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भारतीय मानक मसौदा

वस्त्रादि – परीक्षण की विधि – गैस क्रोमैटोग्राफी-मास स्पेक्ट्रोमेट्री द्वारा टोल्यूनि निष्कर्षण के बाद पॉलीसाइक्लिक एरोमैटिक हाइड्रोकार्बन का निर्धारण

Draft *Indian Standard*

Textiles — Method of Test — Determination of Polycyclic Aromatic Hydrocarbons After Toluene Extraction by Gas Chromatography-Mass Spectrometry

ICS 59.080.01

Chemical Methods of Test Sectional Committee TXD 05
Last date for receipt of comments **25 October 2025**

FOREWORD

(*Formal clauses will be added later*)

Polycyclic Aromatic Hydrocarbons (PAHs) are naturally occurring compounds made up of multiple aromatic rings of carbon and hydrogen. They are commonly found in fossil fuels and are formed during the incomplete combustion of organic matter. Polycyclic Aromatic Hydrocarbons (PAHs) are a class of hazardous organic compounds known for their potential carcinogenicity, mutagenicity, and environmental persistence. Their presence in consumer products, particularly those involving rubber, plastic, and textiles, poses significant health risks due to dermal and oral exposure, especially through prolonged or repetitive contact.

In textiles and textile products, PAHs are not intentionally added but may be present as unintended contaminants introduced during the manufacturing process. This contamination can result from the use of certain raw materials such as synthetic rubber, plasticizers, dyes, recycled materials, carbon black, and mineral oil-based processing aids. PAHs are commonly found in rubber or plastic components of textile articles, including coatings, prints, appliqués, soles, logos, and trims. They may be present in various textile products such as clothing, footwear, gloves, accessories, outdoor gear, and children’s items, particularly where there is direct, prolonged, or repeated contact with the skin or oral cavity.

In the preparation of this standard, considerable assistance has been derived from the following references:

- BS EN 17132 (2019): Textiles and textile products - Determination of Polycyclic Aromatic Hydrocarbons (PAH), method using gas chromatography
- ISO 16190 (2021): Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine polycyclic aromatic hydrocarbons (PAHs) in footwear materials

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2: 2022 ‘Rules for rounding off numerical values (*second revision*)’.

Draft *Indian Standard*

TEXTILES — METHOD OF TEST — DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS AFTER TOLUENE EXTRACTION BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

1 SCOPE

1.1 This standard prescribes a test method for determining the content of polycyclic aromatic hydrocarbons (PAHs) in individual material components of textile products. The method involves extraction with toluene followed by analysis using Gas Chromatography–Mass Spectrometry (GC-MS) operated in Selected Ion Monitoring (SIM) mode.

1.2 The method is designed to achieve a limit of quantification of 0.5 mg/kg for the listed PAH compounds (*See* **Table 1**).

2 TERMINOLOGY

2.1 Analyte — The specific substance being measured or identified in the sample.

NOTE — The list of substances covered under this Standard is provided in **Table 1**.

2.2 Calibration Solution — A solution prepared from a secondary standard and/or stock solutions, used to calibrate the instrument's response with respect to analyte concentration.

2.3 GC-MS (Gas Chromatography – Mass Spectrometry) — An analytical method that combines gas chromatographic separation with mass spectrometric detection, enabling the identification and quantification of PAHs at trace levels.

2.4 GC-MS Diagnostic Ion — A selected fragment or molecular ion of the target compound that provides the highest possible specificity for identification during GC-MS analysis.

2.5 Internal Standard — An isotopically labelled PAH, or a PAH unlikely to be present in the sample, added to samples prior to extraction, against which the concentrations of native substances are calculated.

NOTE — The list of relevant Internal Standards for each 24 PAH is given in **Table 2**.

2.6 Selected Ion Monitoring (SIM) Mode — A detection mode in mass spectrometry that focuses on measuring specific diagnostic ions for enhanced sensitivity and selectivity.

3 PRINCIPLE

3.1 The sample of the material of the textile product is extracted using toluene in an ultrasonic bath at (60 ± 5) °C for 60 min. The final filtered extract is then analysed using a gas chromatograph with mass selective detector. The extracted PAHs content shall be expressed in mg PAH per kg of textile product.

4 APPARATUS

4.1 Ultrasonic Cleaner Bath — An ultrasonic cleaner bath capable of heating and maintaining the temperature at (60 ± 5) °C, with an output power of 200 W and an oscillation frequency of 40 kHz, or an equivalent arrangement.

4.2 Membrane Filter — A filter having a pore size in the range of 0.22 µm to 0.45 µm shall be used for filtration. Membrane filters made of polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET), or nylon have been found suitable for this purpose.

