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Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine polycyclic aromatic hydrocarbons (PAHs) in footwear materials

Chaussures — Substances critiques potentiellement présentes dans les chaussures et les composants de chaussures — Méthode d'essai pour déterminer quantitativement les hydrocarbures aromatiques polycycliques (HAP) dans les matériaux de chaussures

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Contents

Page

Foreword ..... **iv**
Introduction ..... **vi**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Principle **1**
5 Reagents **1**
6 Apparatus **5**
7 Sample preparation **5**
8 Procedure **5**
8.1 Extraction 5
8.2 Optional: Solid-phase extraction (SPE) clean-up 6
8.3 Determination by GC-MS or GC-MS/MS 6
9 Expression of results **6**
9.1 Determination of the PAH content 6
9.1.1 For each PAH 6
9.1.2 When a sum of PAHs is requested 6
9.2 Performance of the test method 7
10 Test report **7**
Annex A (informative) **Examples of chromatographic conditions for GC-MS and GC-MS/MS** **8**
Bibliography **11**

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).

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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 Technical Committee ISO/TC 216, *Footwear*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 309, *Footwear*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This first edition cancels and replaces the first edition Technical Specification (ISO/TS 16190:2013), which has been technically revised. The main changes compared with the previous edition are as follows:

— the Introduction has been added;

— in the Scope, editorial changes have been made and a note has been added;

— the Normative references have been updated;

— Clause 3 “Terms and definitions” has been added and the following clauses have been renumbered;

— Clause 5 “Reagents” has been renamed and major technical changes have been made;

— Clause 6 “Apparatus” has been renamed, further equipment has been added and further minor technical changes have been made;

— Clause 7 “Sample preparation” has been added, which has been mainly taken from ISO/TS 16190:2013, 6.2, and the following clauses have been renumbered;

— in Clause 8 “Procedure”, major technical changes and editorial changes have been made;

— Clause 9 “Expression of results” has been renamed and subclause headings have been added;

— 9.1.2 “When a sum of PAH is requested” has been added;

— in 9.2 “Performance of the test method”, the limit of quantification has been changed;

— in Clause 10 g), the option to state a sum of PAH has been added;

— Annex A has been added.

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

Certain polycyclic aromatic hydrocarbons (PAHs) have been identified as carcinogenic. Thus, several countries have restricted them in articles such as footwear, e.g. in the European Union by Commission Regulation (EU) 2018/1513[1] amending Regulation (EC) No 1907/2006[2].

Restricted PAHs according to Regulation (EC) No 1907/2006 are Benzo[a]pyrene (BaP), Benzo[e]pyrene (BeP), Benzo[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbFA), Benzo[j]fluoranthene (BjFA), (g) Benzo[k]fluoranthene (BkFA) and Dibenzo[a,h]anthracene (DBAhA).

Further PAHs are restricted by footwear brands in their restricted substances lists (RSLs).

Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine polycyclic aromatic hydrocarbons (PAHs) in footwear materials

WARNING — The use of this document involves hazardous materials. It does not purport to address all of the safety or environmental problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel and the environment prior to the application of this document, and to fulfil the relevant requirements for this purpose.

1 Scope

This document specifies a method to determine the amounts of polycyclic aromatic hydrocarbons (PAHs) in footwear and footwear components.

NOTE A list of relevant materials can be found in ISO/TR 16178:2021, Table 1[3].

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 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

3 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The test sample is extracted using toluene at 60 °C in an ultrasonic bath for 1 h. An aliquot is then analysed using a gas chromatograph with mass selective detector.

5 Reagents

WARNING — Toluene is flammable. In addition, PAHs can cause cancer. Therefore, they should be treated taking into account relevant regulations on occupational health and safety.

Unless otherwise specified, analytical grade chemicals shall be used.

5.1 Toluene, CAS Registry Number®[1] 108-88-3.

5.2 PAHs. The 24 PAHs given in Table 1 may be relevant.

Table 1 — List of relevant PAHs

Component	CAS Registry Number®[1]
Naphthalene	91-20-3
Acenaphthylene	208-96-8
Acenaphthene	83-32-9
Fluorene	86-73-7
Anthracene	120-12-7
Phenanthrene	85-01-8
Fluoranthene	206-44-0
Pyrene	129-00-0
1-methylpyrene	2381-21-7
Cyclopenta(c,d)pyrene	27208-37-3
Benzo[a]anthracene	56-55-3
Chrysene	218-01-9
Benzo[b]fluoranthene	205-99-2
Benzo[j]fluoranthene	205-82-3
Benzo(k)fluoranthene	207-08-9
Benzo[a]pyrene	50-32-8
Benzo[e]pyrene	192-97-2
Benzo[ghi]perylene	191-24-2
Indeno[1,2,3-cd]pyrene	193-39-5
Dibenzo(a,h)anthracene	53-70-3
Dibenzo[a,l]pyrene	191-30-0
Dibenzo[a,e]pyrene	192-65-4
Dibenzo[a,i]pyrene	189-55-9
Dibenzo[a,h]pyrene	189-64-0

