

# INVESTIGATIONS ON THE EXTRACTION AND MIGRATION BEHAVIOR OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) FROM CURED RUBBER FORMULATIONS CONTAINING CARBON BLACK AS REINFORCING AGENT

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## ABSTRACT

Potential release of polycyclic aromatic hydrocarbons (PAHs) from cured rubber materials containing carbon black as reinforcing agent was studied on the basis of seven standard formulations prepared with different loadings of a carbon black grade specifically selected for its high PAH content. A specific test method involving Soxhlet extraction with toluene was developed and validated for quantification of the US-EPA and EU priority PAHs in the rubber materials containing up to 350 ppm of these compounds. PAH migration into aqueous media was assessed by total immersion of rubber sheets into drinking water, artificial sweat, saliva and rainwater for 7 days at 30 °C. GC/MS and internal deuterated standards were applied for PAH determination in all tests. Migration of PAHs from the cured rubber into aqueous media was not detected for the EU PAHs including benzo(a)pyrene and proved to be very low for the combined US-EPA PAHs, not exceeding 1.2 µg/dm<sup>2</sup>. Migration-derived PAH concentrations for drinking water were at least 10<sup>5</sup> lower than those in the rubber compounds. This study demonstrates that once incorporated into a rubber matrix, the PAHs originating from carbon black are scarcely available to aqueous media. These results should be considered while developing PAH exposure assessments for rubber articles.

## INTRODUCTION

Carbon black is extensively used as a reinforcing agent in rubber formulations composing numerous industrial and consumer products. Examples of such rubber applications are tires, indoor and outdoor floorings, water sealants, hand tool grips or toys for children. Since carbon black may contain traces of polycyclic aromatic hydrocarbons (PAHs), such contaminants can be incorporated into rubber formulations and be present in the end product. Concerns have been raised that the presence of PAHs in rubber formulations might pose a potential risk during the manufacture, handling or disposal of some rubber articles.<sup>1</sup> There seems, however, to be limited documented knowledge about the migration behavior and availability of PAHs from rubber formulations, especially for those originating from the carbon black. It even appears that there currently is no established standard method for the characterization and determination of individual PAHs in rubber products.

This paper first describes and validates a specific extraction method for the quantitative determination of PAHs from cured rubber materials containing carbon black. In the second part

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of this study is examined the potential migration of individual PAHs from these rubber materials into aqueous solutions representing typical human or environmental liquids like sweat, saliva and rainwater. Such migration data are of importance for the development of exposure assessments for various rubber products and articles.

## EXPERIMENTAL SECTION

### EXPERIMENTAL DESIGN

Various standard methods are available for the extraction and determination of individual PAHs from a range of matrices.<sup>2-3</sup> The extraction procedure is usually matrix specific as is the extract clean-up for a given analyte. For the identification and quantification of PAHs, most of these methods recommend High Performance Liquid Chromatography (HPLC) with UV and fluorescence detection, or Gas Chromatography coupled with Mass Spectrometry (GC/MS). Since no standard method seems to have been established for the extraction of PAHs from rubber materials, a specific method was developed and validated.

GC/MS has been selected as the analytical technique for the detection of PAHs because of its higher qualitative resolution and because of the possibility to use deuterated PAHs as internal standards to minimize potential interferences from various matrix components (isotope dilution and internal standard technique).

Toluene was selected as the extracting solvent since it has already been established by various regulations for the characterization of PAHs in carbon black.<sup>4-6</sup> Toluene was also reported as suitable for the extraction and quantification of different additives and organic contaminants in polymeric matrices.<sup>7</sup>

An ASTM carbon black grade with a high PAH content was selected as worst case scenario for the preparation of the rubber specimens. A total of seven rubber formulations were prepared based on the ASTM D 3192 test recipe, with different carbon black loadings and varying proportions of extender oil in polyisoprene (Table I). To represent a wide range of consumer products made out of rubber, the carbon black loadings were varied from 0 to 100 phr (parts per hundred rubber). The extender oil was added to four of the seven formulations at a level of 10 phr to establish if this ingredient had any influence on the extraction or migration of PAHs out of the rubber compounds.

TABLE I  
COMPOSITION OF THE RUBBER TEST SPECIMENS

Rubber sheet No.	1	2	3	4	5	6	7
Unit	[phr]	[phr]	[phr]	[phr]	[phr]	[phr]	[phr]
<b>Component</b>							
Polyisoprene	100	100	100	100	100	100	100
Stearic acid	3	3	3	3	3	3	3
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Vulcanizer	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Zinc oxide	5	5	5	5	5	5	5
<b>Oil</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>10</b>	<b>10</b>	<b>10</b>	<b>10</b>
<b>Carbon black</b>	<b>0</b>	<b>25</b>	<b>50</b>	<b>25</b>	<b>50</b>	<b>75</b>	<b>100</b>
<b>Percentage</b>	[%]	[%]	[%]	[%]	[%]	[%]	[%]
<b>Carbon black</b>	<b>0</b>	<b>18.4</b>	<b>31.0</b>	<b>17.1</b>	<b>29.2</b>	<b>38.3</b>	<b>45.2</b>

The different rubber formulations were prepared in a Tröster WNU 3 mixer applying a 16 minutes mixing procedure. The formulations were vulcanized in 2-mm thick sheets for 45 minutes at 145 °C. These sheets were then cut into smaller pieces and covered with a protective foil until tested. The carbon black content was verified by thermogravimetry (see Figure 1).

