UNSUITABILITY OF THE ZEK/AFPS TEST METHOD FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN CARBON BLACK

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ABSTRACT

The Zentraler Erfahrungsaustauschkreis/Ausschuss für Produktsicherheit (ZEK/AfPS) analytical method established within the Geprüfte Sicherheit (GS) quality label for the determination of 18 polycyclic aromatic hydrocarbons (PAHs) in consumer articles made out of rubber or plastic was demonstrated as unsuitable for carbon black (CB). High molecular weight PAHs are not efficiently extracted from CB through the ZEK/AfPS method when compared with the CB-specific method consisting of 48 h Soxhlet extraction. The low extraction efficiency correlates with the low recovery or loss of the deuterated isotopologues added prior to the 1 h ZEK/AfPS ultrasound extraction of the native PAHs. These phenomena are dependent on the type and concentration level of the various PAHs and are attributed to the relative distribution and adsorption of the native and deuterated PAHs between the CB surface and the toluene phase. These findings are based on comparative extractions of various carbon black grades, use of a larger set of deuterated isotopologues for gas chromatography/mass spectrometry (GC/MS) quantification of native PAHs, and monitoring of the recoveries of the deuterated PAHs added prior to or after the ZEK/AfPS extractions. [doi:10.5254/rct.18.82635]

INTRODUCTION

Industrially manufactured carbon black is widely used as a reinforcing agent and for pigment in tires, rubber and plastic products, printing inks, paints, and coatings. Since carbon black contains traces of polycyclic aromatic hydrocarbons (PAHs), these compounds may be incorporated into many end products.[1]

PAHs are a class of ubiquitous environmental contaminants that comprise hundreds of molecules with two or more fused aromatic rings. Such compounds are primarily formed by incomplete combustion or pyrolysis of organic matter and through various industrial processes.[2] Some of the PAHs are regarded as potentially genotoxic and carcinogenic to humans.[3] Usually, the major route of exposure is consumption of food. However, other pathways, like respiratory uptake (smokers) or dermal uptake (coal tar workers), may also play a role under specific conditions.[4,5] Traditionally, benzo[*a*]pyrene (B[*a*]P) has been used as a qualitative and quantitative marker for monitoring this family of molecules. Over the past several years, however, other individual PAHs have been included in various regulations considering their toxic potency and representativeness due to their respective abundance. For instance, quality standards and regulations are now enforced covering 4, 8, 16, 18, or even 22 priority PAHs for a broad variety of matrices.[6–13] Some regulations directly or indirectly impact carbon black as part of consumer products.

To assure compliance with the various PAH limits and specifications, industrial carbon black is frequently tested. There are currently only two internationally recognized test methods for the determination and quantification of selected PAHs in carbon black. Both methods specify Soxhlet

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extraction with toluene, for 48 h for the U.S. Food and Drug Administration (FDA) method[14] and 16 h for the American Society for Testing and Materials (ASTM) D7771 standard.[15] Gas chromatography in connection with mass spectrometry (GC/MS) is then applied for the identification and quantification of the PAHs of interest in the toluene extract. It is recognized that such severe and exhaustive Soxhlet extractions are in no way representative of what could realistically happen during normal use conditions for carbon black containing articles made out of rubber or plastics. The carbon black specific methods are meant to extract the PAHs from the carbon black surface in an exhaustive manner.

In 2008, the German Zentralstelle der Länder für Sicherheitstechnik (ZLS) introduced a first version of the so-called Zentraler Erfahrungsaustauschkreis (ZEK) method for compliance testing of rubber and plastic parts with respect to the Geprüfte Sicherheit (GS) quality label. The method was first established to determine 16 (now 18) specific individual PAHs in rubber and plastic parts of toys and articles that may come into contact with human skin during intended use.[13] The method consists of a 1 h toluene extraction of the test material in an ultrasonic bath at 60 °C followed by GC/MS quantification. In contrast to the carbon black specific methods, the deuterated internal standards (IStds) are added to the solvent prior to the extraction step and not to the toluene extract after the extraction process. The subsequent extract treatment and GC/MS analysis follow the same principles as for the FDA and ASTM methods, though a minimum of three deuterated internal standards are recommended for the 18 PAHs of interest (latest ZEK version 01.4-08 of November 2011)[16] as opposed to seven in the FDA method for 22 PAHs.

In August 2014, the German commission on Product Safety (Ausschuss für Produktsicherheit [AfPS]) set a series of new requirements for the GS-Mark certification, "AfPS GS 2014:01 PAK," replacing the ZEK specification in July 2015.[11] This change did not alter the analytical method or the number and identity of the 18 individual PAHs but did make the various limits more restrictive and extended the categories of consumer products that were affected. Table I presents the product categories and PAH limits according to the new GS specification.

Although neither intended nor validated for the determination of PAHs in carbon black, the ZEK method is often seen being applied for this specific matrix. Especially with respect to the differences in the extraction methods, application of the ZEK/AfPS method on carbon black may lead to significantly different and inconsistent PAH results in comparison with the established carbon black specific PAH methods. This may result in inadequate product specifications and entail commercial implications. The present research paper demonstrates the unsuitability of the ZEK/AfPS method for the determination of the 18 GS-PAHs in carbon black through a series of comparative tests using the three methods available.

EXPERIMENTAL SECTION

STUDY DESIGN

Three carbon black grades relevant to plastics and rubber applications were selected by the International Carbon Black Association (ICBA) to cover a wide PAH concentration range. Some surface and PAH related data of the three grades are presented in Table II. For the purpose of this study, the three carbon black samples are referred as "L" for the one with the lowest PAH level, "M" for the one with the intermediate level, and "H" for the sample with the highest concentration. All PAH data shown in Table II correspond to mean values of triplicate measurements using the FDA extraction conditions.

