



DPC: 25/30493818 DC

BSI Group Headquarters

389 Chiswick High Road London W4 4AL

Tel: +44 (0)20 8996 9000

Fax: +44 (0)20 8996 7400

www.bsigroup.com

Date: 08 July 2025

Origin: International

Latest date for receipt of comments: 31 August 2025

Project No. 2024/01571

Responsible committee: PRI/200

Interested committees:

Title: Draft BS ISO 21396 Rubber - Determination of the mass concentration of tyre and road wear particles (TRWP) in soil and sediment - Pyrolysis-gas chromatography/mass spectrometry (GC/MS) method.

Please notify admin.start@bsigroup.com if you are aware of any keywords that might assist in clarifying or identifying the standard or of the content of this standard:

- i) has any issues related to 3rd party IPR, patent or copyright
- ii) affects other national standard(s)
- iii) requires additional national guidance or information

WARNING: THIS IS A DRAFT AND MUST NOT BE REGARDED OR USED AS A BRITISH STANDARD. THIS DRAFT IS NOT CURRENT BEYOND 31 August 2025

This draft is issued to allow comments from interested parties; all comments will be given consideration prior to publication. No acknowledgement will normally be sent. **See overleaf for information on the submission of comments.**

No copying is allowed, in any form, without prior written permission from BSI except as permitted under the Copyright, Designs and Patent Act 1988 or for circulation within a nominating organization for briefing purposes. Electronic circulation is limited to dissemination by e-mail within such an organization by committee members.

Further copies of this draft may be purchased from BSI Shop <http://shop.bsigroup.com> or from BSI Customer Services, Tel: +44(0) 20 8996 9001 or email cservices@bsigroup.com. British, International and foreign standards are also available from BSI Customer Services.

Information on the co-operating organizations represented on the committees referenced above may be obtained from <https://standardsdevelopment.bsigroup.com/>.

E-mail: admin.start@bsigroup.com

Introduction

This draft standard is based on national and international discussions. Your comments on this draft are invited and will assist in the preparation of the consequent standard.

For international standards, comments will be reviewed by the relevant UK national committee before sending the consensus UK vote and comments to the international committee, which will then decide appropriate action. If the international standard is approved, it is usual for the text to be published as a British Standard.

For national standards, comments will be reviewed by the relevant UK national committee and the resulting standards published as a British Standard.

UK Vote

Please indicate whether you consider the UK should submit a negative (with supporting technical reasons) or positive vote on this draft. Please indicate if you are aware of any reason why this draft standard should not be published as a British Standard.

Submission of Comments

- **Annotated drafts are not acceptable and will be rejected.**
- All comments should be submitted online at <https://standardsdevelopment.bsigroup.com/>. You will need to register in order to comment.

Template for comments and secretariat observations

Date: xx/xx/20xx	Document: ISO/DIS xxxx
------------------	------------------------

1	2	(3)	4	5	(6)	7
MB	Clause No./ Subclause No./Annex (e.g. 3.1)	Paragraph/ Figure/Table/Note	Type of comment	Comment (justification for change) by the MB	Proposed change by the MB	Secretariat observations on each comment submitted
	3.1	Definition 1	ed	Definition is ambiguous and needs clarifying.	Amend to read '...so that the mains connector to which no connection...'	
	6.4	Paragraph 2	te	The use of the UV photometer as an alternative cannot be supported as serious problems have been encountered in its use in the UK.	Delete reference to UV photometer.	



DRAFT International Standard

ISO/DIS 21396

Rubber — Determination of the mass concentration of tyre and road wear particles (TRWP) in soil and sediment — Pyrolysis-gas chromatography/mass spectrometry (GC/MS) method

ICS: 13.080.01; 83.160.01; 83.060

ISO/TC 45

Secretariat: **DSM**

Voting begins on:
2025-07-08

Voting terminates on:
2025-09-30

This document is circulated as received from the committee secretariat.

THIS DOCUMENT IS A DRAFT CIRCULATED FOR COMMENTS AND APPROVAL. IT IS THEREFORE SUBJECT TO CHANGE AND MAY NOT BE REFERRED TO AS AN INTERNATIONAL STANDARD UNTIL PUBLISHED AS SUCH.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.

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.

Reference number
ISO/DIS 21396:2025(en)

Full document details: 25/30493818 DC

© ISO 2025  **Documents**
Document Sharing Hub



COPYRIGHT PROTECTED DOCUMENT

© ISO 2025

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

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

Published in Switzerland

Contents

Page

Forward	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Principle	2
5 Reagents and materials	3
6 Apparatus	3
7 Specimen preparation laboratory	5
8 Measuring range	5
9 Limit of detection	6
10 Procedure	6
10.1 General	6
10.2 Sample collection	6
10.3 Deuterated internal standard preparation	6
10.4 Calibration curve preparation	7
10.4.1 Stock solutions	7
10.4.2 Calibration curves	7
10.5 Sample preparation	8
10.5.1 Oven drying	8
10.5.2 Sieving and homogenization	8
10.5.3 Sample pretreatment	9
10.6 Sample measurement	9
10.6.1 Sample mass	9
10.6.2 Internal standard addition	9
10.6.3 Pyrolysis-GC/MS measurement	9
11 Analysis	10
11.1 General	10
11.2 TRWP LOD	10
11.3 Quantity of tyre polymer in the sample	11
11.4 Mass concentration of TRWP	11
12 Performance characteristics	11
12.1 General	11
12.2 Specific performance characteristics	11
13 Test report	11
Annex A (informative) Recipe for calibration curves and stock solutions	13
Annex B (informative) Instrument Conditions	15
Annex C (informative) Representative calibration curves and total ion pyrograms	17
Annex D (informative) Calculation of TRWP detection limits	22
Annex E (normative) Calculation of results using dimer markers	24
Bibliography	29

Forward

The International Organization for Standardization (ISO) 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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

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/html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and Rubber Products*. This second edition cancels and replaces the first edition (ISO/TS 21396:2017), which has been technically revised.

