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Rubber — Determination of styrene content — Nitration method

Caoutchouc — Détermination de la teneur en styrène — Méthode par nitration

Reference number
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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 5478 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This third edition cancels and replaces the second edition (ISO 5478:1990), which has been revised to update the normative references.

Rubber — Determination of styrene content — Nitration method

1 Scope

This International Standard specifies a method for the determination of the styrene content of all types of styrene-butadiene rubber (SBR), including oil-extended types.

The method is applicable to styrene-butadiene rubbers reinforced with styrene homopolymer, to give the total styrene content. The method is also applicable for determining the styrene in block copolymers containing up to 50 % (by mass) of styrene.

It is applicable to vulcanizates of mixtures of SBR with other polymers (NR, BR, IR and CR) and is considered a method for estimating the SBR content of mixtures, if the styrene content of the SBR is known and provided that no other styrene-containing materials are present.

Any other non-extractable aromatic material which absorbs in the specified spectral region will interfere with this method.

The procedure may give low results when the content of mineral fillers insoluble in nitric acid exceeds 5 % (by mass).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 1407, *Rubber — Determination of solvent extract*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 4655, *Rubber — Reinforced styrene-butadiene latex — Determination of total bound styrene content*

ISO 4661-2, *Rubber vulcanized — Preparation of samples and test pieces — Part 2: Chemical tests*

3 Principle

3.1 A test portion is extracted with acetone and digested with nitric acid to oxidize the styrene to *p*-nitrobenzoic acid.

3.2 The *p*-nitrobenzoic acid is extracted with diethyl ether.

3.3 The *p*-nitrobenzoic acid is extracted from the ether with sodium hydroxide solution and measured spectrometrically in the ultraviolet spectral region.

4 Reagents and materials

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

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 ether and acids. Extractions shall be carried out in a properly ventilated fume hood and safety glasses shall be worn during these extractions.

4.1 Nitric acid, $\rho = 1{,}43$ g/cm^3.

The nitric acid shall be fresh. Old batches may give inferior nitration.

4.2 Sodium hydroxide, solution, $c(\text{NaOH}) = 5$ mol/dm^3.

Dissolve 200 g of sodium hydroxide in water and dilute to 1 000 cm^3.

4.3 Sodium hydroxide, solution, $c(\text{NaOH}) = 0{,}1$ mol/dm^3.

Dissolve 4 g of sodium hydroxide in water and dilute to 1 000 cm^3.

4.4 Diethyl ether, free from peroxides.

4.5 Sodium chloride, saturated solution.

4.6 Sodium sulfate, anhydrous.

4.7 SBR of known styrene content, preferably in the region of 23,5 % (by mass), for spectrometric calibration.

4.8 Carborundum boiling chips.

4.9 Acetone.

4.10 Dichloromethane.

5 Apparatus

Ordinary laboratory apparatus, plus the following:

5.1 Conical flasks, of capacity 100 cm^3 or 125 cm^3, with 24/29 ground-glass necks (see ISO 383) to fit the Graham condenser.

5.2 Graham condenser, water-cooled, with inner joint, with a 24/29 ground-glass cone to fit the flasks (5.1).

5.3 Separating funnels, of capacity 500 cm^3.

5.4 Spectrometer, with 10 mm silica cells, capable of accurately measuring absorbance within the range 260 nm to 290 nm.

5.5 Hotplate, with variable-heating facility, capable of maintaining concentrated nitric acid at a vigorous boil. (The surface of the hotplate shall be capable of reaching a temperature of approximately 350 °C.)

5.6 Soxhlet extraction apparatus, as in ISO 1407.

6 Sample selection and preparation of test portion

6.1 Sample selection

For raw rubbers, select and prepare a sample in accordance with ISO 1795. For vulcanized rubbers, select a sample in accordance with ISO 4661-2.

