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

1 Aim

Products (according to ProdSG) must comply with legal requirements to avoid health risks, e.g. §§ 30 & 31 of the LFBG, the Prohibition of Chemicals Act, and the § 3 of the ProdSG. 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 validation by GS bodies.

The Board for Technical Work Equipment and Consumer Products (AtAV) on Nov. 20, 2007 has demanded that the consideration of the test for PAH for the GS certification of products has to be mandatory. The implementation takes place by means of this PAH document.

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

3 Procedure

The following steps are to be considered by the GS body at new GS mark awards as well as in the frame of monitoring of existing GS mark certificates:

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

3.1 Risk Analysis

The GS body has to perform a risk analysis and at the same time has to stipulate which (grip) surfaces are possible for a test and which are not as well as to document this. This means, that the GS body first of all has to stipulate for which (grip) surfaces the requirements of the PAH document apply (stipulation of the PAH relevance). As the case may be, the risk analysis can be omitted, if the circle of exchange of experience has already determined a procedure for the product and the product group respectively regarding the (grip) surfaces to be tested. The reference to the EK regulation is to be documented accordingly.

Materials which are not accessible or only accessible with the help of tools needn't to be evaluated. Basically all (grip) surfaces are to be considered, which during intended use or foreseeable misapplication (however not misuse) can be touched or put into the mouth¹

¹ In order to guarantee a consistent and adequate procedure for the GS mark award not all free accessible surface should be checked generally. Intention of this document is that actually only relevant (grip) surfaces are considered. It is no target-oriented to test all product parts or surfaces "for safety".

(This document supersedes the document **ZEK 01.2-08/ZEK 01.3-08** with the date of publications)

Materials which may contain PAH are e.g. elastomeres (plastics and rubber materials) as well as black or dark coloured polymers.

3.2 Categorization

Depending on the result of the risk analysis afterwards the respective products are to be categorized (see table 1) and to be tested regarding the actual content of PAH according to the method of analysis mentioned below. Existing test reports can be considered provided that the ZEK Principle Decision ZEK-GB-2000-01 and the requirements of this PAH document are observed. The categorization can be omitted, if the respective circle of exchange of experiences for a product and a product group respectively has already stipulated a categorization of the (grip) surfaces. Stipulations to products and/or product groups of the individual circles of exchange of experience are published on the ZLS homepage and be valid with the date of publication.

The limits for PAH that must be met for materials of consumer goods are stated in table 1.

The regulations of this document regarding the PAH content do not apply if in other laws corresponding or advanced requirements to the PAH content are given. This applies only for the material or component and assembly group respectively and not for the whole product. Materials and parts of the product which are not covered by other laws are to be evaluated in the frame of the GS mark award according to the specifications of the PAH document².

It must be ensured that the detection limit of 0.2 mg/kg for each of the PAH single component can actually be proved by the test procedure.

In the sum of all **18** PAH according **(extended AtAV material list according to EPA on basis of ZEK document 04-11)** only those PAH components are take into account, which have been specified in the material over the 0.2 mg/kg.

² Example: Water-conducting in coffee machines which are in contact with food (e.g. water etc.) are subjected to the law LFGB, and therefore excluded from the practice of the PAH document. Grip surfaces of the coffee machine however have to be evaluated according to the requirements of the PAH document further on.

Table 1: Limits for PAH content for material of (grip) surfaces, which are to be categorized based on the results of the risk analysis.

Parameter	Category 1	Category 2	Category 3
	Materials indented to be put in the mouth, or materials of toys for children aged < 36 months with intended skin contact ²⁾	Materials not covered by category 1, with foreseeable skin contact for longer than 30 seconds (long-term skin contact)	Materials not covered by category 1 or 2 with foreseeable skin contact up to 30 seconds (short term skin contact)
Benzo[a]pyrene mg/kg	Not detectable (< 0.2) ¹⁾	1	20
Sum 18 PAH ³⁾ 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 stipulations of the EK2.

³⁾ (extended AtAV material list according to EPA on basis of ZEK document 04-11)

3.3 Test and Evaluation

The steps of the *preparation of sampling, extraction of the PAH, purification of the extract, identification and quantitation* are described in the attached test instruction and have to be applied by all performing test laboratories in equal measure.

The GS body evaluates the test result and decides whether the GS mark can be awarded subject to the other requirements.

³⁾ extended AtAV material list according to EPA on basis of ZEK document 04-11

4 Transition Regulations

4.1 Transition Periods

At the award of the GS mark for products this document is mandatory from 1st July, 2012 onwards.

