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Rubber and rubber additives — Determination of total nitrogen content using an automatic analyser

Caoutchouc et additifs pour caoutchouc — Dosage de l'azote total à l'aide d'un analyseur automatique

Reference number
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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15672 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

Rubber and rubber additives — Determination of total nitrogen content using an automatic analyser

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 an instrumental (automatic analyser) method for the determination of total nitrogen in rubber and rubber additives.

2 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

2.1
sample
unit selected to represent the material to be analysed

2.2
test portion
actual material used in the analysis

2.3
control sample
material with a recognized level of nitrogen, analysed with each set of test portions

3 Principle

3.1 Specified is a reliable, rapid, instrumental (automatic) method for determining total nitrogen in rubber and rubber additives. The nitrogen is determined by a single instrumental procedure consisting of weighing a test portion, placing it in the instrument and initiating the (subsequently automatic) analytical process. The analysis may be controlled manually to a limited degree, and a capability to perform computations automatically may be provided by the instrument used to perform the analysis.

3.2 The actual process can vary substantially from instrument to instrument because a variety of means can be used to meet the primary requirements of the method. The method includes the following:

a) conversion of nitrogen-containing materials to nitrogen oxides in an oxygen stream;

b) reduction of the nitrogen oxides to elemental nitrogen by passing them over copper at an elevated temperature;

c) determining the nitrogen by one of three detection schemes.

3.3 In the **thermal conductivity detection** configuration, the combustion gases are conducted through a series of thermal conductivity detectors and gas absorbers aligned so that the gases pass first through the sample side of a water vapour detector, through a water vapour absorber and through the reference side of the detector. The gases are then conducted through the sample side of a carbon dioxide detector, through a carbon dioxide absorber and

through the reference side of the detector. Finally, the resultant gases, which contain only nitrogen and the carrier gas, pass through the sample side of a nitrogen detector and are vented. For this detector, high-purity carrier gas is used as the reference gas. In this way, the detectors determine the thermal conductivities solely of the specified components.

3.4 In the **combined absorbance/conductivity detection** configuration, the carbon dioxide and water vapour are determined by infrared detection, using an aliquot of the combustion gases from which only the halides and sulfur oxides have been removed. These detectors determine the infrared absorbance of the pertinent gases at precise wavelength windows so that the absorbances result from only the specified components. In such a system, nitrogen is determined by thermal conductivity, using a second aliquot of the gases additionally treated to reduce the nitrogen oxides to nitrogen and to remove the residual oxygen, carbon dioxide and water vapour.

3.5 In the **modified chromatographic detection** configuration, which is essentially a modified gas chromatographic system, the nitrogen, carbon dioxide and water vapour in the treated combustion gases are eluted from a chromatographic column and determined (at appropriate retention times) by thermal conductivity detection.

3.6 The concentration of nitrogen is calculated in each configuration as a function of the following:

a) the measured instrumental (automatic analyser) responses per unit mass for elemental nitrogen (established via instrument calibration);

b) the mass of the test portion.

4 Requirements for apparatus

4.1 Because a variety of instrumental (automatic analyser) component configurations can be used satisfactorily for this method, no specifications are presented with regard to overall system design. Functionally, however, the following requirements are specified for all instruments.

4.2 The conditions for combustion of the sample shall be such that (for the full range of applicable samples) nitrogen-containing components shall be converted completely to nitrogen or nitrogen oxides. General instrumental conditions that affect complete combustion include:

a) availability of the oxidant;

b) temperature;

c) time.

4.3 Representative aliquots of the combustion gases shall then be treated to reduce nitrogen oxides to elemental nitrogen.

4.4 For the configuration described in 3.3, halides, sulfur oxides and residual oxygen are removed when water, carbon dioxide and nitrogen are determined sequentially.

4.5 For the configuration described in 3.4, in which nitrogen is determined, water, carbon dioxide and residual oxygen are removed.

4.6 For the configuration described in 3.5, halides and sulfur oxides are removed.

4.7 The detection system shall determine nitrogen without interference.

4.8 The detector should ideally provide a linear response that correlates directly with nitrogen concentration over the full range of possible concentrations from the applicable test samples.

4.9 The system shall include provisions for evaluating nonlinear response appropriately, so that nonlinear responses can be correlated accurately with concentration. Such provisions can be integral with the instrument or be provided by (auxiliary) computation schemes.

