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**Rubber — Determination of mass concentration of tire and road wear particles (TRWP) in soil and sediments — Pyrolysis-GC/MS method**

*Caoutchouc — Détermination de la concentration massique en particules de pneus et d'usure de la route (TRWP) dans le sol et les sédiments — Méthode par pyrolyse-GC/MS*

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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](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 on 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 the following URL: [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html). (standards.iteh.ai)

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## Introduction

Tyre and road wear particles (TRWP) are formed as a result of tread abrasion from the road surface, and subsequent particle release to the environment. TRWP consist of tyre tread particles which include incorporated material from the road surface (Kreider et al. 2010[1]). The elastomeric fraction in TRWP contained in soil or sediment materials is quantified in this document by direct pyrolysis-GC/MS analysis. Mass concentration can be expressed on the basis of the rubber polymer, tyre tread, or TRWP. This method has been used to measure the TRWP concentration in soil and sediment samples from three geographically separated regions (Unice et al. 2012[2]; Unice et al. 2013[3]). The airborne concentration of TRWP in the PM<sub>10</sub> fraction has also been characterized by a similar method (Panko et al. 2013[4]).

Specific chemical markers are generated from intact TRWP by pyrolysis of sample specimens. The chemical markers consist of characteristic and specific pyrolysis dimeric fragments of passenger and truck tyre tread polymers including butadiene rubber, styrene-butadiene rubber, and isoprene rubber. The polymer fragments generated by sample pyrolysis are subsequently separated by gas chromatography, and identified by mass spectroscopy. The TRWP mass concentration is calculated based on market average polymer use rates in tread, and prior characterization of the mineral content of TRWP. Rubber polymer specificity is achieved by quantification of dimeric polymer fragments consisting of two monomer units (Kitamura et al. 2007[5]; Harada et al. 2009[6]). Repeatability is achieved by the use of a deuterated internal standard of similar polymeric structure to the tyre tread polymers. The internal standard corrects for variable analyte recovery caused by sample size, matrix effects, and temporal variation in instrument response. The method is suitable for monitoring changes in soil or sediment TRWP concentrations over time.

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# Rubber — Determination of mass concentration of tire and road wear particles (TRWP) in soil and sediments — Pyrolysis-GC/MS method

**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.

**WARNING 2** — Certain procedures specified in this document may 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 soil or sediment mass concentration ( $\mu\text{g/g}$ ) of tyre and road wear particles (TRWP) in environmental samples.

This document establishes principles for soil or sediment sample collection, the generation of pyrolysis fragments from the sample, and the quantification of the generated polymer fragments. The quantified polymer mass is used to calculate the concentration of TRWP in soil or sediment. These quantities are expressed on a TRWP basis, which includes the mass of tyre tread and mass of road wear encrustations, and can also be expressed on a tyre rubber polymer or tyre tread basis.

**NOTE** Tyre and road wear particles are a discrete mass of elongated particles generated at the frictional interface between the tyre and roadway surface during the service life of a tyre. The particles consist of tyre tread enriched with mineral encrustations from the roadway surface.

## 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 7270-1, *Rubber — Analysis by pyrolytic gas-chromatographic methods — Part 1: Identification of polymers (single polymers and polymer blends)*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

### 3.1

#### deuterated internal standard

compound containing at least one deuterium molecule added to a sample in a fixed amount that is nearly identical to the target analyte used to correct for instrument drift and matrix interference

### 3.2

#### dry mass

mass of solid dried in an oven for a specified time and at a specified temperature

3.3  
monitoring

repeated measurement to follow changes over a period of time

3.4  
percent moisture

mass of water in soil expressed as a percentage of oven dried mass

3.5  
pyrolysis analysis

decomposition of organic polymeric molecules into characteristic fragments separated by gas chromatography and quantified by mass spectroscopy