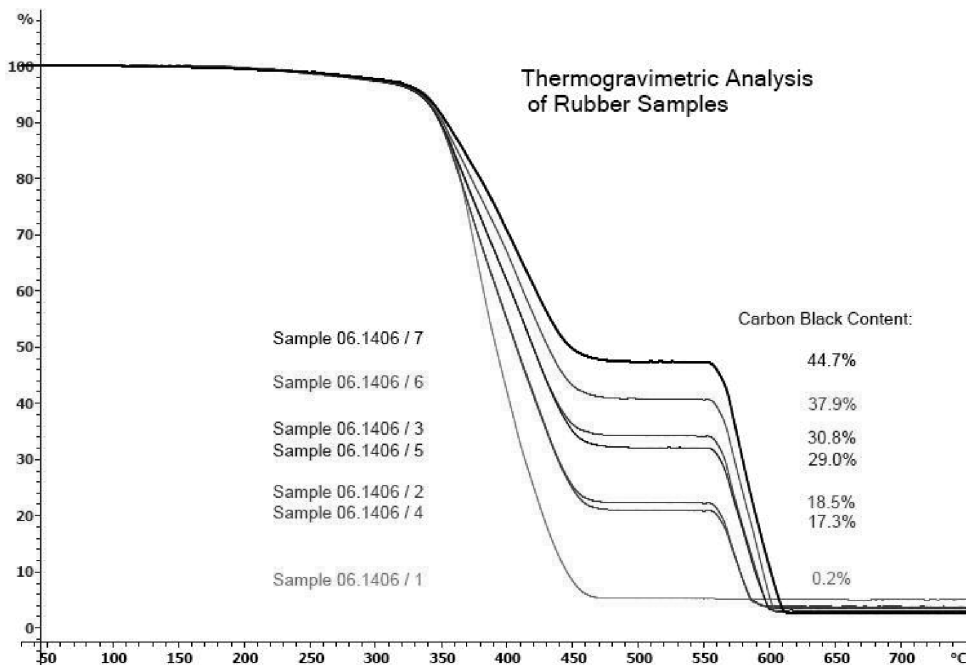


FIG. 1 — Thermogravimetric verification of the carbon black content of the cured rubber samples 1 to 6 prepared for the extraction and migration tests

The cured sheets were used as base material for the extraction and migration tests. Each material was tested for migration of PAHs into drinking water and in three other aqueous solutions simulating sweat, saliva and rain water.<sup>8-10</sup> Rubber sheets of 1-dm<sup>2</sup> surface were totally immersed into these liquids for 7 days at 30 °C<sup>11</sup> and the simulants were subsequently analyzed for PAHs. Compound specific migration rates were calculated when individual PAHs were detected in a test solution. The PAH migration data were compared to the PAH content of the rubber formulations and that of the carbon black. The PAHs could then be traced from the carbon black through to the rubber sheets and to the aqueous simulants used for the migration.

The PAHs considered in this study are the 16 priority PAHs of the US-EPA<sup>12</sup> and the 8 priority compounds specified in the European Directive 2005/69/EC on the restriction of highly aromatic extender oils in tires.<sup>13</sup> From the EU list of PAH compounds, only benzo(j)fluoranthene and benzo(e)pyrene are not covered by the EPA list. Both sets of PAH compounds include benzo(a)pyrene which is often recognized as a qualitative and quantitative marker for the other PAHs. The individual PAHs from both lists are presented in Table II.

TABLE II  
EPA AND EU PRIORITY PAHs, DEUTERATED STANDARDS USED FOR THEIR QUANTIFICATION AND  
MEASUREMENT UNCERTAINTY OF THE ANALYTICAL DETERMINATION

Priority PAHs according to the <b>US-EPA</b>	Priority PAHs according to the <b>EU regulation</b>	<b>Deuterated PAHs used as internal standards</b>	<b>Relative expanded measurement uncertainty, %</b>
Naphthalene		D <sub>8</sub> -naphthalene	25.8
Acenaphthylene		D <sub>8</sub> -acenaphthylene	15.5
Acenaphthene		D <sub>10</sub> -acenaphthene	42.4
Fluorene		D <sub>10</sub> -fluorene	22.2
Phenanthrene		D <sub>10</sub> -phenanthrene	23.9
Anthracene		D <sub>10</sub> -anthracene	22.2
Fluoranthene		D <sub>10</sub> -fluoranthene	19.7
Pyrene		D <sub>10</sub> -pyrene	19.8
Benzo(a)anthracene	Benzo(a)anthracene	D <sub>12</sub> -benzo(a)anthracene	28.3
Chrysene	Chrysene	D <sub>12</sub> -chrysene	22.0
Benzo(b)fluoranthene	Benzo(b)fluoranthene	D <sub>12</sub> -benzo(b)fluoranthene	14.4 <sup>a</sup>
	Benzo(j)fluoranthene <sup>a</sup>	D <sub>12</sub> -benzo(b)fluoranthene	14.4 <sup>a</sup>
Benzo(k)fluoranthene	Benzo(k)fluoranthene	D <sub>12</sub> -benzo(k)fluoranthene	10.6
	Benzo(e)pyrene	D <sub>12</sub> -benzo(a)pyrene	11.9
<b>Benzo(a)pyrene</b>	<b>Benzo(a)pyrene</b>	<b>D<sub>12</sub>-benzo(a)pyrene</b>	<b>11.2</b>
Dibenz(a,h)anthracene <sup>b</sup>	Dibenz(a,h)anthracene <sup>b</sup>	D <sub>14</sub> -dibenzo(a,h)anthracene	(no value available)
Benzo(ghi)perylene		D <sub>12</sub> -benzo(ghi)perylene	11.5
Indeno(1,2,3-cd)pyrene		D <sub>12</sub> -indeno(1,2,3-c,d)pyrene	12.1

*a* Since benzo(b)fluoranthene and benzo(j)fluoranthene are co-eluting on the GC column used, the sum of both PAHs is always reported. Measurement uncertainty therefore also refers to the sum of both PAHs.