The main changes are as follows:

- addition of illustrative instrument conditions for the microfurnace pyrolyser and statement of limitations of the resistive pyrolysers;
- addition of recommendations for sample chemical pretreatment to mitigate interference from co-eluting non-tread synthetic and/or naturally occurring compounds;
- revision and improvement of calculation method to account for differences in elastomer microstructure between calibration standards and marketplace average tread including total 1,4-butadiene content for SBR/BR and styrene content for SBR;
- addition of 4-phenylcyclohexene marker, which may be used as a marker for SBR or alternative marker for SBR/BR when an estimate of the SBR:BR ratio is available.

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

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 (gas chromatography/mass spectrometry) 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 (Unice et al. 2012^[2]; Unice et al. 2013^[3]; Barber et al., 2023^[4]). The airborne concentration of TRWP in the PM_{2.5} and PM₁₀ fraction has also been characterized by a similar method (Panko et al. 2013^[5]; Panko et al. 2019^[6]).

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 (GC) and identified by mass spectrometry (MS). 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^[7]; Harada et al. 2009^[8]). 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.

Rubber — Determination of the mass concentration of tyre and road wear particles (TRWP) in soil and sediment — Pyrolysis-gas chromatography/mass spectrometry (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 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 mass concentration ($\mu\text{g/g}$) of tyre and road wear particles (TRWP) in soil or sediment 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 17257, *Rubber — Identification of polymers — Pyrolytic gas-chromatographic method using mass-spectrometric detection*

ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

3 Terms and definitions

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

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/>

3.1

deuterated internal standard

monomer 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**wet mass**

mass of solid before drying in an oven

3.4**monitoring**

repeated measurement to follow changes over a period of time

3.5**percent dry mass**

dry mass of sample solids expressed as a percentage of the sample wet mass

3.6**pyrolysis analysis**

decomposition of organic polymeric molecules into characteristic fragments separated by GC and quantified by MS

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) (CAS 9006-04-6), styrene-butadiene rubber (SBR) (CAS 9003-55-8) and butadiene rubber (BR) (CAS 9003-17-2) polymers depend on the abundance of polymers in the sample. SBR pyrolysis generates butadiene (CAS 106-99-0), 4-vinylcyclohexene (butadiene dimer;VCH) (CAS 100-40-3), styrene (CAS 100-42-5), and 4-phenylcyclohexene (PCH) (CAS 4994-16-5), whereas BR generates butadiene monomer and VCH (Miller et al. 2022^[9]). NR is associated with isoprene (CAS 78-79-5) monomer and dipentene (isoprene dimer;DP) (CAS 138-86-3). Quantification of the synthetic fraction (SBR and BR) by the VCH marker is preferred based on the increased response ratio and contribution as compared to the PCH marker, which estimates the synthetic fraction based on SBR only (Miller et al. 2022^[11]).

The dimer fragments have good specificity for rubber polymers, whereas both anthropogenic and natural organic substances are sources of the monomer markers (Kitamura 2007^[2]). 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^[10]). The tyre polymers and pyrolysis fragment dimers used for quantification of TRWP are shown in [Figure 1](#).

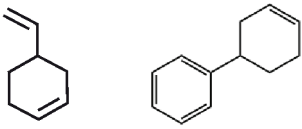
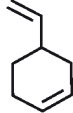
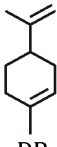
Polymer Formula	Dimer
$\left(\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right)_m \left(\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_n$ SBR	 VCH PCH
$\left[\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right]_n$ BR	 VCH
$\left[\text{CH}_2 - \underset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_2 \right]_n$ NR	 DP

Figure 1 — Dimeric pyrolysis products of tyre rubber polymers

5 Reagents and materials

Use only reagents of recognized analytical grade.

- 5.1 **Chloroform**, analytical grade. (non-deuterated CAS 67-66-3 or deuterated CAS 865-49-6)
- 5.2 **Helium**, purity 99,999 5 % by volume. (CAS 7440-59-7)
- 5.3 **Potassium hydroxide 10 % (100 g/l)**, purity >86 % by volume. (CAS 1310-58-3)
- 5.4 **Purified water**, Type I ultrapure.
- 5.5 Deuterated poly(1,4-isoprene) (d-IR), for internal standard.
- 5.6 Deuterated polystyrene polybutadiene (d-PSPB), for internal standard.
- 5.7 Poly(1,4-isoprene) rubber (IR) (CAS 9003-31-0), for calibration polymer.
- 5.8 Styrene-butadiene rubber (SBR), for calibration polymer.

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 Stantec Consulting Services, Inc.

Figure 2 — Collection of sample with clamshell dredge device

6.1.2 Sample containers.

Samples shall 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 Consulting Services, Inc..

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) 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 shall be 1 mm as specified in ISO 3310-1.