4.3 Gas Chromatograph with Mass Selective Detector (GC-MS) — Shall be used for the detection and quantification of extracted PAHs from textile products.

NOTE — For details of chromatographic conditions of suitable GC-MS equipment, see **Annex A**.

4.4 GC Vial with Cap — of capacity 2 mL.

4.5 Injection Syringes — of capacity 5 µL and 10 µL.

4.6 Micropipette — of capacity 50 µl and 100 µL.

4.7 Pipette — of capacities 0.5 mL to 5 mL.

4.8 Volumetric Flasks — of capacity 10 mL and 100 mL.

4.9 Glass Vial with Screw Cap — of capacity 40 mL.

4.10 Analytical Balance, with an accuracy of 0.1 mg.

5 REAGENTS

Unless otherwise specified, only analytical grade chemicals and reagents shall be used.

5.1 Toluene

Toluene shall be of analytical grade, suitable for chromatographic analysis.

5.2 Polycyclic Aromatic Hydrocarbons (PAHs)

The PAHs listed in **Table 1** shall be used for calibration and quantification.

Table 1 List of relevant PAHs

(*Clause* 5.2)

Sl. No. (1)	Component (2)	CAS Number (3)	Molecular Formula (4)
i)	Naphthalene	91–20–3	$C_{10}H_8$
ii)	Acenaphthylene	208–96–8	$C_{12}H_8$
iii)	Acenaphthene	83–32–9	$C_{12}H_{10}$
iv)	Fluorene	86–73–7	$C_{13}H_{10}$
v)	Phenanthrene	85–01–8	$C_{14}H_{10}$
vi)	Anthracene	120–12–7	$C_{14}H_{10}$
vii)	Fluoranthene	206–44–0	$C_{16}H_{10}$
viii)	Pyrene	129–00–0	$C_{16}H_{10}$
ix)	Benzo[a]anthracene	56–55–3	$C_{18}H_{12}$
x)	Benzo[e]pyrene	192–97–2	$C_{20}H_{12}$
xi)	Benzo[j]fluoranthene	205–82–3	$C_{20}H_{12}$
xii)	Chrysene	218–01–9	$C_{18}H_{12}$
xiii)	Benzo[b]fluoranthene	205–99–2	$C_{20}H_{12}$
xiv)	Benzo[k]fluoranthene	207–08–9	$C_{20}H_{12}$
xv)	Benzo[a]pyrene	50–32–8	$C_{20}H_{12}$
xvi)	Indeno[1,2,3-cd]pyrene	193–39–5	$C_{22}H_{12}$
vii)	Dibenzo[a,h]anthracene	53–70–3	$C_{22}H_{14}$
viii)	Benzo[g,h,i]perylene	191–24–2	$C_{22}H_{12}$
xix)	Dibenzo[a,e]pyrene	192-65-4	$C_{24}H_{14}$
xx)	Dibenzo[a,h]pyrene	189-64-0	$C_{24}H_{14}$
xxi)	Dibenzo[a,i]pyrene	189-55-9	$C_{24}H_{14}$
xii)	Dibenzo[a,l]pyrene	191-30-0	$C_{24}H_{14}$
xiii)	1-Methylpyrene	2381-21-7	C_7H_{12}
xiv)	Cyclopenta (c,d)pyrene	27208-37-3	$C_{18}H_{10}$

5.3 Standard Solutions of PAHs (100 µg/mL)

The eighteen PAH components listed in **5.2** shall be used either as commercially available certified mixes or as individual components in solution.

5.3.1 PAHs - Stock Solution (0.5 µg/mL)

To prepare the stock solution, pipette 50 µL of the PAH standard solution (**5.3**) into a 10 mL volumetric flask containing approximately 9 mL of toluene. Make up the volume to the mark with toluene and mix thoroughly.

5.3.2 PAHs - Working (Calibration) Solutions

Prepare a minimum of four calibration solutions of PAHs in toluene with concentrations such as 0.025 µg/mL, 0.050 µg/mL, 0.100 µg/mL, and 0.500 µg/mL. Each solution shall contain a fixed concentration of internal standard, typically 0.050 µg/mL.

To prepare, pipette the appropriate volume of the PAH stock solution (**5.3.1**) and 0.1 mL of the internal standard working solution (**5.4.2**) into a 10 mL volumetric flask. Dilute to the mark with toluene and mix thoroughly.

5.4 Internal Standards

Certified internal standards shall be used to ensure accurate quantification of PAHs. Examples of suitable isotopically labelled compounds and their corresponding CAS numbers are provided below:

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
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 internal standards.

