

# **Product Safety Commission (AfPS)**

## **GS Specification**

**Testing and assessment of polycyclic aromatic hydrocarbons (PAHs) in the course of awarding the GS mark**

**- Specification pursuant to article 21(1) no. 3 of the Product Safety Act (ProdSG) –**

AfPS GS 2014:01 PAK

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# Testing and assessment of polycyclic aromatic hydrocarbons (PAHs) in the course of awarding the GS mark

## Preliminary observations

On Aug. 4<sup>th</sup> 2014 the Product Safety Commission (AfPS) has assigned the requirements of PAH testing in the course of GS mark certification as specification according to art. 21 Product Safety Act (ProdSG) para. 1 no. 3. The implementation is achieved by means of this PAH document.

## 1. Purpose / Intention

Products (pursuant to the Product Safety Act) must comply with legal requirements to avoid health risks, e.g. art. 30 & 31 of the LFGB (Foodstuffs, Consumer Goods and Feedstuffs Code – LFGB), the Prohibition of Chemicals Ordinance, and the art. 3 of the ProdSG (Product Safety Act). This document and, in particular, the testing instructions (see Annex) specify the requirements with respect to the level of PAHs in products. In addition, the document harmonises the testing methodology for assessment by GS bodies.

## 2. Basics

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

- PAH contaminated softening oils in rubber and flexible (soft) plastics
- PAH-contaminated carbon black as a black pigment in rubber, plastics and paints.

PAH contamination has previously been detected not only in rubber but also in various types of plastic, e.g. ABS and PP, and various paints/coatings, as well as in a variety of natural materials.

## 3. Procedure

The GS body must take the following steps into account 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. Testing and assessment

### 3.1 Risk assessment

The GS body must carry out a risk assessment and, in doing so, define which relevant contact/grip and operating surfaces of the product are to be considered for testing and which are not, and must make a record of these (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 should be not applied, where appropriate, if the respective “Erfahrungsaustauschkreis” (“Exchange of Experience Group”, EK) has already defined a procedure for the product or product group with regard to the contact/grip

and operating surfaces to be tested. A reference to the EK's definition is to be included in the documentation accordingly.

Materials that cannot be accessed or that can only be accessed by using tools need not be assessed, with the exception of samples with a conspicuous odour.

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 during proper or foreseeable use (but not misuse).<sup>1</sup>

### 3.2 Categorisation

Depending on the results of the risk assessment, the corresponding product parts are then to be categorised (see Table 1) and to be analysed on their actual PAH content according to the analysis method below. Existing test reports can be taken into account if they are compliant with the "Grundsatzbeschluss" ("principle decision") ZEK-GB-2012-01 of the ZEK ("Central Exchange of Experience Group") and the requirements of this PAH document. Categorisation can be dispensed with if the respective "Erfahrungsaustauschkreis" ("Exchange of Experience Group", EK) has already defined a categorisation of the contact/grip and operating surfaces for a product or product group. Definitions for products or product groups from the individual EKs are published on the ZLS website<sup>2</sup> and apply from the time of publication.

Table 1 presents the maximum levels of PAH in product materials, which must not be exceeded. The provisions of this document with regard to the PAH content do not apply if other legislation lays down corresponding or further requirements for the PAH content. This applies only to the material or component/assembly and not to the 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 the PAH document.

It must be ensured that the method of testing can actually achieve the limit of quantification of 0.2 mg/kg for each individual PAH component<sup>3</sup>.

At the same time, method and matrix effects, as well as the measurement uncertainty, the efficiency of extraction and losses during purification must be considered.

Based on the findings of the United States Environmental Protection Agency (EPA) (according to the list in the ZEK document 04-11), the total of 18 PAHs (extended substance list of the AtAV, the predecessor committee of the AfPS) only considers PAH components whose level in the material is found to exceed 0.2 mg/kg.

