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

Caoutchouc butadiène-styrène brut — Détermination de la teneur en savons et acides organiques

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This fifth edition cancels and replaces the fourth edition (ISO 7781:2008), which has been technically revised.

The main changes compared to the previous edition are as follows:

— addition of a new Method C (8.4) for the back titration using automatic potentiometric titrator;

— update of Method B (8.3) for the titration method using automatic potentiometric titrator;

— deletion of buffer solutions of pH 7, pH 4 and pH 9 (former 4.6 to 4.8);

— addition of pipette (6.9) and automatic potentiometric titrator (6.11);

— update of the expression of results (Clause 9);

— addition of precision data in informative Annex B;

— addition of a bibliography.

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

1 Scope

This document specifies three methods for the determination of the soap and organic-acid content of raw styrene-butadiene rubber (SBR).

— Method A is the titration method using indicator reagent.

— Method B is the titration method using an automatic potentiometric titrator.

— Method C is the back titration method using an automatic potentiometric titrator.

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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

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

ISO 4799, *Laboratory glassware — Condensers*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

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

— Method A: Titrate with standard acid for the determination of soap and with standard alkali for the determination of organic acid using indicator reagent.

— Method B: Titrate with standard acid for the determination of soap and with standard alkali for the determination of organic acid using automatic potentiometric titrator. The titration equivalence point is determined by inflection point.

— Method C: Back titrate with standard alkali for the determination of soap and organic acid after adding sufficient acid. The titration equivalence point is determined by inflection point.

For methods A and B, there are no precision data available. Therefore their precision is not known. For method C, if the quantity of soap is very low, the standard deviation of the measurement of soap content should be looked at carefully.

5 Reagents

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

5.1 Ethanol-toluene azeotrope (ETA).

Mix seven volumes of absolute ethanol with three volumes of toluene. Alternatively, mix seven volumes of commercial-grade ethanol with three 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.

5.2 Ethanol-toluene-water mixture.

Mix 95 cm^3 of ETA (5.1) and 5 cm^3 of water.

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

5.4 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.

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

6 Apparatus

Use ordinary laboratory apparatus and the following.

6.1 Balance, accurate to 1 mg.

6.2 Hotplate.

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

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

6.5 Reflux condenser, complying with the requirements of ISO 4799.

6.6 Conical flask, of capacity 250 cm^3.

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

6.7 Burette, of capacity 25 cm^3, complying with the requirements of ISO 385.

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

6.9 Pipette, of capacity 2 cm^3, complying with the requirements of ISO 648.

6.10 Magnetic stirrer, with a polytetrafluoroethylene-coated stirrer bar.

6.11 Automatic potentiometric titrator, including an electrode which is applicable to test the pH of organic solution.

7 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 and no wider than 5 mm. Weigh a test portion of approximately 2 g to the nearest 0,001 g.

8 Procedure

8.1 Preparation of the test solution

Place a circular filter paper in the bottom of the wide-mouthed conical flask (6.3), and add 100 cm^3 of ETA extraction solvent (5.1) for all rubbers except alum-coagulated rubbers. For alum-coagulated rubbers, use an ethanol-toluene-water mixture (5.2).

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

Transfer the extract to the volumetric flask (6.4), 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.

Alternatively, the weighed strips of sample can be wrapped in filter paper and placed in a Soxhlet extractor (see Note to 6.6) and extracted with an ETA (5.1) or ethanol-toluene-water mixture (5.2) under reflux for a minimum of 4 h.

8.2 Method A — Titration method using indicator reagent

8.2.1 Procedure for determination of soap content

After thorough mixing, pipette 100 cm^3 of the diluted extract into the 250 cm^3 conical flask (6.6), add six drops of thymol blue indicator (5.4) and titrate the solution with hydrochloric acid solution (5.5) 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 used for titration of the test portion (V_2).

8.2.2 Procedure for determination of organic-acid content

Proceed exactly as in 8.2.1, but titrate the aliquot portion with sodium hydroxide solution (5.3), again using thymol blue indicator (5.4) (V_3).

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

8.3 Method B — Titration method using automatic potentiometric titrator

8.3.1 Procedure for determination of soap content

Turn on the automatic potentiometric titrator (6.11), and allow the electronic circuit to stabilize.

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 (6.10). Insert the electrode into the test solution in the beaker.

While stirring, titrate the test solution with hydrochloric acid solution (5.5). Record the volume of hydrochloric acid solution used at the equivalence point that is given as the inflection point of the titration curve (V_1).