*b* Dibenz(a,h)anthracene co-elutes with dibenz(a,c)anthracene on the GC column used. For this reason, all results refer to the sum of these two PAHs

#### PAH EXTRACTION FROM THE CARBON BLACK

In the first series of tests, the extraction behavior of PAHs from carbon black was examined to ensure a quantitative extraction under reasonable experimental conditions. For this purpose, the carbon black used for the preparation of the rubber sheets was Soxhlet extracted with toluene, stepwise for up to 48 hours as follows:

10 g of the carbon black were poured into a cellulose extraction thimble (MN 645, Macherey-Nagel, Düren, Germany), covered with a glass wool plug and placed in a 100 mL Soxhlet extractor equipped with a 250-mL solvent flask and a Dimroth condenser on the top. To minimize the potential decomposition of PAHs, the extraction device was wrapped up with aluminum foil for light protection and the condenser slightly purged with gaseous nitrogen. The carbon black was extracted with toluene at 20 extraction cycles per hour (toluene for residue analysis, LGC Promochem GmbH, Wesel, Germany). After 8 h, 16 h, 32 h and 48 h of extraction, the partial extracts were removed and analyzed for PAHs. The solvent was renewed after each extraction period. This stepwise extraction of the carbon black was crosschecked by a separate continuous 48 h Soxhlet extraction.

Table III summarizes the PAH data on the successive extractions for the carbon black. When normalized and compared against the total amount of PAHs extracted after 48 hours, the data suggest that less than 1% of the total EPA and the total EU PAHs are extracted during the last 16 hours of the entire 48 hours (32 to 48 h period). The percentages of some individual PAH compounds can be slightly higher but none are exceeding 3%. This clearly indicates that after 48 hours and 960 extraction cycles, the EPA and EU PAHs are in effect quantitatively extracted from the carbon black.

TABLE III  
PAH DATA ON THE SUCCESSIVE EXTRACTIONS OF THE CARBON BLACK

Matrix extracted	Carbon black								
Parameter considered	PAH amount extracted					Percentage of 48 h total			
Extraction period	8h	8–16h	16–32h	32–48h	48 h total	8h	8–16h	16–32h	32–48h
Unit	ppm <sup>b</sup>	ppm <sup>b</sup>	ppm <sup>b</sup>	ppm <sup>b</sup>	ppm <sup>b</sup>	% <sup>c</sup>	% <sup>c</sup>	% <sup>c</sup>	% <sup>c</sup>
<b>PAH compound</b>									
Naphthalene <sup>d</sup>	26.3	1.95	1.59	0.538	30.4	86.6	6.4	5.2	1.8
Acenaphthylene <sup>d</sup>	101	2.97	2.38	0.871	107.4	94.2	2.8	2.2	0.8
Acenaphthene <sup>d</sup>	0.40	0.017	0.015	<0.01	0.43	92.5	3.9	3.5	< 2.3
Fluorene <sup>d</sup>	1.27	0.105	0.095	0.044	1.51	83.8	7.0	6.3	2.9
Phenanthrene <sup>d</sup>	77.9	3.46	3.18	1.43	85.9	90.6	4.0	3.7	1.7
Anthracene <sup>d</sup>	5.00	0.361	0.335	0.147	5.84	85.6	6.2	5.7	2.5
Fluoranthene <sup>d</sup>	164	2.59	2.09	0.952	169	96.7	1.5	1.2	0.6
Pyrene <sup>d</sup>	335	3.88	3.00	1.35	344	97.6	1.1	0.9	0.4
Benzo(a)anthracene <sup>d,e</sup>	0.72	0.055	0.059	0.026	0.86	83.8	6.3	6.9	3.0
Chrysene <sup>d,e</sup>	1.27	0.106	0.099	0.046	1.52	83.5	7.0	6.5	3.0
Benzo(b,j)fluoranthene <sup>a,d,e,f</sup>	9.27	0.222	0.188	0.080	9.76	95.0	2.3	1.9	0.8
Benzo(k)fluoranthene <sup>d,e</sup>	2.88	0.122	0.104	0.043	3.15	91.4	3.9	3.3	1.4
Benzo(c)pyrene <sup>e</sup>	16.2	0.135	0.102	0.043	16.5	98.3	0.8	0.6	0.3
Benzo(a)pyrene <sup>d,e</sup>	24.8	1.05	0.815	0.313	27.0	91.9	3.9	3.0	1.2
Dibenz(a,h/a,c)anthracene <sup>a,d,e,g</sup>	<0.1	<0.01	<0.01	<0.01	<0.13	nc	nc	nc	nc
Benzo(ghi)perylene <sup>d</sup>	102	15.6	1.73	0.482	120.2	85.2	13.0	1.4	0.4
Indeno(1,2,3-cd)pyrene <sup>d</sup>	27.2	5.50	1.50	0.429	34.6	78.6	15.9	4.3	1.2
<b>Total 16 EPA PAHs <sup>h</sup></b>	<b>880</b>	<b>38.0</b>	<b>17.2</b>	<b>6.75</b>	<b>942</b>	93.4	4.0	1.8	0.7
<b>Total 8 EU PAHs <sup>h</sup></b>	<b>55.2</b>	<b>1.69</b>	<b>1.37</b>	<b>0.55</b>	<b>58.8</b>	93.9	2.9	2.3	0.9

nc not calculated since not detected

a Co-eluting PAH compounds

b ppm is equivalent to mg/kg

c percentage relative to the cumulated concentration after 48 hours extraction

d EPA priority PAH

e EU priority PAH

f Benzo(j)fluoranthene is included in the EU priority PAHs but not in the EPA priority PAHs

g only dibenz(a,h)anthracene is on the EPA and EU priority lists but is co-eluting with dibenz(a,c)anthracene

h Total of specified compounds; concentrations of not detected compounds were set to zero

After 16 hours of extraction, between 90% and 99% of the individual PAHs were transferred into the toluene extract. For the EPA and EU totals, the extraction efficiency was found to be close to 97% while for benzo(a)pyrene, a value of nearly 96% was measured. When compared with the expanded uncertainties associated with the analytical determination of the PAHs (Table II), the proportions of the PAHs remaining in the carbon black after 16 hours of extraction are much lower. It seems therefore meaningless to extend the extraction over 16 hours.