The documents ZEK 01.2-08 is getting invalid from 1st July, 2012

As the test regarding the PAH contents in products represents a comprehensive requirement to nearly all members of the circles of exchange of experience the following procedure is determined by the ZLS:

4.1.1. **GS mark certificates, date of issue from 2012-07-01 onwards (including ongoing projects, which will be completed after 2012-07-01)**

Mandatory application on the PAH document ZEK 01.4-08 from 1st July, 2012 onwards (exception: see 4.1.3).

4.1.2. **GS mark certificates, issued before 1st July, 2012**

For the time being, existing GS mark certificates remain valid.

Within the framework of regular control measures for monitoring the production (at the latest within 1 year and in those cases respectively, when the regular control period is two years, within 2 years) the requirements of paragraph 3 of the EK 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. The ZEK Principle Decision ZEK-GB-2006-01 is to be observed.

4.1.3 **New issue of existing GS mark certificates – Exceptional Rules**

An immediate consideration is not necessary in case of a new issue of an existing GS mark certificate for the following reasons

In case that the trade name is changed normally new GS mark certificates are issued. As the product is not modified regarding the construction as well as other properties and the new issue of the GS mark certificate is more or less a mere formality, a consideration of the requirements of the PAH resolution is only necessary when the control measure for monitoring the production takes place.

(Note: With the new issue of the GS mark certificate the already specified periods for the control measures of the manufacture of the product do not change.)

The same applies in an analogous manner at a relocation of the GS mark certificate owner provided that the product is not changed concerning all properties and no additional safety-related examination of the product is necessary.

For the area of the secondary certificates (OEM certificates) the same procedure mentioned

(This document supersedes the document **ZEK 01.2-08/ZEK 01.3-08** with the date of publications)

above can be applied. In these cases an examination according to the specifications of the PAH document until the next control measure for the manufacture of the product is mandatory. This has to take place according the already determined periods of the “main certificate” and until 30th June, 2013 at the latest. Control periods in excess thereof are not allowed in these cases.

Concerning the OEM certificates and therefore also for the „main certificates“ the PAH document has to be applied – as stipulated – until **30th June, 2013** at the latest.

Test Instruction

Harmonised Method for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in **Polymere**

1 Aim

To identify PAH Polycyclic Aromatic Hydrocarbons in **Polymere** sampling.

2.1 Short Description of the Procedure

2.1.1 General Procedure

A representative partial sample is taken from the material and cut with scissors, side cutters etc. 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. At **Polymeres** (e.g. plastic or rubber material respectively) at which matrix problems occur during the examination, an additional column-type chromatographic purification step is performed.

The quantification is done with a gas chromatograph with a mass specific detector (GC-MSD) in SIM method.

2.1.2 Procedure with Minor Quantities

If the total mass of the material for the evaluation is below 500 mg, the following applies:

Identical materials of the product can be united and regarded as one sample.

Additional product samples may not be used.

Individual samples will not be examined, if less than 50 mg material is available for these samples.

If the available mass of the cut up material amounts to only between 50 mg and 500 mg, then the sample is to be examined according 2.1.1, and the toluene quantity is to be converted proportional respectively to be adapted. The actual mass of the sample is to be specified accordingly in the test report.

2.2 Equipment

- Ultrasonic bath: minimum power is 200 W for a bath surface of 706 cm² 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 and 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: 18 PAH-substances according to **material list**³, mixed or individual.
- Petroleum ether
- Silicia 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 extended AtAV material list according to EPA on basis of ZEK document 04-11

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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.

3.1.2 Column-type chromatographic extract purification step

At some **Polymeres** (e.g. plastic or rubber material respectively), especially such, which are dissolved with toluene to a very large degree under the described extraction conditions, a purification of the extract with silica gel adsorption chromatography is necessary.

Hereto a clean-up column with "Hahnschliff" (ca. 220 x 15 mm) with fibreglass, 4 g silica gel and 1 cm sodium sulphate.

The silica gel first is to be deactivated by addition of 10 % water (in the glass flask the silica gel is mixed with the appropriate amount of water and afterwards 1 h homogenized on the rotary vaporizer at 760 Torr and room temperature. The silica gel then can be stored in the closed flask at room temperature).

The conditioning of the packed column is done with 10 ml petroleum ether.

Then the toluene extract aliquot in the rotary vaporizer is reduced to ca. 1 ml and given upon the column. The pointed piston is rinsed with ca. 20 ml elution agent which is also transferred to the clean-up column. The elution is done with 50 ml petroleum ether. The collected petroleum ether eluate is spiked with 1 ml toluene and reduced at the TurboVap with nitrogen to ca. 1 ml. Afterwards it is replenished with toluene to a defined volume and the extract then is analysed by means of GC-MS.