5.3 PAH standard solution(s) (100 µg/ml)

Based on its tasks, a laboratory shall decide which PAHs from Table 1 need to be determined. Based on this decision, standard stock solutions for each PAH (c = 100 µg/ml for each PAH) shall be available either as commercially available certified mixes or as individual components in solution.

5.4 Target PAHs — Stock solution 1 (5 µg/ml)

Put 9 ml of toluene (5.1) in a 10 ml amber volumetric flask (6.6), add 500 µl of PAH stock solution (5.3) and fill the flask up to the calibration mark with toluene (5.1).

5.5 Target PAHs — Stock solution 2 (0,5 µg/ml)

Put 8 ml of toluene (5.1) in a 10 ml amber volumetric flask (6.6), add 1 ml of stock solution 1 (5.4) and fill the flask up to the calibration mark with toluene (5.1).

1) CAS Registry Number® (CAS RN®) is a trademark of CAS corporation. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.6 Internal standards (IS) solution(s) (100 µg/ml)

5.6.1 General

The following IS shall be used either as commercially available certified mixes or as individual components in solution.

5.6.1.1 Naphthalene-d8, CAS RN®[1)] 1146-65-2.

5.6.1.2 Fluorene-d10, CAS RN®[1)] 81103-79-9.

5.6.1.3 Pyrene-d10, CAS RN®[1)] 1718-52-1.

5.6.1.4 Chrysene-d12, CAS RN®[1)] 1719-03-5.

5.6.1.5 Benzo[a]pyrene-d12, CAS RN®[1)] 63466-71-7.

5.6.1.6 Benzo[ghi]perylene-d12, CAS RN®[1)] 93951-66-7.

5.6.1.7 Dibenzo[a,h]anthracene-d14 CAS RN®[1)] 13250-98-1.

5.6.2 Correspondence between PAH and IS

Use the IS for the determination of the corresponding PAH according to Table 2. The number of IS can be reduced to a minimum of five if method validation demonstrates sufficient recovery rates for the corresponding PAH[7].

Table 2 — List of relevant internal standards

Component	CAS RN®[1)]	Internal standard
Naphthalene	91-20-3	Naphthalene-d8 (5.6.1.1)
Acenaphthylene	208-96-8	Pyrene-d10 (5.6.1.3)
Acenaphthene	83-32-9	Pyrene-d10 (5.6.1.3)
Fluorene	86-73-7	Fluorene-d10 (5.6.1.2)
Anthracene	120-12-7	Pyrene-d10 (5.6.1.3)
Phenanthrene	85-01-8	Pyrene-d10 (5.6.1.3)
Fluoranthene	206-44-0	Pyrene-d10 (5.6.1.3)
Pyrene	129-00-0	Pyrene-d10 (5.6.1.3)
1-methylpyrene	2381-21-7	Pyrene-d10 (5.6.1.3)
Benzo[a]anthracene	56-55-3	Chrysene-d12 (5.6.1.4)
Chrysene	218-01-9	Chrysene-d12 (5.6.1.4)
Cyclopenta(c,d)pyrene	27208-37-3	Benzo[a]pyrene-d12 (5.6.1.5)
Benzo[b]fluoranthene	205-99-2	Benzo[a]pyrene-d12 (5.6.1.5)
Benzo[j]fluoranthene	205-82-3	Benzo[a]pyrene- d12 (5.6.1.5)
Benzo(k)fluoranthene	207-08-9	Benzo[a]pyrene- d12 (5.6.1.5)
Benzo[a]pyrene	50-32-8	Benzo[a]pyrene- d12 (5.6.1.5)
Benzo[e]pyrene	192-97-2	Benzo[a]pyrene- d12 (5.6.1.5)
Benzo[ghi]perylene	191-24-2	Benzo[ghi]perylene- d12 (5.6.1.6)
Indeno[1,2,3-cd]pyrene	193-39-5	Benzo[ghi]perylene- d12 (5.6.1.6)
Dibenzo(a,h)anthracene	53-70-3	Dibenzo[a,h]anthracene-d14 (5.6.1.7)

Table 2 *(continued)*

Component	CAS RN®[1)]	Internal standard
Dibenzo[a,l]pyrene	191-30-0	Dibenzo[a,h]anthracene- d14 (5.6.1.7)
Dibenzo[a,e]pyrene	192-65-4	Dibenzo[a,h]anthracene- d14 (5.6.1.7)
Dibenzo[a,i]pyrene	189-55-9	Dibenzo[a,h]anthracene- d14 (5.6.1.7)
Dibenzo[a,h]pyrene	189-64-0	Dibenzo[a,h]anthracene-d14

5.6.3 Internal standard — Stock solution (each 100 µg/ml)

Internal standards are commercially available as certified solutions, or solutions of certified individual compounds may be prepared.

