BS ISO 19051:2015

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Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content by Micro Dumas combustion method

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee PRI/23, Test methods for rubber and non-black compounding ingredients.

A list of organizations represented on this committee can be obtained on request to its secretary.

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INTERNATIONAL STANDARD

ISO 19051

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Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content by Micro Dumas combustion method

Latex de caoutchouc brut — Détermination de la teneur en azote par la méthode de combustion de Micro Duma

Reference number
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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

Introduction

The Dumas combustion method has become the most frequently used method worldwide for the accurate and fast determination of nitrogen. Compared to the wet chemical Kjeldahl method, it is superior in terms of speed, safety, and environmental friendliness. The representative analysis of a natural product requires a larger sample size of up to 1 g or more.

The nitrogen content of natural rubber is related to the protein level. The protein content of natural rubber varies depending upon its source and methods used in its processing. Generally, raw natural rubber is expected to have a nitrogen content in the range of 0,3 % to 0,6 %. The normal latex grades have lower levels of nitrogen than the "dry" rubbers, with values around 0,2 %. However, "skim" rubber, with its high protein content, will have appreciably higher values, in the range of 1,5 % to 2,5 %.

This test method will help determine the nitrogen content of the raw natural rubber in the shortest possible time and will be helpful for laboratory quality control testing.

INTERNATIONAL STANDARD ISO 19051:2015(E)

Rubber, raw natural, and rubber latex, natural — Determination of nitrogen content by Micro Dumas combustion method

WARNING 1 — Persons using this International Standard should be familiar with normal laboratory practice. This International 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.

WARNING 2 — Certain procedures specified in this International Standard 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 International Standard specifies a test method for the determination of nitrogen content of raw natural rubber using the Micro Dumas combustion method. This method is also applicable to natural rubber latex.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 124:2014, *Latex, rubber — Determination of total solids content*

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

ISO 18899:2013, *Rubber — Guide to the calibration of test equipment*

3 Principle

In the combustion process (furnace at ca. 1 000 °C), nitrogen is converted to nitrogen gas/oxides. If other elements are present, they will also be converted to different combustion products. A variety of absorbents are used to remove these additional combustion products.

The combustion products are swept out of the combustion chamber by an inert carrier gas such as helium and passed over heated (about 600 °C) high purity copper. This copper can be situated at the base of the combustion chamber or in a separate furnace. The function of this copper is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas. The gases are then passed through the absorbent traps.

Detection of the gases can be carried out in a variety of ways, including the following:

a) GC separation followed by quantification using thermal conductivity detection;

b) partial separation by GC (“frontal chromatography”) followed by thermal conductivity detection;

c) series of separate infrared and thermal conductivity cells for detection of individual compounds.

Quantification of nitrogen requires calibration with high purity "micro-analytical standard" standard reference compounds with known nitrogen content.

During the combustion process, organic compounds are oxidized at high temperature to yield carbon dioxide, water, and oxides of nitrogen:

$$\text{CHN Compound} \xrightarrow{O_2;1000\ ^\circ C} CO_2 + H_2O + NO_x$$

The oxides of nitrogen are then converted to nitrogen gas in the presence of metallic copper:

$$NO_x \xrightarrow{Cu;\ 600\ ^\circ C} N_2$$

4 Reagents

4.1 **Helium (99,99 %)**, as carrier gas and **high purity (99,99 %) oxygen** as combustion gas.

4.2 **Analytical standards**, as per Table 1.

