Fraunhofer
IVV

Test report, part 1

Determination of metals soluble in hydrochloric acid from a graphite films

Customer:	SGL Carbon GmbH 86400 Meitingen
IVV Order no.:	PA/4148/17
Date of order:	31.03.2017
Sample receipt:	31.03.2017
Testing period:	04.04. – 13.04.2017
Date of report	09.05.2017
Sample storage:	Remaining test material will be stored in the institute for six months.
Total pages of the report:	6

The results relate only to the investigated samples.

1 Scope

The investigated graphite material is intended to be used in food processing machines (repeated use, huge amounts of food) as sealing materials and not in food packaging applications.

In the USA there are no statutory regulations for the composition resp. the purity of graphite (CAS 7782-42-5) in contact with food. However, substances used as components of articles that contact food shall be of a purity suitable for its intended use according to 21 CFR 174.5 "General provisions applicable to indirect food additives".
The restriction of various metals/elements in the graphite film is determined according to the BfR recommendations IX (pigments) and LII (filler). For this purpose the substances soluble in 0.07 N hydrochloric acid were analysed according DIN 53770 part 1.

2 Sample material

The customer provided the following sample material:

Sample: SIGRAFLEX® graphite film F05010Z

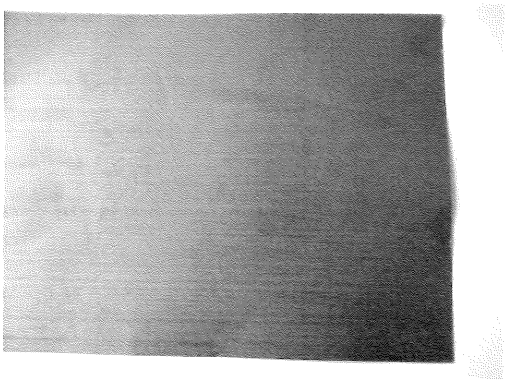

Figure 1: Sample – SIGRAFLEX® graphite film F05010Z

3 Method

Determination of metal content soluble in 0.07 N hydrochloric acid

Extraction and quantification was determined by an external laboratory which is accredited for both methods.

The extraction with 0.07 N hydrochloric acid was performed according to DIN 53770 part 1.

The elements were determined quantitatively according to DIN EN ISO 17294-2 "Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements". Rhodium and Rhenium are used as internal standards. Calibration was performed by using multi element standards (simple linear).

4 Results

Table 1: Quantification of element content soluble in 0,07 N hydrochloric acid

Element	Symbol	Soluble content [mg/kg]	Quantification limit [mg/kg]
Aluminium	Al	< 1	1
Arsenium	As	< 0.1	0.1
Barium	Ba	< 0.5	0.5
Cadmium	Cd	< 0.1	0.1
Cerium	Ce	< 0.1	0.1
Cobalt	Co	< 0.1	0.1
Chromium	Cr	< 0.5	0.5
Caesium	Cs	< 0.1	0.1
Copper	Cu	< 0.5	0.5
Iron	Fe	1	1
Gallium	Ga	< 0.1	0.1
Hafnium	Hf	< 0.1	0.1
Mercury	Hg	< 0.02	0.02
Lanthanum	La	< 0.1	0.1
Lithium	Li	< 0.1	0.1

Manganese	Mn	< 1	1
Molybdenum	Mo	< 0.5	0.5
Nickel	Ni	< 0.5	0.5
Lead	Pb	**0.05**	0.05
Rubidium	Rb	< 0.1	0.1
Antimony	Sb	< 0.1	0.1
Selenium	Se	< 0.5	0.5
Tin	Sn	< 0.5	0.5
Strontium	Sr	< 1	1
Tantalum	Ta	< 0.1	0.1
Tellurium	Te	< 0.1	0.1
Thorium	Th	< 0.1	0.1
Titanium	Ti	< 1	1
Uranium	U	< 0.1	0.1
Vanadium	V	< 0.5	0.5
Wolfram	W	< 0.5	0.5
Yttrium	Y	< 0.1	0.1
Zinc	Zn	< 1	1
Zirconium	Zr	< 1	1

5 Food regulatory assessment

In the 0.07 N hydrochloric acid extraction of the investigated sample material iron (Fe) and lead (Pb) were found at the respective quantification limits.