4 Principle

Tyre tread polymer is quantified using internal standard calibration and the peak area of characteristic fragment ions corresponding to dimers of the raw polymer by pyrolysis-GC/MS. The thermal decomposition products of cross-linked natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR) polymers depend on the abundance of polymers in the sample. SBR pyrolysis generates butadiene, vinylcyclohexene (butadiene dimer) and styrene, whereas BR generates only butadiene monomer and vinylcyclohexene. NR is associated with isoprene monomer and dipentene (isoprene dimer). The dimer fragments have good specificity for rubber polymers, whereas both anthropogenic and natural organic substances are sources of the monomer markers (Kitamura 2007[5]). Therefore, the monomeric pyrolysis marker compounds are subject to interference from non-TRWP environmental sources, and are not suitable for quantification of TRWP mass concentration in soil or sediment. One well-known example is styrene, which is generated from pyrolysis of both SBR and diesel exhaust particles (Pierson and Brachaczek 1974[7]). The tyre polymers, and pyrolysis fragment dimers used for quantification of TRWP are shown in Figure 1.

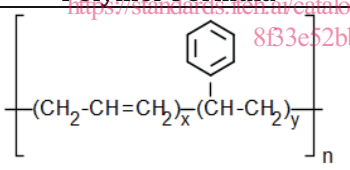
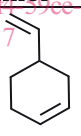
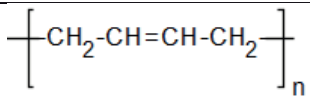
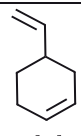
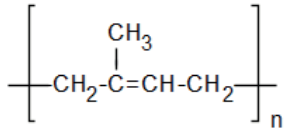
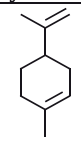
Polymer Formula	Dimer
 SBR	 vinylcyclohexene
 BR	 vinylcyclohexene
 NR	 dipentene

Figure 1 — Dimeric pyrolysis products of tyre rubber polymers

5 Reagents

Use only reagents of recognized analytical grade.

5.1 Chloroform, analytical grade.



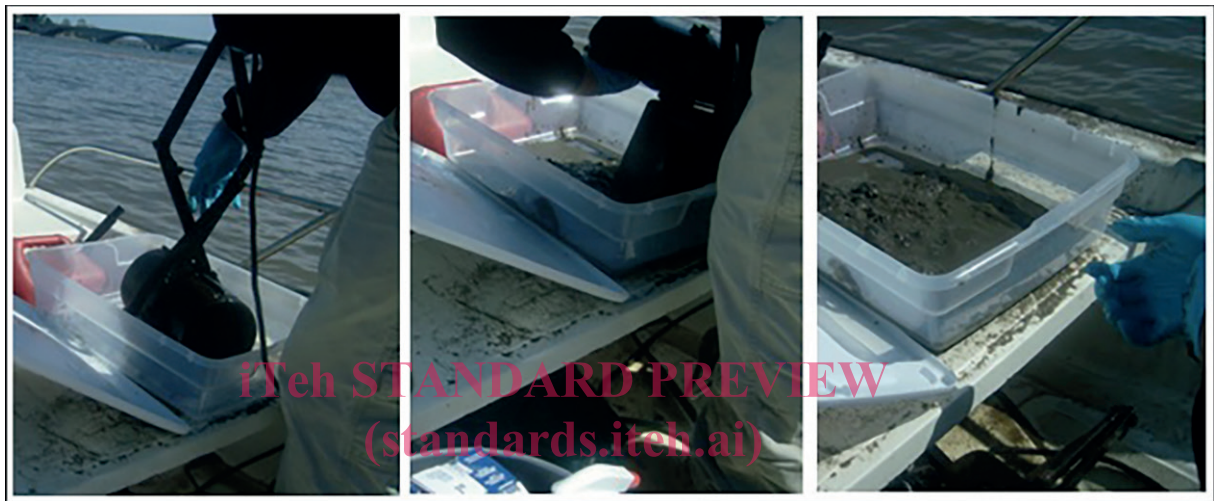
5.2 Helium, purity 99,999 5 % by volume.

## 6 Apparatus

6.1 Soil or sediment sampling — Equipment and consumable supplies.

### 6.1.1 Sampling device.

The sampling device shall be suitable for the collection of soil or sediment samples. Suitable devices include pre-cleaned stainless steel hand trowels, coring tools or clamshell dredge devices. The collection of a sediment sample with a clamshell dredge device is illustrated in [Figure 2](#).



