

(This document replaces document ZEK 01.1-08 at the date of publication)

Not authorized translation of original document

Testing and Validation of Polycyclic Aromatic Hydrocarbons (PAH) in the course of GS-Mark Certification

1. Aim

Products (technical work products and Consumer products must comply with legal requirements to avoid health risks, e.g. §§ 30 & 31 of the LFBG, the Prohibition of Chemicals Act (ChemVerbotsV), and the § 4 of the GPSG (Equipment and Product Safety Act). With this document and the attached test procedure the requirement regarding

PAH in products is substantiated. In addition, the test method is harmonized for the test institutes. The Board for Technical Work Equipment and Consumer Products (AtAV) has decided that the consideration of PAH for the GS certification of products has to be mandatory.

2. Basics

The main reasons for PAH contamination in materials is the use of:

- PAH contaminated softening oils in rubber and flexible (soft) plastics
- PAH contaminated soot as a black pigment dye in rubber and plastics and lacquer

PAH contamination could be proven so far not only in rubber, but also in various plastic materials, such as ABS, PP and various lacquer / coating and in natural materials.

3. Procedure

The following steps have to be considered by the GS-body either for new GS-mark-granting procedures as well as for the follow up of existing GS-mark certificates:

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

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3.1 Risk assessment

The GS-body has to perform a risk assessment and determine which (handle) areas of the product have to be considered for a test and which are not and to document this (this means that the GS-body has to decide first to which (handle) areas the requirements of PAH document should be applied (definition of relevance of PAH)). The risk assessment may be omitted if the respective exchanges group has already decided an approach for the product or the product group with respect to the (handle) areas, which need to be tested. The reference to the EK's determination has to be documented.

Materials that are not accessible or only accessible by use of a tool must not be assessed.

Basically, all (handle) areas need to be taken into account which can be touched during intended use or foreseeable misuse (but not abuse) or which can be put in the mouth. ¹

Materials that may contain PAHs are, for example, elastomers (plastics and rubber materials) and black or dark colored polymers.

3.2 Categorization

Depending on the outcome of the risk assessment the relevant parts of the product are then categorized (see Table 1) and measured for the actual content of PAH according to the method of analysis below. Existing test reports may be considered if the ZEK-principle decision ZEK-GB-2000-01 and the requirements of this PAH document are met. The categorization may be omitted if the respective experience group for a product or a product group has decided on a categorization of the (handle) areas. Provisions for products or product groups of the various experience exchange committees will be published on the ZLS website published and will apply from the date of publication.

The maximum levels of PAHs contained in materials of products are listed in Table 1.

The provisions of this document regarding the PAH content do not apply in case other legislation specifies appropriate or more stringent requirements for PAH content. This applies only to the material or component or assembly and not for the whole product. Materials and parts of the product, which are not covered by other legislation are to be considered during the GS-mark recognition procedure as required by the PAH document.²

It must be ensured that the detection limit of 0.2 mg / kg for each individual PAH component actually can be demonstrated.

In the sum of all 16 PAH according to EPA (Environmental Protection Agency) only those with a result over the 0.2 mg/kg shall be taken into account.

¹ To ensure a uniform and fair approach of the GS-bodies generally not all freely accessible areas should be examined. Intention of the document is that only relevant handle) areas to be considered. It is not targeting, "for safety reason" to examine all product parts or areas

² Example: water carrying parts in coffee machines, which are in contact with food (such as water, etc.) are subject to the LFGB legislation and are therefore exempt from the application of PAH document.. Grip surfaces of the coffee machine, however, further are required to be assessed in accordance with the requirements of PAH.

Table 1: Limits for PAH in Products

Parameter	Category 1	Category 2	Category 3
	Material indented to be put in the mouth, or materials of toys for children <36 months with normal skin contact ²⁾	Materials that are not included in Category 1, with predictable skin contact for longer than 30 seconds (long-term skin contact)	Materials that are not included in Category 1 or 2, with predictable skin contact up to 30 s (short-term skin contact)
Benzo[a]pyrene Mg/kg	Not detectable (< 0.2) ¹⁾	1	20
Sum 16 PAH (EPA) mg/kg	Not detectable (< 0.2) ¹⁾	10	200

¹⁾ If the limits of category 1 are surpassed but the limits of category 2 still met, the confirmation of suitability of contact with foodstuff or the oral mucosa can be verified by an additional specific migration test of the PAH components according to EN 1186, ff. and § 64 LFBG 80.30-1. The results of the migration test shall be evaluated according to law criteria for foodstuff.