Iron, elemental (CAS 7439-89-6) is defined as ´generally recognized as safe´ (GRAS) according 21 CFR 184.1375 and therefore no limits for the use in food contact materials exist.

Lead is not regulated according the 21 ´Code of Federal Regulations´ (CFR) for the use in food contact materials. For the food regulatory assessment BfR recommendation IX and LII are used.
According to the BfR recommendation IX on pigments and BfR recommendation LII on fillers the lead content soluble in 0.07 N hydrochloric acid must not exceed 0,01 % (100 mg/kg).

The BfR recommendation IX on pigments and BfR recommendation LII on fillers gives the following limits for the content of elements which are soluble in

hydrochloric acid according to DIN 53770 (see Table 2 and Table 3).

Table 2: Restrictions of elements soluble in 0.07 N hydrochloric acid according to BfR recommendation IX

Element	Symbol	Restriction [%]	Restriction [mg/kg]
Lead	Pb	0.01	100
Arsenium	As	0.01	100
Mercury	Hg	0.005	50
Selenium	Se	0.01	100
Barium	Ba	0.01	100
Chromium	Cr	0.1	1000
Cadmium	Cd	0.01	100
Antimony	Sb	0.05	500

Table 3: Restrictions of elements soluble in 0.1 N hydrochloric acid according to BfR recommendation LII

Element	Symbol	Restriction [%]	Restriction [mg/kg]
Lead	Pb	0.01	100
Arsenium	As	0.01	100
Mercury	Hg	0.0005	5
Barium (from Barium sulfate)	Ba	0.01	100
Cadmium	Cd	0.01	100
Antimony	Sb	0.005	50

The quantification limits obtained by the used analytical method are below these restrictions given in the BfR recommendations IX and LII.

Therefore, the investigated graphite film is in compliance with the specifications for metals/elements given in the BfR recommendations IX and LII.

6 Signatures

Fraunhofer Institute
Process Engineering
and Packaging

Dr. Diana Kemmer
(Dep. Head of Migration Laboratory)

Freising. 09.05.2017

Maria Gierl
(Scientist in charge)

Fraunhofer
IVV

Test report, part 2

Determination of polycyclic aromatic hydrocarbons (PAHs) in the material

Customer:	SGL Carbon GmbH 86400 Meitingen
IVV Order no.:	PA/4148/17
Date of order:	31.03.2017
Sample receipt:	31.03.2017
Testing period:	03.04. – 26.06.2017
Date of report	27.07.2017
Sample storage:	Remaining test material will be stored in the institute for six months.
Total pages of the report:	6

The results relate only to the investigated samples.

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-11140-04-00

Fraunhofer-Institut für Verfahrenstechnik und Verpackung, Giggenhauser Str. 35, D-85354 Freising

1 Scope

The investigated graphite material is intended to be used in food processing machines (repeated use, huge amounts of food) as sealing materials and not in food packaging applications.

In USA there are no statutory regulations for the composition resp. the purity of graphite (CAS 7782-42-5) in contact with food. However, substances used as components of articles that contact food shall be of a purity suitable for its intended use according to 21 CFR 174.5 "General provisions applicable to indirect food additives".

High temperature is needed for the production of synthetic graphite. Thereby various polycyclic aromatic hydrocarbons (PAH) can be generated. The US Environmental Protection Agency (EPA) has selected 16 PAH-substances from more than 100 substances and compiled in a list, that are most frequently found in the environment ("EPA-PAH").

These 16 EPA-PAHs were analysed in the investigated graphite film.