Based on these findings, for practical and reduced energy consumption considerations, it was elected to set the standard toluene Soxhlet extraction conditions for carbon black and for the cured rubber materials at 16 hours with 20 cycles per hour.

Table III provides also the basic PAH concentrations for the carbon black used in the rubber formulations. Individual PAH levels ranged from 0.43 to 344 mg/kg (ppm) while the totals of the 8 EU priority PAHs and the 16 EPA PAHs amounted to 59 and 942 ppm, respectively. Benzo(a)pyrene showed a concentration level of 27 ppm.

As potential source of PAHs within the rubber formulations, polyisoprene and extender oil

were also analyzed. The polyisoprene polymer showed minor traces for some PAHs (not shown) while none of the individual EPA and EU PAHs were detected in the extender oil. The other constituents of the rubber formulations were not analyzed since none were expected to contain significant amounts of PAHs. The carbon black was thus by far the main PAH source in the rubber formulations which were specifically prepared for these extraction and migration tests.

#### PAH EXTRACTION FROM CURED RUBBER MATERIALS

Duplicate Soxhlet extractions with toluene for 16 hours at a rate of 20 extraction cycles per hour were performed for all rubber materials prior to the quantification of the relevant PAHs. For extraction, the rubber sheet materials were cut into smaller pieces of approximately 3 mm x 2 mm, which were subsequently cryogenically ground down to < 2 mm particulates by means of an ultra centrifugal mill using liquid nitrogen as cooling agent (Pulverisette 14 with a 2-mm sieve, Fritsch, 55743 Idar-Oberstein, Germany). An alternative approach by directly extracting the 3 mm x 2 mm pieces was tested for rubber No. 7. Identical PAH results for both sample preparations indicated that the cost- and labor-intensive cryogenic grinding treatment seems not to be necessary for efficient PAH extraction from such rubber materials. Further details of the extraction procedures are presented in Table V and the PAH analytical method section below.

#### PAH MIGRATION TESTS ON THE CURED RUBBER SHEETS

The basic experimental conditions applied for the migration tests are summarized in Table IV and are as specified in the DIN EN 1811 standard.<sup>11</sup>

TABLE IV  
MIGRATION TEST CONDITIONS

<b>Test specimen</b>	rubber sheets of 10 cm x 5 cm x 0.2 cm
<b>Kind of exposure</b>	Total immersion
<b>Temperature</b>	30 °C ± 1 °C, as per DIN EN 1811 [11]
<b>Duration</b>	7 days (168 h), as per DIN EN 1811 [11]
<b>Exposed surface</b>	1 dm <sup>2</sup> , total surface of both sides of the rubber sheets
<b>Volume of stimulant</b>	170 mL
<b>Migration cell</b>	Glass Petri dishes (ø 14 cm) closed with lids and kept in the dark (oven)
<b>Simulants</b>	<ul style="list-style-type: none"> <li>• Saliva, prepared as per pre-draft DIN 53160-1, pH 6.8 ± 0.1 [8]</li> <li>• Sweat, prepared as per pre-draft DIN 53160-2, pH 6.5 ± 0.1 [9]</li> <li>• Rainwater, prepared as per BCR reference 409; pH 4.3 ± 0.1 representing "simulated rainwater - high contents [10]</li> <li>• Drinking water (local drinking water of Münster city). pH 7.5 ± 0.1</li> </ul>
<b>Analysis</b>	Simulant solutions and blanks for the EPA and EU priority PAHs

All simulant solutions were freshly prepared prior to the migration tests. The chemicals used for the preparation of the simulants were exclusively of p.A. grade (pro analysis, AppliChem GmbH, D-64291 Darmstadt, Germany). The pH adjustment and control was verified by a pH-meter (HI 83141, HANNA Instruments, D-77694 Kehl, Germany).

For migration testing, the rubber pieces were cut into rectangular sheets of exactly 10 cm x 5 cm to get an overall exposed surface of 1 dm<sup>2</sup> when the sheets are totally immersed into the aqueous simulant. The 2-mm thick cutting edges of the sheets were not taken into account as they were compensating, to some extent, for the loss of surface that the upper and lower sample holders of the migration cell covered.

For each test, 170 mL of the aqueous simulant were poured into a glass Petri dish and the rubber sheet fixed between a lower and an upper glass holder to guarantee complete immersion into the simulant. Care was taken to ensure no air bubble remained under the sheet. The Petri dishes were closed with a glass lid, weighed and transferred into the pre-heated oven (UM 500, Memmert GmbH Co. KG, D-91126 Schwabach, Germany). Since the oven had no transparent walls, the cells were not exposed to daylight except for short control periods or when removing old cells and introducing new ones. The oven temperature was adjusted to 30 °C and additionally monitored by means of an external testo 110 thermometer equipped with an air heat sensor which was placed inside the oven (testo AG, Testo-Straße 1, D-79853 Lenzkirch, Germany). The external controller was used to ensure the temperature deviations were not to exceed 1 °C. Once the migration tests were completed and the cells weighed again, the rubber specimens were removed and the aqueous simulants transferred into a separatory funnel for PAH analysis.

For each migration test, the total amount of PAHs detected in the 170 mL of simulant was related to the exposed surface area of the rubber specimen (1 dm<sup>2</sup>). Specific migration rates, expressed as µg PAH/dm<sup>2</sup>, were calculated for each of the individual PAHs detected in the aqueous simulants or in the drinking water. For those which were not detected, the limit of quantification (LOQ) was used to derive a limit of determination (LOD). The LODs for the migration rates were found to be 0.012 µg/dm<sup>2</sup> for naphthalene and 0.002 µg/dm<sup>2</sup> to 0.006 µg/dm<sup>2</sup> for the other PAHs. For benzo(a)pyrene, an LOD of 0.002 µg/m<sup>2</sup> was determined.