To prepare an internal standard solution, use the analytical balance (6.1) and weigh 10 mg, with an accuracy of 0,1 mg, of each selected internal standard (5.6.1) into 100 ml amber volumetric flasks and fill it up to the mark with toluene (5.1).

5.6.4 Internal standard — Working solution (5 µg/ml)

Transfer 0,5 ml of each internal standard stock solution (5.6.3) to a 10 ml amber volumetric flask and fill it up to the mark with toluene (5.1).

5.7 Target PAHs — Calibration solutions

Prepare at least four calibration solutions of PAHs (see Table 3), including internal standard, in toluene, at suitable concentrations for the analysis. Put the required volume of PAH standard stock solution(s) (5.3) and 100 µl of internal standard working solution(s) (5.6.4) into a 10 ml amber volumetric flask (6.6) and fill it up to the mark with toluene (5.1).

Table 3 — Preparation of calibration standards suitable for GC-MS (example)

Calibration solution PAH concentration (µg/ml)	Calibration solution IS concentration (µg/ml)	Volume of PAH working solution c = 5 µg/ml (5.4) (µl)	Volume of PAH working solution 2 c = 0,5 µg/ml (5.5) (µl)	Volume of IS working solution c = 5 µg/ml (5.6.4) (µl)	Volume of volumetric flask (6.6) (ml)
0,005	0,050		1 000	100	10
0,025		50			
0,100		200			
0,500		1 000			

5.8 Extraction solution with internal standard (0,050 µg/ml)

Prepare the extraction solution with an internal standard concentration of 0,050 µg/ml by diluting internal standard stock solution (5.6.2) with toluene (5.1) in a suitable volumetric flask. The solution shall be stored in an amber bottle in the dark. Exposure to direct sun irradiation shall be avoided. The solution is stable for seven days.

5.9 Preservation

All PAH standard solutions (5.3), (5.4), (5.5) and internal standard solutions (5.6.2), (5.6.3) shall be stored in amber glassware in a refrigerator, at about (5 ± 3) °C and preserved in the dark.

6 Apparatus

The usual laboratory apparatus and amber laboratory glassware, in accordance with ISO 4787, shall be used, in addition to the following.

NOTE Plastic equipment can contain traces of PAHs.

6.1 Analytical balance, with a readability of at least 0,1 mg.

6.2 Glass vial, with screw cap (e.g. volume of 40 ml).

6.3 Ultrasonic bath, with adjustable temperature suitable for operation at about 60 °C.

6.4 Micropipettes, 50 µl and 100 µl.

6.5 Pipettes, 0,5 to 5 ml.

6.6 Amber volumetric flasks (e.g. volume of 10 ml).

6.7 Gas chromatograph, coupled with single-quad mass spectrometer (GC-MS) or triple-quad mass spectrometer (GC-MS/MS)

6.8 PTFE-membrane filter, pore size 0,45 µm.

6.9 Amber GC vials, with cap (e.g. volume of 2 ml).

7 Sample preparation

The exposure to light can change the concentration of PAHs in the samples. Samples shall be stored in the dark at 18 to 25 °C.

Dismantle the footwear and separate the different material types.

Each test specimen shall consist of a single material type (leather or textile or polymer), which is tested separately.

Up to three test specimens (of equal mass) of the same material type may be tested together taking into consideration the limits of detection and quantification.

Each material type shall cut into pieces of about 3 mm to 5 mm edge length.

8 Procedure

8.1 Extraction

Weigh (0,500 ± 0,100) g of the sample by using an analytical balance (6.1) in a glass vial (6.2). Record the mass to the nearest 1 mg. Add 10 ml of extraction solution with internal standard (5.7) and seal the vial.

Extract the specimen at (60 ± 5) °C for (60 ± 5) min in an ultrasonic bath (6.3).

After cooling below at least 27 °C, filter this solution through a PTFE membrane filter (6.8).

Transfer an aliquot of the extract to a GC-MS vial (6.9) and seal with a cap.

8.2 Optional: Solid-phase extraction (SPE) clean-up

In cases of an interfering matrix, an SPE clean-up by using an SPE column which is highly selective for PAHs and suitable for use with toluene may be performed.