2 Sample material

The customer provided the following sample material:

Sample: SIGRAFLEX® graphite film F05010Z

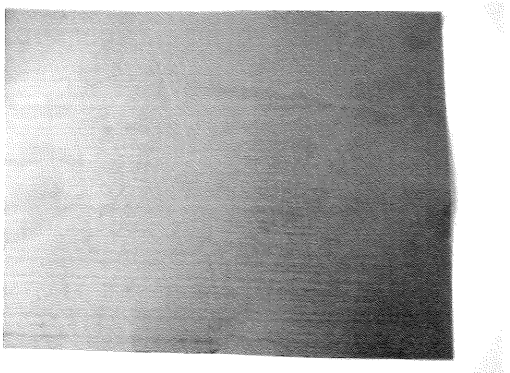

Figure 1: Sample – SIGRAFLEX® graphite film F05010Z

3 Method

Determination of 16 polycyclic aromatic hydrocarbons (PAHs) in the material

Accredited Fraunhofer IVV method PA 1.601

a) Extraction

The sample was ground with a centrifugal mill (Retsch ZM-200) to a particle size of ≤ 250 µm. Approx. 0.5 g of the ground and homogenized sample were spiked with a mixture of isotope labeled PAH-standard (internal standard) solution was extracted under the following extraction conditions:
pressure: 100 bar, temperature: 120 °C, cycles: 3 cycles each 15 min (static)

The sample extracts were reduced to a small volume and measured by GC-MS.

The analysis was performed in triplicate.

b) Quantification of 16 EPA – PAHs

The PAH content of the extraction solutions was determined by a low resolution mass spectrometer (Shimadzu QP 2010 plus) in the single ion monitoring (SIM) mode.

The PAH content in the sample solutions was determined by the ratio of an external calibration and the isotopic labeled standard substances. All values were corrected by blank samples.

4 Results

Polycyclic hydrocarbons (PAH) in the material

Analyt	Concentration in the material [µg/kg]	Area related migration [µg/dm²][1]
Naphthalene	**105** *(d.l.: 10)*	**0.5** *(d.l.: 0.05)*
Acenaphthylen	< d.l. *(d.l.: 10)*	< d.l. *(d.l.: 0.05)*
Acenaphthen	< d.l. *(d.l.: 20)*	< d.l. *(d.l.: 0.1)*
Fluoren	< d.l. *(d.l.: 50)*	< d.l. *(d.l.: 0.3)*
Phenanthren	**39** *(d.l.: 20)*	**0.2** *(d.l.: 0.1)*
Anthracene	< d.l. *(d.l.: 25)*	< d.l. *(d.l.: 0.1)*
Fluoranthene	**34** *(d.l.: 10)*	**0.2** *(d.l.: 0.05)*
Pyrene	< d.l. *(d.l.: 600)*[2]	< d.l. *(d.l.: 2.9)*
Benzo(a)anthracene	< d.l. *(d.l.: 10)*	< d.l. *(d.l.: 0.05)*
Chrysene	**220** *(d.l.: 10)*	**1.1** *(d.l.: 0.1)*
Benzo(b)fluoranthene	< d.l. *(d.l.: 10)*	< d.l. *(d.l.: 0.05)*
Benzo(k)fluoranthene	< d.l. *(d.l.: 10)*	< d.l. *(d.l.: 0.05)*
Benzo(a)pyrene	< d.l. *(d.l.: 5)*	< d.l. *(d.l.: 0.03)*
Indeno(1,2,3-cd)pyrene	< d.l. *(d.l.: 10)*	< d.l. *(d.l.: 0.05)*
Dibenz(a,h)anthracene	< d.l. *(d.l.: 20)*	< d.l. *(d.l.: 0.1)*
Benzo(g,h,i)perylene	< d.l. *(d.l.: 20)*	< d.l. *(d.l.: 0.1)*

d.l. detection limit
[1] calculated with a grammage of approx. 4.9 g/dm²
[2] due to matrix influence the detection limit of pyrene is 600 µg/kg material

5 Food regulatory assessment

The US Environmental Protection Agency (EPA) has selected16 PAH-substances from more than 100 substances and compiled in a list, that are most frequently found in the environment ("EPA-PAH").

