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Rubber and rubber products — Determination of 2-mercaptobenzothiazole content by high performance liquid chromatography (HPLC)

Caoutchouc et produits à base de caoutchouc — Détermination de la teneur en 2-mercaptobenzothiazole par chromatographie en phase liquide haute performance
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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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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).

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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 ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

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

2-Mercaptobenzothiazole (sometimes also referred to as: MBT; 2-MBT; 2-benzothiazolethione, or BTSH) is used in the rubber industry as a curing agent. MBT is in the group of thiazoles and is considered as scorch fast when used as a primary accelerator.

2-Mercaptobenzothiazole as the acidic sulfur accelerator is widely used in rubber materials because of its good characteristics: stable sulfides, good vulcanization, and a low critical temperature to accelerate vulcanization so that the rubber product can reach higher tensile strength and hardness levels.

Measuring 2-mercaptobenzothiazole concentration in rubber compounds at different stages of curing the rubber product is an excellent means to define the optimal curing conditions of temperature and time in order to obtain the right properties for the products at the best cost.

During the curing of rubber compounds sulfenamides are used as accelerators, which chemically react at an early stage of the curing to produce 2-mercaptobenzothiazole and other species. 2-Mercaptobenzothiazole then contributes to the initiation of the mechanism which creates the sulfur crosslinks between the rubber macromolecules at the end (an example is given in [Figure A](#)). To ensure continuous progress, it is important to know the chemical mechanisms involved at each stage. Thus, it is necessary to quantify the content of 2-mercaptobenzothiazole during the decomposition of the sulfenamide and to know whether 2-mercaptobenzothiazole has disappeared in any further chemical reactions.

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Rubber and rubber products — Determination of 2-mercaptobenzothiazole content by high performance liquid chromatography (HPLC)

1 Scope

This document specifies a quantitative test method to determine the 2-mercaptobenzothiazole content in rubber and rubber products by high performance liquid chromatography (HPLC).

This document delivers a method for quantifying 2-mercaptobenzothiazole in rubber products for a better selection of curing conditions.

This document provides a method to follow the curing of rubber with sulfur- and benzothiazole-based accelerators using a chemical measurement which is complementary to the classical rheometric technique.

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Principle

The 2-mercaptobenzothiazole in rubber is ultrasonically extracted with a chloroform-methanol solution determined and confirmed with HPLC-DAD (high performance liquid chromatography equipped with a diode-array detector).

Note There is a risk of neo-formed MBT from MBTs if a thiazole accelerator is used in the formulation of the sample.

5 Reagents and materials

Unless otherwise specified, analytical grade chemicals should be used. Water shall be distilled or deionized to fulfil grade 3 in accordance with ISO 3696.

5.1 Methanol, of analytical grade.

- 5.2 **Chloroform**, of analytical grade.
- 5.3 **Acetonitrile**, of chromatographic grade.
- 5.4 **2-Mercaptobenzothiazole standard material**, of purity $\geq 99,1$ %.
- 5.5 **Filtration membrane**, with a pore size of 0,45 μm .
- 5.6 **Chloroform-methanol solution**, 2 V+1 V.

6 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

- 6.1 **HPLC-DAD**.
- 6.2 **Analytical balance**, accuracy $\pm 0,1$ mg.
- 6.3 **Ultrasonic extraction apparatus**.
- 6.4 **One-mark volumetric flask**, 100 ml.
- 6.5 **Quantitative filter paper**.
- 6.6 **Flask with stopper**, 20 ml.
- 6.7 **Pipette**, 10 ml.

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7 Sampling

Prepare the sample according to ISO 4661-2, cut it into pieces smaller than 0,1 cm \times 0,1 cm. Store the sample pieces in a dry and cool place, and avoid their contamination.

8 Procedure

8.1 Sample preparation

Weigh approximately 0,4 g (accurate to 0,1 mg) of a homogeneous test sample and put it into a 20 ml flask with a stopper. Add accurately, by pipette, 10 ml chloroform-methanol solution (5.6) and stopper the flask. Extract for 14 h in the ultrasonic extraction apparatus (6.3) at a temperature not exceeding 40 °C.