Table 1 — Reference standards

Sample	Molecular formula	Theoretical %C	Theoretical %H	Theoretical %N	Theoretical %S
Tryptophan	$C_{11}H_{12}N_2O_2$	64,69 %	5,92 %	13,72 %	0 %
Imidazole	$C_3H_4N_2$	52,93 %	5,92 %	41,15 %	0 %
Isatin	$C_8H_5NO_2$	65,31 %	3,43 %	9,52 %	0 %
Alanine	$C_3H_7NO_2$	40,44 %	7,92 %	15,72 %	0 %
Nicotinamide	$C_6H_6N_2O$	59,01 %	4,95 %	22,94 %	0 %
Lysine	$C_6H_{14}N_2O_2$	49,30 %	9,65 %	19,16 %	0 %
Cyclohexanone	$C_6H_{10}O$	73,43 %	10,27 %	0 %	0 %
Acetanilide	C_8H_9NO	71,09 %	6,71 %	10,36 %	0 %
Urea	CH_4N_2O	20,00 %	6,71 %	46,65 %	0 %
Atropine	$C_{17}H_{23}NO_3$	70,56 %	8,01 %	4,84 %	0 %
Cystine	$C_6H_{12}N_2O_4S_2$	29,99 %	5,03 %	11,66 %	26,69 %
Sulphanilamide	$C_6H_8N_2O_2S$	41,84 %	4,68 %	16,27 %	18,62 %
BBOT	$C_{26}H_{26}N_2O_2S$	72,53 %	6,09 %	6,51 %	7,44 %

5 Apparatus

5.1 Combustion elemental analysers are manufactured in a variety of configurations to suit specific applications and the choice will depend on the elements of interest, the sample type and size, and the concentration of the analyte.

All instruments require two gas supplies: an inert carrier gas (helium recommended) and high purity oxygen (minimum 99,99 %). The strict specification for oxygen and the carrier gas is associated with the need to reduce the nitrogen "blank" contribution to an inconsequential level. Additionally, GC-type gas filters are also usually fitted to prevent trace organic species and water entering the combustion system.

The choice of test piece introduction system will depend on the application and the nature of the material. For solids or viscous liquids, the test pieces are weighed out into tin capsules. For liquids, the test pieces can be sealed in individual aluminium vials or introduced through a liquid auto-sampler. Both capsules

and vials are pre-cleaned and dried to avoid trace contamination from oils and water acquired during their manufacture. Instruments are marketed with either simple "one shot" introduction interfaces or a carousel type auto-sampler. In some instances, a microbalance is directly interfaced with the analyser to allow the automatic recording of the weight of each test piece.

The combustion section of the analyser is designed to achieve both complete combustion of the test piece and conversion of oxides of nitrogen to nitrogen gas (N_2). Although different approaches have been chosen by different manufacturers, the use of high purity copper is universal for the reduction stage. In some instruments, the combustion and reduction stages are housed in separate furnaces. In others, the reactions are combined in a single two-tier furnace. Catalysts are usually added to the combustion section to aid complete combustion along with absorbents to remove potential contaminants. Both the catalysts/absorbents and copper metal are packed into readily exchangeable tubes made of ceramic material or high quality silica.

The detection system within the analyser can take several forms depending on the combustion mode and test piece size. With small test pieces, the combustion gases can be separated on a GC column and quantified using a thermal conductivity detector. A schematic diagram of such a system is shown in Figure 1. If larger test pieces are required, an instrument employing "frontal" chromatography can be chosen. The latter approach employs a GC column with thermal conductivity detection but provides a step-wise profile for integration. Other detection approaches do not require a separation step but use separate infrared and thermal conductivity cells to respond to individual elements.

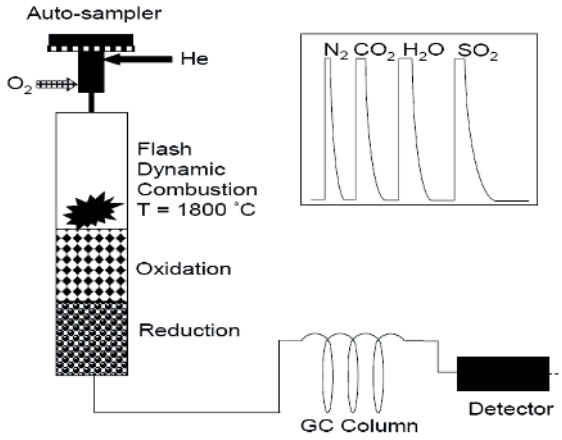

Figure 1 — Different components of elemental analyser (Micro Dumas method)

5.2 **Analytical balance**, capable of weighing to the nearest 0,000 01 g.