NOTE The x-axis value of the inflection point of the titration curve is shown as the x-axis value of maximal value point of the derivative of the titration curve. This x-axis value is the volume of hydrochloric acid solution used at the equivalence point.

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

8.3.2 Procedure for determination of organic-acid content

Proceed exactly as in 8.3.1, but titrate the aliquot portion with sodium hydroxide solution (5.3). Record the volume of sodium hydroxide solution used at the equivalence point that is given as the inflection point of the titration curve (V_3).

NOTE The x-axis value of the inflection point of the titration curve is shown as the x-axis value of the maximal value point of the derivative of the titration curve. This x-axis value is the volume of sodium hydroxide solution used at the equivalence point.

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

8.4 Method C — Back titration method using automatic potentiometric titrator

8.4.1 Preparation

Turn on the automatic potentiometric titrator (6.11), expel the air from the dosing tube and titration tube of the titrator. Set the main parameters referring to Table 1 which gives some recommended values.

NOTE The experimenter can also set the parameters based on his/her own experience, but he/she is supposed to obtain a sample titration curve similar to Figure 1 and a blank titration curve similar to Figure 2.

Table 1 — Parameters of automatic potentiometric titrator

Parameters	Set value
Test mode	pH dynamic titration
Volume of dosing tube	5 cm^3
Stirring rate	A small vortex should be formed but no splash
Regulation of signal drift	50 mV
Minimum waiting time	0 s
Maximum waiting time	25 s
Minimum dosing increment	0,01 cm^3
Maximum dosing increment	Close
Stop condition	After adding 4 cm^3 of titrant