NOTE Photo courtesy of Cardno ChemRisk.  
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**Figure 2 — Collection of sample with clamshell dredge device**

### 6.1.2 Sample containers.

Samples should be collected in clean sample containers supplied by the laboratory, or clean sample container handled in a manner consistent with laboratory standard operating procedures. The placement of a soil sample into a sample container with a trowel is illustrated in [Figure 3](#).



NOTE Photo courtesy of Cardno ChemRisk.

**Figure 3 — Placement of sample in container with trowel**

## 6.2 Equipment for analysis.

**6.2.1 Laboratory oven**, for drying field collected sample(s) at a temperature of 105 °C for 24 h in a suitably clean laboratory-supplied container.

**6.2.2 Sieve**, for removing large aggregates unsuitable for the pyrolyser unit. The nominal opening for dry sieving can be 1 mm.

**6.2.3 Precision analytical balance**, for determination of sample mass as collected, after oven drying, and after dry sieving. Measurements shall be conducted in an environment of controlled temperature and humidity. The balance shall be accurate to 0,01 mg and be maintained, calibrated and certified in accordance with the manufacturer's recommendations.

**6.2.4 Pyrolyser**, operating at a temperature of 670 °C for 5 s in a helium atmosphere with an induction time of less than 0,2 s. A single-use or reusable sample holder shall be selected in accordance with the manufacturer's recommendation. Examples of pyrolyser systems are provided in ISO 7270-1, and include micro-furnace with quartz tube, Curie-point with holder, and platinum filament with holder. An example of one type of pyrolyser that can be used is described in [Annex B](#).

**6.2.5 Gas chromatograph/mass spectrometer**, operated and maintained in accordance with the manufacturer's instructions.

### 6.2.5.1 Gas chromatograph, as specified below:

- carrier gas flow rate: 1,0 ml/min to 2,0 ml/min;
- injector temperature: 300 °C;
- oven temperature programme: initial temperature 50 °C for 5 min, heating at 25 °C /min up to 300 °C, maintained at 300 °C for 10 min.

### 6.2.5.2 Column, as specified below:

- length: 25 m to 60 m;
- diameter: 0,25 mm to 0,35 mm;

- liquid phase: 5 % diphenyl-, 95 % polydimethylsiloxane;
- film thickness: 0,20 µm to 1,0 µm.

**6.2.5.3 Mass spectrometer**, quadrupole mass spectrometer, magnetic-sector-type mass spectrometer or any other suitable type, having the characteristics specified below:

- interface temperature: 300 °C to 350 °C;
- ionization method: electron ionization;
- ion source temperature: 230 °C;
- ionizing voltage: 70 eV;
- scan range: mass/charge ratio: 35 m/z to 500 m/z.

## 7 Specimen preparation laboratory

The specimen preparation laboratories and sample containers selected for analysis shall be sufficiently free of contamination that blank analyses demonstrate an absence of polymer as established by the method detection limit (MDL). At least one laboratory blank analysis shall be performed for each type of sample container used for sample collection, and following modifications to laboratory standard operating procedures or equipment.

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## 8 Measuring range

The range of SBR/BR polymer that can be determined in a soil or sediment sample is approximately 0,09 µg to 90 µg, and the range of NR polymer that can be determined is approximately 0,03 µg to 50 µg. Assuming a total sample mass of 0,020 g, this mass range corresponds to a TRWP concentration range in soil or sediment of approximately 24 µg/g to 28 000 µg/g.

**NOTE** The TRWP concentration range is based on Formula (E.2). For example, the low end of the TRWP concentration range is  $(0,09 \mu\text{g} + 0,03 \mu\text{g}) / 0,5 / 0,5 / 0,020 \text{ g} = 24 \mu\text{g/g}$ . The first factor of 0,5 accounts for the polymer fraction in tyre tread. TRWP consists of tyre tread enriched with mineral encrustations from the roadway surface. The second factor of 0,5 accounts for the fraction of tyre tread in TRWP.

