
**Ambient air — Determination of the
mass concentration of tire and road
wear particles (TRWP) — Pyrolysis-
GC-MS method**

*Air ambient — Détermination de la concentration en masse de
particules provenant de l'usure des pneumatiques et des chaussées
(TRWP) — Méthode par pyrolyse-GC/SM*

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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).

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).

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.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

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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.[3] The elastomeric fraction in TRWP contained in PM_{2,5} or PM₁₀ is quantified in this document by direct pyrolysis-GC-MS analysis of a sample filter. Mass can be expressed on the basis of the rubber polymer, tyre tread, or TRWP. This method has been used to measure the airborne concentration of TRWP in the PM₁₀ fraction for three geographically separated regions.[4] The TRWP concentration in soil and sediment has also been characterized by a similar method.[5]

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.[6][7] 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 ambient air TRWP concentrations over a specified averaging time.

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Ambient air — Determination of the mass concentration of tire and road wear particles (TRWP) — 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 and to ensure compliance with any national regulatory conditions.

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 airborne concentration ($\mu\text{g}/\text{m}^3$), mass concentration ($\mu\text{g}/\text{g}$) and mass fraction (%) of tyre and road wear particles (TRWP) in ambient particulate matter (PM) samples.

This document establishes principles for air 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 fraction of tyre tread in PM and concentration of tyre tread in air. 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.

Air sample collection is on quartz fibre filters with size-selective input in a range of $\text{PM}_{2,5}$ or PM_{10} . The method is suitable for the determination of TRWP in indoor or outdoor atmospheres.

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 4225, *Air quality — General aspects — Vocabulary*

ISO 7708:1995, *Air quality — Particle size fraction definitions for health-related sampling*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4225 and the following 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 <http://www.iso.org/obp>

3.1

ambient air

outdoor air to which people, plants, animals, or material may be exposed

3.2

averaging time

interval of time over which the air quality has been expressed as an average

3.3

continuous sampling

sampling, without interruptions, throughout an operation or for a predetermined time

3.4

deuterated compound

compound containing at least one *deuterium* (3.5) molecule

3.5

deuterium

minor and stable isotope of hydrogen with one proton and one neutron

3.6

internal standard

compound 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

3.7

measurement period

interval of time between first and last measurement

3.8

monitoring

repeated measurement to follow changes over a period of time

3.9

natural background concentration

concentration of a given species in a pristine air mass in which anthropogenic emissions are negligible

3.10

particle aerodynamic diameter

diameter of a sphere of density 1 g/cm³ with the same terminal velocity due to gravitational force in calm air as the particle, under the prevailing conditions of temperature, pressure, and relative humidity

3.11

particle

small discrete mass of solid or liquid matter

3.12

particulate matter — 2,5 µm

PM_{2,5}

airborne *particles* (3.11) passing a size selective inlet with 50 % efficiency cut-off at a *particle aerodynamic diameter* (3.10) of 2,5 µm

Note 1 to entry: See Thoracic Convention in ISO 7708:1995, Clause 6.

3.13

particulate matter — 10 µm

PM₁₀

airborne *particles* (3.11) passing a size selective inlet with 50 % efficiency cut-off at an aerodynamic diameter of 10 µm

Note 1 to entry: See High-Risk Respirable Convention in ISO 7708:1995, Clause 7.

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3.14**pyrolysis analysis**

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

Note 1 to entry: The principle of sample decomposition is the application of thermal energy to a sample encapsulated in a pyrolyser in the absence of oxygen. Secondary reactions are minimized by rapid heating of the pyrolyser to the target temperature.

3.15**sampling time**

interval of time over which a single sample is taken

3.16**tyre and road wear particles****TRWP**

discrete mass of elongated *particles* (3.11) generated at the frictional interface between the tread of the tyre and the roadway surface during the service life of a tyre

Note 1 to entry: The particles consist of tyre tread enriched with mineral encrustations from the roadway surface.

3.17**thoracic convention**

mass fraction of inhaled *particles* (3.11) which penetrate beyond the larynx

3.18**respirable convention**

target specification for sampling instruments when the respirable fraction is of interest

4 Symbols and abbreviated terms

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4.1 Symbols of units (see also ISO 4226)

µg	microgram (10 ⁻⁶ gram)
cm	centimeter (10 ⁻² meter)
m ³	cubic meter
cm ²	square centimeter
µg/m ³	microgram per cubic meter

4.2 Abbreviated terms

BdD	vinylcyclohexene (butadiene dimer)
d-BdD	deuterated butadiene dimer
d-IpD	deuterated isoprene dimer
d-PI	deuterated polyisoprene
d-PB	deuterated polybutadiene
BR	butadiene rubber
GC-MS	gas chromatograph/mass spectrometer

IpD	dipentene (isoprene dimer)
IR	isoprene rubber
LOD	limit of detection
LOQ	limit of quantification
PM	particulate matter
PM _{2,5}	airborne particles with an aerodynamic diameter less than 2,5 µm
PM ₁₀	airborne particles with an aerodynamic diameter less than 10 µm
NR	natural rubber
SBR	styrene-butadiene rubber
TRWP	tyre and road wear particles

5 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. 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.^[6] Therefore, the monomeric pyrolysis marker compounds are subject to interference from non-TRWP environmental sources and are not suitable for quantification of TRWP mass or fraction in air. One well-known example is styrene, which is generated from pyrolysis of both SBR and diesel exhaust particles.^[8] The tyre polymers and pyrolysis fragment dimers used for quantification of TRWP are shown in [Figure 1](#).