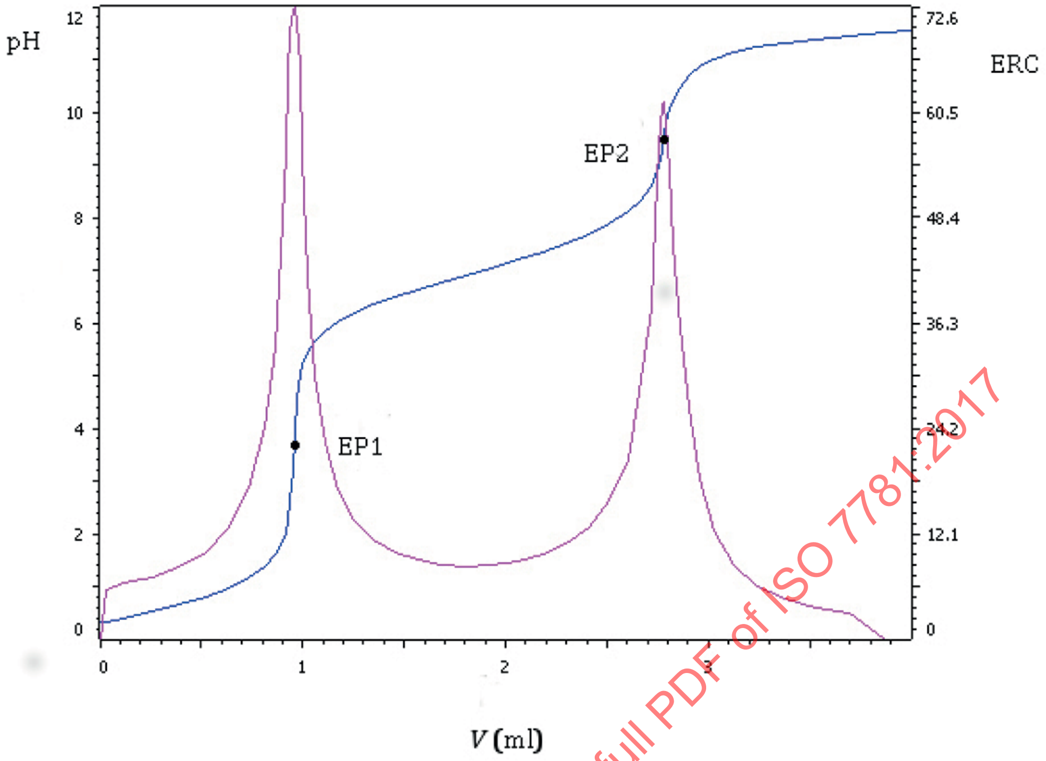

Figure 1 — Typical titration curve of sample

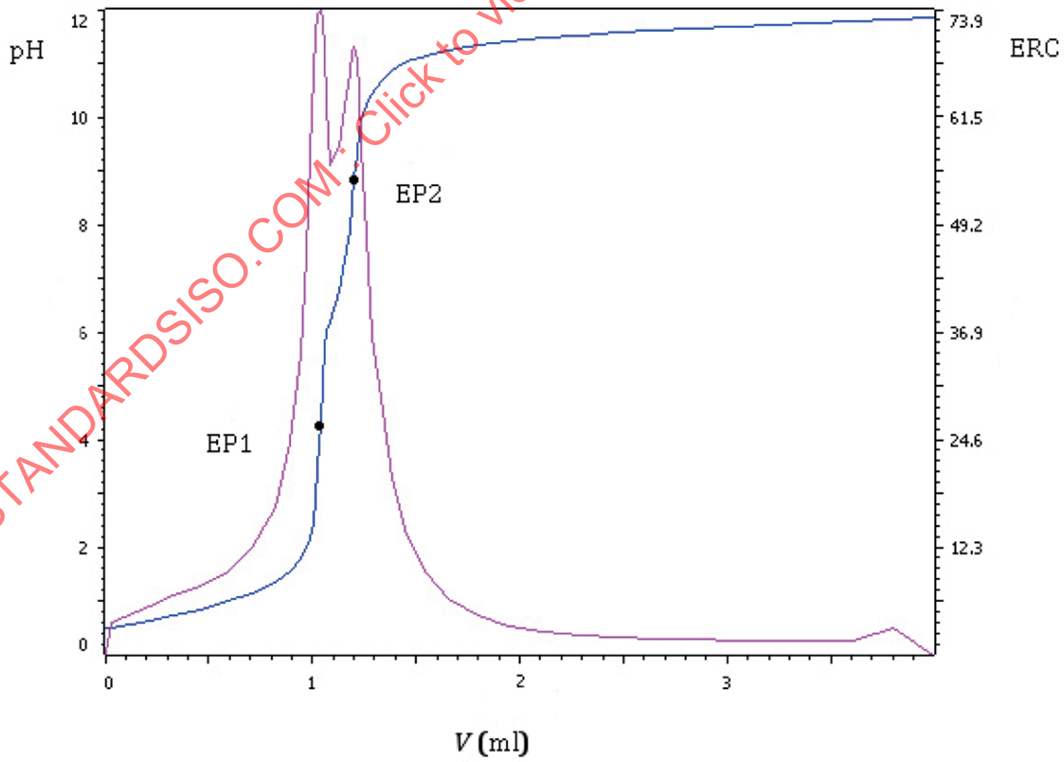

Figure 2 — Typical titration curve of blank

8.4.2 Sample titration procedure

Pipette 100 cm^3 of the sample solution into a 150 cm^3 beaker containing a stirrer bar, add 2 cm^3 hydrochloric acid solution (5.5) using the pipette (6.9) or the titrator, then place the beaker on the test stand. Insert the electrode and stir 2 min, titrate with sodium hydroxide solution (5.3).

NOTE For Method C, the concentration of hydrochloric acid solution does not appear in the calculation formula. Therefore it is not necessary to accurately standardize its concentration.

8.4.3 Blank titration procedure

Pipette 100 cm^3 extraction solvent into a 150 cm^3 beaker containing a stirrer bar, add 2 cm^3 hydrochloric acid solution (5.5) using the pipette (6.9) or the titrator, titrate using the same method as is used in the sample test.

8.4.4 Determination of equivalence points

Figures 1 and 2 present the typical titration curves of the sample and the blank. The s-shaped curve is the titration curve, the curve having two peaks shows the derivative of the titration curve.

As shown in Figures 1 and 2, there should be two equivalence points (EP1 and EP2) on the titration curve.

For the titration curve of the sample, EP1 indicates the reaction end of sodium hydroxide and the surplus hydrochloric acid, and it is determined by the position of the first peak on the derivative curve. EP2 indicates the reaction end of sodium hydroxide and the organic-acid existing in the sample or derived from the soap, and it is determined by the position of the second peak on the derivative curve.

For the titration curve of the blank, EP1 and EP2 have the same meaning as that of the sample, and can be determined in the same way.

Record the volume of sodium hydroxide solution (5.3) at each equivalence point. The volumes of sodium hydroxide solution, corresponding to EP1 and EP2 on the sample titration curve, are recorded as V_5 and V_6. The volumes of sodium hydroxide solution, corresponding to EP1 and EP2 on the blank titration curve, are recorded as V_7 and V_8 respectively.

