

# *Not authorized translation of original document*

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

*Based on the document ZEK 01-08 issued by the Central Experience Exchange Committee (ZEK) in connection with the German Accreditation Body for GS Mark issuing Bodies (ZLS) the following shows the translated document.*

### **1. Aim**

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
- PAH contaminated lacquers
- naphthalene as preservative for transport and storage

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 (preserving agent for bristle of brushes, leather, wood etc).

### **3. Requirements**

The limits for PAH that must be met for materials of consumer goods are stated in table 1. The test procedure must ensure at least a detection limit of 0.2 mg/kg for each of the PAH components.

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.

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Table 1: Limits for PAH in Products

Parameter	Category 1	Category 2	Category 3
	Material in contact with foodstuff, or materials intended to be put in the mouth and toys for children aged < 36 months	Materials with foreseeable contact to skin for longer than 30 seconds (long-term skin contact) and toys not covered by category 1	Materials with foreseeable contact to skin up to 30 seconds (short term skin contact) or without skin contact.
Benzo[a]pyrene mg/kg	Not detectable (< 0.2)*	1	20
Sum 16 PAH (EPA) mg/kg	Not detectable (< 0.2)*	10	200

\* 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 LFGB 80.30-1. The results of the migration test shall be evaluated according to law criteria for foodstuff.

## **4. Procedure**

### **4.1 Scope of testing / sampling**

The following components and materials need to be covered during a PAH examination of products: All (grip) surfaces, which may contain PAH and that are touched or put into the mouth during intended use or foreseeable misapplication (however not misuse).

The following materials are examples that may contain PAH

- elastomers (plastics and rubber materials)
- black or dark colored polymers
- coatings and varnish
- materials treated with conservation agents (naphthalene) (e.g. leather products, wood, bast and natural bristles).

The testing body has to evaluate which parts of the product have to be considered for testing and which parts not and to document it accordingly.

The following materials do not need to be included in the evaluation:

- Materials which are not accessible or only accessible with the help of tools
- Materials which, through a risk analysis, are identified as not relevant for testing for PAH

### **4.2 Testing**

The following steps are described in the attached test instruction and have to be used by all test laboratories in exactly the same way.

- preparation of samples
- extraction of PAH
- identification and quantification

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## **Test Instruction Harmonized Method for Determination of PAH in Plastic Sampling**

### **1 Aim**

To identify PAH Polycyclic Aromatic Hydrocarbons in plastic sampling (material).

### **2 Description**

#### 2.1 Short description of the 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.

#### 2.2 Equipment

- Ultrasonic bath: minimum power is 200 W for a bath surface of 706 cm<sup>2</sup> which compares to 0,28 W/cm<sup>2</sup> without basket with internal or external thermostat (temperature controller)
- Gas chromatograph with mass selective detector

#### 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 to be mixed with toluene as extraction agent.

- External standard: 16 PAH-substances according to EPA, mixed or individual.

##### 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 Process**

#### 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.

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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.

### 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
- BENZO(a)ANTHRACENE
- CHRYSENE
- INDENO(1,2,3-cd)PYRENE
- BENZO(b)FLUORANTHENE
- BENZO(k)FLUORANTHENE
- BENZO(a)PYRENE
- DIBENZO(a,h)ANTHRACENE
- BENZO(g,h,i)PERYLENE

#### 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:

- |                          |  |
|--------------------------|--|
| - 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      |
| - INDENO(1,2,3-cd)PYRENE | benzo(a)pyrene-d12 or perylene-d12 or triphenylbenzene |
| - 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 |

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- 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 aforementioned 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.

### 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 6 of the ZEK document