

**SLOVENSKI STANDARD**  
**kSIST-TS FprCEN/TS 17307:2018**  
**01-december-2018**

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**Snov iz izrabljenih avtomobilskih gum - Granulati in praški - Identifikacija elastomerov: odkrivanje piroliznih produktov v raztopinah z uporabo plinske kromatografije in masne spektrometrije**

Material derived from End-of-Life tyres - Granulates and powders - Elastomers identification: Gas-chromatography and mass-spectrometric detection of pyrolysis products in solution

Material aus Altreifen - Granulat und Mehle - Identifizierung von Elastomeren: Gaschromatographie und massenspektrometrische Detektion von Pyrolyseprodukten in Lösung

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Matériaux obtenus à partir de pneumatiques en fin de vie - Granulats et poudrette - Identification des élastomères : Détection par chromatographie en phase gazeuse et spectrométrie de masse des produits de pyrolyse en solution

**Ta slovenski standard je istoveten z: FprCEN/TS 17307**

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71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
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SPÉCIFICATION TECHNIQUE  
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**FINAL DRAFT**  
**FprCEN/TS 17307**

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English Version

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powders - Elastomers identification: Gas-chromatography  
and mass-spectrometric detection of pyrolysis products in  
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Identifizierung von Elastomeren: Gaschromatographie  
und massenspektrometrische Detektion von  
Pyrolyseprodukten in Lösung

This draft Technical Specification is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 366.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

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## European foreword

This document (FprCEN/TS 17307:2018) has been prepared by Technical Committee CEN/TC 366 “Materials obtained from End-of-Life Tyres (ELT)”, the secretariat of which is held by UNI.

This document is currently submitted to the Vote on TS.

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## Introduction

**WARNING —** Persons using this European Standard should be familiar with normal laboratory practice. This 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.

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## 1 Scope

This document specifies a method for the identification of the elastomers in granulates or powder derived from End-of-Life Tyres.

The method specified is a qualitative method only.

## 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 1407, *Rubber — Determination of solvent extract*

## 3 Principle

A sufficient amount of granules or powder is compacted and homogenized in a laboratory mill and a small aliquot of the homogenized sample is then solvent extracted and subjected to pyrolysis at elevated temperature. Few drops of the liquid pyrolysis products are then diluted in dichloromethane for the GC/MS analysis. The use of the mass-spectrometric detector is a mean for improving the sensitivity and reliability of the identification of the elastomers present in low or trace amount, with threshold limit estimated to about 5 %.

The use of this standard pre-supposes sufficient working knowledge of the principles and techniques of gas chromatography/mass-spectrometry (GC/MS) for the analyst to perform the operations described and interpret the results correctly.

## 4 Reagents

### 4.1 Dichloromethane

### 4.2 Acetone

### 4.3 Nitrogen, for flushing the pyrolysis product.

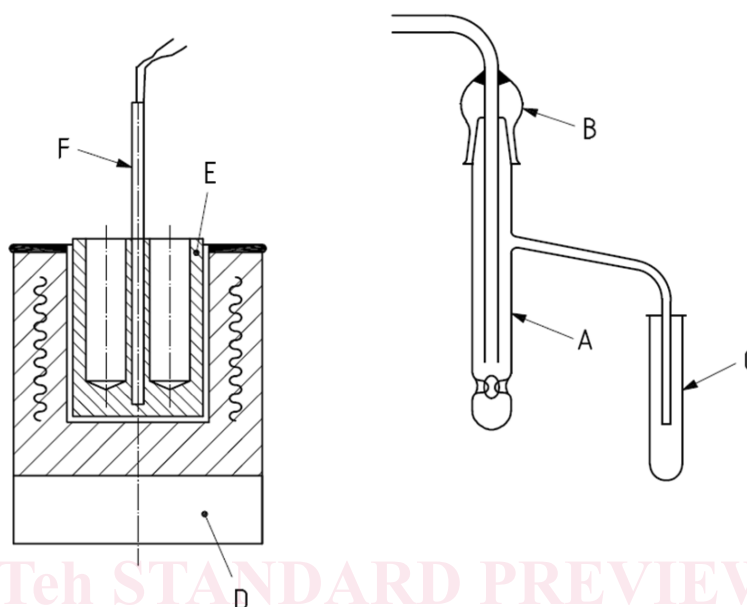
## 5 Apparatus

All reagents shall be of analytical grade

### 5.1 Extraction apparatus. The apparatus specified in ISO 1407 is satisfactory.

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**5.2 Pyrolysis apparatus** (see Figure 1), comprising a glass tube A having inward projections to prevent the sample from falling to the bottom of the tube, and a lateral condenser tube. The tube A has a standard ground-glass joint B that carries a small glass adductor tube for the connection to flowing nitrogen. A collecting tube C is placed under the condenser tube. A thermo-regulated electric furnace D accommodates an aluminium block E with holes for one or more tubes A. A thermocouple F

**Key**

A glass tube for sample

B ground-glass joint

C collecting tube <https://standards.iteh.ai/catalog/standards/sist/143e46e2-5e8a-4df3-b4fd-8009c8830b06/sist-ts-cen-ts-17307-2019>