6.2 Preparation of test portion

6.2.1 Mill the raw rubber or product to produce a sheet (or crumb) less than 0,5 mm thick and weigh, to the nearest 0,1 mg, a test portion such that its mass, in grams, multiplied by the estimated styrene content, expressed as a percentage by mass, is equal to 4,5. (The intention is to obtain an ultimate absorbance value between 0,3 and 0,8.)

6.2.2 If the styrene content is completely unknown, use a 0,5 g test portion.

6.3 Extraction of test portion

6.3.1 Extract the test portion (see 6.2) overnight with acetone (4.9) in the extraction apparatus (5.6).

NOTE 1 The object of this preliminary extraction is to remove oil and non-rubber additives. It is not intended to remove styrene homopolymers or styrene resins if it is desired to determine the total styrene content.

NOTE 2 Acetone will not dissolve styrene homopolymers and is a good extractant for raw rubbers, raw rubber mixes and vulcanizates, all of which may be extracted with this solvent.

6.3.2 If bituminous material is present in a vulcanizate, extract additionally with dichloromethane (4.10). This is not applicable to unvulcanized materials, which should be appropriately vulcanized to enable them to be analysed. Vulcanization can be achieved at 110 °C for 45 min.

6.3.3 Dry the rubber until free of solvent (usually 1 h at 100 °C is sufficient to remove the acetone).

7 Procedure

7.1 Place the extracted, dry rubber (see 6.3) in a flask (5.1), together with 20 cm^3 of nitric acid (4.1). Add a few carborundum boiling chips (4.8).

7.2 Place the flask on the cold hotplate (5.5) and connect to the Graham condenser (5.2). Heat cautiously until the initial vigorous reaction has subsided. This reduces the risk of rapid oxidation, which might cause the rubber to burst into flames. If flames are observed, repeat the procedure from the beginning.

7.3 Boil vigorously for at least 16 h, continuing the boiling until a clear straw-coloured solution is obtained.

7.4 Turn off the heat, allow to cool to room temperature, add 10 cm^3 to 20 cm^3 of water to the top of the condenser and allow the water to be drawn into the flask as it cools.

7.5 Remove the flask from the condenser, rinsing the glass joint. Perform the following transfer and extraction operations with care, as the skill with which these are performed determines the accuracy of the analysis.

7.6 Transfer the reaction mixture to a 400 cm^3 beaker, rinsing with small portions of distilled water. Cool to ambient temperature and carefully add 50 cm^3 of sodium hydroxide solution (4.2) while swirling the beaker. Verify that the solution is still strongly acidic with a pH-meter or pH-indicating paper; if it is not, add nitric acid (4.1) drop-wise until the solution is strongly acidic.

7.7 Cool to ambient temperature and transfer the solution to a separating funnel (5.3).

7.8 Shake the solution in the separating funnel with 50 cm^3 of diethyl ether (4.4) and allow the layers to separate. Drain the lower, aqueous layer into the original 400 cm^3 beaker (see 7.6).

7.9 Add 25 cm^3 of sodium chloride solution (4.5) to the funnel. Drain a few cubic centimetres into the beaker to rinse out the stem, shake vigorously and allow the layers to separate.

7.10 Drain off the lower, aqueous layer into the 400 cm^3 beaker (see 7.8) and pour off the ether layer into a 250 cm^3 beaker containing 5 g of sodium sulfate (4.6).

7.11 Swirl the ether with the sodium sulfate, and allow the latter to settle. Transfer the dried ether extract to a dry 500 cm^3 separating funnel.

7.12 Carry out a total of three extractions, repeating the procedures specified in 7.8 to 7.11 and drying each ether extract over the same 5 g of sodium sulfate.

7.13 Combine the ether extracts by transferring each one, after drying, to the same dry 500 cm^3 separating funnel and, after the three extracts have been combined, add 50 cm^3 of sodium hydroxide solution (4.3). Shake and allow the layers to separate. Allow a few cubic centimetres of each fresh portion of sodium hydroxide solution to flow through the stem of the separating funnel to rinse out the previous hydroxide wash before shaking with additional sodium hydroxide solution.