²⁾ according to the provisions of EK 2.

3.3. Test and Evaluation

The steps *Sample Preparation, Extraction of PAHs, Purification of the Extract, Identification and Quantification* are described in the attached test instruction and must equally be applied by all testing laboratories.

The GS-body evaluates the test result and decides whether the GS-mark may be granted based on compliance with the other requirements.

4. Transition arrangements

4.1 Transition periods

The application of ZEK document ZEK 01-08 is, by virtue of an AtAV decision dated 2007-11-20, mandatory for GS mark certifications as of 2008-04-01.

Since the evaluation of PAH contents in products represents a comprehensive requirement to almost all members of all EKs, ZLS has specified the following procedure:

4.1.1 Certificates, date of issue from 2008-04-01 onwards (including ongoing projects, which will be completed after 2008-04-01):

Mandatory application of the PAH document ZEK 01-08 from 2008-04-01 onwards, respectively ZEK 01.1-08 from date of publication (exceptions: see 4.1.3).

4.1.2 Certificates, issued before 2008-04-01

For the time being, existing GS certificates remain valid.

Within the framework of periodical control measures (at the latest within 1 year respectively. in those cases, where the surveillance period is two years, within two years) the requirements of paragraph 3 of the PAH document according to the risk analysis have to be considered, regardless whether the product was inspected in the factory or not. In case it can be concluded that the respective requirements are not met, the certificate has to be withdrawn immediately. ZEK-principle decision ZEK-GB-2006-01 has to be respected.

4.1.3 Re-issue of existing GS-Certificates – Exceptions

For the following cases, an immediate consideration is not requested when re-issuing a current GS Mark Certificate:

If the company name has been changed, normally new GS Mark Certificates are issued. Since the construction of the product as well as other properties are not modified and therefore the re-issue of the GS Mark Certificate is a formal procedure only, the requirements of the PAH Decision shall be considered during the next factory surveillance.

(Remark: The re-issue of a GS Mark Certificate does not influence and change the fixed intervals for the performance of surveillance measures for the production of the product.)

The same applies in case the GS Mark Certificate Holder moves to another place, as far as the properties of the product are not modified and no additional safety-related check of the product is necessary.

As far as Second-Certificates (OEM-Certificates) are concerned, the same procedure can be applied. In these cases, a check according to the requirements specified in the PAH document has to be made until the next surveillance measure for the production of the product which has been scheduled for the product covered by the „Main Certificate“, but not later than 31 March 2009. Other surveillance intervals are not allowed.

Regarding the OEM Certificates and therefore also the „Main Certificates“ the PAH document has to be implemented - as stipulated – **until 31 March 2009** at the latest.

Test Instruction

Harmonized Method for Determination of polycyclic aromatic Hydrocarbons (PAH) in Plastic Sampling

ZEK
01.2-08

1 Aim

To identify PAH polycyclic aromatic hydrocarbons in plastic sampling (material).

2.1 Short description of the procedure

2.1.1 Standard Procedure

A representative partial sample is taken from the material and cut with scissors (or similar) into particles of max 2-3 mm in size. Of that 500 mg shall be weighed for extraction. Use 20 ml toluene mixed with internal standard. Place for 1 hour into the ultrasonic bath at a temperature of 60° C for extraction. After cooling to room temperature take an Aliquot from the extract. The quantification is done with a gas chromatograph with a mass specific detector (GC-MSD) in SIM method.

2.1.2 Procedures in case of small quantities

Should the **total** mass of material to be analyzed be below 500 mg, the following applies: Identical materials of the same product can be united and be considered to be as one sample. Additional product samples may not be used.

Is for individual samples **less than 50 mg** of material available, they will not be tested.

If the available mass of the crushed material is only between 50 mg and 500 mg, then the sample has to be tested according to 2.1.1 and the amount of Toluol is to be converted proportional or adapted. The actual mass of the sample has to be listed in the in the test report.

