INTERNATIONAL
STANDARD

ISO
24698-2

First edition
2008-05-15

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

Reference number
ISO 24698-2:2008(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 24698-2:2008

COPYRIGHT PROTECTED DOCUMENT

© ISO 2008

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

© ISO 2008 – All rights reserved

Contents

Page

1 Scope 1
2 Normative references 1
3 Principle 1
4 Reagents and materials 1
5 Apparatus 2
6 Sampling, preparation of the sample for the determination and preparation of reagents 3
7 Procedure 3
8 Calculation of bound acrylonitrile content 4
9 Precision 5
10 Test report 5
Annex A (informative) Examples of automatic analysers based on the Kjeldahl method 6
Annex B (informative) Precision 8

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 24698-2 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

ISO 24698 consists of the following parts, under the general title *Rubber, raw — Determination of bound acrylonitrile content in acrylonitrile-butadiene rubber (NBR)*:

- *Part 1: Combustion (Dumas) method*
- *Part 2: Kjeldahl method*

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

Part 2:
Kjeldahl method

WARNING — Persons using this part of ISO 24698 should be familiar with normal laboratory practice. This part of ISO 24698 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.

CAUTION — Certain procedures specified in this part of ISO 24698 may 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 part of ISO 24698 specifies a method for the determination of the bound acrylonitrile content in NBR by an automatic analyser which uses the Kjeldahl method.

NOTE Parts 1 and 2 of this International Standard may not necessarily give the same result for any given rubber sample.

2 Normative references

The following referenced documents are indispensable for the application 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 1407:1992, *Rubber — Determination of solvent extract*

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

3 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.

4 Reagents and materials

4.1 Reference material: ammonium sulfate, purity $\geqslant$ 99,5 %.

4.2 Standard volumetric acid solutions:

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

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

4.3 Sulfuric acid, $\rho = 1{,}84$ g/cm^3.

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

4.5 Potassium sulfate (K_2SO_4).

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

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

- methyl red;
- methylene blue;
- bromophenol blue.

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

4.9 Ethanol, purity $\geqslant$ 95 % by volume.

4.10 Methanol, purity $\geqslant$ 99,8 % by volume.

5 Apparatus

5.1 Automatic analyser.

5.1.1 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.

5.1.2 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 $\pm$ 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 Relative standard deviation (%) $= \frac{s}{w_N} \times 100$

where

s is the standard deviation;

w_N is the mean nitrogen content, in mass %.

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

5.3 Extraction apparatus, as specified for method B in ISO 1407:1992.

5.4 Beaker, capacity 300 cm^3.

5.5 Stirrer.

5.6 Sieve, aperture 150 µm.

5.7 Absorbent tissue.

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

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

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

6.1 Sampling and preparation of the sample for the determination

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 B in ISO 1407:1992 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 0,1 mg over a period of 10 min.

6.2 Preparation of reagents

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

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

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

7 Procedure

7.1 Operate the apparatus in accordance with the manufacturer's instructions. A general procedure is as described in 7.2 to 7.12.

7.2 Take as the test portion 50 mg to 500 mg of the extracted material prepared by the method in 6.1 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.

7.3 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.

7.4 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).

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

7.6 Place the digestion tube in the distillation unit.

7.7 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.

7.8 The distillate is collected by absorbtion in boric acid solution in the titration vessel.

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

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

7.11 Carry out a blank determination in the same way.

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

8 Calculation of bound acrylonitrile content

8.1 When sulfuric acid (0,05 mol/dm^3) is used as the standard volumetric solution

Calculate the bound acrylonitrile content w_A of the sample, in mass %, from the following equation:

$$w_\mathrm{A} = \frac{10{,}61 \times c_\mathrm{S}(V_1 - V_2)}{m}$$

where

c_S is the exact concentration of the sulfuric acid solution, in mol/dm^3;

V_1 is the volume of sulfuric acid solution required for the titration, in cm^3;

V_2 is the volume of sulfuric acid solution required for the blank determination, in cm^3;

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

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

8.2 When hydrochloric acid (0,05 mol/dm^3) is used as the standard volumetric solution

Calculate the bound acrylonitrile content w_A of the sample, in mass %, from the following equation:

$$w_\mathrm{A} = \frac{5{,}306 \times c_\mathrm{H}(V_1' - V_2')}{m}$$

where

c_H is the exact concentration of the hydrochloric acid solution, in mol/dm^3;

V_1' is the volume of hydrochloric acid solution required for the titration, in cm^3;

V_2' is the volume of hydrochloric acid solution required for the blank determination, in cm^3;

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 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).