In the investigated sealing SIGRAFLEX® material naphthalene, phenanthrene, fluoranthene and chrysene were detected at the detection limit of 10 resp. 20 µg/kg material. Due to strong matrix influence the detection limit of pyrene is 600 µg/kg material.

Naphthalene was quantified to be 105 µg/kg in the material. The oral reference dose in drinking water is 20 µg/kg body weight / day for naphthalene according to US-EPA[1]. For an adult person with 60 kg body weight, this reference dose corresponds to 1200 µg naphthalene (1200 µg/kg food under the assumption that 1 kg food will be consumed per day).
Calculating with the grammage of approx. 4.9 g/dm², the amount of 105 µg/kg corresponds to an area related migration potential of 0.5 µg/dm² (under assumption of total transfer – worst case scenario). Therefore the maximum possible migration of naphthalene from the investigated graphite film is below the described reference dose for all practicable surface-to-volume ratios for the real application as sealing material in the food industry.

Fluoranthene was quantified to be 34 µg/kg in the material. The oral reference dose of fluoranthene is 40 µg/kg body weight / day according to EPA[2]. For an adult person with 60 kg body weight, this reference dose corresponds to 2400 µg fluoranthene (2400 µg/kg food under the assumption that 1 kg food will be consumed per day).
Calculating with the grammage of approx. 4.9 g/dm², the amount of 34 µg/kg corresponds to an area related migration potential of 0.2 µg/dm² (under assumption of total transfer – worst case scenario). Therefore the maximum possible migration of fluoranthene from the investigated graphite film is below the described reference dose for all practicable surface-to-volume ratios for the real application as sealing material in the food industry.

Chrysene is classified as a possible human carcinogenic substance[1,3]. Until now an oral reference dose for drinking water is not set by the EPA.
Until now phenanthrene is not classified as a human carcinogenic substance ("classification – D, not classifiable as to human carcinogenicity")[1,4].

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[1] 2012 Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001, Office of Water U.S. Environmental Protection Agency Washington, DC, Date of update: April, 2012
[2] Integrated Risk Information System (IRIS) U.S. Environmental Protection Agency Chemical Assessment Summary, STATUS OF DATA for Fluoranthene
[3] Integrated Risk Information System (IRIS) U.S. Environmental Protection Agency Chemical Assessment Summary, STATUS OF DATA for Chrysen
[4] Integrated Risk Information System (IRIS) U.S. Environmental Protection Agency Chemical Assessment Summary, STATUS OF DATA for Phenanthrene

Many polycyclic aromatic hydrocarbons (PAHs) are classified as human carcinogenic substances. Thereby benzo(a)pyrene is used as an indicator substance for the PAHs substances because, beside its carcinogenic property benzo(a)pyrene is almost certainly a mutagenic and reprotoxic substance[5]. According to the EPA a maximum amount of benzo(a)pyrene of 0.0002 mg/liter (0.2 µg/liter) in the drinking water is acceptable. For the assessment of phenanthrene and chrysene the described limit of benzo(a)pyrene is used. Phenanthrene was quantified to be 39 µg/kg in the graphite film. Calculating with the grammage of approx. 4.9 g/dm² the amount corresponds to an area related migration potential of 0.2 µg/dm² (under assumption of total transfer – worst case scenario). Up to a surface-to-volume ratio of maximum 1 dm²/kg food the maximum possible migration of phenanthrene from the investigated graphite film meets the described limit.
Chrysene was quantified to be 220 µg/kg in the graphite film. Calculating with the grammage of approx. 4.9 g/dm² the amount corresponds to an area related migration potential of 1.1 µg/dm² (under assumption of total transfer – worst case scenario). Up to a surface-to-volume ratio of maximum 0.18 dm²/kg food the maximum possible migration of chrysene from the investigated graphite film meets the described limit.

