INTERNATIONAL STANDARD PCD13(2168) ISO 7781:2001(E)

Styrene-butadiene rubber, raw — Determination of soap and organic-acid content

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies methods for the determination of the soap and organic-acid content of raw styrene-butadiene rubber (SBR). Method A is suitable for non-oil-extended styrene-butadiene rubbers. Method B is applicable to oil-extended styrene-butadiene rubbers.

The methods depend on the extraction of the organic acids and soaps from the rubber by means of a specified solvent. In practice, therefore, it is convenient to determine both organic-acid and soap contents on separate portions of the same solvent extract. Since the soaps and organic acids present in the rubber are not single chemical compounds, the method gives only an approximate value for the soap and organic-acid content.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 648:1977, *Laboratory glassware — One-mark pipettes*

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*

ISO 1795:2000, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 4799:1978, *Laboratory glassware — Condensers*

3 Principle

A weighed test portion of the rubber, in the form of thin strips, is extracted by ethanol-toluene azeotrope, or, for alum-coagulated rubber, ethanol-toluene-water mixture. After making up to a standard volume, an aliquot portion of the extract is withdrawn and titrated with standard acid for the determination of soap and with standard alkali for the determination of organic acid.

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4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. Use commercially available analytical-grade buffer solutions of known pH or, in the absence of commercial buffer solutions, prepare the solutions required (4.6, 4.7 and 4.8).

4.1 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 (quicklime) under reflux for 4 h. Cool to room temperature and decant through No. 42 filter paper.

4.2 Ethanol-toluene-water mixture.

Mix 95 cm^3 of ETA (4.1) and 5 cm^3 of water.

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

4.4 Thymol blue indicator.

Dissolve 0,06 g of thymol blue in 6,45 cm^3 of 0,02 mol/dm^3 sodium hydroxide solution and dilute to 50 cm^3 with water.

4.5 Hydrochloric acid, $c(HCl) = 0{,}05\ mol/dm^3$, accurately standardized.

4.6 Buffer solution of nominal pH 7.

Dissolve 3,40 g of potassium dihydrogen phosphate (KH_2PO_4) and 3,55 g of disodium hydrogen phosphate (Na_2HPO_4) in water and make up to 1 000 cm^3 in a volumetric flask. The pH of this solution is 6,87 at 23 °C.

Store the solution in a glass or polyethylene vessel that is resistant to chemicals.

4.7 Buffer solution of nominal pH 4.

Dissolve 10,21 g of potassium hydrogen phthalate ($HOOCC_6H_4COOK$) in water and make up to 1 000 cm^3 in a volumetric flask. The pH of this solution is 4,00 at 23 °C.

Store the solution in a glass or polyethylene vessel that is resistant to chemicals.

4.8 Buffer solution of nominal pH 9.

Dissolve 3,814 g of sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in water and make up to 1 000 cm^3 in a volumetric flask. The pH of this solution, when freshly prepared, is 9,20 at 23 °C.

Store the solution in a glass or polyethylene vessel that is resistant to chemicals and fitted with a soda lime carbon dioxide trap. Replace the solution after 1 month.

5 Apparatus

5.1 Balance, accurate to 1 mg.

5.2 Hotplate.

5.3 Wide-mouthed conical flask, capacity 400 cm^3 to 500 cm^3.

5.4 Volumetric flask, capacity 250 cm^3, complying with the requirements of ISO 1042.

5.5 **Reflux condenser**, complying with the requirements of ISO 4799.

5.6 **Conical flask**, capacity 250 cm^3.

NOTE Alternatively, a Soxhlet extractor may be used instead of a reflux condenser and a conical flask.

5.7 **Burette**, capacity 25 cm^3, complying with the requirements of ISO 385-1.

5.8 **Pipette**, capacity 100 cm^3, complying with the requirements of ISO 648.

5.9 **Automatic titrator or pH-meter**, including a calomel electrode and glass electrode, accurate to within 10 mV or 0,1 pH-units.

5.10 **Magnetic stirrer**, with a polytetrafluoroethylene-coated stirrer bar.

6 Sampling and sample preparation

Sheet out 2 g to 6 g of rubber, selected and prepared in accordance with ISO 1795. Cut into pieces no larger than 2 mm × 2 mm or strips no longer than 10 mm or wider than 5 mm. Weigh a test portion of approximately 2 g to the nearest 0,001 g.

7 Procedure

7.1 Preparation of the test solution

Place a circular filter paper in the bottom of the wide-mouthed conical flask (5.3) and add 100 cm^3 of ETA extraction solvent (4.1) for all rubbers except alum-coagulated rubbers. For alum-coagulated rubbers, use ethanol-toluene-water mixture (4.2).

Introduce the strips of rubber separately into the flask, swirling after each addition so that the strips are thoroughly wetted with solvent and sticking is minimized.

Fit the reflux condenser (5.5) to the flask and boil the solvent very gently under reflux for 1 h.

Transfer the extract to the volumetric flask (5.4), and treat the rubber with a second 100 cm^3 portion of extraction solvent under reflux for 1 h. Add this extract also to the volumetric flask. Rinse the strips with three successive 10 cm^3 portions of extraction solvent, add these washings to the volumetric flask and, after cooling to room temperature, adjust the final volume to 250 cm^3 with appropriate extraction solvent.

NOTE Alternatively, the weighed strips of sample may be wrapped in filter paper and placed in a Soxhlet extractor (see note to 5.6) and extracted with ETA (4.1) or ethanol-toluene-water mixture (4.2) under reflux for a minimum of 4 h.

