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## Rubber — Determination of total sulfur content by ion chromatography

*Caoutchouc — Détermination de la teneur en soufre total par  
chromatographie ionique*

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# Contents

Page

<b>Foreword</b>	iv
<b>Introduction</b>	v
<b>1 Scope</b>	1
<b>2 Normative references</b>	1
<b>3 Terms and definitions</b>	1
<b>4 Principle</b>	2
4.1 Combustion	2
4.1.1 Tubular furnace combustion method	2
4.1.2 Oxygen combustion flask method	2
4.2 Determination	2
<b>5 Reagents</b>	2
<b>6 Apparatus</b>	2
<b>7 Procedure</b>	3
7.1 Preparation of sample solutions	3
7.1.1 Tubular furnace combustion method	3
7.1.2 Oxygen combustion flask method	3
7.2 Determination of sulfate by ion chromatography	3
7.2.1 Setting up the ion chromatograph	3
7.2.2 Measuring calibration solutions	3
7.2.3 Measuring blank solutions and sample solutions	4
<b>8 Calculations</b>	4
<b>9 Precision</b>	4
<b>10 Test report</b>	4
<b>Annex A (normative) Preparation of sample solutions by the tubular furnace combustion method</b>	5
<b>Annex B (normative) Preparation of sample solutions by the oxygen combustion flask method</b>	8
<b>Annex C (informative) Examples of conditions for ion chromatography</b>	11
<b>Annex D (informative) Precision data from an interlaboratory test programme</b>	13
<b>Bibliography</b>	15

## 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.

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](http://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](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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](http://www.iso.org/iso/foreword.html).

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

This second edition cancels and replaces the first edition (ISO 19242:2015), of which it constitutes a minor revision. The main changes compared to the previous edition are as follows:

- the CAS numbers have been added for all chemicals listed in this document;
- [Clause 3](#) on “Terms and definitions” has been added.

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](http://www.iso.org/members.html).

## Introduction

Titration methods using thiorin, a toxic arsenic compound as a reagent, have been used to determine the total sulfur content in raw rubber and rubber compounds. In this document, the sulfur in a test piece is burnt and oxidized to sulfur dioxide, which is then absorbed into a hydrogen peroxide solution and converted to sulfuric acid for determination by ion chromatography.

No hazardous reagents are required, thus improving the working environment as well as being eco-friendly. In addition, ion chromatography is used worldwide for its simplicity and high accuracy.

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# Rubber — Determination of total sulfur content by ion chromatography

**WARNING 1** — 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 and to ensure compliance with any national regulatory conditions.

**WARNING 2** — The use of this document pre-supposes sufficient working knowledge of the principles and techniques of ion chromatography for the analyst to perform the operations described and interpret the results correctly.

**CAUTION** — Certain procedures specified in this document can 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 document specifies a method for the determination of the total sulfur content of raw rubber and unvulcanized or vulcanized rubber compounds by ion chromatography following the preparation of a sample solution using either a tubular furnace combustion or an oxygen combustion flask method.

The tubular furnace combustion method is applicable for rubbers with sulfur content less than 0,1 % as it is possible that the oxygen combustion flask method will not give sufficiently accurate results.

The oxygen combustion flask method is not applicable to rubbers containing a metal salt that forms an insoluble metal sulfate, such as barium sulfate (CAS 7727-43-7).

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4661-2, *Rubber, vulcanized — Preparation of samples and test pieces — Part 2: Chemical tests*

## 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

### 4.1 Combustion

#### 4.1.1 Tubular furnace combustion method

A test piece is burnt in an oxygen (CAS 7782-44-7) stream in a tubular furnace with an electrical heater. The sulfur in the test piece is oxidized to sulfur dioxide (CAS 7446-09-5), which is absorbed into hydrogen peroxide (CAS 7722-84-1) solution and converted to sulfuric acid (CAS 7664-93-9).

#### 4.1.2 Oxygen combustion flask method

A test piece is burnt in the presence of oxygen in a flask. The sulfur in the test piece is oxidized to sulfur dioxide, which is absorbed into hydrogen peroxide solution and converted to sulfuric acid.

### 4.2 Determination

The sulfate from either the tubular furnace combustion or the oxygen combustion flask method is quantitatively analysed by ion chromatography, and the result is converted to the total sulfur content of the original rubber sample.

## 5 Reagents

Use only reagents of recognized analytical grade and only water as specified in 5.1. The reagents for the tubular furnace combustion method are given in A.2. The reagents for the oxygen combustion flask method are given in B.2.

#### 5.1 Water, of grade 1 or higher as specified in ISO 3696.

#### 5.2 Sulfate stock standard solution, of a commercial standard solution with a certified sulfate concentration, e.g. 1 000 mg/dm<sup>3</sup> of sulfate, traceable to national standards.

Observe the manufacturer's expiry date or recommended shelf-life.

#### 5.3 Sulfate calibration solutions, prepared by dilution of the sulfate stock standard solution (5.2) with water (5.1).

Prepare at least four solutions of different concentration of sulfate covering the expected concentration from the sample. The solutions shall be prepared every analytical day.

#### 5.4 Eluent solution, capable of eluting sulfate to a proper retention time in selected column.

Follow the column manufacturer's instructions. Some examples of eluent are shown in Annex C.