The procedure relies on deuterated homopolymer internal standards to increase the precision and accuracy of the measured TRWP concentration. An internal standard is a chemical compound that is nearly identical to the target analyte, but with sufficient differences in mass or functional groups to be discriminated from the target analyte by the analytical method. The internal standard is used to correct for matrix effects that affect polymer pyrolysis and fragment recovery. This correction is made by comparing the instrument response for the internal standard of known amount to the instrument response for the target analytes. 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 (m/z) from the dipentene and vinylcyclohexene markers associated with NR and SBR/BR, respectively.

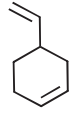
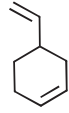
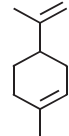
Polymer Formula	Dimer
$\left[(\text{CH}_2-\text{CH}=\text{CH}_2)_x (\text{CH}-\text{CH}_2)_y \right]_n$ <p style="text-align: center;">SBR</p>	 <p style="text-align: center;">Vinylcyclohexene</p>
$\left[\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right]_n$ <p style="text-align: center;">BR</p>	 <p style="text-align: center;">Vinylcyclohexene</p>
$\left[\text{CH}_2-\overset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2 \right]_n$ <p style="text-align: center;">NR</p>	 <p style="text-align: center;">dipentene</p>

Figure 1 — Dimeric pyrolysis products of tyre rubber polymers

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6 Reagents

During the analysis, use only reagents of recognized analytical grade.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

6.1 Chloroform, analytical grade.

6.2 Helium, purity 99,999 5 %.

7 Apparatus

7.1 Air sampling — Equipment and consumable supplies

7.1.1 Quartz fibre filter.

A 47-mm quartz fibre filter consisting of woven filaments is required for compatibility with the pyrolysis-GC-MS method. The filter should be suitable for PM_{2,5} or PM₁₀ measurement by forming an appropriate seal with the sampling device. The filters shall lie flat in the sampling device remaining intact during handling. The filter selected shall be compatible with the ambient air particulate sampling device. Quartz fibre filters are brittle and shall be handled with care for accurate mass measurement. Preparation of the filter is not required, but the absence of contamination should be verified by at least one blank filter analysis in accordance with 7.2.

7.1.2 Ambient air particulate sampling device.

The ambient air particulate sampling device shall be designed in a manner consistent with an identified national or international guideline or reference method for the collection of PM samples.

7.2 Specimen preparation laboratories

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

7.2.1 Gravimetric PM determination laboratory.

Samples shall be prepared for gravimetric PM determination in an environment free of polymer and particulate contamination. Samples shall not be prepared for analysis until acceptable blank filter analyses have been completed. The laboratory shall condition the quartz fibre filters in accordance with the national or international reference method identified in the collection of the PM_{2,5} or PM₁₀ sample.

7.2.2 Pyrolysis analysis laboratory.

Samples shall be prepared for pyrolysis analysis in an environment free of polymer contamination. Samples shall not be prepared for analysis until acceptable blank filter analyses have been completed.

7.3 Equipment for analysis

7.3.1 General

Prior to pyrolysis analysis, the total mass of PM collected on the filter is determined gravimetrically. After determination of PM mass, the destructive pyrolysis analysis is completed using an integrated system consisting of a pyrolyser interfaced to a gas chromatograph/mass spectrometer (GC-MS).

7.3.2 Precision analytical balance, for determination of total mass collected on the quartz filter and operated in accordance with the national or international reference method identified in the collection of the PM_{2,5} or PM₁₀ sample. Measurements shall be conducted in an environment of controlled temperature and humidity. The balance shall be maintained, calibrated and certified in accordance with the manufacturer's recommendations.

7.3.3 Pyrolyser, operated 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](#).

7.3.4 Gas chromatograph/mass spectrometer, operated and maintained in accordance with the manufacturer's instructions, with a split ratio suitable for the sample density, and pyrolysis-GC interface and transfer line temperature maintained at 300 °C. A DB-5MS equivalent ultra inert column (30 m × 0,25 mm i.d., 1 µm film thickness) shall be used to separate the pyrolysis products. The initial GC temperature shall be 50 °C for 5 min followed by heating to 300 °C at a rate of 25 °C min⁻¹. The MS shall be operated in scan mode with *m/z* range of 35 to 500 and tuned using perfluorotributylamine at *m/z* = 69, 212, and 502 prior to each analysis sequence in accordance with the manufacturer's instructions.

7.4 Consumables

7.4.1 Pyrolyser sample holders, selected in accordance with the pyrolyser manufacturer's instructions and operated at a target temperature of 670 °C with a tolerance of ±0,1 °C. An example of one type of sample holder that can be used is described in [Annex B](#).