भारतीय मानक

Indian Standard

IS 16848 (Part 2) : 2024

(*Superseding IS 14789 : 2000/ ISO 5478 : 1990*)

रबड़ — परीक्षण पद्धतियाँ

भाग 2 स्टाइरीन सामग्री का निर्धारण — नाइट्रेशन पद्धति

Rubber — Methods of Test

Part 2 Determination of Styrene Content — Nitration Method

ICS 83.060

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September 2024 **Price Group 5**

Methods of Test for Rubber and Rubber Products Sectional Committee, PCD 29

FOREWORD

This Indian Standard (Part 2) was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Test for Rubber and Rubber Products Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

This standard was first published in 2000, as a dual numbered standard identical to ISO 5478 : 1990. In 2015, ISO 5478 was withdrawn by International Organization of Standardization as advanced methods of test standard has been published.

The Committee responsible for formulation of this standard decided to prepare an indigenous standard based on IS 14789 : 2000/ISO 5478 : 1990 as this method is being used by the industries as well as laboratories even till date and withdrawal of this standard will affect MSMEs as well as large industries as this test method is largely used and other methods like FTIR or FTIR with ATR is too costly for our industry.

This standard is being incorporated into IS 16848 series that is, methods of test for rubber series. This standard shall supersede IS 14789 : 2000/ISO 5478 : 1990.

The composition of the Committee responsible for formulation of this standard is given in Annex B.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 ‘Rules for rounding off numerical values (*second revision*)’.

Indian Standard

RUBBER — METHODS OF TEST

PART 2 DETERMINATION OF STYRENE CONTENT — NITRATION METHOD

1 SCOPE

1.1 This standard (Part 2) specifies a method for the determination of the styrene content of all types of styrene-butadiene rubber (SBR), including oil-extended types.

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

1.3 The method is also applicable for determining the styrene in block copolymers containing up to 50 percent (*m*/*m*) of styrene.

1.4 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.

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

1.6 The procedure may give low results when the content of mineral filters insoluble in nitric acid exceeds 5 percent (*m/m*).

2 REFERENCES

The standards listed in Annex A contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent edition of these standards.

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 — ρ 1.43 g/cm^3

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

4.2 Sodium Hydroxide Solution — $c(\mathrm{NaOH}) = 5$ mol/dm^3

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

4.3 Sodium Hydroxide Solution — $c(\mathrm{NaOH}) = 0.1$ 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 percent (*m/m*), for spectrometric 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 cm^3 or 125 cm^3, with 24/29 ground-glass necks (*see* IS 5165) 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 IS 3660 (Part 9)

6 SAMPLE SELECTION AND PREPARATION OF TEST PORTION

6.1 Sample Selection

For raw rubbers, select a sample in accordance with IS 5599 and prepare it in accordance with the appropriate clause of IS 5599. 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).

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 in a vulcanizate (*see* 1.4), extract additionally with dichloromethane (4.10). This is not applicable to unvulcanized materials, which should be appropriately vulcanized to enable them to be analyzed. 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 the 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 the sodium hydroxide solution (4.2) while swirling the beaker. Verify that the solution is still strongly acidic with a *p*H-meter or *p*H-indicating paper; if it is not, add nitric acid (4.1) dropwise 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 the 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 the sodium chloride solution (4.5) to the funnel. Drain a few cubic centimeters 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 the sodium sulfate (4.6).

7.11 Swirl the ether with the sodium sulphate, 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 the sodium hydroxide solution (4.3). Shake and allow the layers to separate. Allow a few cubic centimeters 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 260 cm^3 volumetric flask. Remove any ether which comes to the top of the volumetric flask using a pipette. Soluble ether should 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 the 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 as 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 uncompounded unfilled standard sample may be determined, for example, by the method described in ISO 2453.

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 percent (*m*/*m*), 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 = absorptivity of nitrated styrene at the appropriate wavelength;

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

V = 2.5 dm^3, if the dilution in **7.15** is used;

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

K' = the absorptivity of the nitration product from polybutadiene, that is:

0.373 at 265 nm,
0.310 at 274 nm,
0.265 at 285 nm;

X = 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 = $(100\ A_1/C - 37.3)/(K_1 - 0.373)$;

S_2 = $(100\ A_2/C - 31.0)/(K_2 - 0.310)$;

S_3 = $(100\ A_3/C - 26.5)/(K_3 - 0.265)$;

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

C = concentration, in grams per cubic decimetre, of the test sample in the test solution (*see* **7.15**); and

K_1, K_2 and K_3 = absorptivities of nitrated styrene as defined and calculated in **8.6**.