## 9 Limit of detection

The TRWP limit of detection depends on mass of sample pyrolysed. In practice, sampling constraints and the capacity of the pyrolysis unit determine the lowest achievable limit of detection. For a nominal sample mass of 0,020 g, the limit of detection is approximately 24 µg/g TRWP in soil or sediment.

An alternative limit of detection can be achieved by changing the calibration curve range and mass of internal standard used in the analysis. Alternative limits of detection based on adjustment of the calibration curve range and internal standard masses shall be verified by a method detection limit study.

The target TRWP detection limit shall be determined as part of the sampling plan prior to sample collection. The sample plan shall specify field and laboratory conditions sufficient to ensure that the target detection limit satisfies the sample campaign goals and objectives. A sample-specific detection limit shall be calculated based on the conditions of the analysis. The detection limit calculations are specified in 11.1.

## 10 Procedure

### 10.1 General

The method is defined for a sample mass of oven-dried soil or sediment suitable for the pyrolyser unit. Thermal energy is applied to a sample encapsulated in a pyrolyser in the absence of oxygen to decompose the sample. Secondary reactions are minimized by rapid heating of the pyrolyser to the target temperature. The nominal sample mass for the example pyrolysis unit described in [Annex B](#) is 0,020 g. The sample collection and laboratory pyrolysis-GC/MS procedure consists of the following six steps and is described in [10.2](#) to [10.6](#) respectively:

- a) sample collection;
- b) deuterated internal standard preparation;
- c) calibration curve preparation;
- d) sample preparation;
- e) sample pyrolysis with polymer decomposition under defined thermal conditions;
- f) dimer measurement using gas-chromatographic (GC) separation and mass spectroscopy (MS).

The procedure relies on deuterated homopolymer internal standards to increase the precision and accuracy of the measured TRWP concentration. The internal standard is used to correct for matrix effects that affect polymer pyrolysis and fragment recovery. The internal standard also corrects for changes in the mass spectrometer ion source condition and fluctuations in carrier gas flow rates. The internal standards are deuterated polyisoprene (d-PI) and deuterated polybutadiene (d-PB), which are polymers labelled with the minor stable hydrogen isotope deuterium. The pyrolysis-GC/MS thermal decomposition products of d-PI and d-PB are discriminated based on retention time and mass to charge ratio from the dipentene and vinylcyclohexene markers associated with NR and SBR/BR, respectively.

### 10.2 Sample collection

A soil or sediment sample is collected in clean laboratory supplied or approved sample containers. The sample shall be collected using a clean device suitable for the collection of soil or sediment samples, such as stainless steel hand trowels, coring tools or clamshell dredge devices. The standard operating procedure for sample collection shall be approved by the laboratory. A chain-of-custody form documenting sample collection and relinquishment shall be maintained. A soil or sediment mass of at least 10 g to 50 g should be collected to ensure adequate homogenization.

### 10.3 Deuterated internal standard preparation

Deuterated standards d-PI (1,4-d8) and d-PB (1,4-d6) of known purity shall be obtained prior to analysis (see [Table 1](#)). The purity of the standards shall be sufficiently high to prevent interference for TRWP sample concentrations at or above the detection limit or reporting limit of the analysis.

A recipe for stock internal standard solution preparation that should be used is specified in [Annex A](#). Alternative recipes may be used to meet the objectives of the analysis. To prepare the stock solutions, raw d-PI or d-PB polymer is weighed and placed in a graduated flask. Chloroform shall be poured to two-thirds of the total volume specified in the recipe, and allowed to settle overnight to achieve complete dissolution. Immediately prior to analysis, chloroform shall be added to achieve the total volume specified in the recipe. The raw polymers should be dissolved in chloroform prior to the day of analysis to ensure sufficient time for dissolution. The stability of the internal standard solutions shall be determined by comparing the instrument response after expected storage times to that of a freshly prepared solution. The peak area should decrease by no more than 25 % to that of the freshly prepared solution at expected storage times.