

Product Safety Commission (AfPS)

GS Specification

Testing and assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in the awarding of GS Marks

- Specification pursuant to Article 21 (1) No. 3 of the Product Safety Act (ProdSG) -

AfPS GS 2019:01 PAK

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Testing and assessment of polycyclic aromatic hydrocarbons (PAHs) in the awarding of GS marks

Preliminary observations

On 4 August 2014 the Product Safety Commission (AfPS) has determined the requirements of PAH testing in the awarding of the GS mark as specification according to Article 21 (1) No. 3 of the Product Safety Act (ProdSG). On 15 May 2019 the requirements were reviewed and revised. The GS specification AfPS GS 2014:01 PAK shall be replaced by this document. The implementation is achieved by means of this PAH document.

1 Purpose / Intention

A GS mark may be awarded only if the prerequisites of Article 21 (1) of the Product Safety Act are fulfilled. Above all, GS certified products, i.e. the examined type in sense of Article 21 (1) sentence 1 of the ProdSG (Product Safety Act), shall comply with the essential requirements set out in Article 3, and in case of consumer products, the additional requirements set out in Article 6 of the ProdSG.

Based on the general clauses (especially Article 3 (1) No. 2 and Article 3 (2) sentence 1 of the ProdSG), the GS body is obliged to identify and evaluate known risks to health during a risk assessment. In addition to the ProdSG the GS body must consider also other applicable legal provisions such as the Chemicals Prohibition Ordinance (ChemVerbotsV) or the Articles 30, 31 of the German Food and Feed Code (LFGB) or the REACH Regulation (EC) No 1907/2006, especially Annex XVII.

This document and, in particular, the testing instructions (Annexe) specify the requirements with respect to the contents of PAHs in products. Furthermore, the methodology for the evaluation by GS bodies is harmonised.

2 Basics

PAH contamination of materials is primarily due to the use of:

- PAH contaminated extender oils in rubber and flexible plastics (soft plastics)
- PAH contaminated carbon black as black pigment in rubber, plastics and paints
- hydrocarbon solvents (e.g. solvent naphtha)

PAH contamination has previously been detected not only in rubber but also in various types of plastic, e.g. ABS, PP and in different synthetic fibers, natural latex, paints as well as in materials treated with naphthalene.

3 Procedure

The GS body must take into account the following steps both in the process of awarding a new GS mark and within the framework of monitoring existing GS mark certificates:

1. Risk assessment
2. Categorisation
3. Test and evaluation

3.1 Risk assessment

The GS body must carry out a risk assessment and, in doing so, lay down which relevant contact/grip and operating surfaces of the product are to be considered for testing and which are not. And these shall be documented (this means that the GS body must first specify the contact/grip and operating areas, to which the requirements of the PAH document must be applied (specification of PAH relevance)). The risk assessment can be suspended with, where appropriate, if the respective Erfahrungsaustauschkreis (“Exchange of Experience Forum”, EK) has already defined a procedure for the product or product group regarding the contact/grip and operating surfaces to be tested. A reference to the EK’s definition shall be included in the documentation accordingly.

Materials that cannot be accessed or that can only be accessed using tools need not be considered, with the exception of samples with a conspicuous odour. Components that are rarely and only briefly accessible to the user during simple maintenance or expansion work do not need to be considered.

In principle, account must be taken of all contact/grip and operating surfaces that can come into direct contact with the skin or that can be put into the mouth (in the latter case regardless of accessibility) during intended or reasonable foreseeable use (but not misuse) .¹

3.2 Categorisation

Depending on the results of the risk assessment, the corresponding product parts are then to be categorised (see Table 1) and their actual PAH contents are to be analysed according to the analysis method as mentioned below. Existing test reports can be taken into account subject to compliance with the Grundsatzbeschluss (“principle decision”) ZEK-GB-2012-01

¹ However, in order to ensure a consistent and appropriate procedure during the awarding of GS marks, it is not generally necessary to analyse all freely accessible surfaces. The intention of this document is that only relevant contact/grip and operating surfaces are to be considered. It is not expedient to test all product parts or surfaces in order “to be on the safe side”.

rev.1 of the ZEK (“Central Exchange of Experience Forum”) and the requirements of this PAH document. Categorisation can be dispensed with if the respective Erfahrungsaustauschkreis (“Exchange of Experience Forum”, EK) has already defined a categorisation of the contact/grip and operating surfaces for a product or group of products.

Table 1 presents the maximum limits of PAH in materials of products, which shall not be exceeded.