The principles of the three test methods applied to carbon black in this study are summarized in Table III. The main difference between the two methods specific to carbon black and the ZEK/AfPS method is the extraction procedure. The most vigorous extraction procedure is presumably the 48 h

TABLE I
PRODUCT CATEGORIES AND PAH MAXIMUM LEVELS ACCORDING TO THE GS-MARK SPECIFICATION AFPS GS 2014:01 PAK

PAH compound (maximum level mg/kg)	Item regulated				
	Category 1[a]	Category 2[b]		Category 3[c]	
		Toys[d]	Other products[e]	Toys[d]	Other products[e]
Naphthalene	<1	<2	<2	<10	<10
Seven AFP-PAHs[f]	<1	<5	<10	<20	<50
Benzo[*a*]anthracene	<0.2	<0.2	<0.5	<0.5	<1
Chrysene	<0.2	<0.2	<0.5	<0.5	<1
Benzo[*b*]fluoranthene	<0.2	<0.2	<0.5	<0.5	<1
Benzo[*k*]fluoranthene	<0.2	<0.2	<0.5	<0.5	<1
Benzo[*j*]fluoranthene	<0.2	<0.2	<0.5	<0.5	<1
Benzo[*e*]pyrene	<0.2	<0.2	<0.5	<0.5	<1
Benzo[*a*]pyrene	<0.2	<0.2	<0.5	<0.5	<1
Dibenz[*a,h*]anthracene	<0.2	<0.2	<0.5	<0.5	<1
Benzo[*ghi*]perylene	<0.2	<0.2	<0.5	<0.5	<1
Indeno[1,2,3-*cd*]-pyrene	<0.2	<0.2	<0.5	<0.5	<1
Total 18 PAHs	<1	<5	<10	<20	<50

[a] Category 1 includes materials intended to be taken into the mouth or materials of toys with intended and prolonged skin contact (>30 s).
[b] Category 2 includes non–category 1 materials with foreseeable skin contact >30 s (prolonged skin contact) or short term repetitive skin contact. "Repeated short termed skin contact" as defined under REACH, attachment XVII No. 50 amendment regulation EU 1272/2013.
[c] Category 3 includes materials not in category 1 and category 2 with foreseeable skin contact up to 30 s (short term skin contact).
[d] Toys in the scope of the EU directive 2009/48/EC on the safety of toys, dated June 18, 2009.
[e] Other products in the scope of the German law on product safety of November 08, 2011, BGBl. I page 2178, 2179; 2012 BGBl. I, page 131.
[f] The sub-group of seven PAHs, which includes acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene, with specific limits for its sum are partly denoted as "seven AFP-PAHs" in the text since all compound names start either with an A, an F or a P, in contrast to the names of the other GS-PAHs.

Soxhlet extraction of the FDA method. ASTM D7771 and its 16 h Soxhlet extraction was included in the investigation to examine its potential for the determination of PAHs other than B[*a*]P in carbon black. At a minimum, it is expected that for carbon blacks with high PAH content, the 16 h Soxhlet extraction should provide similar quantitative PAH results compared with the FDA method.[17,18]

TABLE II
SOME BASIC CHARACTERISTICS OF THE THREE CARBON BLACK GRADES USED IN THIS STUDY

Parameter	CB Sample L	CB Sample M	CB Sample H
Nitrogen surface adsorption, m^2/g	182	40	78
Oil adsorption number, mL/100 g	94	121	72
Iodine number, mg/g	191	43	82
Benzo[*a*]pyrene concentration, mg/kg[a]	0.0195	0.572	2.38
Total of 18 GS-PAHs, mg/kg[a]	8.30	29.1	162

[a] Mean of triplicate determinations by applying the FDA-based method (48 h Soxhlet extraction with toluene).

TABLE III
PRINCIPLES OF THE THREE PAH TEST METHODS USED IN THIS STUDY

Analytical method	U.S. FDA[14]	ASTM D7771[a,15]	ZEK/AfPS[b,10]
Established for	carbon black	carbon black	rubber and plastics
Sample amount, g	10	10	0.5
Extraction technique	Soxhlet	Soxhlet	ultrasonic treatment; at least 0.28 W/cm^2
Solvent for extraction	toluene	toluene	toluene
Extraction time, h	48	16	1
Extraction conditions	$\geq$10 cycles/h[c] boiling toluene	$\geq$10 cycles/h boiling toluene	60 °C
Number of individual PAHs quantified	22	1	18
Minimum number of internal standards	7	1	3
Addition of internal standards	after extraction	after extraction	prior to extraction
Extract purification	Solid Phase Extraction	Solid Phase Extraction	Solid Phase Extraction (optional)
Recovery standard	none	none	none
Instrumental analysis	GC/LRMS	GC/LRMS	GC/LRMS
MS-Mode	SIM	SIM	SIM
Quantification method	isotope dilution and internal standard	isotope dilution	isotope dilution and internal standard
Limit of quantification, mg/kg	0.001	0.01[d]	0.2[e]

[a] ASTM D7771-11 and current version ASTM D7771-15.
[b] Method according to ZEK 01.4-08, now GS specification AfPS 2014:01 PAK.
[c] Not specified in the method but applied in this study.
[d] Lower LOQs of 0.001 mg/kg were applied within this study.
[e] Lower LOQs of 0.01 mg/kg were applied within this study.

Another significant difference between the methods is that the addition of the internal standards is done prior to the extraction for the ZEK/AfPS, while for both the FDA and ASTM methods, the deuterated PAHs are added to the toluene extract or an aliquot of it. Furthermore, the ZEK/AfPS method prescribes the use of only three internal standards as a minimum for the quantification of the 18 PAHs, while the FDA requires seven. All three analytical methods are covered by the International Organization for Standardization/International Electrotechnical Commission (ISO/IEC) 17025:2005 accreditation scope of the münster analytical solutions (mas) laboratory.

The three carbon black samples were extracted in triplicate for the FDA and ASTM methods and five times for the ZEK/AfPS. A blank analysis was also performed for each of the three extraction procedures. To get a deeper insight into the effects of the ZEK/AfPS extraction process when applied to carbon black, additional tests were performed by adding the internal standards after the extraction process. Other complementary tests involved re-extracting the carbon black samples with no additional spiking with internal standards. A summary of the extraction tests conducted within this project is presented in Table IV.

Overall, 23 different individual PAHs are considered in the FDA, GS-Mark specification, the U.S. EPA and the European Regulation 1272/2013/EC; 22 from the FDA method plus benzo[*j*]fluoranthene. Owing to the complete co-elution of dibenz[*a,c*]anthracene with

TABLE IV
EXTRACTION TESTS PERFORMED WITHIN THIS STUDY

Extraction procedure	U.S. FDA 48 h Soxhlet	ASTM D7771 16 h Soxhlet	ZEK/AfPS 1 h ultrasonic treatment at 60 °C	ZEK/AfPS 1 h ultrasonic treatment at 60 °C	ZEK/AfPS 1 h ultrasonic treatment at 60 °C and re-extraction by applying the same procedure
Addition of the internal standards	to the extract[a]	to the extract[a]	prior to the extraction[a]	to the extract	prior to the first extraction
CB L	3	3	5	1	1
CB M	3	3	5	1	1
CB H	3	3	5	1	1
Method blank	1	1	1	—	—

[a] According to the method provisions.