4.10 Finally, except for those systems in which the nitrogen concentration is expressed as a direct output, the instrument shall include an appropriate detector response readout device.

5 Reagents

Reagent grade chemicals shall be used in all analyses, unless otherwise indicated.

5.1 **Helium**, carrier gas, as specified by the instrument manufacturer.

5.2 **Oxygen**, as specified by the instrument manufacturer.

5.3 **Additional reagents**, as specified by the instrument manufacturer.

This specification refers to the reagents used to meet the requirements cited in 3.3 to 3.5. These reagents can vary substantially for different instruments; in all cases, however, the reagents specified by the manufacturer shall be used.

6 Instrument (automatic analyser) preparation and calibration

6.1 Assemble the instrumental (automatic analyser) system in accordance with the manufacturer's instructions.

6.2 For the response (drift) adjustment, weigh and analyse (in accordance with the manufacturer's instructions) an appropriate test portion of the nitrogen calibrating agent. Repeat this procedure, adjusting instrument response as recommended by the manufacturer, until the absence of drift is indicated.

6.3 For the calibration, select calibrating agents and materials specified by the manufacturer that have certified nitrogen contents lying within the range of those of the samples to be analysed. At least three such calibrating agents are recommended for each range of nitrogen contents to be determined. When possible, two of the calibrating agents shall bracket the range of nitrogen contents to be determined, with the third falling within the range.

6.4 For the calibration procedure, analyse portions of the calibrating agent chosen (see 6.3) to represent the nitrogen content in the samples to be tested. Continue analysing until the results from five consecutive determinations fall within the repeatability interval (see 9.3) of this method. Calibrate the instrument in accordance with the manufacturer's instructions using these values. The results obtained shall be within the precision limits stated for the calibrating agent, otherwise the calibration procedure shall be repeated.

6.5 For the periodic calibration verification and recalibration, analyse a control sample on a periodic basis. The results obtained for the control sample shall be within established limits. If not, all results obtained since the last successful control check shall be rejected and the calibration procedure repeated.

7 Procedure

Analyse a test portion of the sample in accordance with the manufacturer's instructions.

Carry out the analysis in duplicate.

8 Calculation

Calculate the percent nitrogen N as follows:

$$N = \frac{B \times C}{m} \times 100\ \%$$

where

B is the detector response for nitrogen;

C is the detector response per unit mass established for nitrogen during calibration;

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

9 Precision

9.1 Although the precision of this method was calculated from data obtained from the analysis of bituminous coal that contained nitrogen in the range 0,69 % to 1,57 %, it is considered to be directly applicable to the analysis for nitrogen in rubber compounds. The precision is expressed in terms as specified in ISO/TR 9272, on the basis of a 95 % confidence level for the values established for repeatability r and reproducibility R .

9.2 The precision data given in this clause give an estimate of the precision of this method with the materials used in the particular interlaboratory test programme. The precision parameters shall not be used for acceptance or rejection testing of any group of materials without documentation that the parameters are applicable to the particular group of materials and the specific test protocols of the method.

9.3 The **repeatability** r, in percent nitrogen, has been established as the value in Table 1. Two results, obtained in one laboratory (same instrument, material, operator) under normal procedures, that differ by more than this tabulated value shall be considered to have come from different or non-identical sample populations.

9.4 The **reproducibility** R, in percent nitrogen, has been established as the value in Table 1. Two results, obtained in different laboratories (same material, but different instrument and different operator) under normal procedures, that differ by more than this tabulated value shall be considered to have come from different or non-identical sample populations.

9.5 **Bias** is eliminated when the apparatus is calibrated properly against certified reference standards. Proper calibration includes comparison of test data on calibrating agents that have certified nitrogen contents.

Table 1 — Nitrogen analysis precision

Within labs r	**Between labs** R
0,11	0,17
$r = 2{,}83 \times s_r$ where s_r is the repeatability standard deviation. $R = 2{,}83 \times s_R$ where s_R is the reproducibility standard deviation.	

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

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

c) the procedure used (thermal conductivity detection, combined absorbance/conductivity detection or modified chromatographic detection);

d) the duplicate percent nitrogen results to the nearest 0,1 %;

e) the instrument (automatic analyser) make and model;

f) any deviations from the method;

g) the date of the analysis.

Bibliography

[1] ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards*.

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