5.3 **Micro syringe**, calibrated.

5.4 **Test piece holder**, generally, a tin capsule.

6 Calibration

The instrument shall be calibrated in accordance with the schedule given in Annex A.

7 Sampling and preparation of test piece

7.1 For the determination of nitrogen in raw solid rubber, take the laboratory sample in accordance with the method specified in ISO 1795 and prepare the test piece from the laboratory sample. The test piece is to be cut into small thin pieces using suitable tools such as scissors or knife.

7.2 For the determination of nitrogen in raw latex, take the laboratory sample in accordance with ISO 123.

To prepare the dried latex test piece, take an accurately weighed clean and dry aluminium foil dish. Measure 10 ml from the laboratory sample and put it in the aluminium foil dish. Put the aluminium foil dish in a 110 °C vacuum oven and heat for 15 min until completely dry. Remove the aluminium foil dish from the oven and cool in a desiccator. If the dried sample becomes excessively sticky, sample can be dried at 70 °C ± 2 °C.

A dried latex test piece can also be prepared in accordance with ISO 124:2013, 6.2.

7.3 Weigh the test piece within the range of 0,50 mg to 1,50 mg using the analytical microbalance nearest to 1,00 mg ± 0,01 mg.

7.4 Allow all the weighed test pieces and the analytical microbalance to equilibrate to room temperature for at least 30 min.

7.5 Use a pair of tweezers to place an empty tin capsule on balance and tare the weight.

7.6 Remove the tin capsule using a pair of tweezers and place on metal sample prep block.

7.7 Fill capsule with the desired test piece (generally 0,50 mg to 1,50 mg) and ensure that the test piece is fully encapsulated.

7.8 Tap the encapsulated test piece on a clean surface to remove any remnants on the outside of the encapsulated test piece.

7.9 Place the encapsulated test piece on the balance and record the weight.

7.10 Put the encapsulated test piece in numbered sample tray.

8 Procedure

8.1 General

Turn on the power to the instrument as per instruction of the instrument manufacturer.

8.2 Equipment check

8.2.1 Blank run

a) It is used to establish the instrumental readings for carbon, hydrogen, nitrogen, and sulfur, so as to apply the required correction during the actual test run. It also indicates the stability of the system.

b) Run the empty tin capsules as per manufacturer's instruction.

8.2.2 K-Factor run

a) It is the sensitivity factor which is required to convert the electrical signal from the detector to weight percent results.

b) Run analytical standards of known composition, mentioned under the reagent list as per manufacturer's instruction.

8.2.3 Test run

Set the instrument as per manufacturer's instruction. A general method for instrument set up may be as follows.

Table 2 — Typical instrument condition

Carrier flow (ml/min)	~115
Carrier (kPa)	80
Purge (ml/min)	80
Oxygen (ml)	20
$\Delta P\ O_2$ (kPa)	35
Sampling delay (s)	10
Run time (s) (CHN)	180
TCD (baseline)	1 mV
TCD polarity	(+)
TCD gain	10 or (1 less sensitive)
Front furnace temperature (°C)	1 000
Rear furnace temperature (°C)	600 to 1 000
GC oven temperature (°C)	85

a) Weigh out, at minimum, five different weights of the calibration standards in the range 0,5 mg, 0,7 mg, 1,0 mg, 1,3 mg, and 1,5 mg to account for variation between samples.

b) Weigh out, at minimum, three test pieces of different weights from the laboratory sample in the range of 0,5 mg to 1,5 mg.

c) Generally, the weights of the test pieces should be sufficient to produce an area of N that lies in the middle of the standard curve or in the range of the K-Factor.

d) Carry out the test run in the following order:

   1) blank (tin capsule only–balled up), do not perform more blanks than necessary as it will consume the copper reduction catalyst faster;

   2) set of calibration standards;

   3) test pieces;

   4) blank (15 to 20 tests after the last blank);

   5) repeat steps 1) through 5) until the total analysis is completed.