In order to maintain the bath below 40 °C, it is necessary to periodically add cold water or another cooling agent to the bath during the extraction.

Transfer the extracted solution into a 100 ml volumetric flask (6.4) with funnel and filter paper (6.5), dilute it to the mark with methanol and mix thoroughly.

8.2 Chromatographic conditions

Since the test results depend on the equipment that is used, there are no universal parameters for chromatographic analysis (see example in [Annex B](#)). The following parameters have been proven to be suitable for testing as reference:

- column: C18, 4,6 mm × 250 mm × 5 µm, or chromatographic column with the similar performance;
- temperature of column: 35 °C;
- wavelength range: 200 nm to 400 nm;
- test wavelength: 320 nm;
- mobile phase A (water containing 1 % acetonitrile) and mobile phase B (acetonitrile);
- flow: 1,0 ml/min;
- injection volume: 10 µl.

8.3 Preparation of standard working solutions and the calibration curve

Weigh 100 mg of a 2-mercaptobenzothiazole standard material and put it into a 100 ml volumetric flask. Fill the flask with methanol to obtain a 1 mg/ml standard stock solution. The standard stock solution is diluted with methanol stepwise into 0,005 mg/ml, 0,010 mg/ml, 0,020 mg/ml, 0,030 mg/ml and 0,050 mg/ml standard working solutions (see example in [Annex C](#)).

Inject those solutions using the analytical conditions described in [8.2](#), and the calibration curve is obtained by plotting the peak area of each standard against their concentration. Because of the instability of MBT, standard working solutions shall be analysed without delay to avoid systematic errors in the calibration.

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8.4 HPLC-DAD testing

Filter the solution through the filtration membrane for HPLC detection.

Analyse the sample solutions (10 µl) and standard working solutions (10 µl) by HPLC-DAD separately. To ensure that the peak of response in the extracts is indeed 2-mercaptobenzothiazole, it is necessary to verify that the retention time and the UV-visible spectrum of the peak are identical for the extracts and standard solutions (see example in [Annex D](#)).

A blank test shall be carried out in parallel with the determination. The blank test is performed according to [8.1](#) but omitting the test sample.

To avoid column damages, appropriate measures should be taken such as washing the column after testing.

9 Test results

9.1 Calibration curve

The linear calibration equation is determined by plotting the standard working solution concentration (ordinate) against the peak area (abscissa). An example of a calibration curve is given in [Annex C](#). Through the least square fitting, the linear determination coefficient R^2 should be greater than 0,995.

The 2-mercaptobenzothiazole content in standard solution can be calculated by [Formula \(1\)](#).

$$c = K \times A + b \quad (1)$$

where

- c is the 2-mercaptobenzothiazole content in the standard solution, in mg/ml;
- K is the slope of the calibration curve;
- A is the chromatography area of 2-mercaptobenzothiazole in the standard solution;
- b is the intercept of the calibration curve.

9.2 Calculation

The 2-mercaptobenzothiazole content in sample is calculated according to [Formula \(2\)](#).

$$W = \frac{(c - c_0) \cdot V}{m} \quad (2)$$

where

- W is the 2-mercaptobenzothiazole concentration in the sample, in g/kg;
- c is the 2-mercaptobenzothiazole concentration in the extracted solution, in mg/ml;
- c_0 is the 2-mercaptobenzothiazole concentration in the blank, in mg/ml;
- V is the final constant volume of the extracted solution, in ml;
- m is the sample mass, in g.

10 Precision

See [Annex E](#).

11 Test report

The test report shall include the following information:

- a) reference to this document, i.e. ISO 21490:—;
- b) detailed description of the test sample;
- c) content of the 2-mercaptobenzothiazole in the test sample for each curing temperature and time condition, g/kg;
- d) the difference between the test procedure and the specified steps;
- e) any deviations during the analytical procedure;
- f) date of the test.

Annex A (informative)

Schematic chemical reactions during curing of rubber with sulfenamide that gives 2-MBT

Figure A provides a schematic representation of the reaction of sulfenamides during the curing of a rubber compound. The level of the curing process can be followed chemically by the concentration of 2-MBT, the reaction of crosslinking with 2-MBT ends on a plateau.