9.2 In the cases where a reference 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

$$S_1 = \frac{A_{265} \times 3.83}{c} - 0.57;$$

$$S_2 = \frac{A_{274} \times 3.61}{c} - 0.45;$$

$$S_3 = \frac{A_{285} \times 4.01}{c} - 0.43;$$

A = absorbance at the specified wavelength; and

C = mass of rubber, in grams per 2.5 dm^3, in the test solution (*see* **7.15**) if the dilution in **7.15** is used.

10 TEST REPORT

The test report shall include the following particulars:

a) a reference to this standard;
b) complete identification of the sample;
c) the results, the units in which they are expressed and the method of calculation used (whether as in **9.1** or in **9.2**);
d) any unusual features noted during the determination; and
e) any operation not included in this standard or in the standards to which reference is made, as well as any operation regarded as optional.

ANNEX A

(*Clause 2*)

LIST OF REFERRED STANDARDS

IS No./Other Standards	*Title*
IS 3660 (Part 9) : 2016/ISO 1407 : 2011	Methods of test for natural rubber: Part 9 determination of solvent extract [NR : 10] (*second revision*)
IS 5165 : 2017/ISO 383 : 1976	Laboratory glassware — Interchangeable conical ground joints (*first revision*)
ISO 4661-2 : 2018	Rubber vulcanized — Preparation of samples and test pieces — Part 2: Chemical tests
IS 5599 : 1999	Rubber — Raw, natural and synthetic — Methods for sampling and sample preparation (*first revision*)
ISO 2453 : 2020	Rubber, raw styrene-butadiene, emulsion-polymerized — Determination of bound styrene content — Refractive index method

To access Indian Standards click on the link below:
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ANNEX B

(*Foreword*)

COMMITTEE COMPOSITION

Methods of Test for Rubber and Rubber Products Sectional Committee, PCD 29

Organization	*Representative(s)*
Indian Rubber Manufacturers Research Association, Mumbai	Dr K. Raj Kumar **(*Chairperson*)**
All India Rubber Industries Association, Mumbai	Shri Srikanth Krishnamurthy Shri Chinmoy Ray (*Alternate*)
Apcotex Industries Ltd, Mumbai	Dr S. V. Govindaraju
Association of Latex Producers of India, Kottayam	Shri Satish Abraham
Attuned Polymers Limited, Mumbai	Shri Mehul Patel
Automotive Tyres Manufacturers Association, New Delhi	Shri Rajiv Budhraja Shri Niteesh Shukla (*Alternate*)
Central Institute of Plastic Engineering and Technology, Guindy	Shri M. Navaneethan
Central Institute of Plastics Engineering and Technology, Murthal	Dr Smita Mohanty
Central Institute of Road Transport, Pune	P. S. Dahia
Directorate General of Quality Assurance, Ministry of Defence, New Delhi	Shri Jabar Mohammad
Hari Shankar Singhania Elastomer and Tyre Research Institute, Mysuru	Shri Saikat Das Gupta
Indian Oil Corporation (R and D Centre), Faridabad	Dr Pankaj Bhatnagar Dr S. Paul (*Alternate*)
Indian Rubber Manufacturers Research Association, Mumbai	Dr Bharat Kapgate
Indian Synthetic Rubber Private Limited, Noida	Shri Lalit Kumar Sharma Shri Bhanu Pratap Singh (*Alternate* I) Shri Tuhin Kanti Das (*Alternate* II)
L.P.G. Equipment Research Centre, Bengaluru	Shri Santosh K Gupta Shri Ashish Kumar Bera (*Alternate*)
MRF Limited, Chennai	Shri G. Shyju Dr P. Indumathi (*Alternate*)
National Test House, Kolkata	Shrimati Saly C. M. Dr Nishi Srivastava (*Alternate*)
NOCIL Limited, Chennai	Dr N. D. Gangal
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Organization	*Representative(s)*
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Rubber Research Institute of India, Rubber Board, Kottayam	DR SIBY VARGHESE
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Member Secretary
SHRI RAJAT GUPTA
SCIENTIST 'B'/ASSISTANT DIRECTOR
(PETROLEUM COAL AND RELATED PRODUCTS), BIS

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