8.3 Determination by GC-MS or GC-MS/MS

Calibrate the GC-MS or the GC-MS/MS (6.7) with at least four calibration solutions (5.7) and determine the extracted PAHs.

Examples of the GC-MS and GC-MS/MS conditions are given in Annex A.

If required to verify the compliance of PAH content with legal requirements, the capillary column used shall be able to achieve a sufficient resolution of 0,8 between the chromatographic peaks of critical pairs as benzo(b)fluoranthene and benzo(k)fluoranthene as well as of benzo(a)pyrene and benzo(e) pyrene.

Depending on the equipment used, it is not always possible to achieve calibration down to the concentration required to verify the compliance of PAH content with legal requirements. In such cases, it is permissible to concentrate the test specimen extract to about 2 ml. When the extract is concentrated, it is necessary to decrease the concentration of IS in the initial extraction solution. The last step of the concentration may be done using a gentle stream of nitrogen at room temperature.

NOTE Due to the volatility of naphthalene, it can be partly lost during this concentration step.

9 Expression of results

9.1 Determination of the PAH content

9.1.1 For each PAH

The content of individual substances is calculated according to Formula (1) as a mass fraction w in mg/kg:

$$w = \frac{A_{\text{PAH-S}} \times c_{\text{PAH-Std}} \times V}{A_{\text{PAH-Std}} \times m_{\text{S}}} \times \frac{A_{\text{int.Std}}}{A_{\text{int.S}}} \quad (1)$$

where

$A_{\text{PAH-S}}$ is the peak area of a PAH component in the test specimen extract;

$A_{\text{PAH-Std}}$ is the peak area of the same PAH component in the calibration solution;

$c_{\text{PAH-Std}}$ is the concentration of the PAH component in the calibration solution (µg/ml);

V is the final volume of the sample (ml) (V = 10 ml according to 8.1);

m_{S} is the mass of the sample (g);

$A_{\text{int.Std}}$ is the peak area of the appropriate internal standard in calibration solution;

$A_{\text{int.S}}$ is the peak area of the same internal standard in the test specimen extract.

9.1.2 When a sum of PAHs is requested

In certain cases, a final requested result can be expressed as a sum of different PAHs.

All the PAHs included in the sum shall be clearly identified.

The results of the identified PAH (as obtained in 9.1.1) are added to give the result of the sum. If the result for a single PAH is lower than the limit of quantification of the test method (see 9.2), this result is considered as zero and shall not be included in the sum.

9.2 Performance of the test method

This method is able to determine the PAHs listed in Table 1 with a limit of quantification of 0,5 mg/kg or lower.

NOTE For complex matrix (e.g. leather, rubber, materials with a high amount of phthalates and/or paraffines), this limit of quantification can be difficult to achieve.

10 Test report

The test report shall include at least the following:

a) a reference to this test method, i.e. ISO 16190:2021;

b) the date of the test;

c) all the details necessary for complete identification of the sample tested;

d) that different material types (see Clause 7) that have been tested;

e) the conditions of storage before the test, if available;

f) the mass fraction determined for each of the 18 PAH in mg/kg; and as sum in mg/kg of certain PAHs if required;

g) any deviation(s) from the given procedure.

Annex A
(informative)

Examples of chromatographic conditions for GC-MS and GC-MS/MS

A.1 Suitable GC-MS conditions

Column:	(5 %-phenyl)-methylpolysiloxane; length: 20 m, interior diameter: 0,18 mm, film thickness: 0,18 µm
Carrier gas:	Hydrogen
Flow rate:	0,8 ml/min
Injector temperature:	280 °C, pulsed splitless, 0,5 min
Injection volume:	1,0 µl
Temperature programme:	95 °C for 1 min to 350 °C at 30 °C/min 350 °C for 1,5 min
Transfer line temperature:	300 °C
MS mode:	Electron impact
Detection mode:	Selected ion monitoring (SIM) Typical quantification ions for PAHs are shown in Table A.1.

Table A.1 — Typical quantification ions for PAHs

PAH	Quantifier (m/z)	Quantifier (m/z)
Naphthalene-d8	136	108
Naphthalene	128	102
Acenaphthylene	152	76
Acenaphthene	154	76
Fluorene-d10		
Fluorene	166	82
Phenanthrene	178	89
Anthracene	178	89
Fluoranthene	202	101
Pyrene-d10		
Pyrene	202	101
1-methylpyrene	216	108
Cyclopenta[c,d]pyrene	226	113
Chrysene-d12	240	120
Chrysene	228	114
Benzo[a]anthracene	228	114