TABLE V
NATIVE PAHS CONSIDERED AND DEUTERATED PAH COMPOUNDS USED

Native PAH compounds[a]	No. of aromatic rings	Deuterated PAHs used as internal standards within this study[b]	Internal PAH standards required by the ZEK/AFPS method[c]
Naphthalene	2	D_8-naphthalene	D_8-naphthalene[c]
Acenaphthylene[d]	3	D_8-acenaphthylene	
Acenaphthene[d]	3	D_{10}-acenaphthene	
Fluorene[d]	3	D_{10}-fluorene	
Phenanthrene[d]	3	D_{10}-phenanthrene	
Anthracene[d]	3	D_{10}-anthracene	
Fluoranthene[d]	4	D_{10}-fluoranthene	
Pyrene[d]	4	D_{10}-pyrene	D_{10}-pyrene[c,e]
Benzo[*ghi*]fluoranthene[f]	5	D_{12}-chrysene	na
Benzo[*a*]anthracene[g]	4	D_{12}-benzo[*a*]anthracene	
Cyclopenta[*cd*]pyrene[f]	5	D_{12}-chrysene	na
Chrysene[g]	4	D_{12}-chrysene	
Benzo[*b/j*]fluoranthene[g,h]	5	D_{12}-benzo[*b*]fluoranthene	
Benzo[*k*]fluoranthene[g]	5	D_{12}-benzo[*k*]fluoranthene	
Benzo[*e*]pyrene[g]	5	D_{12}-benzo[*a*]pyrene	
Benzo[*a*]pyrene[g]	5	D_{12}-benzo[*a*]pyrene	D_{12}-benzo[*a*]pyrene[c,i]
Perylene[f]	5	D_{12}-benzo[*a*]pyrene	na
Dibenz[*a,h/a,c*]anthracene[g,h]	5	D_{14}-dibenz(a,h)anthracene	
Benzo[*ghi*]perylene	6	D_{12}-benzo[*ghi*]perylene	
Indeno[1,2,3-*cd*]pyrene	6	D_{12}-indeno(1,2,3-c,d)pyrene	
Anthanthrene[f]	6	D_{12}-benzo[*ghi*]perylene	na
Coronene[f]	7	D_{12}-coronene	na

Na, the corresponding native PAH is not part of the 18 GS-PAHs.
[a] The 18 PAHs highlighted in bold are part of the GS-Mark specification.
[b] Some of the deuterated internal standards were used for quantification not only of the corresponding native compound but also for other native PAHs as indicated in the far left column.
[c] The deuterated PAH contained within a cell is specified as internal standard by the ZEK/AfPS method for the corresponding series of native PAHs.
[d] The sub-group of seven PAHs with specific limits for its sum are partly denoted as "seven AFP-PAHs" in the text since all compound names start either with an A, an F or a P, in contrast to the names of the other GS-PAHs.
[e] D_{10}-anthracene or D_{10}-phenanthrene may be used instead of D_{10}-pyrene per ZEK/AfPS.
[f] The PAH compound is part of the 24 PAHs determined here but is not considered within the GS-Mark specification.
[g] Eight EU PAHs considered by the Commission Regulation (EU) No. 1272/2013 (exclusive of the co-eluting dibenz[*a,c*]anthracene).
[h] PAH compounds co-eluting on the GC columns used.
[i] D_{12}-perylene or triphenyl benzene may be used instead of D_{12}-benzo(a)pyrene per ZEK/AfPS.

dibenz[*a,h*]anthracene on the GC/MS column used, a total of 24 PAH compounds are considered throughout this project. Comparison of the FDA and ZEK/AfPS results, however, was mostly done on the basis of the 18 GS-PAHs. The 24 PAHs are listed in Table V based on the elution sequence from the GC/MS column used. The order follows in general the increasing number of aromatic rings, combined with the decreasing volatility and water solubility of the PAHs. The most volatile, naphthalene, is the only 2-ring molecule, whereas the seven AFP-PAHs have three or four rings. The other 10 higher boiling GS-PAHs contain four to six rings and are consequently

more potent in terms of human carcinogenicity. These large PAHs are classified by the International Agency for Research on Cancer (IARC) as probably (2A) or possibly (2B) carcinogenic to humans and, for the case of benzo[*a*]pyrene, as carcinogenic (1). The IARC does not classify the seven AFP-PAHs as carcinogenic (3), whereas naphthalene is suspected to be carcinogen to humans (2B).[3]

In this study, to get a deeper insight into the extraction behavior of individual PAHs and for sake of accuracy and precision, 17 deuterated analogues were used as internal standards for the quantification of the 24 native PAHs. Furthermore, though not required by any of the three methods, an additional quality control was implemented. D_{12}-perylene was used as a recovery standard and added to each extract prior to the GC/MS analysis to monitor the recovery of the internal standards after the extraction and/or the extract purification step; this is of special interest for the ZEK/AfPS method. Since D_{12}-perylene is specified as one of the internal standards in the FDA method, it had to be substituted with another deuterated compound; D_{12}-benzo[*a*]pyrene was used instead. All deuterated internal and recovery standards were added at a level of 200 ng per carbon black sample or extract portion. All native PAH standards were provided by Dr. Ehrensdorfer GmbH, Augsburg, Germany, with a minimum certified purity of 98.5%. The deuterated PAH standard solutions were from Chiron AS (Trondheim, Norway), except the D_{12}-coronene and D_{12}-perylene solutions, which were provided by Cambridge Isotope Laboratories Inc. (Andover, MA, USA). The chemical purity of the deuterated PAH compounds was certified to be at least 98%.

The limits of quantifications (LOQs) for the three methods are presented at the bottom of Table III. The ZEK/AfPS method stipulates a sample amount of only 0.5 g, as compared to 10 g for both the FDA and ASTM methods, and this is the main reason behind the difference in the reported LOQs. The sensitivity of the GC/MS instrument used for this study, however, enabled an LOQ of 0.01 mg/kg for most of the PAHs through the ZEK/AfPS method.

When analyzing rubber and plastic parts with the ZEK/AfPS method, uptake of an aliquot of the toluene extract after the extraction can easily be done, since separation with the sample matrix occurs by gravity. This is not the case when extracting carbon black by sonication treatment, where a fine dispersion of carbon black in the solvent is obtained. For this reason, a specific procedure for separating the toluene extract from the finely dispersed carbon black had to be developed. Centrifugation proved to be easy and suitable and was applied to all carbon black analyzed through the ZEK/AfPS method.

For the three test methods, the final toluene extracts were all processed in the same way, based on common principles, namely, treatment with a silica gel column, GC/MS analysis with PAH identification, and quantification via internal standards. This consistent approach implied that not all provisions of the various methods for the extract treatment were followed in detail. However, potential impact on PAH results caused by such modifications is deemed minor. Applying the same extract treatment and GC/MS analysis procedure helps in focusing on the extraction mode, which is the most critical difference between the three methods.