D thermo-regulated electric furnace

E aluminium block, bored to hold tubes

F thermocouple

**Figure 1 — Pyrolysis apparatus**

**5.3** The chromatographic equipment consists of three associated parts:

**5.3.1** Gas chromatograph equipped with chromatographic columns; capillary column in fused silica of 0,20 mm diameter and 30 m long, of apolar type. Stationary phase – film of dimethyl polysiloxane, 1 µm thick;

**5.3.2** Mass detector in electronic impact mode.

**5.3.3** These elements are connected with an acquisition and data processing system.

**5.4 Glassware**

**5.4.1** Vials of 2 ml capacity: caps with silicone septum, PTFE lined.

**5.4.2** Capillary pipettes.



## 6 Procedure

**6.1** On a laboratory mill, thinly sheet, to about 0,25 mm to 0,5 mm thickness, a representative sample of about 0,5 kg of the rubber granulates or powder.

**6.2** Extract with acetone (4.2) 2 g to 5 g of the homogenized sample in accordance with the procedure given in ISO 1407.

**6.3** Depending on the nature of the composition of the unknown vulcanisate and of the type of apparatus used, place 0,5 g to 2 g of the extracted, dried test sample in the pyrolysis tube A (see Figure 1).

**6.4** Bring the electric furnace D to  $525\text{ °C} \pm 50\text{ °C}$  and hold within this temperature range. This temperature range is recommended to obtain rapid pyrolysis without excessive degradation or carbonization. A temperature of  $475\text{ °C}$  is advised, however, to obtain the maximum quantity of pyrolysate for NR, IR, BR, SBR, IIR, BIIR and CIIR.

**6.5** Pass a slow stream of nitrogen (4.3) through the pyrolysis tube A and introduce the tube containing the prepared test sample into a hole in the aluminium block E. Nitrogen serves to displace air, prevent oxidation and facilitate transfer of the pyrolysis products into the collecting tube C. Maintain the nitrogen flow at  $10\text{ cm}^3/\text{min} \pm 2\text{ cm}^3/\text{min}$ .

**6.6** Continue the heating to complete distillation, i.e. for about 10 min.

**6.7** Place a few drops (1 mg to 5 mg) of the homogenized pyrolysate into the vial (5.4.1), add about 1 ml of dichloromethane (4.1) and seal the vials with the cap and silicon septum.

**6.8** Inject  $1\text{ }\mu\text{L}$  of the dichloromethane solution in the GC/MS analyser and acquire the data. The following conditions were tested for a quadrupole mass detector: other condition can be used provided that they provides similar results:

**6.8.1** Gas-chromatograph set-up:

**6.8.1.1** Carrier gas: helium

**6.8.1.2** Constant pressure: 70 kPa: corresponding to a linear velocity of approximately 40 cm/s

**6.8.1.3** Injector temperature:  $300\text{ °C}$

**6.8.1.4** Injector: Splitless with gold-plated seal, Injection volume:  $1,0\text{ }\mu\text{L}$

**6.8.1.5** Thermal program:

Isothermal for 4 min at  $50\text{ °C}$

Heating from  $50\text{ °C}$  to  $300\text{ °C}$  at the rate of  $10\text{ °C}/\text{min}$

Isothermal for 10 min at  $300\text{ °C}$

**6.8.2** Mass spectrometric detector

**6.8.2.1** Transfer line temperature:  $280\text{ °C}$

**6.8.2.2** Source temperature:  $230\text{ °C}$

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- 6.8.2.3** Quadrupole temperature: 150 °C (if available)
- 6.8.2.4** Electron energy: 70 eV
- 6.8.2.5** Ionization mode: EI
- 6.8.2.6** Mass range: 50 to 550 atomic mass units (a.m.u), SCAN data acquisition
- 6.8.2.7** Scan time: at least three scans per peak
- 6.8.2.8** Solvent delay: 4 min (to protect mass detector)

**7 Interpretation of the GC/MS data**

**7.1** The object of the interpretation is to identify the elastomers in the blend, looking for pyrolysate products (markers) specific for each elastomer. A set of reference chromatograms and mass spectra shall be produced using samples of known composition. The following table is given for reference purpose: it includes the marker compound to be used for the identification of the different rubbers, together with the mass fragments characteristic of the mass spectrum.

**Table 1 — Main markers detected by GC/MS of common elastomers**

<b>Elastomer</b>	<b>Marker</b>	<b>Identification mass, m/z</b>
NR and polyisoprene	limonene	136, 93, 68
SBR	1-vinyl-3cyclohexene styrene	108, 93, 79 104, 78, 51
BR	1-vinyl-3cyclohexene	108, 93, 79
IIR and X-IIR	2,5 -dimethyl-2,4-hexadiene	110, 95, 67
NBR	$\alpha$ -allylacrylonitrile	93, 60, 39
CR	chloro-4-(1-chlorophenyl)-cyclohexene	176, 141, 88
EPDM	n-octane, n-nonane, n-decano	128, 85, 57

The following gas-chromatograms are an example of the results obtained from compound with single elastomer composition: