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International Standard



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Rubber — Determination of styrene content — Nitration method

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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

International Standard ISO 5478 was developed by Technical Committee ISO/TC 45, *Rubber and rubber products*, and was circulated to the member bodies in March 1977.

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

Australia
Austria
Belgium
Brazil
Canada
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United Kingdom

USA

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The member body of the following country expressed disapproval of the document on technical grounds :

India

Rubber — Determination of styrene content — Nitration method

1 Scope and field of application

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

1.2 The method is applicable to styrene-butadiene rubbers, reinforced with styrene homopolymer, to give the total styrene content.

1.3 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.

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

1.5 The procedure may give low results when the content of mineral fillers, insoluble in nitric acid, exceeds 5 %.

2 References

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

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

ISO 1796, *Rubber, raw — Sample preparation.*¹⁾

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

3 Principle

3.1 Extraction of the test portion, and refluxing with nitric acid to oxidize the styrene to *p*-nitrobenzoic acid.

3.2 Extraction of the *p*-nitrobenzoic acid into diethyl ether.

3.3 Extraction of the *p*-nitrobenzoic acid into sodium hydroxide solution and spectrophotometric measurement 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, ρ 1,43 g/cm³.

4.2 Sodium hydroxide, 5 mol/dm³ solution.

Dissolve 200 g of sodium hydroxide in water and dilute to 1 000 cm³.

4.3 Sodium hydroxide, 0,1 mol/dm³ solution.

Dissolve 4 g of sodium hydroxide in water and dilute to 1 000 cm³.

4.4 Diethyl ether, free from peroxides.

4.5 Sodium chloride, saturated solution.

4.6 Sodium sulphate, anhydrous.

4.7 SBR of known styrene content, preferably in the region of 23,5 % (*m/m*) for spectrophotometric calibration.

4.8 Carborundum boiling chips.

4.9 Acetone.

4.10 Dichloromethane.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Conical flasks, of capacity 100 or 125 cm³, with ground glass necks to fit the Graham condenser.

1) At present at the stage of draft. (Revision of ISO 1796-1972.)

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

5.3 Separating funnels, of capacity 500 cm³.

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

5.5 Hot-plate, capable of maintaining a rolling boil of concentrated nitric acid for 16 to 18 h. (The surface of the hot-plate will need to reach a temperature of approximately 350 °C.)

5.6 Extraction apparatus.

See ISO 1407.

6 Sample selection and preparation of test portion

6.1 Sample selection

For raw rubbers, select a sample according to ISO 1795 and prepare it according to the appropriate clause of ISO 1796.

6.2 Preparation of test portion

6.2.1 Comminute the rubber and weigh, to the nearest 0,000 1 g, 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 (6.2) overnight with the acetone (4.9) in the extraction apparatus (5.6).

NOTES

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.

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, extract additionally with the dichloromethane (4.10). Mixes shall be cured before extraction with dichloromethane. This extraction shall not be used for raw polymers which would dissolve in dichloromethane.

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 (6.3) in a flask (5.1), together with 20 cm³ of the nitric acid (4.1). (The nitric acid should be fresh. Old batches may give inferior nitration.) Add a few carborundum boiling chips (4.8).

7.2 Place the flask on the cold hot-plate (5.5), connect to the Graham condenser (5.2) and heat at a rolling boil for 16 to 18 h or until the solution is clear and free from haziness. (Starting on a cold hot-plate allows oxidation to proceed slowly, reducing the chance of rapid oxidation, which might cause the rubber to burst into flames. If flames are observed, repeat the procedure from the beginning.)

7.3 Turn off the heat, add 10 to 20 cm³ of water to the top of the condenser and allow the water to be drawn into the flask as it cools.

7.4 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.

7.5 Transfer the reaction mixture to a 400 cm³ beaker, rinsing with small portions of distilled water. Cool to ambient temperature and carefully add 50 cm³ of the sodium hydroxide solution (4.2). With a piece of litmus paper or pH indicating paper, verify that the solution is still strongly acid; if not, add nitric acid (4.1) dropwise until the litmus paper turns red or the pH indicating paper shows a pH of 1.

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

7.7 Shake the solution in the separating funnel with 50 cm³ of the diethyl ether (4.4) and allow the layers to separate. Drain the lower aqueous layer into the original 400 cm³ beaker (see 7.5).

7.8 Add 25 cm³ of the 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.

7.9 Drain off the lower aqueous layer into the 400 cm³ beaker (see 7.7) and pour off the ether layer into a 250 cm³ beaker containing 5 g of the sodium sulphate (4.6).

7.10 Swirl the ether with the sodium sulphate, and allow the latter to settle.

7.11 Carry out a total of three extractions, repeating the procedures specified in 7.7 to 7.10 and dry each ether extract over the same 5 g of sodium sulphate.

7.12 Combine the ether extracts by transferring each one, after drying, to the same dry 500 cm³ separating funnel and, after the three extracts have been combined, add 50 cm³ of the 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.

NOTE — Use care when shaking ether because of pressure build-up. Stopping 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.

7.13 Repeat the extractions of 7.12 three times for a total of four extractions, combining each alkaline aqueous extract in a single 250 cm³ volumetric flask. Any ether which comes to the top of the volumetric flask should be removed using a pipette. Soluble ether should be disregarded.

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

7.14 Dilute the combined extracts of 7.13 with the sodium hydroxide solution (4.3) to the mark of the volumetric flask. Shake and transfer a 25 cm³ aliquot portion to a clean, dry 250 cm³ volumetric flask. Make up to the mark with the sodium hydroxide solution (4.3) and mix thoroughly. This is the test solution.

7.15 Using the spectrophotometer (5.4), measure the absorbance of the test solution (7.14) in a 10 mm silica cell at 265 nm, 274 nm and 285 nm, using the sodium hydroxide solution (4.3) as the reference (instrument blank) liquid.

7.16 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 (7.14).

7.17 Calculate the styrene content according to 9.1 if a standard SBR is available, or according to 9.2 if a standard SBR is not available.

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

8.1 For the most accurate analysis, a spectrophotometric calibration is desirable, using a standard sample of styrene containing copolymer, having a styrene content approximately the same as that in the unknown sample. The styrene content of an uncompounded 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 %, calibration should 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 should be carried out when obtaining calibration constants.

8.5 Prepare the calibration sample as specified in 7.1 to 7.16 and determine the calibration constants K_1 , K_2 and K_3 according to 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 385 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 spectrophotometer;

V is 2,5 dm³, if the dilutions of 7.13 and 7.14 are used;

m is the mass, in grams, of standard 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 standard 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

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

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

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

and

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

C is the concentration, in grams per cubic decimetre, of the test sample in the test solution (7.14);

K_1 , K_2 , K_3 are the absorptivities of nitrated styrene as defined and calculated in 8.6.

9.2 In cases where a standard SBR of known styrene content is unavailable, the total styrene content, expressed as a percentage by mass, is given by the formula

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

where

$$S_1 = \frac{A_{265} \times 3,83}{C} - 0,57$$

$$S_2 = \frac{A_{274} \times 3,61}{C} - 0,45$$

$$S_3 = \frac{A_{285} \times 4,01}{C} - 0,43$$

and

A is the absorbance at the specified wavelength;

C is the mass of rubber, in grams per 2,5 dm³, in the test solution (7.14) if the dilutions of 7.13 and 7.14 are used.

10 Test report

The test report shall include the following particulars :

- a) complete identification of the sample;
- b) reference to this International Standard;
- c) results and method of expression used (whether as in 9.1 or 9.2);
- d) any unusual features noted during the determination;
- e) any operation not included in this International Standard or in the International Standards to which references are made, or regarded as optional.

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