PREPARATION AND EXTRACTION OF THE CARBON BLACK SAMPLES

Basic characteristics of the three carbon black samples (L, M, and H) are summarized in Table II. These were received as fine beaded materials, which were crushed in a mortar with a pestle to get homogeneous powders prior to extraction.

A 100 mL Soxhlet apparatus equipped with a 250 mL round bottom flask was used for both the FDA and ASTM procedures. In both cases, 10 g of carbon black was weighed in a cellulose extraction thimble (MN 645, Macherey-Nagel, Düren, Germany), and a glass wool plug was placed on the top of the carbon black. The plug was subsequently covered with a layer of cellulose pieces

cut from an extraction thimble to avoid carbon black overflow with the solvent. All materials and glassware were pre-extracted with toluene specified for residue analysis (LGC Promochem GMBH, Wesel, Germany). After assembly of the Soxhlet apparatus and addition of toluene, a gentle nitrogen flush through a manifold connected to the condenser was applied. The whole apparatus was thoroughly wrapped with aluminum foil for light protection. Extraction cycles were adjusted to approximately 10 cycles per hour, and the extraction continued under constant conditions for 16 h in case of the ASTM and for 48 h when following the FDA protocol. The resulting raw extracts were concentrated to slightly over 5 mL by means of a rotary evaporator operated at 40 °C and a pressure reduction of 5 kPa as a minimum (Büchi Rotavapor R-200, Büchi Labortechnik AG, 9230 Flawil, Switzerland). The extracts were then transferred to a 10 mL volumetric flask and brought to the mark by adding fresh toluene. Suitable aliquots of the extracts were used for the PAH determination. In contrast to the FDA protocol, the internal standards were added not prior to, but after, this concentration step.

For the ZEK/AfPS procedure, 0.5 g of carbon black was weighed in a 50 mL glass vial, and 20 mL of toluene was added along with 200 µL of the internal standard solution. The vial was capped and transferred into an ultrasonic bath with no basket, providing a power of 0.31 W/cm^2 (Sonorex Super RK 156 BH, Bandelin Electronic GmbH & Co. KG, 12207 Berlin, Germany; bath surface: 700 cm^2, HF-power: 215 W). The water bath temperature was kept at 60 °C, and the carbon black suspension in toluene was extracted for 1 h. Separation of the carbon black from the toluene was performed using centrifugation (SIGMA 2-6E centrifuge, Sigma Laborzentrifugen GmbH, Osterrode am Harz, Germany). For this separation step, the suspension was allowed to cool down to room temperature before being thoroughly shaken for homogenization. An aliquot of 15 mL was then transferred to a tube and centrifuged for 4 min at 3000 rpm. A clear extract was obtained above the carbon black layer from which 10 mL were removed by means of a pipette.

EXTRACT PROCESSING

The ASTM and FDA methods require purification of the toluene extract by means of a silica column prior to the GC/MS analysis. This purification is an option for the ZEK method but proves necessary in cases where the polymer matrix is dissolved by the solvent. In order to treat all toluene solutions identically, a silica clean-up was systematically applied during this project. Though deviating from the FDA and ZEK method, it is recognized that this well established silica clean-up protocol does not greatly affect the PAH results. A silica gel/13% H_2O gravity column with 10 mm inner diameter and 5 cm^3 capacity, containing 1 g of silica gel/13% H_2O adsorbent, was used (silica gel, high purity grade, type 60, particle size 0.063 to 0.200 mm). Preparation of the column followed the procedure described in section 7.7.2 of the ASTM D7771-15 standard.[15] For purification, the extract aliquots, containing the internal standards, were concentrated to approximately 1 cm^3 and quantitatively transferred to the top of the pre-eluted and cyclohexane-wetted silica gel/13% H_2O column. The PAH fraction was eluted by means of cyclohexane (Cyclohexane Picograde® for residue analysis, LGC Promochem, Wesel, Germany) and collected in a conical-bottom centrifuge tube. A nitrogen blow-down apparatus (TurbVap LV, Biotage, Uppsala, Sweden) was used to further reduce the volume to approximately 0.25 cm^3 by applying suitable conditions (28 ± 2 kPa pressure and 40 ± 2 °C bath temperature). Finally, the concentrated eluate was quantitatively transferred to a GC/MS amber vial that already contained 100 µL (200 ng) of the D_{12}-perylene recovery standard. This solution was used for GC/MS injection.

TABLE VI
GC/MS INSTRUMENTATION AND OPERATION CONDITIONS

GC/MS parameters
Gas chromatograph: Thermo Scientific GC-Ultra with PTV injector, GC-column: 60 m DB5-MS, 0.25 mm ID, 0.25 μm Film
Mass spectrometer: Thermo Scientific Trace DSQ LRMS—Low resolution mass spectrometer, operated in the electron impact mode (EI) and Selected Ion Monitoring (SIM Mode); Resolution: 1 amu
Identification and quantification of PAHs
Identification: relative retention time, molecular and fragment ions, fragmentation ratio
Quantification: via the deuterated internal PAHs (see Table V) (isotope dilution and internal standard method)
Calibration
Seven-point calibration for each PAH compound with linear curve fitting
GC/MS calibration range: 1 ng to 500 ng or 1000 ng
Check of calibration within each analysis sequence by injection of a mixture of 23 native and 18 deuterated PAHs including the recovery standard D_{12}-perylene (see Table V)

GC/MS ANALYSIS FOR PAHS

Details of the GC/MS analytical method are presented in Table VI. A low resolution mass spectrometer (LRMS) operated in the selected ion mode (SIM) was used for PAH identification and quantification. Calibration check of the instrument was performed for each analysis sequence by injection of mixtures containing all native PAHs of interest, the 17 deuterated internal standards (Table V), and the recovery standard, D_{12}-perylene.

Since benzo[*b*]fluoranthene and benzo[*j*]fluoranthene are not baseline separated on the GC column used, they were always quantified as the total of the two compounds. Furthermore, dibenz[*a,c*]anthracene, a PAH not considered by the GS-Mark specification, co-elutes with dibenz[*a,h*]anthracene. For this reason, the values for dibenz[*a,h*]anthracene have always been considered as a potential total of both compounds.

RESULTS AND DISCUSSION

PAH RESULTS BASED ON THE FDA EXTRACTION MODE

Table VII shows the mean concentrations and standard deviations for the triplicate analyses on the three carbon black samples after 48 h Soxhlet extraction per the FDA-based method. Since this was the most vigorous extraction procedure, these results were taken as reference values for all comparisons, and considerations were made in the following sections.