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1 However, in order to ensure a consistent and appropriate procedure during the awarding of GS mark, it is not generally necessary to analyse all freely accessible surfaces. It is this document's intention to limit the consideration to relevant contact/grip and operating surfaces. It is not expedient to test all product parts or surfaces in order "to be on the safe side".

2 Homepage of ZLS (Central Authority of the Laender for Safety): <http://www.zls-muenchen.de>

3 Example: Water-carrying parts in coffee machines that come into contact with foodstuffs (e.g. water, etc.) are subject to the Food and Feed Code legislation and are therefore excluded from the PAH document's field of application. However, grip surfaces on the coffee machine must still be assessed according to the requirements of the PAH document.

**Table 1:** Maximum PAH levels to be complied with for the materials in 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	
		Materials indented to be put in the mouth, or materials of toys with intended long-term skin contact (longer than 30 s)	Materials not covered by category 1, with foreseeable skin contact for longer than 30 seconds (long-term skin contact) or repeated short-term skin contact <sup>1)</sup>	Toys in the scope of 2009/48/EC	Other products in the scope of ProdSG
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 E mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
DIBENZO(a,h)ANTHRACENE mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
BENZO(g,h,i)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
ACENAPHTHYLENE, ACENAPHTHENE, FLUORENE, PHENANTHRENE, PYRENE, ANTHRACENE, FLUORANTHENE mg/kg	<1 sum	< 5 sum	< 10 sum	< 20 sum	< 50 sum
NAPHTHALENE mg/kg	< 1	< 2		< 10	
Sum 18 PAH <sup>3</sup> mg/kg	< 1	< 5	< 10	< 20	< 50

\* Wording "short-term repetitive skin contact" from supplement to REACH annex XVII no. 50 (REGULATION (EU) No 1272/2013)

### **3.3 Testing 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 carrying out testing.

The GS body assesses the test results and decides whether the GS mark can be awarded in compliance with the other requirements.

### **4. Transitional regulations/periods**

From July 1<sup>st</sup> 2015 (issue date of the GS mark certificate), it is compulsory to apply this document when awarding the GS mark to products.

The document ZEK 01.4-08 will cease to be valid from June 30<sup>th</sup> 2015.

Since testing for PAH levels in products constitutes an overarching requirement for almost all of the members of all of the "Erfahrungsaustauschkreise" ("Exchange of Experience Groups"), the following procedure is defined:

#### **4.1 GS mark certificates, issued from July 1<sup>st</sup> 2015 onwards**

(incl. ongoing procedures that are concluded after July 1<sup>st</sup> 2015)

Compulsory application of this GS specification from July 1<sup>st</sup> 2015 onwards (exception: see 4.3).

#### **4.2 GS mark certificates, issued before July 1<sup>st</sup> 2015**

Existing GS mark certificates initially remain valid.

Within the framework of regular checks to monitor the manufacturing process (at the latest within one year or, in cases where the regular monitoring period is two years, within two years), the requirements under no. 3 of the ZEK ("Central Exchange of Experience Group") document with regard to the risk assessment must be taken into account, regardless of whether the product was found in the manufacturing facility or not. If, in the process, it is found that the corresponding requirements are not met, the GS mark certificate must be withdrawn immediately. The ZEK "Grundsatzbeschluss" ("principle decision") ZEK-GB-2006-01 must be complied with.

#### **4.3 Reissuing of existing GS mark certificates – exemptions**

For the reissuing of an existing GS mark certificate, immediate consideration is not required in the following circumstances:

If the company name is changed, new GS mark certificates are usually issued. However, since the product does not change in terms of construction or other properties, and the reissuing of the GS mark certificate is more or less a pure formality, it is not necessary to consider the requirements of the PAH decision until the time of the check which must be performed for the purposes of monitoring the manufacturing process.

(Please note: The reissuing of the GS mark certificate does not alter the previously defined periods for carrying out checks on the product's manufacturing process.)

The same applies by analogy when the holder of the GS mark certificate changes address provided none of the product's properties change and the product does not require an additional safety check.