The provisions of this document regarding the PAH contents are not applicable, if in other legal provisions corresponding or further stricter requirements for the PAH content are provided. This applies only to the material, component, or component group but not to the integral product as a whole. Materials and parts of the product that are not covered by other legislative provisions must be assessed within the framework of the procedure for awarding the GS mark in accordance with the requirements of this PAH document.²

It must be ensured that for each single PAH component the limit of quantification of 0.2 mg/kg can be actually achieved with the test procedure.

Meanwhile the influences of the procedure and the matrix, as well as measurement uncertainty and efficiency of extraction but also losses during purification must be taken into consideration.

As total amount of 15 PAHs, only those individual PAH content which is from 0,2 mg/kg and onwards will be calculated.

² Example: internal, accessible water-carrying parts in coffee machines getting in contact with food (e.g. water etc.) are subject to the legislation of the German Food and Feed Act Code (LFGB) and therefore are exempted from the application of this PAH documents. However, grip surfaces of coffee machines have to be assessed according to the requirements of this PAH document.

Table 1: Maximum PAHs limits for the materials with relevant contact/grip and operating surfaces that are to be categorised based on the results of the risk assessment

Parameter	Category 1	Category 2		Category 3	
		a. use by children	b. other consumer products	a. use by children	b. other consumer products
	Materials intended to be placed in the mouth, or materials coming into long-term contact with skin (more than 30s) during the intended use - in toys according to Directive 2009/48/EC or - for the use by children ^{a,b} up to 3 years of age				
Benzo[a]pyrene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[e]pyrene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[a]anthracene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[b]fluoranthene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[j]fluoranthene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[k]fluoranthene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Chrysen mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Dibenzeno[a,h]anthracene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[ghi]perylene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Indeno[1,2,3-cd]pyrene mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Phenanthrene, Pyrene, Anthracene, Fluoranthene mg/kg	< 1 Sum	< 5 Sum	< 10 Sum	< 20 Sum	< 50 Sum
Naphthalene mg/kg	< 1	< 2		< 10	
Sum 15 PAH mg/kg	< 1	< 5	< 10	< 20	< 50

^a A "child" is legally defined as a person before reaching the age of 14 years.

^b Use by children includes both active and passive direct contact by children.

^c Definition "short-term repetitive contact" taken from REACH Annex XVII entry 50 amendment (Regulation (EC) No.1272/2013)

^d According to the definition of the Product Safety Act (ProdSG) (Chapter 1 Article 2 No. 28) "foreseeable use" shall mean the use of a product in a manner that the person placing it on the market, has not intended, but which could be reasonably foreseeable.

3.3 Test and assessment

The testing instructions found in the annex describe the steps of sample preparation, extraction of the PAHs, purification of the extract, identification and quantification; these must be applied uniformly by all laboratories.

The GS body assesses the test results and decides whether the GS mark can be awarded provided that the other requirements are fulfilled.

4 Transitional regulations/periods

From 1 July 2020 (date of issuing the GS mark certificate), it is compulsory to apply this document when awarding the GS marks to products.

The document AfPS GS 2014:01 PAK will cease to be valid after 30 June 2020.

4.1 GS mark certificates, issued from 1 July 2020 onwards

Compulsory application of this GS specification from 1 July 2020 onwards (incl. ongoing procedures that are concluded after 1 July 2020)

4.2 GS mark certificates, issued before 1 July 2020

Existing GS mark certificates remain valid.

Annex: Test instructions

Harmonised method for determining polycyclic aromatic hydrocarbons (PAHs) in polymers

1 Aim and purpose

Determination of polycyclic aromatic hydrocarbons (PAHs) in polymer samples

2 Procedure

2.1 Brief description

2.1.1 Standard procedure

A representative partial sample is taken from the material and cut up into pieces with a maximum size of 2–3 mm using scissors, wire cutters, etc. Then, 500 mg of the sample is weighed and extracted with 20 ml of toluene (to which an internal standard has been added) for 1 h at 60 °C in an ultrasonic bath. An aliquot is taken from the extract once it has cooled down to room temperature. In the case of polymers (e.g. plastics or rubber products) for which matrix problems arise during the analysis, an additional purification step is carried out using column chromatography. Quantification is performed on a gas chromatograph with a mass-selective detector (GC/MSD) using the SIM method.

2.1.2 Procedure for insufficient quantities

If the total mass of material to be analysed is less than 500 mg, it should be proceeded as follows: Identical materials from this product item can be combined and considered as one sample. However, additional product specimens must not be used.

If less than 50 mg of material is available for individual samples, these are not tested.

If the available mass of chopped-up material is between 50 mg and 500 mg, the sample must be tested according to 2.1.1 and the quantity of toluene has to be converted or adjusted proportionally. The actual mass of the sample is to be recorded in the test report accordingly.