Use care when shaking ether because of pressure build-up. Stoppering the funnel and shaking in an inverted position with the stop-cock alternately closed when shaking and open when not shaking, to release pressure, eliminates possible loss of liquid.

7.14 Repeat the extractions described in 7.13 three times for a total of four extractions, combining each alkaline aqueous extract in a single 250 cm^3 volumetric flask. Remove any ether which comes to the top of the volumetric flask using a pipette. Dissolved ether can be disregarded.

WARNING — Do not distil to expel ether because of the risk of explosion.

7.15 Dilute the combined extracts of 7.14 with sodium hydroxide solution (4.3) to the mark of the volumetric flask. Shake, and transfer a 25 cm^3 aliquot portion to a clean, dry 250 cm^3 volumetric flask. Make up to the mark with sodium hydroxide solution (4.3) and mix thoroughly. This is the test solution.

7.16 Using the spectrometer (5.4), measure the absorbance of the test solution (see 7.15) in a 10 mm silica cell at 265 nm, 274 nm and 285 nm, using sodium hydroxide solution (4.3) as the reference (instrument blank) liquid.

7.17 If the absorbance is above 0,8, repeat the analysis using a smaller test portion, or take a smaller aliquot portion in the preparation of the test solution (see 7.15).

7.18 Calculate the styrene content in accordance with 9.1 if a reference SBR is available, or in accordance with 9.2 if a reference SBR is not available.

8 Determination of calibration constants (K_1, K_2 and K_3)

8.1 For the most accurate analysis, a spectrometric calibration is desirable, using a reference sample of styrene-containing copolymer having a styrene content approximately the same as that in the unknown sample. The styrene content of an un-compounded unfilled standard sample may be determined, for example, by the method described in ISO 4655.

8.2 With mixtures containing other rubbers, calibration to give maximum accuracy requires the use of a known SBR together with the same proportion of any other rubber present in the test sample, in order to obtain a correction for the absorptivity of nitrated products of these other rubbers.

8.3 For the most accurate results, when mineral fillers insoluble in nitric acid are present at a level of more than 5 % (by mass), calibration shall be carried out using a known SBR mixed with a similar level of the appropriate filler.

8.4 When extreme accuracy is required, replicate analysis shall be carried out when obtaining calibration constants.

8.5 Prepare the calibration sample as specified in 7.1 to 7.17 and determine the calibration constants (absorptivities) K_1, K_2 and K_3 in accordance with 8.6.

8.6 Calculate the average absorptivities (K_1, K_2, K_3) of nitrated styrene at the wavelengths 265 nm, 274 nm and 285 nm, respectively, from the formula

$$K = \frac{\left(A \times \frac{V}{m}\right) - K' (1 - X)}{X}$$

where

K is the absorptivity of nitrated styrene at the appropriate wavelength;

A is the absorbance (optical density) at the appropriate wavelength, read on the spectrometer;

V is 2,5 dm^3, if the dilution in 7.15 is used;

m is the mass, in grams, of reference SBR in the volume V;

K' is the absorptivity of the nitration product from polybutadiene, i.e.

0,373 at 265 nm,

0,310 at 274 nm,

0,265 at 285 nm;

X is the fraction of styrene in the reference SBR.

9 Expression of results

9.1 The total styrene content, expressed as a percentage by mass, is given by the formula

$$\frac{S_1 + S_2 + S_3}{3}$$

where

$S_1 = (100A_1/C - 37{,}3)/(K_1 - 0{,}373)$

$S_2 = (100A_2/C - 31{,}0)/(K_2 - 0{,}310)$

$S_3 = (100A_3/C - 26{,}5)/(K_3 - 0{,}265)$

and

A_1, A_2 and A_3 are the absorbances of the solution at wavelengths 265 nm, 274 nm and 285 nm, respectively;