9 Expression of results

9.1 Soap content

For Method A and Method B, calculate the soap content W_s using Formula (1). For Method C, calculate the soap content W_s using Formula (2).

$$W_s = \frac{0{,}25 \times (V_1 - V_2) \times c_1 \times Ks}{m} \qquad (1)$$

$$W_s = \frac{0{,}25 \times \left(V_7 - V_5\right) \times c_2 \times Ks}{m} \qquad (2)$$

where

W_s is the soap content, expressed as a percentage by mass;

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

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

V_5	is the volume of sodium hydroxide solution used to titrate the sample solution at EP1, in cubic centimetres;
V_7	is the volume of sodium hydroxide solution used to titrate the blank at EP1, in cubic centimetres;
c_1	is the actual concentration of the hydrochloric acid solution, in moles per cubic decimetre;
c_2	is the actual concentration of the sodium hydroxide solution, in moles per cubic decimetre;
m	is the mass of the test portion, in grams;
Ks	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.

For samples of lower soap content, the results might be a minus value, and the soap content should be considered as 0.

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

9.2 Organic-acid content

For Method A and Method B, calculate the organic-acid content W_o using Formula (3). For Method C, calculate the organic-acid content W_o using Formula (4).

$$W_o = \frac{0{,}25 \times (V_3 - V_4) \times c_2 \times Ko}{m} \tag{3}$$

$$W_o = \frac{0{,}25 \times (V_6 - V_8) \times c_2 \times Ko}{m} \tag{4}$$

where

W_o	is the organic-acid content, expressed as a percentage by mass;
V_3	is the volume of sodium hydroxide solution used to titrate the test solution, in cubic centimetres;
V_4	is the volume of sodium hydroxide solution used to titrate the blank, in cubic centimetres;
V_6	is the volume, in cubic centimetres, of sodium hydroxide solution used to titrate the sample solution at EP2;
V_8	is the volume, in cubic centimetres, of sodium hydroxide solution used to titrate the blank at EP2;

c_2 is the actual concentration, in moles per cubic decimetre, of the sodium hydroxide solution;

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

Ko 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_o gives only an approximate value for the organic-acid content. A test for rosin is given in Annex A.

10 Precision data

See Annex B.

11 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 7781;

b) all details necessary for the identification of the sample;

c) the method used (A, B or C);

d) test details: details of any deviation from this document;

e) the test results and the units in which they were expressed: the calculated soap content (9.1) and/or organic-acid content (9.2), and the value of K_s and/or K_o used;

f) the date of the test.

Annex A
(informative)

Test for rosin

A.1 Reagents

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

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, $c(\text{KMnO}_4)$ = 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 two drops of sulfuric acid (A.1.2). The reaction is positive for rosin if a temporary violet colour appears which, at its moment of maximum intensity, is stronger than the colour of the potassium permanganate solution.

Annex B
(informative)

Precision data for method C

B.1 General

An interlaboratory test programme (ITP) to determine the precision of Method C of this document was conducted in July 2016 in China and Japan, using automatic potentiometric titrators. The precision evaluated was a type 1 precision in accordance with ISO/TR 9272.

B.2 Precision details

Six laboratories participated in the ITP, and two different materials (SBR rubbers) were used in the ITP. A test result was taken to be the value from a single determination of soap content or organic-acid content. Test results from each laboratory were obtained on three different days in two weeks.

B.3 Precision results

The precision results are given in Table B.1 for determination of soap content and Table B.2 for determination of organic-acid content. These results were obtained using outlier AOT replacement procedures as described in ISO/TR 9272.

a) Repeatability: the repeatability, *r*, of the test method has been established as the appropriate value tabulated in Table B.1 or Table B.2 for each material. Two single test results that differ by more than this value should be considered suspect and suggest that some appropriate investigative action be taken.

b) Reproducibility: the reproducibility, *R*, of the test method has been established as the appropriate value tabulated in Table B.1 or Table B.2 for each material. Two single test results that differ by more than this value should be considered suspect and suggest that some appropriate investigative action be taken.

Table B.1 — Precision data for determination of soap content

Material	Mean content	Within laboratory			Between laboratories			Number of laboratories[a]
		s_r	r	(r)	s_R	R	(R)	
SBR1723	0,05	0,019	0,055	120,28	0,035	0,099	217,96	6
SBR1502	0,25	0,019	0,055	21,55	0,030	0,085	33,48	6
Pooled values	0,18	0,019	0,055	86,41	0,033	0,092	155,93	—

s_r is the repeatability standard deviation;

r is the repeatability, in measurement units;

(r) is the repeatability, in percent (relative);

s_R is the reproducibility standard deviation;

R is the reproducibility, in measurement units;

(R) is the reproducibility, in percent (relative).

[a] Final number of laboratories in the ITP after (option 2) AOT replacement of outliers.