Table 2 List of relevant Internal Standards

(*Clause* 5.4)

Sl. No. (1)	PAH references substances (2)	Labelled Internal Standard Substances (3)
i)	Naphthalene	Naphthalene-d8
ii)	Acenaphthylene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
iii)	Acenaphthene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
iv)	Fluorene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
v)	Phenanthrene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
vi)	Anthracene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
vii)	Fluoranthene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
viii)	Pyrene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
ix)	Benzo[a]anthracene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
x)	Benzo[e]pyrene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
xi)	Benzo[j]fluoranthene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
xii)	Chrysene	Pyrene-d10 or Anthracene-d10 or Phenanthrene-d10
xiii)	Benzo[b]fluoranthene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
xiv)	Benzo[k]fluoranthene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
xv)	Benzo[a]pyrene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
xvi)	Indeno[1,2,3-cd]pyrene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
vii)	Dibenzo[a,h]anthracene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene
viii)	Benzo[g,h,i]perylene	Benzo[a]pyrene-d12 or Perylene-d12 or Triphenylbenzene

5.4.1 *Internal Standard - Stock Solution (each 100 µg/mL)*

To prepare an internal standard solution, weigh 10 mg of each selected internal standard (**5.4**) into 100 mL volumetric flask and fill up to the mark with toluene and mix thoroughly.

5.4.2 *Internal Standard - Working Solution (5 µg/mL)*

Pipette 0.5 mL of each internal standard stock solution into a 10 mL volumetric flask and dilute to the mark with toluene.

5.5 Extraction Solution with Internal Standard (0.050 µg/mL)

Prepare by diluting the working solution (**5.4.2**) in toluene to yield an internal standard concentration of 0.050 µg/mL.

6. TEST SPECIMEN SAMPLING AND PREPARATION

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

6.2 Dismantle the textile product and separate the different material types.

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

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

6.4 Prepare the test specimen by cutting each material type into pieces of about 0.3 cm to 0.5 cm edge length. Record the mass to the nearest 0.01 g as m_S (**8.1**).

6.5 Up to three test specimens of the same mass may be tested together, considering the limits of detection and quantification.

7 PROCEDURE

7.1 Extraction

7.1.1 Weigh (1 g ± 0.1) g of the test specimen, record the mass to the nearest 1 mg, and transfer it into a clean 40 mL glass vial equipped with screw cap.

7.1.2 Add 10 mL of toluene to the glass vial along with internal standard (**5.5**), and seal the vial.

7.1.3 Place the sealed vial in an ultrasonic cleaner bath maintained at (60 ± 5) °C, and sonicate the sample for (60 ± 5) minutes.

7.1.4 After extraction, allow the vessel to cool to room temperature. Filter the extract through a 0.22 µm PTFE membrane filter.

7.1.4 Transfer an aliquot of the extract to a clean 2 mL GC vial. Seal the vial with a cap.

7.1.5 Inject 1 µL of the filtrate into the GC-MS instrument for analysis.

7.2 Determination by Gas Chromatography-Mass Spectrometry (GC-MS)

7.2.1 The GC-MS instrument (**4.3**) shall be calibrated using a minimum of four calibration solutions (**5.3.2**), and the extracted PAHs shall be quantified accordingly.

Example of GC-MS operating conditions are provided in **Annex A**.

7.2.2 To verify compliance with regulatory limits on PAH content, the capillary column employed must provide adequate resolution. Specifically, it should achieve a minimum resolution of 0.8 between critical peak pairs such as benzo(b)fluoranthene and benzo(k)fluoranthene, as well as benzo(a)pyrene and benzo(e)pyrene.

7.2.3 Depending on the instrument used, calibration down to 0.2 mg/kg may not always be feasible required to verify the compliance of PAH content with legal requirements. In such cases, it is acceptable to concentrate the extract of the test specimen to approximately 2 mL. When concentrating the extract, the concentration of the internal standard in the initial extraction solution must be adjusted (decreased) accordingly. The final concentration step may be performed by gently evaporating the extract under a stream of nitrogen at room temperature.

NOTE — Naphthalene is volatile and may partially evaporate during this concentration step.

8 CALCULATIONS AND EXPRESSION OF RESULTS

8.1 Calculation of Individual PAH Content

8.1.1 The mass fraction (w) of each PAH in the test specimen, expressed in milligrams per kilogram (mg/kg), shall be calculated using the following formula:

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

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 same PAH component in the calibration solution (µg/mL);
V	is the final volume of the sample (mL) (V = 10 mL according to **7.1**);
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.