Standard deviations below 10% were obtained for most of the PAHs, except for naphthalene, which showed deviations of up to 17%. In matrices other than carbon black, naphthalene often shows higher variations than the other PAHs owing to its higher volatility. As expected, variations of the seven AFP-PAHs, the 18 GS-PAHs, and the 24 PAH totals are much lower (0.8 to 3.2%). Such standard deviations can be considered relatively low compared with routine PAH analyses in other matrices, such as plants or soil.[19–21]

The rates of recovery (not shown) for the internal standards were generally in the range of 60 to 90%, with a tendency to lower values for the more volatile PAHs, especially naphthalene (49 to 62%). This fact can certainly be attributed to higher loss during the volume reduction process of the extract. The recovery results are, however, in a reasonable and acceptable range where no impact on

TABLE VII
PAH RESULTS OF THE THREE CARBON BLACK GRADES FOR THE FDA-BASED METHOD, 48 H SOXHLET EXTRACTION (REFERENCE VALUES)

	CB Sample L		CB Sample M		CB Sample H	
PAH compound[a]	MC, $n = 3$	SD, $n = 3$	MC, $n = 3$	SD, $n = 3$	MC, $n = 3$	SD, $n = 3$
Naphthalene	**1.93**	±0.0774	**1.52**	±0.257	**7.57**	±1.12
Acenaphthylene[b]	**0.232**	±0.0114	**0.687**	±0.0293	**4.19**	±0.141
Acenaphthene[b]	**0.0353**	±0.0022	**0.0157**	±0.0004	**0.0174**	±0.0007
Fluorene[b]	**0.0071**	±0.0004	**0.134**	±0.0086	**0.0383**	±0.0001
Phenanthrene[b]	**0.474**	±0.0122	**4.38**	±0.158	**6.07**	±0.0391
Anthracene[b]	**0.0286**	±0.0005	**0.736**	±0.0447	**0.397**	±0.0045
Fluoranthene[b]	**0.880**	±0.0070	**5.73**	±0.212	**14.1**	±0.200
Pyrene[b]	**4.57**	±0.0623	**10.1**	±0.290	**92.7**	±1.84
Benzo[*ghi*]fluoranthene[c]	**0.166**	±0.0124	**0.818**	±0.0050	**14.8**	±0.0946
Benzo[*a*]anthracene	**0.0086**	±0.0002	**0.381**	±0.0235	**0.0476**	±0.0029
Cyclopenta[*cd*]pyrene[c]	**0.164**	±0.0091	**0.568**	±0.0533	**8.62**	±0.871
Chrysene	**0.0141**	±0.0005	**0.380**	±0.0168	**0.0583**	±0.0044
Benzo[*b/j*]fluoranthene[d]	**0.0150**	±0.0010	**0.935**	±0.0288	**0.412**	±0.0089
Benzo[*k*]fluoranthene	**0.0025**	±0.0002	**0.370**	±0.0196	**0.0781**	±0.0038
Benzo[*e*]pyrene	**0.0428**	±0.0039	**0.493**	±0.0039	**2.52**	±0.0478
Benzo[*a*]pyrene	**0.0195**	±0.0014	**0.572**	**±0.0166**	**2.38**	**±0.0884**
Perylene[c]	**0.0037**	±0.0004	**0.148**	±0.0067	**0.220**	±0.0039
Dibenz[*a,h/a,c*]anthracene[d]	**<0.001**	nc	**0.0258**	±0.0008	**<0.001**	nc
Benzo[*ghi*]perylene	**0.0360**	±0.0033	**2.09**	±0.153	**28.3**	±0.570
Indeno[1,2,3-*cd*]pyrene	**0.0050**	±0.0003	**0.507**	±0.0308	**2.97**	±0.0886
Anthanthrene[c]	**0.0037**	±0.0002	**0.291**	±0.0300	**9.16**	±0.580
Coronene[c]	**0.0059**	±0.0006	**1.92**	±0.406	**21.8**	±3.10
Total 7 AFP[b]-PAHs	**6.23**	±0.0620	**21.8**	±0.174	**118**	±2.14
Total 18 GS-PAHs	**8.30**	±0.0954	**29.1**	±0.351	**162**	±2.65
Total 24 PAHs	**8.64**	±0.0871	**32.8**	±0.814	**216**	±6.86

[a] The 18 PAHs highlighted in bold are part of the GS-Mark specification. All values are given in units of mg/kg. MC, mean concentration; SD, standard deviation.
[b] Sub-group of seven PAHs for which a specific limit for its sum is specified in the GS-Mark.
[c] The PAH compound is part of the 24 PAHs determined here but is not considered within the GS-Mark specification.
[d] Co-eluting PAH compounds; values have to be considered as sum of both compounds. Less than sign indicates not detected at levels above the LOQ; nc, not calculated since not detected at levels above the LOQ.

the quantification of the native PAHs is to be expected. The standard deviations for the IStd-recovery rates were consistently below 10%, similar to the repeatability of the native PAH results.

PAH RESULTS BASED ON THE ASTM D7771 STANDARD

Table VIII shows the mean concentrations and standard deviations after the 16 h Soxhlet extraction per the ASTM D7771 standard. While the ASTM method is only intended for the determination of benzo[a]pyrene, all 24 PAHs were quantified using the same principles to examine the impact of the shorter extraction time versus the 48 h of the FDA method.