The above procedure can also be applied in relation to duplicate certificates (also referred to as OEM certificates). In such cases, a review pursuant to the requirements of the PAH document must strictly be carried out by the time of the next product-manufacturing check according to the periods already defined in the “main certificate” or, at the latest, by December 28<sup>th</sup> 2015.

Monitoring intervals beyond this date are not permissible in such cases.

With regard to the OEM certificates and therefore also the “main certificates”, the PAH document – as specified – must be applied by December 28<sup>th</sup> 2015 at the latest.

## **Annex: Testing instructions**

### **Harmonised method for the determination of polycyclic aromatic hydrocarbons (PAHs) in polymers**

#### **1 Aim and purpose**

Determination of polycyclic aromatic hydrocarbons (PAHs) in polymer samples.

#### **2 Method**

##### **2.1 Brief description**

###### **2.1.1 Standard method**

A representative partial sample is taken of 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 into a container 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 Method for insufficient quantities**

If the total mass of material to be analysed is less than 500 mg, one should proceed as follows: Identical materials from the product 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 converted or adapted in proportion. The actual mass of the sample is to be recorded in the test report accordingly.

#### **2.2 Equipment**

- Ultrasonic bath with a minimum power of 200 W and a bath area of 706 cm<sup>2</sup>, corresponding to 0.28 W/cm<sup>2</sup>, without a 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 used; these are added to the extraction solvent (toluene).

- External standard: 18 PAH substances according to Table 1 or those listed under no. 3.2, as a mix 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 execution

### 3.1 Sample preparation

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

#### 3.1.1 Extraction

500 mg of the sample is placed in a glass "Bördelglas" ("vial"). To this 20 ml of toluene, previously amended with internal standards, are added. The sample is then extracted for 1 h in the ultrasonic bath at a temperature of 60 °C throughout. For this purpose, the vials are placed or suspended in the ultrasonic bath without using a basket. The vials are then removed, the extract is left to cool to room temperature and shaken briefly, and an aliquot is taken from the extract and measured either directly or following dilution with toluene.

#### 3.1.2 Column chromatography extraction 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 clean the extract using adsorption chromatography on silica gel.

For this purpose, a clean-up column with "Hahnschliff" ("stopcock") (approx. 220 mm 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 (the corresponding volume of water is added to the silica gel in a glass flask, and the mixture is homogenised on the rotary

evaporator for 1 h at 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. Elution is performed with 50 ml of petroleum ether. The collected petroleum ether eluate is amended with 1 ml of toluene and evaporated to a volume of approx. 1 ml under a nitrogen stream (e.g. on the TurboVap). This is then made 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 18 PAHs are to be determined:

- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Chrysene
- Benzo[a]anthracene
- Benzo[b]fluoranthene
- Benzo[k]fluoranthene
- Benzo[j]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 determined by the analytes.

#### 3.2.2 Analysis

Internal standards: at least three internal standards must be used. For these three standards, the internal standards and the correction ranges are defined as followed:

**Parameter Internal standards with recommended reference**

- |                          |  |
|--------------------------|--|
| • 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       |
| • 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[j]fluoranthene   | Benzo[a]pyrene-d12 or perylene-d12 or triphenylbenzene |
| • Benzo[a]pyrene         | Benzo[a]pyrene-d12 or perylene-d12 or triphenylbenzene |
| • Benzo[e]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 |
- 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**

The limit of quantification for material samples is 0.2 mg/kg per parameter.

**3.3 Special characteristics**

Because it is relatively volatile compared to the other 17 PAHs, naphthalene constitutes a parameter that is hard to assess in products that come into contact with the skin. Experience from the testing institutes indicates that it is possible to identify instances of both naphthalene depletion in materials and secondary contamination. The result obtained for naphthalene therefore only ever reflects the test specimen's current situation at the time of measurement.