## 6 Apparatus

#### 6.1 Balance, of accuracy to the nearest 0,1 mg.

#### 6.2 Apparatus for the tubular furnace combustion method, as specified in A.3.

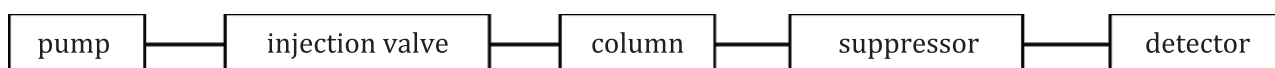
#### 6.3 Apparatus for the oxygen combustion flask method, as specified in B.3.



**6.4 Ion chromatograph**, consisting of a pump to supply eluent, injection valve, column and conductivity detector specified as follows:

- pump: capable of delivering a constant flow within the range of 0,1 cm<sup>3</sup>/min to 2,0 cm<sup>3</sup>/min;
- injection valve: capable of injecting a constant volume of solution;
- column: filled with anion exchange resin suitable for resolving sulfates from other inorganic anions; some examples are shown in [Annex C](#);
- suppressor: used for reducing the conductivity of high ionic eluent;
- detector: for detecting conductivity.

An ion chromatograph fitted with a suppressor is suitable for sensitive analysis (see [Figure 1](#)). The suppressor is attached between the column and the detector. However, an ion chromatograph without a suppressor may also be selected (see [Figure 2](#)). For the conditions of these methods, see [Annex C](#).



**Figure 1 — Example of basic ion chromatography system with suppressor**



**Figure 2 — Example of basic ion chromatography system without suppressor**

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## 7 Procedure

### 7.1 Preparation of sample solutions

#### 7.1.1 Tubular furnace combustion method

Follow the method specified in [Annex A](#). Repeat the procedure to obtain two solutions for each sample.

#### 7.1.2 Oxygen combustion flask method

Follow the method specified in [Annex B](#). Repeat the procedure to obtain two solutions for each sample.

### 7.2 Determination of sulfate by ion chromatography

#### 7.2.1 Setting up the ion chromatograph

Set up the ion chromatograph in accordance with the manufacturer's instructions.

#### 7.2.2 Measuring calibration solutions

Inject the calibration solutions in order of increasing concentration and measure the conductivity of sulfate peak area in each solution. Determine the correlation formula (calibration curve) by plotting the peak area as a function of concentration by means of linear regression.

### 7.2.3 Measuring blank solutions and sample solutions

Inject the blank solutions and sample solutions (obtained in 7.1) to measure the peak area. Then determine the sulfate concentration of the blank  $C_B$  and that of the individual sample solution  $C_S$  by using the calibration curve determined in 7.2.2.

## 8 Calculations

Calculate the sulfur content of the sample in percentage from each value determined in 7.2.3. Average the two content values and round to the second decimal place, using Formula (1):

$$\frac{(C_S - C_B) \times V}{m \times 1000} \times \frac{32,06}{96,06} \times 100 \quad (1)$$

where

$m$  is the mass of the test piece, in mg;

$C_S$  is the sulfate concentration of the sample solution, in mg/dm<sup>3</sup>;

$C_B$  is the sulfate concentration of the blank solution, in mg/dm<sup>3</sup>;

$V$  is the volume of the volumetric flask, in cm<sup>3</sup>;

32,06 is the atomic weight of sulfur;

96,06 is the molecular mass of sulfate.

## 9 Precision

See Annex D.

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## 10 Test report

The test report shall include the following particulars:

- a) sample details:
  - 1) a full description of sample;
  - 2) if appropriate, the brief preparation procedure of the test piece from the sample;
- b) test method:
  - 1) a reference to this document (i.e. ISO 19242:2021);
  - 2) the combustion method used: “tubular furnace combustion method” or “oxygen combustion flask method”;
  - 3) the ion chromatography system used: with suppressor or without suppressor;
  - 4) the column and eluent used;
- c) details of any procedures not specified in this document;
- d) the test results;
- e) the date(s) of the test.

## Annex A (normative)

### Preparation of sample solutions by the tubular furnace combustion method

#### A.1 General

This annex specifies the preparation procedure of sample solutions by the tubular furnace combustion method.

#### A.2 Reagents and materials

**A.2.1 Hydrogen peroxide solution of 500 µg/g**, prepared by diluting hydrogen peroxide of 30 % mass fraction solution with water to 500 µg/g.

**A.2.2 Oxygen** (CAS 7782-44-7), of mass fraction > 99,7 %.

**A.2.3 Argon** (CAS 7440-37-1), of mass fraction > 99,98 %.

**A.2.4 Air** (CAS 132259-10-0), of certified quality in contamination and purity.

NOTE Air is an alternative to the combustion gas of oxygen mixed with argon. The certification of the air quality can be judged by individual laboratories in so far as it does not affect the test result.

#### A.3 Apparatus

The apparatus consists of combustion furnace, quartz tube, and absorbing vessel as shown in [Figure A.1](#).

**A.3.1 Combustion furnace**, with an electric heater capable of heating at a temperature of 1 000 °C and maintaining the temperature for a certain period of time.

**A.3.2 Quartz tube**, having heat-resistance enough to be heated at the maximum temperature (e.g. 1 000 °C) by the electric heater and capable of holding a sample boat inside.

A gas consisting of oxygen mixed with argon, or air which is supplied by the system, passes through the tube.

**A.3.3 Sample boat**, made of quartz, ceramic, or platinum and capable of carrying a test piece.

It shall have heat-resistance enough to be heated by the electric heater at the maximum temperature (e.g. 1 000 °C).

**A.3.4 Absorption vessel**, made of borosilicate glass with sufficient volume to allow the gas to bubble through the absorbent solution in it when it is filled at a certain level.

Other types of apparatus than those specified in [A.3.1](#) through [A.3.4](#) may be used when they are proven to give the same result.