TABLE VIII
PAH RESULTS OF THE THREE CARBON BLACK GRADES FOR THE ASTM D7771-BASED METHOD, 16 H SOXHLET EXTRACTION

	CB Sample L		CB Sample M		CB Sample H	
PAH compound[a]	MC, $n = 3$	SD, $n = 3$	MC, $n = 3$	SD, $n = 3$	MC, $n = 3$	SD, $n = 3$
Naphthalene	**1.70**	±0.251	**1.27**	±0.500	**7.27**	±0.437
Acenaphthylene[b]	**0.181**	±0.0155	**0.593**	±0.0779	**3.65**	±0.194
Acenaphthene[b]	**0.0323**	±0.0021	**0.0139**	±0.0020	**0.0150**	±0.0014
Fluorene[b]	**0.0065**	±0.0005	**0.116**	±0.0094	**0.0327**	±0.0008
Phenanthrene[b]	**0.436**	±0.0081	**4.11**	±0.180	**5.76**	±0.099
Anthracene[b]	**0.0245**	±0.0004	**0.649**	±0.0334	**0.375**	±0.0071
Fluoranthene[b]	**0.763**	±0.0188	**5.52**	±0.224	**13.7**	±0.210
Pyrene[b]	**3.70**	±0.224	**9.69**	±0.365	**93.1**	±6.50
Benzo[*ghi*]fluoranthene[c]	**0.0673**	±0.0066	**0.815**	±0.0269	**15.3**	±1.02
Benzo[*a*]anthracene	**0.0042**	±0.0004	**0.359**	±0.0179	**0.0445**	±0.0023
Cyclopenta[*cd*]pyrene[c]	**0.0704**	±0.0030	**0.478**	±0.0279	**7.30**	±0.636
Chrysene	**0.0069**	±0.0006	**0.355**	±0.0143	**0.0582**	±0.0027
Benzo[*b/j*]fluoranthene[d]	**0.0045**	±0.0003	**0.890**	±0.0431	**0.404**	±0.0065
Benzo[*k*]fluoranthene	**<0.001**	nc	**0.342**	±0.0115	**0.0726**	±0.0046
Benzo[*e*]pyrene	**0.0126**	±0.0011	**0.480**	±0.0133	**2.41**	±0.041
Benzo[*a*]pyrene	**0.0054**	**±0.0007**	**0.512**	**±0.0152**	**2.13**	**±0.108**
Perylene[c]	**<0.001**	nc	**0.138**	±0.0072	**0.213**	±0.0038
Dibenz[*a,h/a,c*]anthracene[d]	**<0.001**	nc	**0.0214**	±0.0005	**<0.001**	nc
Benzo[*ghi*]perylene	**0.0113**	±0.0022	**1.64**	±0.179	**23.5**	±2.27
Indeno[1,2,3-*cd*]pyrene	**<0.001**	nc	**0.350**	±0.0347	**2.03**	±0.280
Anthanthrene[c]	**<0.001**	nc	**0.154**	±0.0201	**5.30**	±0.928
Coronene[c]	**<0.001**	nc	**0.923**	±0.189	**9.00**	±1.93
Total 7 AFP-PAHs[b]	**5.14**	±0.255	**20.7**	±0.459	**117**	±6.69
Total 18 GS-PAHs	**6.89**	±0.447	**26.9**	±0.981	**155**	±6.11
Total of 24 PAHs	**7.03**	±0.453	**29.4**	±1.01	**192**	±5.94

[a] The 18 PAHs highlighted in bold are part of the GS-Mark specification. MC, mean concentration; SD, standard deviation. All values are given in units of mg/kg. Less than sign indicates not detected at levels above the LOQ; nc, not calculated since not detected at levels above the LOQ.
[b] Sub-group of seven PAHs for which a specific limit for its sum is specified in the GS-Mark.
[c] The PAH compound is part of the 24 PAHs determined here but is not considered within the GS-Mark specification.
[d] Co-eluting PAH compounds; values have to be considered as sum of both compounds.

A comparison in relative terms to the FDA concentration levels is presented in Table IX. In general, for all three carbon black samples, the 16 h results tend to be slightly lower. For the medium and high levels carbon blacks, M and H, mostly 80 to 100% of the FDA results are obtained. The 18 GS-PAH results are in line with what Hamm et al. reported.[17] After 16 h of extraction, 89 to 99% of the amounts extractable in 48 h are being transferred into the toluene for these medium to high PAH level carbon blacks. Similar findings were reported with the use of a fluidized-bed extractor by Bergmann et al.[18] For the low-PAH–containing sample L, the more volatile PAHs, from naphthalene to pyrene, return 78 to 92% of the FDA values. However, of the larger, less volatile and less abundant PAHs that were detected in the 16 h extractions, only 27 to 49% of the FDA levels are

TABLE IX
COMPARISON OF THE ASTM D7771 RELATIVE TO THE FDA RESULTS (16 H VS 48 H SOXHLET EXTRACTION)

PAH compound	CB Sample L, %	CB Sample M, %	CB Sample H, %
Naphthalene	88	84	96
Acenaphthylene[a]	78	86	87
Acenaphthene[a]	91	89	87
Fluorene[a]	92	87	85
Phenanthrene[a]	92	94	95
Anthracene[a]	86	88	94
Fluoranthene[a]	87	96	97
Pyrene[a]	81	96	100
Benzo[*a*]anthracene	49	94	94
Chrysene	49	94	100
Benzo[*b/j*]fluoranthene[b]	30	95	98
Benzo[*k*]fluoranthene	nd	93	93
Benzo[*e*]pyrene	30	97	95
Benzo[*a*]pyrene	27	89	89
Dibenz[*a,h/a,c*]anthracene[b]	nc	83	nc
Benzo[*ghi*]perylene	31	79	83
Indeno[1,2,3-*cd*]pyrene	nd	69	68
Total 7 AFP-PAHs[a]	83	95	99
Total 18 GS-PAHs	83	93	95
Total 24 PAHs	81	90	89

[a] Sub-group of seven PAHs for which a specific limit for its sum is specified in the GS-Mark. nc, not calculated since not detected in both methods; nd, not detected in the analyses based on the 16 h Soxhlet extraction.
[b] Co-eluting PAH compounds.

extracted after 16 h, with the lowest percentage obtained for benzo[*a*]pyrene at 27%. Also, some of the larger PAHs that were detected in the 48 h extracts were not detected in the 16 h extracts so, for these PAHs, relative percentages to the 48 h results were not calculated. All these results suggest that at least in case of very low-PAH carbon black, the combination of extraction time and number of cycles per ASTM D7771 is not sufficient to extract the PAHs of interest with an acceptable efficiency.

The standard deviations measured for the ASTM D7771 are slightly higher than those of the FDA-based method but are still acceptable. For naphthalene, standard deviations between 6 and 39% were found, while for the other PAHs variations below 15% were obtained. For the PAH sums presented in Table VIII (7 AFP, 18 GS, and 24 PAH) even lower standard deviations, from 2.0 to 6.5%, were obtained. The recovery rates of the deuterated internal standards were in the same range as for the FDA.

PAH RESULTS BASED ON THE ZEK/AFPS METHOD

Table X shows the mean concentrations and standard deviations of five replicates for the three carbon black samples per the ZEK/AfPS-based method. The corresponding internal standards recovery rates are provided in Table XI, and relative comparisons to the FDA results are summarized in Tables XII through XIV.