**Annex: Measuring conditions for gas chromatography (for information)**

Injected volume: 1 µl pulsed splitless

Column: HT8 25m, ID 0.22mm, film

thickness: 0.25µm

Injector temperature: 280°C

Transfer-line temperature: 260°C

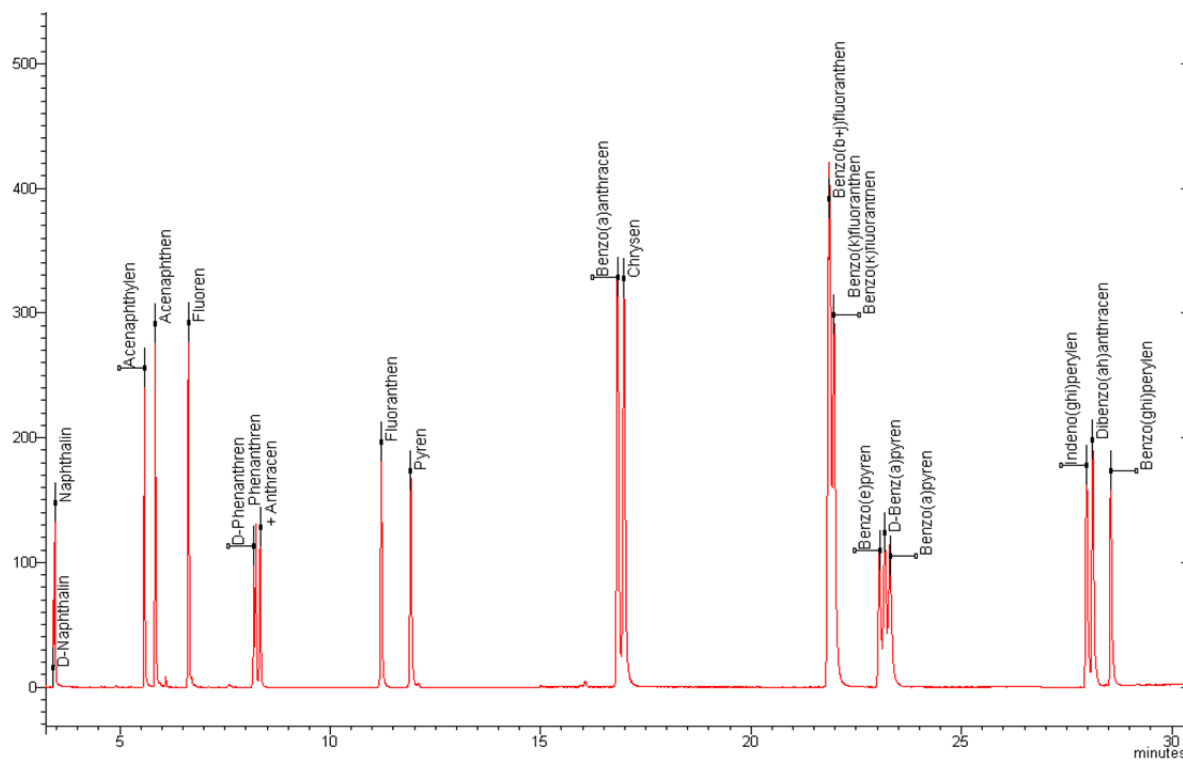
Initial temperature: 50°C

Initial time: 2 min

Heating rate: 11°C/min

Final temperature: 320°C

Final time: 8 min



3,418	D-naphthalene
8,186	D-phenanthrene
23,182	D-benzo[a]pyrene
3,459	Naphthalene
5,586	Acenaphthylene
5,845	Acenaphthene
6,634	Fluorene
8,235	Phenanthrene
8,337	Anthracene
11,217	Fluoranthene
11,914	Pyrene
16,830	Benzo(a)anthracene
16,982	Chrysene
21,860	Benzo(b+j)fluoranthene
21,964	Benzo(k)fluoranthene
23,055	Benzo(e)pyrene
23,302	Benzo(a)pyrene
27,974	Indeno(ghi)perylene
28,121	Dibenzo(ah)anthracene
28,549	Benzo(ghi)perylene