For pyrene an area-related migration potential of 2.9 µg/dm², assuming a grammage of 4.9 g/dm², was determined. For pyrene an oral reference dose of 30 µg/kg body weight / day for drinking water is laid down by EPA (2012 Edition of the Drinking Water Standards and Health Advisories[6]). For an adult person with 60 kg body weight, this reference dose corresponds to 1800 µg pyrene (1800 µg/kg food under the assumption that 1 kg food will be consumed per day). Therefore the maximum possible migration of pyrene from the investigated graphite film is below the described reference dose for all practicable surface-to-volume ratios for the real application as sealing material in the food industry.

6 Signatures

Fraunhofer Institute
Process Engineering
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Freising. 27.07.2017

M. Gierl

Maria Gierl
(Scientist in Charge)

Ludwig Gruber
(Head of Contaminants Laboratory)

[5] Bundesinstitut für Risikobewertung (BfR), Polyzyklische aromatische Kohlenwasserstoffe (PAK) in Spielzeug, 2009
[6] 2012 Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001, Office of Water U.S. Environmental Protection Agency Washington, DC, Date of update: April, 2012

Fraunhofer
IVV

Test report, part 3

Screening analysis of a graphite film

Customer:	SGL Carbon GmbH 86400 Meitingen
IVV Order no.:	PA/4148/17
Date of order:	30.03.2017
Sample receipt:	30.03.2017
Testing period:	04.04. – 26.04.2017
Date of report:	28.07.2017
Sample storage:	Remaining test material will be stored in the institute for six months.
Total pages of the report:	7

The results relate only to the investigated samples.

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-11140-04-00

1 Scope

The investigated graphite material is intended to be used in food processing machines (repeated use, huge amounts of food) as sealing materials and not in food packaging applications.

In USA there are no statutory regulations for the composition resp. the purity of graphite (CAS 7782-42-5) in contact with food. However, substances used as components of articles that contact food shall be of a purity suitable for its intended use according to 21 CFR 174.5 "General provisions applicable to indirect food additives".
The extractions of the graphite film are tested with respect to possible migratable organic contaminations by screening analysis.

2 Sample material

The customer provided the following sample material:

Sample: SIGRAFLEX® graphite film F05010Z

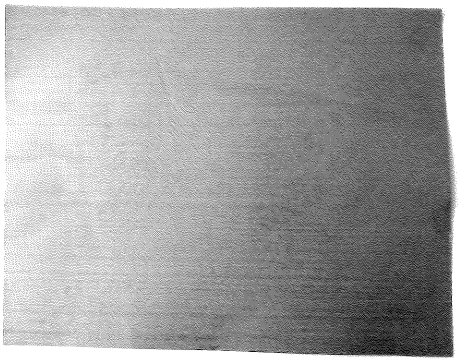

Figure 1: Sample – SIGRAFLEX® graphite film F05010Z

3 Methods

Screening analysis of migratable compounds by extraction

Accredited Fraunhofer IVV method 1.337

0.5 dm^2 of the sample (corresponding to 2.5 g film) cut in small pieces were extracted with 10 ml dichloromethane (DCM) for 3 days at 40 °C resp. with 10 ml 95 % ethanol for 3 days at 60 °C by total immersion (in duplicate). An internal standard of butylated hydroxyanisole (BHA) und Tinuvin 234 was added to an aliquot of the extracts, and analysed by gas chromatography with flame

ionisation detection (GC-FID) for semi-volatile compounds. To enhance the detection limit the internal standard was added to the rest of the extraction solutions which were then reduced to approx. 1 ml under a nitrogen stream and then analysed by GC-FID. Peaks of interest were semi-quantified using the internal standard BHA.