Prior to use, each simulant and the drinking water were tested for PAHs. Migration blanks were also carried out under the standard experimental conditions with the aqueous solutions in the migration cells but with no rubber specimen. None of the 16 EPA or 8 EU priority PAHs were detected in any of the four aqueous solutions. The migration blanks showed traces of acenaphthylene in three cases, acenaphthene in two and naphthalene in one (drinking water). However, all the resulting blank migration rates calculated on the basis of a hypothetical exposed surface of 1 dm<sup>2</sup>, were less than twice the LOD.

The migration tests were performed in triplicate for each rubber sheet and showed reasonable repeatability. For the detected PAHs, the relative standard deviations (RSD) on the migration rates were generally below 15 % and even below 12 % for the EPA totals. As expected, instances of higher RSDs were observed for migration rates close to the LOD, e. g. acenaphthene. This was especially the case in drinking water where the lowest migration rates were observed.

#### ANALYTICAL METHODS FOR THE QUANTIFICATION OF PAHS

The PAH determination in the toluene extracts from the migration solutions, the carbon black, and the other rubber formulation ingredients and the cured rubber specimens were performed according to the validated and ISO/IEC 17025 accredited MAS house methods MAS\_PA017<sup>14</sup> and MAS\_PA018<sup>15</sup>. These analytical protocols follow the principles of international standard procedures for the analysis of PAHs in various matrices using GC/MS with deuterated PAHs as internal standards for quantification (e.g ISO 18287<sup>2</sup> or EPA Method 610<sup>3</sup>). Details of the analytical procedure are provided in Table V with the internal PAH-standards listed in Table II.

TABLE V  
DETAILS OF THE PAH ANALYTICAL METHODS APPLIED

<b>Extraction</b>	<ul style="list-style-type: none"> <li>• Solid materials: Soxhlet / toluene</li> <li>• Aqueous liquids: 3 subsequent liquid/liquid extractions with 25 mL of toluene each</li> </ul>
<b>PAH standards used</b>	<ul style="list-style-type: none"> <li>• Calibration check: mixture of 17 native and 16 deuterated PAH standards (see Table II)</li> <li>• Internal Standards: 16 deuterated PAHs (see Table II)</li> <li>• Recovery standard: D<sub>12</sub>-perylene</li> </ul>
<b>Addition of PAH standards</b>	<ul style="list-style-type: none"> <li>• Internal standard: prior to the extraction or extract clean up</li> <li>• Recovery standard: prior to the GC/MS analysis</li> </ul>
<b>Extract clean up</b>	<ul style="list-style-type: none"> <li>• 8-mm ID chromatographic column packed with 1 g silica gel / 10 % H<sub>2</sub>O and flushed and eluted with 1.5 mL and 9 mL Cyclohexane</li> <li>• Cyclohexane eluate concentrated to 0.5 mL by means of a Turbovap® LV at 40 °C and 4.0 psi nitrogen pressure</li> </ul>
<b>GC/MS analysis</b>	<ul style="list-style-type: none"> <li>• Gas chromatography: Thermo Finnigan GC-Ultra, PTV injector GC-column: 60m DB5 MS, 0.25mm ID, 0.25µm Film</li> <li>• Mass spectrometry: Thermo Finnigan Trace DSQ LRMS -Low resolution mass spectrometer SIM-Mode (Selected Ion Monitoring) Resolution: 1 amu</li> </ul>
<b>Identification and Quantification of PAHs</b>	<ul style="list-style-type: none"> <li>• Identification: relative Retention time, molecular and fragment ions fragmentation ratio</li> <li>• Quantification: via the internal deuterated PAHs (isotope dilution and internal standard method)</li> </ul>
<b>Calibration</b>	<ul style="list-style-type: none"> <li>• 7-point calibration for each PAH compound with linear curve fitting</li> <li>• GC/MS calibration range: 1 ng to 500 ng / 1000 ng</li> <li>• Check of calibration within each analysis sequence by injection of a mixture of 17 native and 16 deuterated PAHs (QC sample)</li> </ul>
<b>Limits of quantification</b>	<ul style="list-style-type: none"> <li>• Solid materials: 0.002 – 0.2 mg/kg for naphthalene 0.001 – 0.1 mg/kg for the other PAHs</li> <li>• Aqueous liquids: 0.012 µg/L for naphthalene 0.002 to 0.006 µg/L for the other PAHs</li> </ul>
<b>Analytical method</b>	<ul style="list-style-type: none"> <li>• Solid materials: MAS_PA018, ISO 17025 accredited [14]</li> <li>• Aqueous liquids: MAS_PA017, ISO 17025 accredited [15]</li> </ul>

For the aqueous solutions, the liquids were transferred into a separatory funnel with an addition of a first toluene portion of 25 mL and a mixture of the 16 deuterated standards. While for the aqueous solutions, the internal standards were added prior to the extraction, for the solid materials, the standards were added after the extraction but prior to the extract clean-up. The latter option was preferred since the PAH levels in solid materials may vary significantly. The raw toluene extracts were concentrated by means of a rotary evaporator (Büchi Rotavapor R-200, Büchi Labortechnik AG, 9230 Flawil, Switzerland), operated at 40 °C water bath temperature and pressure reduction to maximum 70 mbar) and cleaned-up through a silica column. D<sub>12</sub>-perylene was added as “recovery standard” prior to the GC/MS analysis.

The low resolution mass spectrometer (LRMS, see Table V) was operated in EI-Mode (Electron Impact Mode) monitoring the molecular ions and fragment ions of the native PAHs and



the deuterated standards. Native PAHs were quantified via the 16 deuterated standards (isotope dilution and internal standard technique). Six of the eight EU priority PAHs were quantified via their corresponding deuterated compound. Since benzo(j)fluoranthene co-eludes with benzo(b)-fluoranthene on the GC column used, the sum of both compounds was quantified in all cases with D<sub>12</sub>-benzo(b)fluoranthene as internal standard. As no deuterated equivalent could be sourced for benzo(e)pyrene, D<sub>12</sub>-benzo(a)pyrene was taken for this specific PAH.