2.2 Equipment

- Ultrasonic bath: minimum power is 200 W for a bath surface of 706 cm which compares to 0,28 W/cm² without basket with internal or external thermostat (temperature controller)
- Gas chromatograph with mass selective detector

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2.3 Chemicals & solutions

2.3.1 Chemicals

- toluene
- Internal standards:
 - Standard 1: naphthalene - d8
 - Standard 2: pyren-d10 or anthracene-d10, or phenanthrene-d10
 - Standard 3: benzo(a)pyrene-d12 or perylene-d12 or triphenylbenzene

At least 3 internal standards shall be used and mixed with toluene as extraction agent.

- External standard: 16 PAH-substances according to EPA, mixed or individual
- Petroleum ether
- Silica gel
- Sodium sulphate

2.3.2 Calibration solutions

The concentration of the calibration solutions must be selected in such way that a 3-point-calibration covers the range of the samples from 0.1 to 10 mg/kg. This compares to a concentration range in the calibration solutions of 2.5 to 250 ng/ml.

3.1 Sample preparation

Take a representative partial sample from the material. The dimensions of the particles shall not be larger than 2-3 mm. Use scissors, side cutters, pliers to generate the particles from the sample.

3.1.1 Extraction

500 mg of the sample shall be mixed with the toluene (already mixed with the internal standards) in a (flange-)glass. This is then placed into the ultrasonic bath for 1 hour at constant 60°C for extraction. Place the glasses into the bath standing without the basket or hang them. Afterwards the glasses are taken out and an aliquot of the extract is taken after cooling to room temperature and short shaking. Measure directly from the aliquot or after thinning with toluene.

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3.1.2 Column chromatographic extract purification step

Some plastic or rubber products, especially those that under the described extraction conditions were largely resolved with toluene, a cleaning of the extract by silica gel-Adsorption chromatography is necessary.

A Clean-up column with Hahnschliff) Hahn cut (approximately 220 x 15 mm) will be filled with glass wool, 4 g silica gel and 1 cm sodium sulfate.

The silica gel will be deactivated by the addition of 10% water. (the silica gel in the glass flask will be mixed with the required amount of water and then homogenized for 1 h at the Rotary evaporator at 760 Torr and room temperature. The gel can then be stored in the closed glass bulb at room temperature).

The conditioning of the packed column has to be done with 10 ml of petroleum ether.

Thereafter the Toluolextraktaliquot in the rotation evaporator will be reduced to about 1 ml and added to the column. The Spitz flask will be rinsed with about 20 ml Elution, which is also added to the Clean-up column. The elution is done with 50 ml of petroleum ether. The caught Petrolethereluat will be mixed with 1 ml of toluene and reduced with nitrogen to about 1 ml on the Turbo Vap. Then it will be filled up with toluene to a defined value and the extract then analyzed by using GC-MS.

3.2 Measurement procedure

The determination method to be used is the gas chromatography with mass selective detection in SIM Mode.

The following 16 PAH must be identified according to EPA:

- NAPHTHALENE
- ACENAPHTHYLENE
- ACENAPHTHENE
- FLUORENE
- PHENANTHRENE
- ANTHRACENE
- FLUORANTHENE
- PYRENE
- CHRYSENE
- BENZO(a)ANTHRACENE
- BENZO(b)FLUORANTHENE
- BENZO(k)FLUORANTHENE
- BENZO(a)PYRENE
- INDENO(1,2,3-cd)PYRENE
- DIBENZO(a,h)ANTHRACENE
- BENZO(g,h,i)PERYLENE

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3.2.1 Gas Chromatographic Measurement Conditions

The equipment parameters (temperature, columns, mass traces) are to be decided by the lab respectively, by its staff analysts.

3.2.2 Evaluation

Internal standards: use of at least 3 internal standards. They and the correction range are defined as follows:

Parameter	Int. Standards with recommended reference
NAPHTHALENE	naphtalene - 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(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

- External calibration: for each single PAH at least one 3-point-calibration with reference to the afore mentioned internal standardization must be done. Hereby a work range of 0.1 - 10 mg/kg is recommended
- Concentrations above the calibration range can be determined by thinning of the extract.

3.2.3 Determination limit

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

Test Instruction
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3.3 Special characteristics

Based on its relative volatility against the other 15 PAH (according to EPA), naphthalene represents a parameter difficult to evaluate in close to skin products.

Experience of the testing bodies show that loss of naphthalene as well as secondary contamination can be found.

The developed naphthalene result will always only show the momentary situation of the test sample at the time of measurement.

Attachment: gas chromatic measurement conditions (informative)
See page 13 of the ZEK document.