The extraction solutions were analysed by gas chromatography with flame ionisation detection (GC-FID): DB-1-capillary column (length 30 m, inner diameter 0.25 mm, film thickness 0.25 µm) and the following temperature programme: 50 °C (2 min isotherm) up to 340 °C with a heating rate of 10 °C/min, then 10 min isotherm at 340 °C.

With this method organic components with molecular range of 150 – 700 Dalton will be determined.

The identification of the main compounds was done by GC analysis coupled with mass spectrometry. GC/MS-System: ThermoFinnigan SSQ, column: Optima-5-MS - 30 m length - 0.25 mm i.d. - 0.25 µm film thickness, temperature programme: 50 °C (2 min), heating rate 10 °C min^{-1}, 340 °C (30 min), full scan mode, mass range *m/z* 40 - 800.
The identification of the spectra was done by comparison with the NIST spectra library. A confirmation of the suggested spectra by analysis of a respective standard was not done.

4 Results

The gas chromatograms of the extraction solutions are displayed in Figure 2 to Figure 5. Characteristic peaks in the extracts were defined as fingerprint components and semi-quantified using the internal standard BHA (Table 1).

The detected peaks were too small on identification using GC-MS analysis.

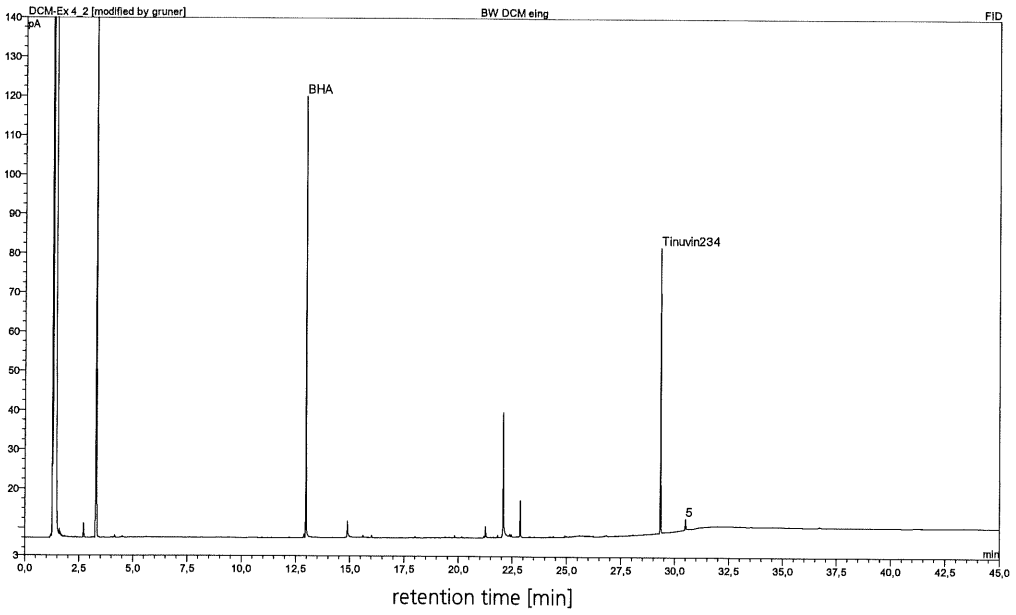

Figure 2: Gas chromatogram of the DCM solvent blank

