# DRAFT MALAYSIAN STANDARD

**LGM17ISC/N004R0**

**STAGE : PUBLIC COMMENT (PC)**
**PC Duration : 30/11/2018 – 28/01/2019**



## Rubber, vulcanised rubber – Determination of free sulphur content

**ICS: 83.040.01**

Descriptors: rubber, vulcanised rubber, free sulphur, determination



**DEPARTMENT OF STANDARDS MALAYSIA**

## DEVELOPMENT OF MALAYSIAN STANDARDS

The **Department of Standards Malaysia (STANDARDS MALAYSIA)** is the national standards and accreditation body of Malaysia.

The main function of STANDARDS MALAYSIA is to foster and promote standards, standardisation and accreditation as a means of advancing the national economy, promoting industrial efficiency and development, benefiting the health and safety of the public, protecting the consumers, facilitating domestic and international trade and furthering international cooperation in relation to standards and standardisation.

Malaysian Standards (MS) are developed through consensus by committees which comprise balanced representation of producers, users, consumers and others with relevant interests, as may be appropriate to the subject at hand. To the greatest extent possible, Malaysian Standards are aligned to or are adoption of international standards. Approval of a standard as a Malaysian Standard is governed by the Standards of Malaysia Act 1996 [Act 549]. Malaysian Standards are reviewed periodically. The use of Malaysian Standards is voluntary except in so far as they are made mandatory by regulatory authorities by means of regulations, local by-laws or any other similar ways.

For the purposes of Malaysian Standards, the following definitions apply:

**Revision:** A process where existing Malaysian Standard is reviewed and updated which resulted in the publication of a new edition of the Malaysian Standard.

**Confirmed MS:** A Malaysian Standard that has been reviewed by the responsible committee and confirmed that its contents are current.

**Amendment:** A process where a provision(s) of existing Malaysian Standard is altered. The changes are indicated in an amendment page which is incorporated into the existing Malaysian Standard. Amendments can be of technical and/or editorial nature.

**Technical corrigendum:** A corrected reprint of the current edition which is issued to correct either a technical error or ambiguity in a Malaysian Standard inadvertently introduced either in drafting or in printing and which could lead to incorrect or unsafe application of the publication.

NOTE: Technical corrigenda are not to correct errors which can be assumed to have no consequences in the application of the MS, for example minor printing errors.

Standards Malaysia has appointed **Malaysian Rubber Board** as its Standards Development Agency (SDA). **Malaysian Rubber Board** is tasked to develop, distribute & sell Malaysian Standards according to its designated scope(s).

For further information on Malaysian Standards, please contact:


**Department of Standards Malaysia**
Ministry of Science, Technology and Innovation
Level 1 & 2, Block 2300
Century Square Jalan Usahawan
63000 Cyberjaya
Selangor Darul Ehsan
MALAYSIA

Tel: 60 3 8318 0002
Fax: 60 3 8319 3131
http://www.jsm.gov.my
E-mail: central@jsm.gov.my

**OR**

**Malaysian Rubber Board (MRB)**
Standards Development Agency (SDA)
Quality & Technical Services Division
RRIM Sungai Buloh
47000 Sungai Buloh
Selangor Darul Ehsan
MALAYSIA

Tel: +603-6145 9400
Fax: +603-6157 6525
http://www.lgm.gov.my
Email: sda@lgm.gov.my

**Contents**

Page

Committee representation ..... ii

Foreword ..... iii

1 Scope ..... 1

2 Normative references ..... 1

3 Principles ..... 1

4 Apparatus ..... 1

5 Reagents and materials ..... 2

6 Instruments preparation and calibration ..... 2

7 Sampling and preparation of the sample ..... 3

8 Procedure ..... 3

9 Calculation of free sulphur content ..... 4

10 Precision ..... 4

11 Test report ..... 5

Bibliography ..... 6



 

## Committee representation

The Industry Standards Committee on Rubber and Rubber Products (ISC N) under whose authority this Malaysian Standard was developed, comprises representatives from the following organisations:

Department of Standards Malaysia

Institute of Materials Malaysia

Malaysian Association of Standards Users

Malaysian Rubber Board

Malaysian Rubber Board (Secretariat)

Malaysian Rubber Export Promotion Council

Malaysian Rubber Glove Manufacturers' Association

Malaysian Rubber Products Manufacturers' Association

Ministry of International Trade and Industry

The Plastics and Rubber Institute of Malaysia

Universiti Kuala Lumpur

Universiti Selangor

Universiti Teknologi MARA

The Technical Committee on Raw Materials and Chemical Test which developed this Malaysian Standard consists of representatives from the following organisations:

Ansell Shah Alam Sdn Bhd

Getahindus Sdn Bhd

Kuala Lumpur Kepong Berhad

MAPA Gloves Sdn Bhd

MARDEC Berhad

Malaysian Rubber Board

Malaysian Rubber Board (Secretariat)

Malaysian SMR Rubber Processors Association

Scientia Solutions Sdn Bhd

Sime Darby Research Sdn Bhd

Synthomer (M) Sdn Bhd



 

## Foreword

This Malaysian Standard was developed by the Technical Committee on Raw Materials and Chemical Test under the authority of the Rubber and Rubber Products Industry Standards Committee.