The relative measurement uncertainties associated with the analytical determination of the individual PAHs are shown in Table II. For the EPA and EU totals, the relative uncertainties are 11.3 % and 10.0 %, respectively. The reported values are relative expanded measurement uncertainties calculated with a coverage factor of 2 for an approximate 95% confidence level. These relative uncertainties were experimentally determined through repeated analyses on a given carbon black extract and are valid for the analytical procedure, excluding the extraction step.

## RESULTS AND DISCUSSION

### PAHS IN CURED RUBBER MATERIALS

Mean values for the duplicate PAH determinations from the seven rubber compounds are presented in Table VI. Table VII summarizes the benzo(a)pyrene values and the totals for the EU and EPA PAHs. For clarity, the carbon black loadings are not only reported as “phr” but also as weight percentages. A clear correlation is observed between the PAH levels measured on the cured rubber compounds and the carbon black loading (see Figure 2 for EPA totals as an example). This is also demonstrated by the “recovery” factor reported in Table VII where the theoretical PAH content is based on the carbon black loading and the PAH content determined in the carbon black itself. The “reference material” No. 1, containing no extender oil nor carbon black, was not included in Table VII since only negligible amounts of PAH were detected.

Based on the results on the rubber sheets, the following conclusion can be drawn:

- The toluene extraction and analytical quantification proved to be suitable for the determination of the EPA and EU priority PAHs from the cured rubber sheets.
- The Soxhlet extraction with toluene for 16 h and 320 extraction cycles yielded high recovery for the PAHs originating from the carbon black. The extraction efficiency for benzo(a)pyrene, the EU and EPA totals from the cured rubber sheets is consistent at  $91\% \pm 4\%$  with the PAH contents from the carbon black.
- Since no noticeable differences were observed for the EPA and EU PAH proportions between the carbon black and the rubber materials, it can be concluded that no significant decomposition or formation of PAHs occurs through the incorporation and curing processes.
- The repeatability (precision) of this test method proved to be quite high. The RSDs on the duplicates were generally below 15% for the individual PAHs, with only a few exceptions (RSDs between 20% and 42 %). For the EU and EPA totals, RSDs of 0.3% to 6.4% were obtained. These values are well within the range of the relative expanded measurement uncertainties, though these uncertainties only refer to the analytical determination with no Soxhlet extraction step.
- The carbon black surface has a relatively strong adsorption affinity for PAHs and should be viewed as worst case scenario in terms of PAH extractability. This method should therefore be also valid for the extraction and quantification of the PAHs associated with the other ingredients of the rubber formulations (e.g. extender oil).
- There is no indication that 10 phr of oil in the rubber formulation have any impact on the extraction efficiency of the PAHs bound to the carbon black once mixed in a rubber matrix.

TABLE VI  
PAH CONCENTRATION FROM THE CURED RUBBER COMPOUNDS

Cured rubber sample No.			1	2	3	4	5	6	7
Carbon black content [phr]			0	25	50	25	50	75	100
Oil content [phr]			0	0	0	10	10	10	10
Unit			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
PAH compound	EPA	EU							
Naphthalene	•		< 0.2	6.30	11.1	6.29	9.89	13.9	15.5
Acenaphthylene	•		0.40	12.7	19.7	12.3	18.2	23.5	22.7
Acenaphthene	•		< 0.1	< 0.1	0.16	0.12	0.11	0.16	0.20
Fluorene	•		< 0.1	0.26	0.46	0.29	0.38	0.55	0.61
Phenanthrene	•		< 0.2	15.9	27.3	14.7	25.4	34.1	38.6
Anthracene	•		< 0.1	1.06	1.69	0.96	1.63	2.16	2.43
Fluoranthene	•		< 0.1	27.9	46.9	25.7	44.1	59.3	64.6
Pyrene	•		0.50	59.4	102	52.8	93.3	118	142
Benz(a)anthracene	•	•	< 0.1	0.23	0.31	0.20	0.26	0.40	0.50
Chrysene	•	•	< 0.1	0.31	0.47	0.31	0.44	0.62	0.73
Benzo(b,j)fluoranthene <sup>a,b</sup>	•	•	< 0.1	1.65	2.92	1.59	2.59	3.50	4.00
Benzo(k)fluoranthene	•	•	< 0.1	0.45	0.86	0.45	0.74	1.06	1.19
Benzo(e)pyrene	•	•	< 0.1	2.61	4.85	2.47	4.20	5.52	6.45
<b>Benzo(a)pyrene</b>	•	•	<b>&lt; 0.1</b>	<b>4.12</b>	<b>7.41</b>	<b>3.87</b>	<b>6.93</b>	<b>8.91</b>	<b>10.8</b>
Dibenz(a,h,a,c)anthracene <sup>a,c</sup>	•	•	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Benzo(ghi)perylene	•		< 0.1	19.2	34.9	18.6	32.7	43.6	50.7
Indeno(1,2,3-cd)pyrene	•		< 0.1	4.98	8.72	4.70	8.44	11.3	13.2
<b>Total 8 EU PAHs <sup>d</sup></b>			<b>nc</b>	<b>9.36</b>	<b>16.8</b>	<b>8.89</b>	<b>15.2</b>	<b>20.0</b>	<b>23.6</b>
<b>Total 16 EPA PAHs <sup>d</sup></b>			<b>0.90</b>	<b>154</b>	<b>265</b>	<b>143</b>	<b>245</b>	<b>321</b>	<b>367</b>

< not detected at levels above the limit of quantification indicated (LOQ)

nc not calculated since none of the compounds was detected at levels above the LOQ

a Co-eluting PAH compounds

b Benzo(j)fluoranthene is included in the EU priority PAHs but not in the EPA priority PAHs

c only dibenz(a,h)anthracene is on the EPA and EU priority lists but is co-eluting with dibenz(a,c)anthracene

d Total of specified compounds; concentrations of not detected compounds were set to zero

