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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**

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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).

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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;
- a note has been added to the Scope;
- the Normative references have been updated;
- the clauses have been renumbered and technical changes have been made throughout;
- [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).

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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

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 16178:2012, 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 at least to five if method validation demonstrates sufficient recovery rates for the corresponding PAH^[7].

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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.