The repeatability of the ZEK/AfPS results seems quite acceptable, at least for the high and medium PAH level samples, H and M (Table X). The variation was mostly below 15% for the

TABLE X
PAH RESULTS OF THE THREE CARBON BLACK GRADES FOR THE ZEK/AFPS-BASED METHOD, WITH 1 H ULTRASONIC EXTRACTION AT 60 °C AND QUANTIFICATION VIA THREE INTERNALS STANDARDS

	CB Sample L		CB Sample M		CB Sample H	
PAH compound	MC, $n = 5$	SD, $n = 5$	MC, $n = 5$	SD, $n = 5$	MC, n=5	SD, $n = 5$
Naphthalene	**1.26**	±0.191	**1.10**	±0.0117	**6.18**	±0.204
Acenaphthylene[a]	**1.13**	±0.388	**0.399**	±0.0187	**2.87**	±0.220
Acenaphthene[a]	**0.144**	±0.0656	**0.0141**	±0.0023	**0.0141**	±0.0021
Fluorene[a]	**0.0499**	±0.0364	**0.0331**	±0.0368	**nc**	nc
Phenanthrene[a]	**1.07**	±0.315	**2.90**	±0.133	**4.05**	±0.190
Anthracene[a]	**0.0612**	±0.0147	**0.395**	±0.0220	**0.237**	±0.0108
Fluoranthene[a]	**0.667**	±0.0913	**4.49**	±0.160	**13.6**	±0.279
Pyrene[a]	**2.96**	±0.110	**8.52**	±0.159	**92.1**	±2.33
Benzo[*a*]anthracene	**na**	na	**0.153**	±0.0074	**0.0169**	±0.0019
Chrysene	**na**	na	**0.177**	±0.0121	**0.0268**	±0.0017
Benzo[*b/j*]fluoranthene[b]	**na**	na	**1.21**	±0.0340	**0.610**	±0.0116
Benzo[*k*]fluoranthene	**na**	na	**0.438**	±0.0166	**0.0789**	±0.0051
Benzo[*e*]pyrene	**na**	na	**0.842**	±0.0269	**5.00**	±0.168
Benzo[*a*]pyrene	**na**	**na**	**0.348**	±0.0157	**2.11**	±0.0689
Dibenz[*a,h*/a,c]anthracene[b]	**na**	na	**0.0135**	±0.0021	**nc**	nc
Benzo[*ghi*]perylene	**na**	na	**0.634**	±0.0350	**13.6**	±0.509
Indeno[1,2,3-*cd*]pyrene	**na**	na	**0.095**	±0.0076	**0.900**	±0.0304
Total 7 AFP-PAHs[a]	**6.08**	±0.970	**16.7**	±0.239	**113**	±2.71
Total 18 GS-PAHs	**7.34**	±1.16	**21.7**	±0.217	**141**	±2.59

[a] Sub-group of seven PAHs for which a specific limit for its sum is specified in the GS-Mark. na, not quantified since the recovery of the internal standard was below 1%; nc, not calculated since not detected at levels above the LOQ. MC, mean concentration; SD, standard deviation. All values are given in units of mg/kg.
[b] Co-eluting PAH compounds.

individual PAHs, and only 1 to 3% for the GS-18 and AFP-7 totals. For the low-PAH containing carbon black, L, only the more volatile PAH compounds (naphthalene plus the seven AFP) could be quantified through ZEK/AfPS and with much larger relative standard deviations (4 to 73%). The other 10 larger PAHs could not be quantified in sample L, since less than 1% of the D_{12}-B[*a*]P internal standard was recovered. The issue of low recovery or loss of internal standards was not restricted to D_{12}-B[*a*]P and sample L but proved to be a systematic effect for the heavier, higher boiling PAHs on all three carbon black samples when applying the ZEK/AfPS extraction mode (Table XI). This could be carved out by using not only the minimum of three internal standards, but 17 deuterated compounds from which 16 were isotopologues of the 18 native GS-PAHs. The recovery data for the 17 deuterated internal standards in Table XI reveal that not only D_{12}-B[*a*]P is affected, but most of the high boiling PAHs. Furthermore, the data clearly indicate that there is a dependency of the IStd-recovery on the overall PAH concentration level in the carbon black and on the volatility and type of the PAH compounds considered. As will be shown later, the IStd-recovery correlates well with the ZEK/AfPS extraction efficiency for the native PAHs when compared with the 48 h Soxhlet extractions.

ZEK/AfPS blank analyses with no carbon black resulted in acceptable recovery rates for all internal standards, suggesting that the losses observed for samples L, M, and H cannot be attributed

TABLE XI
MEAN RECOVERIES OF THE 17 DEUTERATED INTERNAL STANDARDS FOR THE ZEK/AFPS-BASED PROCEDURE

	CB Sample L[a]		CB Sample M[a]		CB Sample H[a]	
Internal PAH standard	MR, $n = 5$	SD, $n = 5$	MR, $n = 5$	SD, $n = 5$	MR, $n = 5$	SD, $n = 5$
D_8-naphthalene[b]	**62**	±8.0	**49**	±5.6	**45**	±4.7
D_8-acenaphthylene	**72**	±9.1	**67**	±4.5	**57**	±5.7
D_{10}-acenaphthene	**62**	±8.2	**60**	±4.1	**57**	±5.7
D_{10}-fluorene	**60**	±7.3	**61**	±4.4	**59**	±5.2
D_{10}-phenanthrene	**44**	±6.4	**63**	±4.6	**63**	±5.4
D_{10}-anthracene	**36**	±5.3	**62**	±4.7	**64**	±5.5
D_{10}-fluoranthene	**16**	±3.6	**65**	±3.8	**70**	±5.3
D_{10}-pyrene[b]	**12**	±2.8	**65**	±3.4	**72**	±5.4
D_{12}-benzo[*a*]anthracene	**2.6**	±0.62	**47**	±1.6	**48**	±2.7
D_{12}-chrysene	**3.2**	±0.68	**48**	±1.1	**50**	±3.3
D_{12}-benzo[*b*]fluoranthene	**<1**	nc	**27**	±0.6	**25**	±1.9
D_{12}-benzo[*k*]fluoranthene	**<1**	nc	**22**	±0.4	**18**	±1.5
D_{12}-benzo[*a*]pyrene[b]	**<1**	nc	**12**	±0.7	**15**	±1.0
D_{14}-dibenzo(a,h)anthracene	**<1**	nc	**7**	±0.14	**7**	±0.70
D_{12}-benzo[*ghi*]perylene	**<1**	nc	**4**	±0.20	**7**	±0.53
D_{12}-indeno[1,2,3-*c,d*]pyrene	**<1**	nc	**3**	±0.09	**5**	±0.44
D_{12}-coronene	**<1**	nc	**1**	±0.12	**2**	±0.17

[a] SD values represent absolute standard deviations as a percentage. MR, mean recovery; SD, standard deviation; less than symbol indicates not detected at levels above the LOQ indicated; nc, not calculated since the recovery of the IStd was below 1%.