Compliance with a Malaysian Standard does not of itself confer immunity from legal obligations.



 

# Rubber, vulcanised rubber — Determination of free sulphur content

## 1 Scope

This Malaysian Standard specifies a method for determination of free sulphur in vulcanised rubber and rubber products by an automatic analyser which uses a combustion process. This method is also applicable for compounded latex.

## 2 Normative references

The following normative references are indispensable for the application of this standard. For dated references, only the edition cited applies. For undated references, the latest edition of the normative reference (including any amendments) applies.

MS 1524, *Rubber – Determination of solvent extract*

MS ISO 124, *Latex, rubber – Determination of total solid content*

ISO 15671, *Rubber and rubber additives – Determination of total sulphur content using automatic analyser*

## 3 Principle

The sulphur is determined by a single instrumental procedure. A weighed test portion from the sample that has undergone solvent extraction is placed in the instrument and the (subsequently automatic) analytical process initiated. The method includes the following:

a) conversion of sulphur-containing materials to sulphur dioxide in an oxygen stream; and

b) determination of the sulphur dioxide generated, by infrared absorption spectroscopy or thermal conductivity or any equivalent detector. A sulphur dioxide standard enables the free sulphur content to be calculated.

NOTE Free sulphur content is determined by calculating the difference in sulphur content from an unextracted and solvent extracted sample

## 4 Apparatus

**4.1 Automatic analyser**, complete with the following components:

a) a combustion unit, capable of maintaining a minimum operating temperature in accordance with the manufacturer's instructions for combustion of the sample in an atmosphere of high purity oxygen;



 

b) a high purity oxygen feeder, capable of feeding enough high purity oxygen for complete combustion where sulphur containing material shall be converted completely to sulphur dioxide;

c) an absorber (or another type of separator) of by products, capable of removing the water and carbon dioxide formed;

d) an infrared absorption or thermal conductivity or any equivalent detector, capable of detecting the sulphur dioxide gas formed;

e) a microprocessor, capable of calibrating the apparatus with a sulphur calibrating agent or material and of converting the detector response into mass % of sulphur in the sample.

**4.2 Analytical balance,** accurate to ± 0.1 mg

**4.3 Soxhlet extraction apparatus**

**4.4 Regulated heating system**

**4.5 Rotary evaporator** or any other suitable type of evaporation equipment

**4.6 Drying oven**

**4.7 Roll mill**

**4.8 Combustion container** as specified by instrument manufacturer

## 5 Reagents and materials

Analytical reagent grade chemical shall be used in all analysis unless otherwise indicated.

**5.1 Acetone,** as specified in MS 1524

**5.2 Sulphur calibrating agents and materials,** as specified by instrument manufacturer

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

**5.4 Carrier gas, helium,** or any other gaseous as specified by the instrument manufacturer

**5.5 Combustion gas, oxygen,** as specified by the instrument manufacturer

## 6 Instrument 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 sulphur calibrating agent. Repeat this procedure, adjusting instrument response, as recommended by the manufacturer, until



 

instrument response, as recommended by the manufacturer, until the absence of drift is accepted.

**6.3** For the calibration, select calibrating agents and materials specified by the manufacturer that have certified sulphur 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 sulphur contents to be determined.

**6.4** For the calibration procedure, analyse portions of the calibrating agent chosen (6.3) to represent the sulphur content in the samples to be tested. Continue analysing until the results from five consecutive determinations fall within the repeatability interval of this test method (r). 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 every ten samples, run one sulphur calibrating agent (5.2) followed by a blank.

**6.6** 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.

## 7 Sampling and preparation of the sample

### 7.1 Vulcanised rubber or rubber products

Weigh, to the nearest 0.1 mg, a sample of 10 g and pass the sample between the surfaces of the laboratory mill rolls.

Take two portions of about 3 g to 5 g from the sample prepared as specified above. Keep one portion for the analysis of total sulphur. Transfer another test portion to the extraction apparatus (4.3) and extract with acetone as specified in MS 1524.

### 7.2 Compounded latex

Take a portion of compounded latex containing about 20 g of total solids and make into a thin film by pouring the portion onto a glass plate. Dry to constant mass as specified in MS ISO 124.

Take two portions of about 3 g to 5 g from the sample prepared as specified above and cut into small pieces. Keep one portion for the analysis of total sulphur. Transfer another test portion to the extraction apparatus (4.3) and extract with acetone as specified in MS 1524.

## 8 Procedure

**8.1** Analyse a test portion of unextracted sample for total sulphur content in accordance with the instrument manufacturer's instruction as specified in ISO 15671.