2.2 Equipment

- Ultrasonic bath: Minimum power 200 W with a bath surface of 706 cm², corresponding to 0.28 W/cm² without basket and with an internal or external thermostat.
- Gas chromatograph with a mass-selective detector

2.3 Chemicals and solutions

2.3.1 Chemicals

- Toluene
- Internal standards
 - Standard 1: naphthalene-d8
 - Standard 2: pyrene-d10 or anthracene-d10 or phenanthrene-d10
 - Standard 3: benzo[a]pyrene-d12 or perylene-d12 or triphenylbenzene

At least three internal standards must be added to the toluene extraction solvent.

- External standard: 15 PAH substances according to Table 1 or those listed under No. 3.2, as a mixture or individually
- Petroleum ether
- Silica gel
- Sodium sulfate

2.3.2 Calibration solutions

The concentrations of the calibration solutions must be chosen so that a three-point calibration covers a working range of 0.1 to 10 mg/kg in the samples. This corresponds to a concentration range of 2.5 to 250 ng/ml in the calibration solutions.

3 Preparation and measurement

3.1 Sample preparation

A representative partial sample is taken from the material. The samples to be analysed will be prepared by chopping up (using scissors, wire cutters, pliers, etc.) and should have a maximum size of 2–3 mm.

3.1.1 Extraction

500 mg sample is mixed with 20 ml toluene in a crimped glass ("vial"), to which the internal standards have already been added, and extracted for 1 h in an ultrasonic bath constantly at 60°C. For this purpose, the crimped glasses are placed or suspended in the ultrasonic bath without using a basket. Afterwards, the vials are taken out. After cooling down to room temperature and short shaking up, an aliquot of the extracts will be taken and measured directly or after dilution with toluene.

3.1.2 Column chromatographic purification step

For some polymers (e.g. plastic or rubber products), especially those that dissolve well in toluene under the described extraction conditions, it is necessary to purify the extract by means of silica gel adsorption chromatography.

For this purpose, a clean-up column with a faucet (approx. 220 x 15 mm) is filled with glass wool, 4 g of silica gel and 1 cm of sodium sulfate.

The silica gel is deactivated beforehand by adding 10% water (in a glass flask an appropriate amount of water is added to the silica gel, and the mixture is homogenised on the rotary evaporator for 1 h under standard pressure and room temperature. The silica gel can then be stored in the sealed glass flask at room temperature).

The packed column is conditioned with 10 ml of petroleum ether.

The aliquot of toluene extract is then evaporated to a volume of approx. 1 ml on the rotary evaporator and poured into the column. The pointed flask is rinsed out with approx. 20 ml of eluent, which is then also transferred to the clean-up column. The Elution is performed with 50 ml of petroleum ether. 1 ml of toluene is added to the collected petroleum ether eluate, which is then evaporated to a volume of approx. 1 ml under a nitrogen stream (e.g. on the TurboVap). This is then filled up to a defined volume with toluene, and the extract is analysed by GC-MS.

3.2 Measuring procedure

The method of determination to be applied is gas chromatography with a mass-selective detector in the SIM mode.

The following 15 PAH are to be determined:

- Naphtalene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Chrysene
- Benzo(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(i)fluoranthene
- Benzo(a)pyrene

- Benzo(e)pyrene
- Indeno(1,2,3-cd)pyrene
- Dibenzo(a,h)anthracene
- Benzo(g,h,i)perylene

3.2.1 Measuring conditions for gas chromatography

The equipment parameters (temperatures, columns, mass traces) may be chosen by the individual laboratory or are defined depending on the analytes.

3.2.2 Evaluation

Internal standards: at least three internal standards must be used. The internal standards and the correction ranges are defined as follows:

Parameters	Internal Standards with recommended reference
Naphthalene	naphthalene-d8
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
Chrysene	pyrene-d10 or anthracene-d10 or phenanthrene-d10
Benzo[b]fluoranthene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Benzo[k]fluoranthene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Benzo[j]fluoranthene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Benzo[a]pyrene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Benzo[e]pyrene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Indeno[1,2,3-cd]pyrene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Dibenzo[a,h]anthracene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene
Benzo[g,h,i]perylene	benzo[a]pyrene-d12 or perlyene or triphenylbenzene

- External calibration: for each individual PAH, at least a three-point calibration must be carried out with reference to the internal standardisation set out above. A working range of 0.1 to 10 mg/kg is recommended here.
- Concentrations above the calibration range can be determined by diluting the extract.

