TECHNICAL SPECIFICATION

ISO/TS 16190

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

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

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ISO/TS 16190 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 309, *Footwear*, in collaboration with ISO Technical Committee ISO/TC 216, *Footwear*, in accordance with the agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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

CAUTION — The use of polycyclic aromatic hydrocarbons (PAH) can be hazardous.

1 Scope

This Technical Specification specifies a method to determine the amounts of polycyclic aromatic hydrocarbons (PAH) in footwear and footwear components.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TR 16178:2012, *Footwear — Critical substances potentially present in footwear and footwear components*

ISO 17993:2002, *Water quality — Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction*

ISO 28540:2011, *Water quality — Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water — Method using gas chromatography with mass spectrometric detection (GC-MS)*

3 Principle

The test sample is extracted using n-hexane at 60 °C in an ultrasonic bath for 1 h. An aliquot is then analysed using chromatographic techniques.

See ISO/TR 16178:2012, Table 1, which defines which materials are concerned by this determination.

4 Chemicals

All chemicals shall be analytical grade.

4.1 n-Hexane, CAS[1)] number: 110-54-3.

4.2 Certificated PAH stock solution, with 18 different components specified in 6.4 to each 100 µg/ml.

NOTE Commercial solutions are available on the market.

4.3 Internal standards:

— Naphthalene-d8, CAS number: 1146-65-2

— Pyrene-d10, CAS number: 1718-52-1

— Perylene-d12, CAS number: 1520-96-3

— Anthracene-d10 CAS number: 1719-06-8

1) CAS: Chemical Abstract Service.

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— Phenanthrene-d10 CAS number 1517-22-2

— Triphenylbenzenze CAS number: 612-71-5

— Benzo[a]pyrene-d12 CAS number: 63466-71-7

NOTE The following list shows examples of correspondence between PAH and deuterated internal standards.

Name	**Internal standard**
Naphthalene	Naphthalene-d8
Acenaphthylene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Acenaphthene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Fluorene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Phenanthrene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Anthracene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Fluoranthene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Pyrene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Benzo[a]anthracene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Benzo[e]pyrene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Benzo[j]fluoranthene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Chrysene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
Benzo[b]fluoranthene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
Benzo[k]fluoranthene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
Benzo[a]pyrene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
Indeno[1,2,3-cd]pyrene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
Dibenzo[a,h]anthracene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
Benzo[g,h,i]perylene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene

4.4 Preservation: Certificated PAH stock solution (4.2) and internal standards (4.3) shall be stored at 4 °C ± 3 °C and preserved in the dark.

5 Apparatus and materials

5.1 Analytical balance.

5.2 Lockable jar with lid.

5.3 Ultrasonic bath (temperature controlled).

5.4 Micropipettes, 50 µl and 100 µl.

5.5 Pipette, 0,5 to 5 ml capacity.

5.6 Volumetric flasks of 10 ml and 100 ml.

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5.7 Suitable chromatographic techniques for PAH analysis.

EXAMPLES High performance liquid chromatography (HPLC) method: fluorescence detector (FLD) and diode array detector (DAD); mass selective detector (MS or MS-MS) method: gas chromatograph with mass selective detector (GC-MS or GC-MS-MS).

5.8 PTFE-membrane filter, pore width 0,45 µm.

6 Procedure

6.1 Preparation of standard solutions

6.1.1 Internal standard stock solution (each 100 µg/ml)

Use the analytical balance (5.1) and weigh 0,01 g of each internal standard (4.3) into several 100 ml volumetric flasks (5.6) and fill up to the mark with n-hexane (4.1).

The maximum shelf life of this internal standard stock solution is 3 months. It shall be stored at 4 °C ± 3 °C and preserved in the dark.

NOTE Commercial solutions are available on the market.

6.1.2 Internal standard solution (5 µg/ml)

Transfer 0,5 ml of each internal standard solution (6.1.1) to a 10 ml volumetric flask (5.6) and fill up to the mark with n-hexane (4.1).

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6.1.3 PAH

The following 18 PAH are relevant:

Naphthalene	CAS number: 91-20-3
Acenaphthylene	CAS number: 208-96-8
Acenaphthene	CAS number: 83-32-9
Fluorene	CAS number: 86-73-7
Phenanthrene	CAS number: 85-01-8
Anthracene	CAS number: 120-12-7
Fluoranthene	CAS number: 206-44-0
Pyrene	CAS number: 129-00-0
Benzo[a]anthracene	CAS number: 56-55-3
Benzo[e]pyrene	CAS number: 192-97-2
Benzo[j]fluoranthene	CAS number: 205-82-3
Chrysene	CAS number: 218-01-9
Benzo[b]fluoranthene	CAS number: 205-99-2
Benzo[k]fluoranthene	CAS number: 207-08-9
Benzo[a]pyrene	CAS number: 50-32-8
Indeno[1,2,3-cd]pyrene	CAS number: 193-39-5
Dibenzo[a,h]anthracene	CAS number: 53-70-3
Benzo[g,h,i]perylene	CAS number: 191-24-2

6.1.4 PAH standard solution (0,5 µg/ml)

Place 9 ml of n-hexane (4.1) in a 10 ml volumetric flask (5.6), add 50 µl of PAH stock solution (4.2) and then top up to the calibration mark with n-hexane (4.1).

6.1.5 PAH calibration solution (0,05 µg/ml)

Put 1 ml of PAH standard solution (6.1.4) and 0,1 ml of internal standard solution (6.1.2) into a 10 ml volumetric flask (5.6) and fill up to the mark with n-hexane (4.1).

6.2 Sample preparation

Dismantle the footwear and separate the different material types into three categories: leather, textile and polymer.

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

Each material type is cut into pieces up to 3 mm edge length.

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6.3 Extraction

Weigh 1 g ± 0,001 g test sample (m_S) with the analytical balance (5.1) into the lockable jar (5.2) and mix with 9,9 ml n-hexane (4.1) and 0,1 ml internal standard solution (6.1.2). Extract at 60 °C in an ultrasonic bath (5.3) for 1 h.

After cooling to room temperature, filter the solution (if necessary through a PTFE membrane filter (5.8).

6.4 Determination

6.4.1 HPLC method

Determine the PAH according to ISO 17993:2002, 8.5. An example of chromatographic conditions is given in ISO 17993:2002, Annex A.

Internal standard use is not mandatory for the HPLC method.

6.4.2 GC-MS method

Determine the PAH according to ISO 28540:2011, Clause 10.

An example of chromatographic conditions is given in ISO 28540:2011, Annex A.

7 Quantification

The content of individual substances is calculated according to the following equation as a mass fraction w in mg/kg:

$$w = \frac{A_{\text{PAH-S}} \cdot c_{\text{PAH-Std}} \cdot V}{A_{\text{PAH-Std}} \cdot m_{\text{S}}} \cdot \frac{A_{\text{int.Std}}}{A_{\text{int.S}}}$$

where

$A_{\text{PAH-S}}$ is the peak area of PAH components in the sample;

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

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

V is the final volume of the sample (ml) (V = 10 ml according to 6.3);

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

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

$A_{\text{int. S}}$ is the peak area of internal standard in the sample.

8 Performance of the method

The laboratory shall determine for each PAH the limit of quantification, taking into account the chosen technique (6.4).

This quantification limit shall be lower or equal to 0,2 mg/kg for each PAH.

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9 Test report

The test report shall include at least the following:

a) reference to this test method;

b) date of the test;

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

d) different material types (6.2) that have been tested;

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

f) the technique chosen in 6.4;

g) the amount determined for each of the 18 PAH in mg/kg;

h) any deviation from the present standard.

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