9 Test report

The test report shall include the following information:

a) sample details

   1) full description of the sample and its origin;

   2) method of preparation of test piece from the laboratory sample;

b) test method

   1) full reference to the test method used, reference to this International Standard, i.e. ISO 19051;

2) test procedure used;

3) type of test piece used;

c) details of any procedures not specified in this International Standard;

d) test results

1) number of test pieces used;

2) mean results;

e) date(s) of test.

Annex A
(normative)

Calibration schedule

A.1 Inspection

Before any calibration is undertaken, the condition of the items to be calibrated shall be ascertained by inspection and recorded on any calibration report or certificate. It shall be reported whether calibration is made in the "as-received" condition or after rectification of any abnormality or fault.

It shall be ascertained that the apparatus is generally fit for the intended purpose, including any parameters specified as approximate and for which the apparatus does not therefore need to be formally calibrated. If such parameters are liable to change, then the need for periodic checks shall be written into the detailed calibration procedures.

A.2 Schedule

Verification/calibration of the test apparatus is a normative part of this International Standard. The frequency of calibration and the procedures used are, unless otherwise stated, at the discretion of the individual laboratory using ISO 18899:2013 for guidance.

The calibration schedule given in Table A.1 has been compiled by listing all of the parameters specified in the test method, together with the specified requirement. A parameter and requirement can relate to the main test apparatus, part of that apparatus, or to an ancillary apparatus necessary for the test.

For each parameter, a calibration procedure is indicated by reference to ISO 18899:2013, to another publication, or to a procedure particular to the test method which is detailed (whenever a more specific or detailed calibration procedure than in ISO 18899:2013 is available, it shall be used in preference).

The verification frequency for each parameter is given by a code-letter.

The code letters used in the calibration schedule are

— R: use of certified reference material, and

— U: in use.

Table A.1 — Calibration frequency schedule

Parameter	Requirement	Subclause in ISO 18899:2013	Verification frequency guide	Notes
Analytical balance	Accurate to ±0,01 mg	22.2	R	Calibrated weight
Reference materials	Different analytical standards as per Table 1		U	

In addition to the items listed in the table, use of the following is implied, which needs calibrating in accordance with ISO 18899:2013:

— thermometer for monitoring the conditioning and test temperatures.

Annex B
(informative)

Technical justification of Micro Dumas combustion process

For total nitrogen and total carbon analysis, sample materials in their naturally occurring solid or liquid state should be converted into simple gases N_2 and CO_2.

For nitrogen (N), the Kjeldahl-Rittenberg procedure is a well-known analytical technique. In this wet-chemistry method, an acid digestion is used to produce an ammonium salt, which is then oxidized to N_2 gas using hypobromite. This procedure is slow and laborious and involves certain hazards, such as hot acid fumes. It also requires care to avoid loss of N during transfer between steps.

The alternative dry Micro Dumas combustion analysis for total carbon and total nitrogen in solid-phase samples is based on transformation to gas phase by extremely rapid and complete flash combustion of the sample material.

CHNS elemental analysers provide a means for the rapid determination of carbon, hydrogen, nitrogen, and sulfur in organic matrices and other types of materials. They are capable of handling a wide variety of sample types, including solids, liquids, volatile, and viscous samples. The analysers are often constructed in modular form such that they can be set up in a number of different configurations to determine, for example, CHN, CHNS, CNS, or N depending on the application. This adaptability allows not only flexibility of operation but also the use of a wide range of sample weights from a fraction of a milligram to several grams.

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