TABLE VII  
PAH CONCENTRATION AND RECOVERY FACTORS FROM THE CURED RUBBER COMPOUNDS

Cured rubber sample No.	2	3	4	5	6	7	
Carbon black content	25 phr	50 phr	25 phr	50 phr	75 phr	100 phr	
	18.4 %	31.0 %	17.1 %	29.2 %	38.3 %	45.2 %	
Oil content [phr]	0	0	10	10	10	10	
Concentration <sup>a</sup>	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Benzo(a)pyrene	4.1	7.4	3.9	6.9	8.9	10.8	
Total 8 EU PAHs	9.4	16.8	8.9	15.2	20.0	23.6	
Total 16 EPA PAHs	154	265	143	245	321	367	
"Recovery" <sup>b</sup>	%	%	%	%	%	%	Mean±SD <sup>c</sup>
Benzo(a)pyrene	87	92	87	91	90	92	90 ± 2.4 %
Total 8 EU PAHs	90	95	92	92	92	92	92 ± 1.8 %
Total 16 EPA PAHs	91	93	91	91	92	88	91 ± 1.5 %

<sup>a</sup> mean values of duplicate analyses

<sup>b</sup> recovery related to the PAH amount extracted from the carbon black in 16 hours

<sup>c</sup> SD = standard deviation

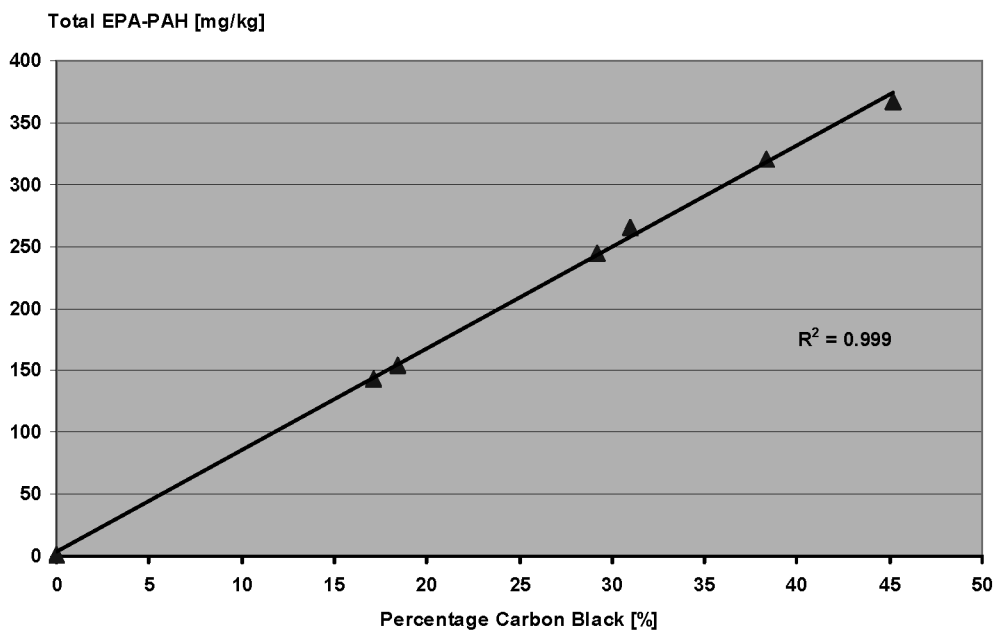


FIG. 2 — Correlation between the EPA-PAH totals and the carbon black content in the rubber materials.

#### PAH MIGRATION FROM THE CURED RUBBER MATERIALS INTO THE AQUEOUS SOLUTIONS REPRESENTING HUMAN AND ENVIRONMENTAL LIQUIDS

The results of the tests examining potential migration of PAHs from the black cured rubber sheets into aqueous media representing environmental or human liquids are summarized in Table VIII. The reported data are mean values of triplicate migration tests per simulant and rubber formulation.

TABLE VIII

BENZO(A)PYRENE, EPA AND EU TOTALS MIGRATION RESULTS FOR THE RUBBER COMPOUNDS IN THE AQUEOUS SIMULANTS

Cured rubber sample No.		1	2	3	4	5	6	7
Oil/carbon black content [phr]		0 / 0	0 / 25	0 / 50	10 / 25	10 / 50	10 / 75	10 / 100
Carbon black content [%]		0 %	18.4 %	31.0 %	17.1 %	29.2 %	38.3 %	45.2 %
Unit		µg/dm <sup>2</sup>	µg/dm <sup>2</sup>	µg/dm <sup>2</sup>	µg/dm <sup>2</sup>	µg/dm <sup>2</sup>	µg/dm <sup>2</sup>	µg/dm <sup>2</sup>
Simulant	PAHs							
Saliva	Total EPA PAHs <sup>a</sup>	0.038	0.605	0.858	0.583	0.853	0.987	0.968
	Total EU PAHs <sup>a</sup>	nd	nd	nd	nd	nd	nd	nd
	Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd
Sweat	Total EPA PAHs <sup>a</sup>	0.025	0.671	0.907	0.606	1.03	1.19	1.03
	Total EU PAHs <sup>a</sup>	nd	nd	nd	nd	nd	nd	nd
	Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd
Rainwater	Total EPA PAHs <sup>a</sup>	0.025	0.560	0.770	0.510	0.796	0.941	0.926
	Total EU PAHs <sup>a</sup>	nd	nd	nd	nd	nd	nd	nd
	Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd
Drinking water	Total EPA PAHs <sup>a</sup>	0.032	0.584	0.598	0.539	0.643	0.626	0.210
	Total EU PAHs <sup>a</sup>	nd	nd	nd	nd	nd	nd	nd
	Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd

nd not detected at levels above the limit of determination (LOD); for LODs see text

<sup>a</sup> Totals include values for detected PAH compounds only

After 7 days of total immersion in the aqueous liquids at 30 °C, no visible change in the constitution of the rubber test specimens was observed with the exception of the sample with no carbon black (No. 1) which developed some whitish spots on the surface.

