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Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content

Caoutchouc brut naturel et latex de caoutchouc naturel — Dosage de l'azote

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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).

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).

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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 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 1656:2014), which has been technically revised.

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

— an introduction has been added to explain the purpose of this revision;

— in Clause 4, a known mass of the sample is now digested with a mixture of sulfuric acid and catalytic amounts;

— the list of reagents in 5.1 and 6.1 has been updated;

— in the formulae, the exact concentration of the standard volumetric solutions are expressed in eq/dm^3 with three significant decimal figures;

— the content of total solids in latex has been changed from 2 g to 10 g in 5.3, and from 0,1 g of total solids to 5 g in 6.3;

— in 5.4.1, the tolerance on weighting of sample has been changed from 0,5 mg to 0,1 mg and the amount of catalyst mixture has been added;

— in 5.5, a note has been added to warn of the non-conformance of the blank test;

— In Figures 8 and 10, the length of the condenser has been changed from 250 mm to 300 mm; and the length of the condenser tube has been changed from 500 mm to 600 mm;

— in Clause 8, the note has been deleted since the concentrations of the standard volumetric solutions used have been standardization;

— the precision data have been updated according to the result of the ITP and former Annex A has been deleted.

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.

Introduction

The purpose of this document is to develop a method to determination of the nitrogen in natural rubber by Kjeldahl process using non-toxic catalyst (no selenium in catalyst mixture). The method is easy to operate, safe and environment friendly. And it does not need alternative analyser.

The previous edition of this document provided a method which had the advantage of being simple and accurate, using ordinary equipment at low cost of analysis. However, it used selenium or sodium selenate in the catalysts which is harmful to environment and human health.

Within Rubber Based Products Working Group of the ASEAN Consultative Committee on Standards and Quality activities, (RPBWG/ACCSQ), Vietnam conducted studies on this matter and finally found some suitable mixtures of catalyst to replace selenium. The mixture of $TiO_2/CuSO_4/K_2SO_4$ is the best catalyst mixture to replace the previous one $Se/CuSO_4/K_2SO_4$. It gives testing results of high accuracy, and compared to the previous one, it is safe to the technicians and the environment and easy to operate.

In addition, the total cost of the new catalyst is much cheaper than the old one (about 50 % compared to the selenium mixture catalyst).

Statistical data are available to prove the reliability of this method and its good repeatability. These data come from an ITP carried out among ASEAN member's laboratories. This ITP was permitted by the ASEAN Secretariat and was organized by the Malaysian Rubber Board (MRB). The ITP was conducted both to compare the results using selenium catalyst with the alternative catalyst, and also to demonstrate the stability of the method.

Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content

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.

1 Scope

This document specifies a macro-method and a semi-micro method for the determination of nitrogen in raw natural rubber and in natural rubber latex using variants of the Kjeldahl process.

NOTE The determination of nitrogen in natural rubber is usually carried out in order to arrive at an estimate of the protein content. Minor amounts of non-proteinous nitrogen containing constituents are also present. However, in the dry solids prepared from natural rubber latex, these materials can make a substantial contribution to the total nitrogen 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 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

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 http://www.electropedia.org/

4 Principle

A known mass of the sample is digested with a mixture of sulfuric acid and catalytic amount converting nitrogen compounds into ammonium hydrogen sulfate from which the ammonia is distilled after making the mixture alkaline.

The distilled ammonia is absorbed either in standard volumetric sulfuric acid solution followed by titration of the excess acid with a standard volumetric base solution or in boric acid solution followed by titration with standard volumetric acid solution (as boric acid is a weak acid, it does not affect the indicator used for this titration).

5 Macro-method

5.1 Reagents

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

5.1.1 Catalyst mixture.

5.1.1.1 Titanium dioxide catalyst mixture.

Mix well these chemicals as follows (it is recommended to use mortar and pestle):

— 100 g of anhydrous potassium sulfate (K_2SO_4);

— 3 g of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$);

— 3 g of titanium dioxide (TiO_2).

5.1.1.2 Selenium catalyst mixture.

CAUTION — When working with selenium, avoid breathing vapours and/or contact with skin or clothing. Work only with adequate ventilation.

Mix well these chemicals as follow (using mortar and pestle are recommended):

— 30 parts by mass of anhydrous potassium sulfate (K_2SO_4);

— 4 parts by mass of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$);

— 1 part of selenium powder or 2 parts by mass of sodium selenate decahydrate ($Na_2SeO_4.10H_2O$).

5.1.2 Sulfuric acid, ρ 1,84 g/cm³.

5.1.3 Disodium tetraborate solution (reference standard solution), $c(Na_2B_4O_7)$ = 0,10 eq/dm³ (0,050 mol/dm³).

Weigh exactly 19,261 6 g of $Na_2B_4O_7 \cdot 10H_2O$ (M = 381,38 g/mol; N = 190,69 g/eq; assay = 99 %) in a beaker, dissolve with some water. Using a glass rod, careful pour them into a 1 000 cm³ volumetric flask, rinse the beaker and glass rod for a few times, and add the rinsing solution into the volumetric flask, make up to mark with water and shake well.

5.1.4 Sulfuric acid standard volumetric solution, $c(H_2SO_4)$ = 0,1 eq/dm³ (0,05 mol/dm³).

Standardization of this solution by a reference standard solution is done as follows.

— Take 10,0 cm³ of $Na_2B_4O_7$, $c(Na_2B_4O_7)$ = 0,10 eq/dm³ (0,050 mol/dm³) (5.1.3) into a 100 cm³ flask.

— Add 2 drops of indicator (5.1.8), titrate this solution with H_2SO_4 (5.1.4). The end of the titration is the change of solution from green colour to pink.

