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Rubber, raw — Determination of bound acrylonitrile content in acrylonitrile-butadiene rubber (NBR) —

Part 2: Kjeldahl method

Caoutchouc brut — Détermination du contenu en acrylonitrile lié dans le caoutchouc acrylonitrile-butadiène (NBR) —
Partie 2: Méthode Kjeldahl

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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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of 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 second edition cancels and replaces the first edition (ISO 24698-2:2008), which has been technically revised.

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

— addition in the scope of two types of raw rubbers, XNBR and NBIR, that contain acrylonitrile;

— addition of NBR latex to the scope and in sample preparation (7.2);

— amendment of of finishing condition of sample weight in 7.1;

— addition of ITP results of NBR latex in a new Annex C.

A list of all the parts in the ISO 24698 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Rubber, raw — Determination of bound acrylonitrile content in acrylonitrile-butadiene rubber (NBR) —

Part 2: Kjeldahl method

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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.

CAUTION — Certain procedures specified in this document might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document specifies a method for the determination of the bound acrylonitrile content in NBR by an automatic analyser which uses the Kjeldahl method. The method is also applicable to XNBR (carboxylic acrylonitrile-butadiene rubber) and NBIR (acrylonitrile-butadiene-isoprene rubber) as well as NBR latex.

NOTE This document and ISO 24698-1 can give different results on the same rubber sample.

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 123, *Rubber latex — Sampling*

ISO 1407:2011, *Rubber — Determination of solvent extract*

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

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:

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

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

4 Principle

The nitrogen in a sample of raw rubber is converted into an ammonium salt by digestion with potassium sulfate, sulfuric acid and a copper sulfate catalyst. Ammonia is then released by the addition of strong alkali and steam-distilled into boric acid solution and titrated with standard volumetric acid solution.

5 Reagents and materials

5.1 Reference material: ammonium sulfate, purity ≥99,5 %.

5.2 Standard volumetric acid solutions:

— sulfuric acid solution, 0,05 mol/dm^3;

— hydrochloric acid solution, 0,05 mol/dm^3.

5.3 Sulfuric acid, ρ = 1,84 g/cm^3.

5.4 Sodium hydroxide solution, 10 mol/dm^3.

5.5 Potassium sulfate (K_2SO_4).

5.6 Copper sulfate ($CuSO_4 \cdot 5H_2O$).

5.7 Indicators, in accordance with the analyser manufacturer's instructions:

— methyl red;

— methylene blue;

— bromophenol blue.

5.8 Boric acid solution, in accordance with the analyser manufacturer's instructions (commonly, 3 % or 4 % solution).

5.9 Ethanol, purity ≥95 % by volume.

5.10 Methanol, purity ≥99,8 % by volume.

6 Apparatus

6.1 Automatic analyser.

6.1.1 General

The automatic analyser consists of the following components:

a) a digestion unit, capable of maintaining a minimum operating temperature in accordance with the manufacturer's instructions for digestion of the sample;

b) a digestion tube, capable of being used for both digestion and distillation;

c) a distillation unit, capable of introducing a fixed volume of sodium hydroxide into the digestion tube when it is placed in the unit and of steam-distilling, for a fixed time, the liberated NH_3 and condensing it into a fixed volume of ammonia-absorbing boric acid solution in a titration vessel;

d) a titration unit, capable of introducing the boric acid solution into the titration vessel before distillation and of titrating the distillate with standard volumetric acid solution photometrically using a photo-cell or potentiometrically;

e) a microprocessor, capable of calibrating the instrument with a reference material and of converting the titration result into mass % of nitrogen in the sample.

6.1.2 Performance requirements

The accuracy of the system shall be demonstrated by performing ten successive determinations using a reference material such as ammonium sulfate. The mean of the ten determinations with the reference material shall be within ±0,2 percentage points of the theoretical value. The relative standard deviation shall be within 0,5 % by mass of nitrogen for the reference material.

NOTE The relative standard deviation, (r), is given by Formula (1):

$$(r) = \frac{s}{w_N} \times 100 \quad (1)$$

where

(r) is the relative standard deviation, in %;

s is the standard deviation;

w_N is the mean nitrogen content, in mass %.

6.2 Balance, weighing to the nearest 0,1 mg.

6.3 Extraction apparatus, as specified for method C in ISO 1407:2011.

6.4 Beaker, capacity 300 cm^3.

6.5 Stirrer.

6.6 Sieve, aperture 150 µm.

6.7 Absorbent tissue.

6.8 Drying oven, capable of maintaining a temperature of 100 °C ± 2 °C.

6.9 Roll mill, the temperature of whose rolls can be maintained at 100 °C ± 5 °C.

7 Sampling, preparation of the sample for the determination and preparation of reagents

7.1 Raw NBR, XNBR or NBIR rubber

Take a sample of 10 g to 50 g in accordance with the method specified in ISO 1795, and pass the sample between the surfaces of the mill rolls with the nip set at 0,2 mm ± 0,05 mm and with the surface temperature of the rolls maintained at 100 °C ± 5 °C.