3.2.3 Limit of quantification

It must be ensured that for each single PAH component the limit of quantification of 0.2 mg/kg can be actually achieved with the test procedure.

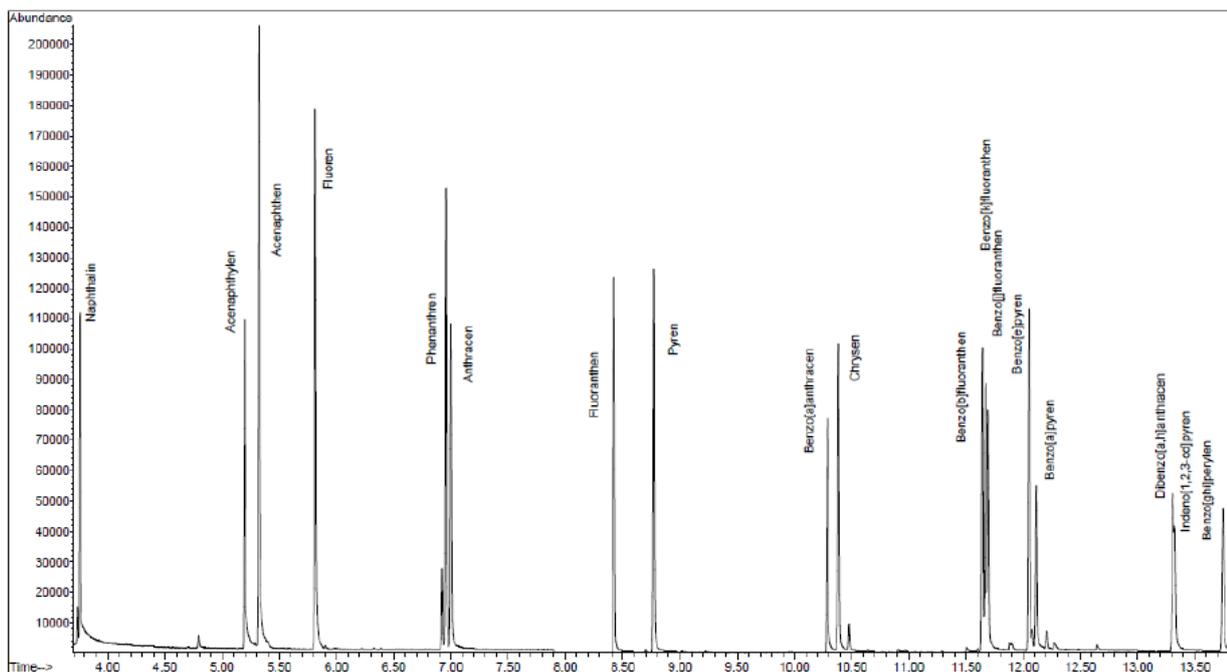
Meanwhile the influences of the procedure and the matrix, as well as measurement uncertainty and efficiency of extraction but also losses during purification must be taken into consideration.

3.3 Special characteristics

Due to its relatively high volatility compared to the other 14 PAH, naphthalene is a parameter, which is difficult to be evaluated in close-to-skin products. Experience from the testing institutes indicates that reductions of naphthalene from materials as well as secondary contamination have been observed. Therefore, the result obtained for naphthalene always shows only the current situation of the test sample at the time of measuring.

Annex: Gas Chromatographic Measurement Conditions (informative)

Injected quantity: 1µl, pulsed splitless
 Column: Rxi-PAH, 40m, ID0.18 mm, film thickness 0.07µm
 Carrier gas: H₂
 Injector temperature: 290°C
 Transfer line temperature: 340°C
 Initial temperature: 90°C → 0.7 min.
 Heating rates: 15°/min. → 120°C
 40°/min. → 170°C
 20°/min. → 340°C



Retention time (min.)	Substance	CAS RN
3.70	Naphthalene	91-20-3
6.95	Phenanthrene	85-01-8
7.00	Anthracene	120-12-7
8.45	Fluoranthene	206-44-0
8.80	Pyrene	129-00-0
10.30	Benzo[a]anthracene	56-55-3
10.40	Chrysene	218-01-9
11.62	Benzo[b]fluoranthene	205-99-2
11.66	Benzo[k]fluoranthene	207-08-9
11.70	Benzo[j]fluoranthene	205-82-3
12.05	Benzo[e]pyrene	192-97-2
12.15	Benzo[a]pyrene	50-32-8
13.35	Dibenz[a,h]anthracene	53-70-3
13.40	Indeno[1,2,3-cd]pyrene	193-39-5
13.85	Benzo[g,h,i]perylene	191-24-2