— Express normal concentration of H_2SO_4, as given by Formula (1).

$$c_2 = \frac{c_1 \times V_1}{V_2} \quad (1)$$

where

V_1 is the volume of $Na_2B_4O_7$ solution (5.1.3), expressed in cm^3;

V_2 is the volume of H_2SO_4 solution (5.1.4) required for the titration, expressed in cm^3;

c_1 is the concentration of the reference solution, $Na_2B_4O_7$ solution (5.1.3) expressed in eq/dm^3;

c_2 is the exact concentration of H_2SO_4 solution (5.1.4), expressed in eq/dm^3.

Calculate and take the correct concentration of the sulfuric acid standard solution with three significant decimal figures.

5.1.5 Sodium hydroxide standard volumetric solution, c(NaOH) = 0,1 eq/dm^3 (0,1 mol/dm^3).

Standardization of this solution is carried out by the same way as demonstrated in 5.1.4, using the 0,1 eq/dm^3 sulphuric acid solution with the exact concentrate as a reference standard solution.

5.1.6 Sodium hydroxide solution, c(NaOH) approximately 10 mol/dm^3 (density of 40 %).

Dissolve 400 g of solid sodium hydroxide in about 600 cm^3 of water and dilute to 1 000 cm^3.

5.1.7 Boric acid solution, $c(H_3BO_3)$ approximately 0,17 mol/dm^3.

Dissolve 10,5 g of solid boric acid in water, warming if necessary, and dilute to 1 000 cm^3, then cool the solution to room temperature.

5.1.8 Mixed indicator solution.

Dissolve 0,1 g of methyl red and 0,05 g of methylene blue in 100 cm^3 of at least 95 % (volume fraction) ethanol.

This indicator might deteriorate during storage and shall therefore be freshly prepared.

5.2 Apparatus

Ordinary laboratory apparatus and Kjeldahl apparatus with a digestion flask of capacity 800 cm^3.

5.3 Sampling and preparation of test portion

For the determination of nitrogen in raw solid rubber, a test portion shall be taken from the homogenized piece, sampled and prepared in accordance with ISO 1795.

For the determination of nitrogen in latex, a representative portion (as specified in ISO 123) of thoroughly mixed latex containing about 10 g of total solids shall be dried to constant mass, as specified in ISO 124.

5.4 Procedure

5.4.1 Cut about 2 g of the rubber or dried latex, weighed to the nearest 0,1 mg, into small pieces and place in the digestion flask (see 5.2). Add about 18 g of the titanium dioxide catalyst mixture (5.1.1.1), or 13 g of the selenium catalyst mixture (5.1.1.2), and 60 cm^3 of the sulfuric acid (5.1.2). Mix the contents of the flask by swirling and then boil gently until the solution is clear. Continue boiling for 1 h.

NOTE Acidic fumes evolved during digestion are trapped in an alkaline solution and are neutralized before being discharged.

Allow the digestion flask and its contents to cool to room temperature then cautiously add 200 cm^3 of water and mix by swirling.

Place the receiving flask containing the absorbing solution in position, connect the distillation unit, and then slowly add 150 cm^3 of the sodium hydroxide solution (5.1.6) to the digestion flask from a dropping funnel.

5.4.2 Carry out the absorption and titration of the liberated ammonia by the procedure described in a) or b). The temperature of the receiving flask shall be maintained below 30 °C to prevent any loss of ammonia. Ensure proper disposal of the selenium-containing waste in the distillation flask.

a) Place 75 cm^3 of water and, by means of a pipette, 25,0 cm^3 of the standard volumetric sulfuric acid solution (5.1.4) in the receiving flask of the distillation unit together with two drops of mixed indicator solution (5.1.8). Position the receiving flask so that the end of the delivery tube from the condenser dips below the surface of the absorbing solution. While holding the stopper of the digestion flask in place, thoroughly mix the contents by swirling. Immediately begin distillation and continue at a steady rate until 200 cm^3 of distillate have been collected. If the colour of the indicator changes, it indicates alkalinity of the absorbing solution. Discontinue the determination and repeat the procedure using more sulfuric acid or a smaller test portion.

   When the distillation is complete (normally, when the volume in the flask reaches about 300 cm^3), titrate the contents with the sodium hydroxide solution (5.1.5), reading the burette to the nearest 0,02 cm^3.

b) Place 100 cm^3 of the boric acid solution (5.1.7) in the receiving flask of the distillation unit with two drops of the mixed indicator solution (5.1.8). Carry out the distillation as described in a) and titrate the distillate with the sulfuric acid solution (5.1.4), reading the burette to the nearest 0,02 cm^3.

5.5 Blank test

In parallel with the determination, carry out a blank test using the same quantities of reagents under the same operating conditions, but omitting the test portion.

NOTE Blank tests within the same laboratory are almost the same across time. Normally, blank test just shows trace of ammonia of almost equal to nil, if the titrant of the blank test is abnormal. It means that this batch of testing is contaminated. An audit of all the processes, including the equipment and the environment of the laboratory is recommended to eliminate the source of the influencing factors.

5.6 Expression of results

5.6.1 When sulfuric acid is used as the absorbing solution as specified in 5.4.2 a), the nitrogen content of the rubber, c_N, expressed as a percentage by mass, is given by Formula (2):

$$c_N = \frac{(V_2 - V_1) \times c \times 1,4}{m} \tag{2}$$

where

V_1 is the volume of sodium hydroxide solution (5.1.5) required for the titration, expressed in cm^3;

V_2 is the volume of sodium hydroxide solution (5.1.5) required for the titration in the blank test, expressed in cm^3;

c is the exact concentration of sodium hydroxide (5.1.5), expressed in eq/dm^3, with three significant decimal figures;

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

Express the results to the nearest 0,01 %.

