chlorine (7.7.3).
IIR	Virtually unattacked but may interfere by preventing complete reaction with NR or IR.