7.2 Method A (for non-oil-extended SBR)

7.2.1 Procedure for determination of soap content

After thorough mixing, pipette 100 cm^3 of the diluted extract into the 250 cm^3 conical flask (5.6), add six drops of thymol blue indicator (4.4) and titrate the solution with hydrochloric acid solution (4.5) to the first colour change (V_1).

Carry out a blank titration on 100 cm^3 of extraction solvent taken from the same stock as was used for the test portion and using the same indicator as was used for titration of the test portion (V_2).

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7.2.2 Procedure for determination of organic-acid content

Proceed exactly as in 7.2.1, but titrate the aliquot portion with sodium hydroxide solution (4.3), again using thymol blue indicator (4.4) (V_3).

Carry out a blank titration on 100 cm^3 of extraction solvent using the same method (V_4).

7.3 Method B (for oil-extended SBR)

7.3.1 Procedure for determination of soap content

Turn on the autotitrator or pH-meter (5.9), and allow the electronic circuit to stabilize. The temperature shown by the temperature compensator indicator shall be same as the temperature of the test solution.

Calibrate the autotitrator or pH-meter using nominally pH 7 buffer solution (4.6) and pH 4 buffer solution (4.7).

Pipette 100 cm^3 of the test solution into a 250 cm^3 beaker containing a stirrer bar, then place the beaker on the magnetic stirrer (5.10). Insert a glass electrode and a calomel electrode into the test solution in the beaker. While stirring, titrate the test solution with hydrochloric acid solution (4.5) to pH 4,8, slowing the titration rate near the equivalence point. Record the volume of hydrochloric acid solution used at the equivalence point (V_1).

Carry out a blank titration on 100 cm^3 of extraction solvent using the same method (V_2).

7.3.2 Procedure for determination of organic-acid content

Calibrate the autotitrator or pH-meter using nominally pH 7 buffer solution (4.6) and pH 9 buffer solution (4.8).

Proceed exactly as in 7.3.1, but titrate the aliquot portion with sodium hydroxide solution (4.3) to pH 11,5, again slowing the titration rate near the equivalence point. Record the volume of sodium hydroxide solution used at the equivalence point (V_3).

Carry out a blank titration on 100 cm^3 of extraction solvent using the same method (V_4).

8 Expression of results

8.1 Calculate the soap content using the equation

$$w_s = \frac{0,25 \times (V_1 - V_2) \times c_1 \times K_s}{m}$$

where

w_s is the soap content, as a percentage by mass;

V_1 is the volume, in cubic centimetres, of hydrochloric acid solution used to titrate the rubber extract;

V_2 is the volume, in cubic centimetres, of hydrochloric acid solution used to titrate the blank;

c_1 is the actual concentration, in mol/dm^3, of the hydrochloric acid solution (4.5);

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

K_s is the appropriate factor selected from the following:

306 when the soap is to be calculated as sodium stearate,

368 when the soap is to be calculated as sodium rosinate,

337 when the soap is to be calculated as a 50:50 mixture of sodium stearate and sodium rosinate,

322 when the soap is to be calculated as potassium stearate,

384 when the soap is to be calculated as potassium rosinate,

353 when the soap is to be calculated as a 50:50 mixture of potassium stearate and potassium rosinate,

345 when the soap is to be calculated as a 50:50 mixture of sodium stearate and potassium rosinate or of sodium rosinate and potassium stearate.

NOTE Since the soaps present in the rubber are not single chemical compounds, the value assigned to K_s gives only an approximate value for the soap content. A test for rosin is given in annex A.

8.2 Calculate the organic-acid content using the equation

$$w_0 = \frac{0,25 \times (V_3 - V_4) \times c_2 \times K_0}{m}$$

where

w_0 is the organic-acid content, expressed as a percentage by mass;

V_3 is the volume, in cubic centimetres, of sodium hydroxide solution used to titrate the test solution;

V_4 is the volume, in cubic centimetres, of sodium hydroxide solution used to titrate the blank;

c_2 is the actual concentration, in mol/dm^3, of the sodium hydroxide solution (4.3);

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

K_0 is the appropriate factor selected from the following:

284 when the acid is to be calculated as stearic acid,

346 when the acid is to be calculated as rosin acid,

315 when the acid is to be calculated as a 50:50 mixture of stearic acid and rosin acid.

NOTE Since the organic acids present in the rubber are not single chemical compounds, the value assigned to K_0 gives only an approximate value for the organic acid content. A test for rosin is given in annex A.

9 Test report

The test report shall include the following information:

a) all details required for the identification of the sample;

b) a reference to this International Standard;

c) the soap and/or organic-acid content and the value of K_0 used;

d) the method used (A or B);

e) details of any deviation from this International Standard;

f) the date of the test.

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Annex A
(informative)

Test for rosin

A.1 Reagents

A.1.1 Acetic anhydride.

A.1.2 *Sulfuric acid solution.*

Carefully add 65 g of sulfuric acid (ρ_{20} = 1,84 g/cm^3) to 35 g of water and mix well.

A.1.3 Potassium permanganate solution, $c(KMnO_4) = 0{,}000\,2$ mol/dm^3.

A.2 Procedure

Mix a small amount of sample with about 3 cm^3 of acetic anhydride (A.1.1). Add 2 drops of sulfuric acid (A.1.2). The reaction is positive for rosin if a temporary violet colour appears which, at the moment of its maximum intensity, is stronger than the colour of the potassium permanganate solution.