Take a portion of about 3 g to 5 g from the sample prepared as specified above.

Extract this portion with ethanol by method C in ISO 1407:2011 and rinse the extracted material twice with a small amount of fresh ethanol. Pour the contents of the flask onto a clean 150 µm sieve to recover the extracted material. Gently blot the extracted material with absorbent tissue to remove excess solvent, and dry the pieces of extracted rubber, separated from each other, in the oven at 100 °C ± 2 °C until the mass does not change by more than 2,0 mg over a period of 10 min.

7.2 NBR Latex

Take about 500 g of NBR latex sample by the appropriate method in ISO 123.

In order to coagulate the latex, add dropwise a small portion of the NBR latex sample, containing approximately 5 g of solid NBR, to 150 cm^3 of ethanol or methanol in the 300 cm^3 beaker, stirring the ethanol or methanol at the same time. After all the latex has been added, continue stirring for another 5 min. Then pour the contents of the beaker onto a clean 150 µm sieve to recover the coagulated polymer. Place the recovered polymer and 100 cm^3 of fresh solvent into the beaker and stir for 5 min. Again pour the contents of the beaker onto the 150 µm sieve to recover the polymer. Finally, dry the recovered polymer between the surfaces of the mill rolls with the nip set at 0,2 mm ± 0,05 mm and with the surface temperature of the rolls maintained at 100 °C ± 5 °C until the mass does not change by more than 2,0 mg over a period of 10 min.

7.3 Preparation of reagents

7.3.1 Catalyst mixture: Prepare a mixture of potassium sulfate and copper sulfate in the fixed ratio in accordance with the analyser manufacturer's instructions.

7.3.2 Indicator solution: Prepare an ethanolic indicator solution in accordance with the analyser manufacturer's instructions.

7.3.3 Boric acid solution: Prepare the ammonia-absorbing solution consisting of boric acid solution and indicator solution in accordance with the analyser manufacturer's instructions.

8 Procedure

8.1 Operate the apparatus in accordance with the manufacturer's instructions. A general procedure is as described in 8.2 to 8.12.

8.2 Take as the test portion 50 mg to 500 mg of the extracted material prepared by the method in Clause 7 and weigh it to the nearest 0,1 mg. The size of the test portion should preferably be chosen so that its total nitrogen content is between 5 mg and 15 mg. Input the mass of the test portion into the microprocessor.

8.3 Place the test portion and the fixed amount of catalyst mixture in the digestion tube and pour the fixed amount of sulfuric acid into the tube.

8.4 Place the digestion tube in the digestion unit and start to digest at the fixed temperature. Allow the digestion to continue until the solution in the tube turns from yellow to a clear blue-green colour and then continue for 30 min longer (the digestion time can be determined before starting the analysis).

8.5 On completion of the digestion, allow the tube to cool to room temperature and then dilute with the fixed amount of water.

8.6 Place the digestion tube in the distillation unit.

8.7 The fixed amount of sodium hydroxide solution and water is poured into the tube, and steam distillation is carried out for a fixed length of time or until a fixed amount of distillate has been collected.

8.8 The distillate is collected by absorption in boric acid solution in the titration vessel.

8.9 The collected distillate is then titrated with standard volumetric acid solution either photometrically using a photo-cell or potentiometrically.

8.10 After the titration, the solution in the titration vessel is exhausted automatically.

8.11 Carry out a blank determination in the same way.

8.12 The microprocessor converts the titration result into the nitrogen content of the test portion, in mass %.

9 Calculation of bound acrylonitrile content

9.1 When sulfuric acid (0,05 mol/dm³) is used as the standard volumetric solution

Calculate the bound acrylonitrile content, w_A, of the sample from Formula (2):

$$w_A = \frac{10{,}61 \times c_s (V_1 - V_2)}{m} \quad (2)$$

where

w_A is the bound acrylonitrile content of the sample, in mass %;

c_s is the exact concentration of the sulfuric acid solution, in mol/dm³;

V_1 is the volume of sulfuric acid solution required for the titration, in cm³;

V_2 is the volume of sulfuric acid solution required for the blank determination, in cm³;

m is the mass of the test portion, in g.

The test result is the value from a single determination of bound acrylonitrile content.

9.2 When hydrochloric acid (0,05 mol/dm³) is used as the standard volumetric solution

Calculate the bound acrylonitrile content, w_A, of the sample from Formula (3):

$$w_A = \frac{5{,}306 \times c_H (V'_1 - V'_2)}{m} \quad (3)$$

where

w_A is the bound acrylonitrile content of the sample, in mass %;

c_H is the exact concentration of the hydrochloric acid solution, in mol/dm³;

V'_1 is the volume of hydrochloric acid solution required for the titration, in cm³;

V'_2 is the volume of hydrochloric acid solution required for the blank determination, in cm³;

m is the mass of the test portion, in g.

The test result is the value from a single determination of bound acrylonitrile content.

10 Precision

An interlaboratory test programme to determine the precision of this Kjeldahl method using automatic analysers was conducted on NBR in 2006 (see Annex B).