The mean migration rates for the EPA total range from 0.025 to 1.2 µg/dm<sup>2</sup> when only the detected compounds are taken into account. None of the 8 EU PAHs were detected in any of the test solutions above their respective LOD. For the EU total, the cumulated LOD is 0.014 µg/dm<sup>2</sup>. Of particular interest, benzo(a)pyrene has **not** been detected in any of the migration test solutions with an LOD of 0.002 µg/dm<sup>2</sup>.

The PAH migration results for the cured rubber sheets do not differ much for the various aqueous simulants. There is a slight trend suggesting that the PAH migration is somewhat higher in the sweat simulant and somewhat lower in the drinking water.

The presence of 10 phr of extender oil does not seem to have any significant effect on the PAH migration into the aqueous simulants.

For the rubber sheet with no carbon black, low levels of naphthalene and acenaphthylene migration were detected though the resulting migration rates were much lower than those observed for the rubber sheets with carbon black. While the naphthalene findings may be attributed to traces of this compound in polyisoprene, the acenaphthylene results may be due to blanks since levels close to the LOD were measured in the migration blank samples.

No clear correlation was found between the PAH levels in the carbon black and the migration rates. For instance, pyrene, fluoranthene and benzo(ghi)perylene were found to be the main PAHs in the carbon black but have much lower migration rates than naphthalene or acenaphthylene. Although present in the rubber material at the mid-ppm level, the main PAHs showed very low migration rates (below 1 µg/dm<sup>2</sup>) or were even undetected in the aqueous simulants.

The data support the expectation that the migration of carbon black bound PAHs from a cured rubber compound into aqueous media is very low under normal environmental conditions.

Regarding PAH migration into food, the European standard EN 13130-1<sup>16</sup> recommends using a conventional surface to volume ratio of 6 dm<sup>2</sup> per 1 kg of water. Taking this model, the PAH migration rates determined in this study have to be multiplied by a factor of 6 to derive the PAH concentrations in the aqueous media after contact with the rubber compounds at 30 °C for 7 consecutive days. These concentrations are provided in Table IX for drinking water with compound No. 5, which had the highest migration rates (0.643 µg/dm<sup>2</sup> for EPA total). When comparing the PAH concentrations calculated for the drinking water with those of the rubber material, ratios in the range of 10<sup>-6</sup> to 10<sup>-5</sup> are obtained. For comparison, the limits set by the German Ordinance on drinking water (TVO<sup>17</sup>) on five PAHs are also listed in Table IX. Since none of the TVO-PAHs, benzo(a)pyrene included, were detected in the drinking water, the LODs were considered. The maximum calculated concentration for benzo(a)pyrene is at the set limit while the sum of the other four TVO-PAHs is below the limit.

TABLE IX  
PAH CONCENTRATION OF RUBBER SAMPLE NO. 5 COMPARED TO DRINKING WATER CONCENTRATIONS  
DERIVED FROM THE MIGRATION TESTS AND TO THE GERMAN TVO REGULATION LIMITS

PAH parameter	Concentration rubber sheet	Migration rate drinking water	Concentration drinking water	Ratio Drinking water / rubber	German limit drinking water (TVO)
Total <b>EPA</b> PAHs	245 mg/kg	0.00064 mg/dm <sup>2</sup>	0.0039 mg/kg	1.6 10 <sup>-5</sup>	na
Total <b>EU</b> PAHs	15.2 mg/kg	< 0.000014 mg/dm <sup>2</sup>	< 0.000084 mg/kg	0.6 10 <sup>-5</sup>	na
Total <b>TVO</b> PAHs <sup>a</sup>	44.5 mg/kg	< 0.000010 mg/dm <sup>2</sup>	< 0.000060 mg/kg	0.1 10 <sup>-5</sup>	0.0001 mg/kg
<b>Benzo(a)pyrene</b>	6.9 mg/kg	< 0.000002 mg/dm <sup>2</sup>	< 0.000012 mg/kg	0.2 10 <sup>-5</sup>	0.00001 mg/kg

*a* Total of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene regulated besides benzo(a)pyrene by the German Ordinance on drinking water (TVO)

*na* not applicable

## CONCLUSIONS

For the first time, an unambiguous test method for the quantification of PAHs in cured rubber materials has been developed and validated. For this purpose, a series of cured rubber sheets with different loadings of a carbon black grade specifically selected for its high PAH content were prepared. The PAHs originating from the carbon black were demonstrated to be quantitatively extracted from the rubber specimens after 16 hours of Soxhlet extraction using toluene. To ensure consistent results, a specific sample preparation prior to the Soxhlet extraction was applied. The analytical determination of the PAHs contained in the toluene extracts is done by GC/MS with addition of deuterated internal standards for quantification.

The cured rubber sheets were also subjected to migration testing into aqueous solutions representing human or environmental liquids, as per international standard protocols. The migration rates of the PAHs from the rubber sheets into the sweat, saliva and rainwater simulants as well as in drinking water, were found to be very low or even below the detection limit. For drinking water, the PAH concentrations after migration were determined to be complying with the German Ordinance on drinking water.<sup>17</sup> It must be noted that the presence of extender oil in the rubber formulation does not seem to have any significant effect on the migration of the carbon black bound PAHs into the aqueous simulants.

These data suggest that even for a worst case scenario (high-PAH carbon black), the PAHs originating from the carbon black, once mixed in a rubber matrix are strongly bound and are

scarcely available to an aqueous surrounding even under severe environmental conditions. These findings should be useful and considered for the development of PAH exposure assessment for various rubber products and articles.

### ACKNOWLEDGEMENT

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