10 Test report

The test report shall include the following particulars:

a) a reference to this part of ISO 24698;

b) full identification of the rubber tested;

c) full identification of the apparatus used;

d) the standard volumetric acid solution used;

e) the result of the test;

f) the date of the test.

Annex A
(informative)

Examples of automatic analysers based on the Kjeldahl method

A.1 General

There are differences between automatic analysers with regard to the digestion conditions (including the digestion temperature) and the catalyst. There are also differences with regard to the methods of distillation, absorption and titration of the ammonia. However, all automatic analysers based on the Kjeldahl digestion method which meet the performance requirements specified in 5.1.2 are suitable for the determination of the bound acrylonitrile content of NBR by the method specified in this part of ISO 24698.

A.2 Examples of suitable automatic analysers

- System A, which is composed of a QDS-10M digestion unit and a KJEL-AUTO DTP-3S distillation and titration unit (Nakayama Rika Seisakusho Inc.);
- System B, which is composed of a Buchi K-435 digestion unit, a B-324 distillation unit (Shibata Scientific Technology Ltd.) and a COM-1500 titration unit (Hiranuma Sangyo Co., Ltd.).

NOTE These are examples of suitable equipment available commercially. This information is given for the convenience of users of this part of ISO 24698 and does not constitute an endorsement by ISO of this equipment.

A.3 Examples of determination conditions

Examples of suitable conditions are given in Table A.1. The following should be noted:

a) Excess sulfuric acid (over and above the amount consumed during the digestion) is needed and the amount depends on the size of the digestion tube.

b) The ratio of K_2SO_4 to $CuSO_4 \cdot 5H_2O$ is between 9:1 and 8:1. The exact ratio and the amount of catalyst mixture used should be determined in advance in accordance with the equipment manufacturer's instructions.

c) The temperature and time of digestion should be fixed in accordance with the equipment manufacturer's instructions.

d) Excess sodium hydroxide (over and above the amount of sulfuric acid used) should be added following digestion so that the solution is strongly alkaline.

e) The time of steam distillation should be fixed in accordance with the steam-generating capability of the distillation unit.

f) The amount of ammonia-absorbing boric acid solution used should be chosen so that the solution remains sufficiently acid during the absorption of the ammonia.

g) In the case of system A, the indicator solution is prepared using 0,1 g of methyl red, 0,05 g of methylene blue and 100 cm^3 of ethanol. In the case of system B, the indicator solution is prepared using 0,1 g of bromophenol blue and 20 cm^3 of ethanol and diluted to 100 cm^3 with water.

h) Since detecting the change in colour of the solution during the titration is important in the case of system A, which involves a photometric titration using a photo-cell, the indicator solution should be used within 48 h of its preparation in order to ensure reproducibility.

Table A.1 — Examples of suitable determination conditions

Procedure subclause	Conditions	System A	System B
7.3	Size of test portion	75 mg	100 mg
	Catalysts		
	K_2SO_4	9,0 g	2,4 g
	$CuSO_4 \cdot 5H_2O$	1,0 g	0,3 g
	Sulfuric acid	15 cm^3	4 cm^3
7.4	Digestion temperature [a]	450 °C	750 °C
	Digestion time (min)	140 min	70 min
7.5	Water	50 cm^3	20 cm^3
7.7	Sodium hydroxide solution	60 cm^3	30 cm^3
	Water	15 cm^3	40 cm^3
	Distillation time	270 s	360 s
	(amount of distillate)	(105 cm^3)	(125 cm^3)
7.8	Strength of boric acid solution	3 %	4 %
	Amount of boric acid solution	25 cm^3	20 cm^3
	Indicator	Mixture of methyl red and methylene blue	Bromophenol blue
	Amount of indicator solution	0,25 cm^3	0,01 cm^3
7.9	Standard volumetric acid solution	0,05 mol/dm^3 sulfuric acid	0,05 mol/dm^3 hydrochloric acid
	Method of titration	Photometric titration using photo-cell	Potentiometric titration

[a] This temperature is the temperature input into the analyser microprocessor and does not represent the actual digestion temperature.