8.1.2 Calculate the average of all the values obtained as in **8.1** to the nearest 0.1 percent.

8.2 Calculation of Total PAHs (If required)

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 **8.1**) 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* **8.3**), this result is considered as zero and shall not be included in the sum.

8.3 Performance of the Test Method

This test method enables the detection and quantification of the 24 PAHs listed in Table **1**, with a limit of quantification of 0.5 mg/kg or lower for each compound.

10 TEST REPORT

10.1 The report shall include the following information:

a) reference to this test method;
b) the date of the test;
c) all the details necessary for complete identification of the sample tested;
d) different material types (*see* **Clause 6**) that have been tested;
e) the conditions of storage before the test, if available;
f) the mass fraction determined for each of the 24 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

(*Clause* 6.1)

(Informative only)

EXAMPLE OF CHROMATOGRAPHIC METHOD

A-1 GAS-CHROMATOGRAPHIC ANALYSIS WITH MASS SPECTROMETRIC DETECTION FOR POLYCYCLIC AROMATIC HYDROCARBON (PAHS)

A-1.1 Setting up the Gas Chromatograph— Set up the gas chromatograph in such a way that optimum separation of the PAH is achieved. For example, optimize the gas chromatograph starting from the following conditions:

Separation column:	95 % dimethylpolysiloxane 5 % diphenylpolysiloxane, (length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm) or Equivalent
Carrier gas:	Helium
Flow rate:	1 mL/min (constant flow)
Oven temperature programme:	Initial (70 °C for 2 min) Ramp 1: 25 °C/min up to 150 °C for 0 min Ramp 2: 4 °C/min up to 200 °C for 2 min Ramp 3: 6 °C/min up to 280 °C for 15 min Ramp 4: 20 °C/min up to 325 °C for 15 min
Injector Temperature:	325 °C
Injection Volume:	1 µL
Injection mode:	Splitless
Injection liner:	Split/Splitless liner

A-1.2 Mass Spectrometric (MS) Conditions —

MSD Transfer line temperature:	300 °C

MS Mode: Electron impact

Detection Mode: Selected ion monitoring (SIM)

Retention Time and Characteristic masses of polycyclic aromatic hydrocarbons (PAHs) are shown in **Table A.1**

Table A.1 Retention Time and Characteristic Masses of Polycyclic Aromatic Hydrocarbons (PAHs)

(*Clause* A-1.2)

SI. No. (1)	**PAHs (2)**	**Retention Time (3)**	**Quantifier (m/z) 1 (4)**	**Qualifier (m/z) 2 (5)**	**Qualifier (m/z) 3 (6)**
i)	Naphthalene	6.88	128	102	129
ii)	Acenaphthylene	10.31	152	76	151
iii)	Acenaphthene	10.83	154	76	153
iv)	Fluorene	12.70	166	83	165
v)	Phenanthrene	16.95	178	76	179
vi)	Anthracene	17.22	178	89	176
vii)	Fluoranthene	22.89	202	101	200
viii)	Pyrene	23.93	202	101	200
ix)	Benzo[a]anthracene	29.53	228	114	226
x)	Benzo[e]pyrene	35.97	252	126	253
xi)	Benzo[j]fluoranthene	34.53	252	126	253
xii)	Chrysene	29.69	228	114	226
xiii)	Benzo[b]fluoranthene	34.54	252	126	253
xiv)	Benzo[k]fluoranthene	34.53	252	126	253
xv)	Benzo[a]pyrene	36.30	252	126	253
xvi)	Indeno[1,2,3-cd]pyrene	44.64	276	138	274
xvii)	Dibenzo[a,h]anthracene	45.13	278	139	276
xviii)	Benzo[g,h,i]perylene	46.88	276	138	274
xix)	Dibenzo[a,e]pyrene	52.48	302	207	151
xx)	Dibenzo[a,h]pyrene	55.33	302	207	282
xxi)	Dibenzo[a,i]pyrene	54.98	302	207	282

xxii)	Dibenzo[a,l]pyrene	54.26	302	207	151
xxiii)	1-Methylpyrene	26.57	216	107	189
xxiv)	Cyclopenta(c,d)pyrene	29.41	226	206	112

NOTES

1 The conditions are for reference purposes. For each piece of equipment, the Lab can follow suitable equipment conditions with proper resolution and response of analytes in the matrix with appropriate run time about the conditions mentioned above. This shall be established through linearity on standard and repeatability on the matrix at the estimated limit of quantification.

2 Retention time given are indicative for information and will differ with different column and instrument conditions. Other column with different stationary phases can also be chosen for further separation and quantification.