**8.2** Analyse a test portion of solvent extracted sample in accordance with the instruments manufacturer's instruction.

**8.3** Carry out the analysis in duplicate.



 

## 9 Calculation of free sulphur content

The percentage of free sulphur ($S_F$) can be calculated by the following equation:

$$S_F = S - S_C$$

where,

$S$ is the sulphur content in an unextracted test portion, in mass %; and

$S_C$ is the sulphur content in a solvent extracted test portion, in mass % x $f$.

where,

$$f = 1 - \left(\frac{\%\ acetone\ extraction}{100}\right)$$

## 10 Precision

The precision data are given in Table 1. The precision parameters should not be used for acceptance or rejection of any group of materials without documentation that the parameters are applicable to those particular materials and specific test protocols of the test method. The precision is expressed on the basis of a 95 % confidence level for the values established for repeatability r and reproducibility R.

The results contained in Table 1 are average values and give an estimate of the precision of this test method as determined in an interlaboratory test programme, carried out in 2018, in which four participants took part, performing duplicate analyses on two types of rubber compound namely rubber compound 1 (RC1) and rubber compound 2 (RC2). The rubber compound was sub-sampled into two pieces labelled A and B (which will be tested on two different weeks. Thus, essentially, samples A and B were the same and were treated as such in the statistical computations. Each participant was required to carry out the test with the specified date.

A type 1 precision was evaluated, based on the method of sampling used for the interlaboratory test programme.

**Table 1: Precision data for the determination of free sulphur in rubber compound**

| Compounded rubber | Average result (µg/cm³) | Within-laboratory | | Between laboratories | |
|---|---|---|---|---|---|
| | | $s_r$ | $r$ | $S_R$ | $R$ |
| RCA | 0,88 | 0,17 | 0,48 | 0,15 | 0,44 |
| RCB | 1,83 | 0,29 | 0,81 | 0,27 | 0,76 |

$s_r$ is the within-laboratory standard deviation
$r$ is the repeatability (in measurement units)
$S_R$ is the between-laboratory standard deviation
$R$ is the reproducibility (in measurement units)



 

**Repeatability:** The repeatability r (in measurement units) of the test method has been established as the appropriate value tabulated in Table 1. Two single test results, obtained in the same laboratory under normal test method procedure, that differ by more than the tabulated value of r (for any given level) should be considered to have come from different, or non-identical, sample populations.

**Reproducibility:** The reproducibility R (in measurement units) of the test method has been established as the appropriate value tabulated in Table 1. Two single test results, obtained in different laboratories under normal test method procedure, that differ by more than the tabulated value of R (for any given level) should be considered to have come from different, or non-identical, sample populations.

**Bias:** In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias cannot therefore be determined for this particular method.

For the general procedure for using precision results, see ISO 19983.

## 11 Test report

The test report shall include the following particulars:

a) reference to this Malaysian Standard;

b) identification of the test sample;

c) the results obtained, free sulphur detected in the sample;

d) the date of the test; and

e) any operation not included in this Malaysian Standard or in the Malaysian Standard to which reference is made, or regarded as optional.



 

## Bibliography

[1] ISO 19242:2015, *Rubber – Determination of total sulphur content by ion chromatography*

[2] ISO 19051:2015, *Rubber, raw natural, and rubber latex, natural – Determination of nitrogen content by Micro Dumas combustion method*

[3] ISO 6528-1:1992, *Rubber – Determination of total sulphur content – Part 1: Oxygen combustion flask method*

[4] ISO 24698-1, *Determination of bound acrylonitrile content in acrylonitrile-butadiene rubber (NBR) – Part 1: Combustion (Dumas) method*

[5] ISO 19983, *Rubber – Determination of precision of test*



 

## Acknowledgements

**Members of Technical Committee on Raw Materials and Chemical Test**

| | |
|---|---|
| Dr Faridah Hanim Ab Hanan (Chairman) | Malaysian Rubber Board |
| Mr Muhammad Syaarani Danya (Secretary) | Malaysian Rubber Board |
| Mr Yeo Chin Huet | Getahindus Sdn Bhd |
| Mr Jason Foong Huey Yuan/<br>Ms Chong Lai Shien | Kuala Lumpur Kepong Berhad |
| Dr Kartini Abdol Rahim | Malaysian Rubber Board |
| Mr Chua Jong Huei | MAPA Gloves Sdn Bhd |
| Mr Ooi Boon Chye/<br>Mr Ho Han Boon | Malaysian SMR Rubber Processors Association |
| Dr Norhayati Moris | Scientia Solutions Sdn Bhd |
| Ms Maizatul Putri Ahmad Sabri | Sime Darby Research Sdn Bhd |
| Mrs Zuridah Manas | Synthomer (M) Sdn Bhd |

**Co-opted members**

| | |
|---|---|
| Dr Rosmahani Che Isa | Malaysian Rubber Board |
| Mrs Ruhida Ab Rahim | Malaysian Rubber Board |