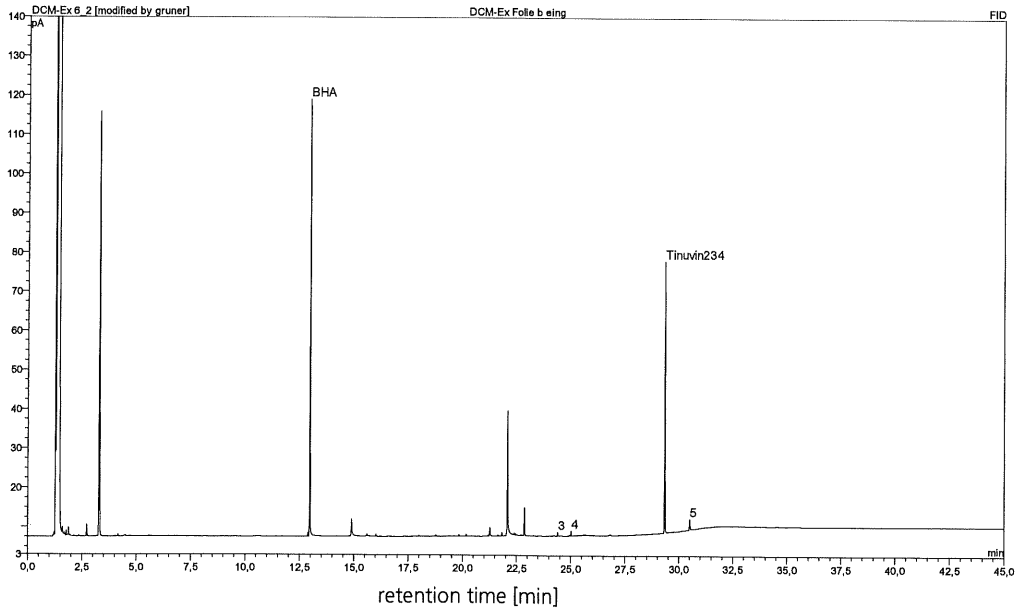

Figure 3: Gas chromatogram of the DCM extract of the sample

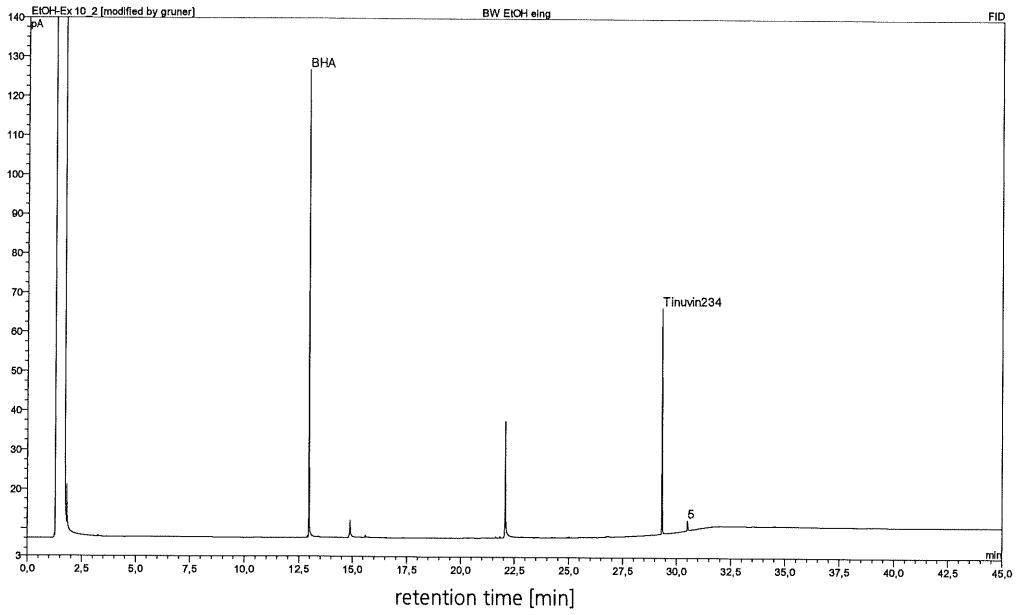

Figure 4: Gas chromatogram of the 95 % ethanol solvent blank

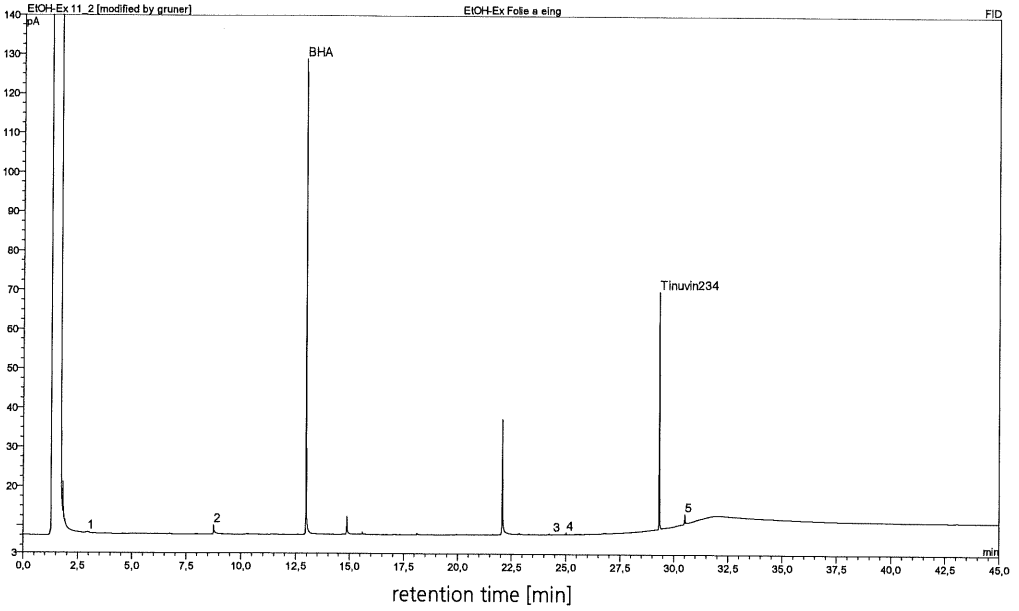

Figure 5: Gas chromatogram of the 95 % ethanol extract of the sample

Table 1 Semi-quantification of fingerprint components in extraction solutions, results given in µg/dm²

	DCM extraction solution [µg/dm²]		95 % ethanol extraction solution [µg/dm²]	
Peak	solvent blank	sample	solvent blank	sample
1	< dl	< dl	< dl	< dl
2	< dl	< dl	< dl	5.4
3	< dl	< dl	< dl	< dl
4	< dl	< dl	0.4	0.3
5	3.8	4.1	3.8	3.1

The detection limit (dl): 0.2 µg/dm²

5 Food regulatory assessment

The evaluation of the applicablility of the graphite film for food processing machines and equipments is based on the possible migration of components from the graphite film into food and the resulting maximum concentrations in food.

With the performed screening analysis of the dichloromethane and 95 % ethanol extraction solutions possible migratable organic contaminants were determined. By comparison with the blank solvents only one not-identified peak (peak 2) in the 95 % ethanol extraction solution was detected. For this peak an area related extraction value of 5.4 µg/dm² results from the semi-quantification.

For the evaluation of the possible mass transfer the Threshold of Regulation – concept (TOR) of the US-FDA is used. On the basis of a statistic evaluation of the toxicological no-effect-level resp. of the tolerable intake of assessed substances, FDA assessed a daily intake of 1.5 µg of a substance as negligibly small, so that no regulation by the authorities for this substance is deemed necessary (21 CFR 170.39). Thereby the derived exposition according FDA results from a daily food intake of 3 kg (including beverages) and the statistic fraction of the assessed material in food contact in relation of all materials in food contact (consumption factor CF).

No statistical data for the use of graphite film in direct food contact was available to us. When the fraction is low and no statistical data are available, a consumption factor of 0.05 is used for the calculation. This corresponds to a maximum migration of 10 µg/kg (10 ppb).

According to the client's information various sizes of the graphite film will be used in contact with food. The above described limit of 10 µg/kg will be met if at least 450 g food will be in contact with 1 dm² contact surface area of the graphite film.

6 Signatures

Fraunhofer Institute
Process Engineering
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Freising, 28.07.2017

M. Gierl

Maria Gierl
(Scientist in Charge)

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