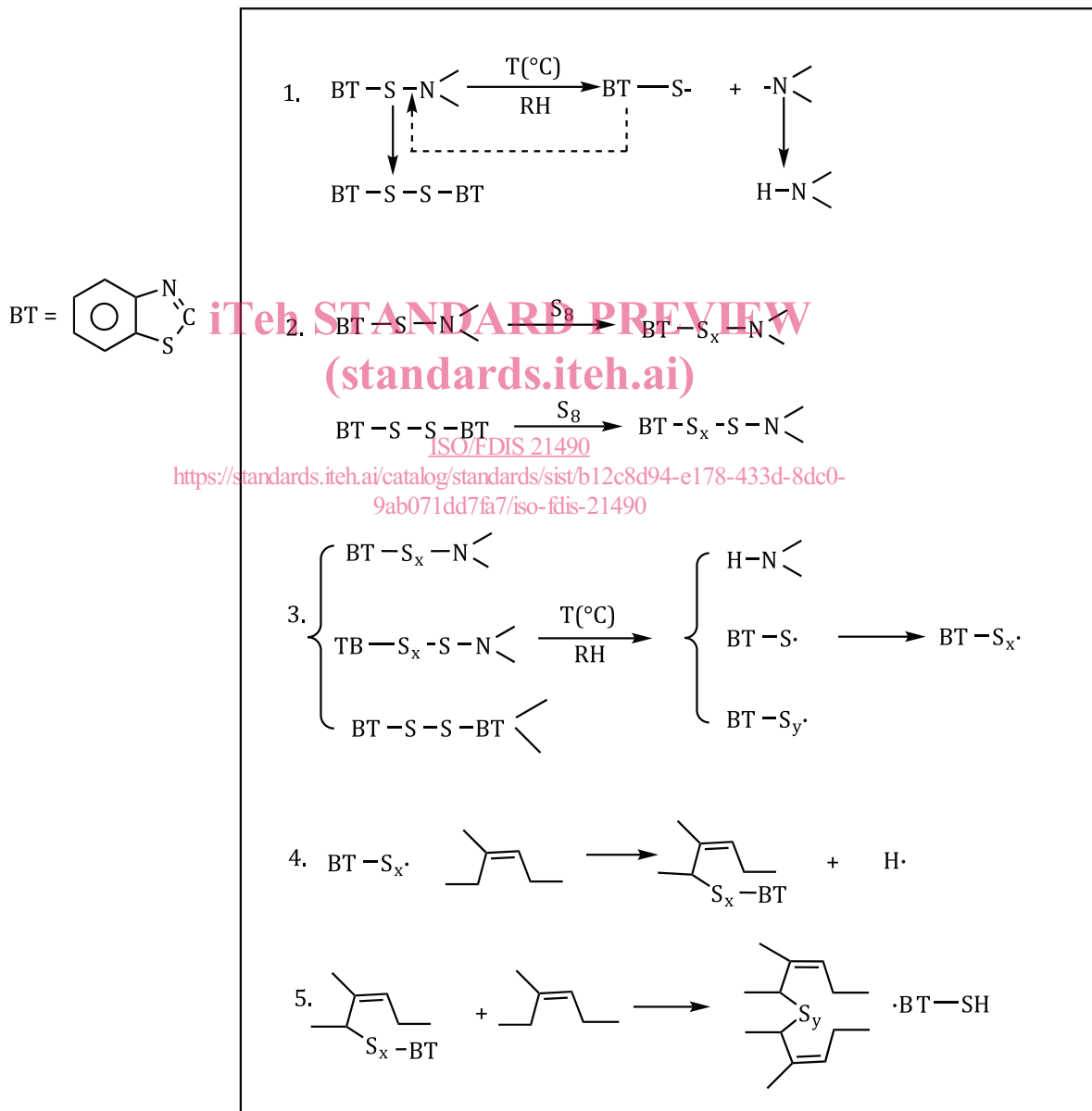


Figure A — Reaction of sulfenamides during the curing of a rubber compound