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Harmonised Method for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in **Polymere**

3.2 Measurement Procedure

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

The following **18** PAH must be identified according to **material list**³:

- 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 Gas Chromatographic Measurement Conditions

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

Test Instruction

Harmonised Method for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in **Polymere**

3.2.2 Evaluation

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

Parameter	Internal 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-dl 0, or phenanthrene-dl 0
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-dl 2 or perylene-dl 2 or triphenylbenzene
BENZO(g,h,i)PERYLENE	benzo(a)pyrene-d!2 or perylene-dl 2 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.

3.3 Special characteristics

Based on its relative volatility against the other **17** PAH according to **material list**³, 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.

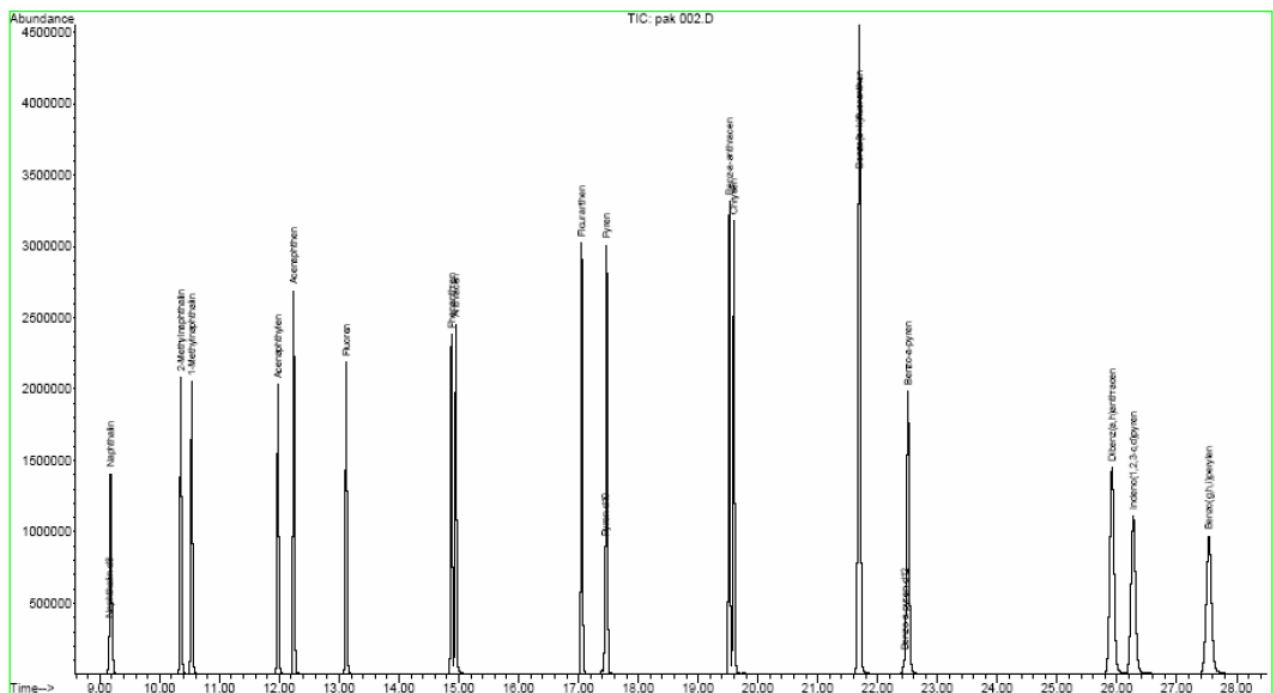
The developed naphthalene result will always only show the momentary situation of the test sample at the time of measurement.

Test Instruction

Harmonised Method for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in **Polymere**

Attachment: Gas Chromatic Measurement Conditions (informative)

Injected amount: 1 µl, pulsed splitlos
 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: 2min
 Heating rate: 11°C/min
 Final temperature: 320°C
 Final time: 8 min



Parameter	RT ca min	MOL-MASS
Naphthalene	10,5	128
Aceraphthylene	14,5	152
Aceraphthene	14,8	153
Fluorene	16,0	166
Phenanthrene	18,3	178
Anthracene	18,4	178
Fluoranthene	21,1	202
Pyrene	21,7	202
Chrysene	24,5	228
Benzo(a)anthracene	24,6	228
Benzo(b)fluoranthene	27,0	252
Benzo(k)fluoranthene	27,0	252
Benzo(a)pyrene	27,8	252
Indeno(1-;2,3-cd)pyrene	31,2	276
Dibenzo(ah)anthracene	31,5	278
Benzo(ghi)perylene	32,7	276

Note: In this evaluation the values of BENZO(j)FLUORANTHENE and BENZO(e)PYRENE are not considered