[b] The three deuterated PAH compounds highlighted in bold are specified as standard and minimum number in the ZEK/AfPS method for the quantification of the 18 PAHs.

to the extraction technique or the extract clean-up but to the specific carbon black matrix. This conclusion is supported by our experience on rubber or plastic materials where no such IStd loss is observed when tested through the ZEK/AfPS method.

As will be shown below through some complementary tests, adsorption of the deuterated PAH standards on the carbon black surface during the sonication treatment or during the matrix separation process appears as the most likely reason for the standard loss. This phenomenon seems to be more significant for the larger PAHs. The postulated adsorption behavior could also explain the dependence of the IStd-recovery on the PAH concentrations in the carbon black and on the volatility of the PAH compounds. Higher concentrations may lead to higher amounts in the ZEK/AfPS extract and, in turn, to higher recovery of the internal standard. A stronger affinity and adsorption of the heavier PAHs on the carbon black surface would lead to a lower recovery of the corresponding IStds, as opposed to the more volatile PAHs (e.g., naphthalene, acenaphthylene, acenaphthene, and fluorene).

Since the adsorption behavior of the native PAHs and their deuterated isotopologues should be very similar, the partition effect should likewise apply to the native PAHs present on the carbon black. This, however, should have a significant impact on the quantitative results when applying the ZEK/AFPS method to carbon black, especially when using different kinds and numbers of internal standards for quantification. Furthermore, this distribution behavior would imply that the PAHs exhibiting a stronger affinity with the carbon black surface are extracted only to a low extent by the

TABLE XII
COMPARISON, RELATIVE TO THE FDA, OF THE ZEK/AFPS RESULTS OBTAINED WITH 3 AND 16 INTERNAL STANDARDS FOR THE H SAMPLE

	CB Sample H				
	FDA	ZEK/3 IStds		ZEK/16 IStds	
PAH compound	MC, $n = 3$, mg/kg	MC, $n = 5$, mg/kg	% of FDA results	MC, $n = 5$, mg/kg	% of FDA results
(1)	(2)	(3)	(4)	(5)	(6)
Naphthalene	7.57	6.18	**82**	6.19	**82**
Acenaphthylene	4.19	2.87	**68**	3.49	**83**
Acenaphthene	0.01737	0.0141	**81**	0.0173	**99**
Fluorene	0.038	<0.01	**<26**	0.0372	**97**
Phenanthrene	6.07	4.05	**67**	4.69	**77**
Anthracene	0.397	0.237	**60**	0.269	**68**
Fluoranthene	14.1	13.6	**96**	13.3	**94**
Pyrene	92.7	92.1	**99**	87.7	**95**
Benzo[*a*]anthracene	0.04760	0.0169	**35**	0.0278	**58**
Chrysene	0.05833	0.0268	**46**	0.0408	**70**
Benzo[*b/j*]fluoranthene[a]	0.412	0.610	**148**	0.374	**91**
Benzo[*k*]fluoranthene	0.07810	0.0789	**101**	0.0660	**85**
Benzo[*e*]pyrene	2.52	5.00	**198**	5.03	**199**
Benzo[*a*]pyrene	2.38	2.11	**89**	2.17	**91**
Dibenz[*a,h/a,c*]anthracene[a]	<0.001	<0.01	**nc**	<0.01	**nc**
Benzo[*ghi*]perylene	28.3	13.6	**48**	28.2	**100**
Indeno[1,2,3-*cd*]pyrene	2.97	0.900	**30**	2.84	**96**
Total 7 AFP-PAHs	118	113	**96**	109	**93**
Total 18 GS-PAHs	162	141	**87**	154	**95**

[a] Co-eluting PAH compounds; values have to be considered as sum of both compounds. nc, not calculated since not detected at levels above the LOQ; less than sign indicates not detected at levels above the LOQ indicated.

ultrasonic treatment of the ZEK/AfPS method. Comparisons of the ZEK/AfPS results relative to 48 h Soxhlet extraction in Tables XII to XVI clearly demonstrate that this is the case. For this comparison, the authors used not only the ZEK/AfPS results, obtained when quantifying methods were compliant with only three internal standards (as provided in Table X), but also data based on quantification via all 16 deuterated analogues, added for the purpose of this study.

When interpreting the data of Tables XII to XIV, one has to consider the IStd-recoveries shown in Table XI. By using just three deuterated internal standards (D_8-naphthalene, D_{10}-pyrene, and D_{12}-benzo[*a*]pyrene), only naphthalene, pyrene, and benzo[*a*]pyrene are quantified via their isotopologues (isotope dilution method). Even with a low IStd-recovery, if a similar partition of the native PAHs and the deuterated analogues added prior to the extraction occurs on the carbon black surface during the ultrasonic treatment, sensible results would be expected. Quantitative extraction of the native PAHs from the carbon black must not necessarily occur in this case. As can be seen from the fourth columns of Tables XII and XIII, percentages between 61 and 99% relative to the FDA data were obtained for these three PAH compounds in samples H and M. The mean recoveries

TABLE XIII
COMPARISON, RELATIVE TO THE FDA, OF THE ZEK/AFPS RESULTS OBTAINED WITH 3 AND 16 INTERNAL STANDARDS FOR THE M SAMPLE

	CB Sample M				
	FDA	ZEK/3 IStds		ZEK/16 IStds	
PAH compound	MC, $n = 3$, mg/kg	MC, $n = 5$, mg/kg	% of FDA results	MC, $n = 5$, mg/kg	% of FDA results
(1)	(2)	(3)	(4)	(5)	(6)
Naphthalene	1.52	1.10	**72**	1.10	**72**
Acenaphthylene	0.687	0.399	**58**	0.449	**65**
Acenaphthene	0.016	0.0141	**90**	0.0153	**98**
Fluorene	0.134	0.0331	**25**	0.0827	**62**
Phenanthrene	4.38	2.90	**66**	2.99	**68**
Anthracene	0.736	0.395	**54**	0.398	**54**
Fluoranthene	5.73	4.49	**78**	4.50	**79**
Pyrene	10.1	8.52	**84**	8.52	**84**
Benzo[*a*]anthracene	0.381	0.153	**40**	0.212	**55**
Chrysene	0.380	0.177	**47**	0.241	**63**
Benzo[*b/j*]fluoranthene[a]	0.935	1.21	**129**	0.549	**59**
Benzo[*k*]fluoranthene	0.370	0.438	**118**	0.237	**64**
Benzo[*e*]pyrene	0.493	0.842	**171**	0.826	**167**
Benzo[*a*]pyrene	0.572	0.348	**61**	0.339	**59**
Dibenz[*a,h/a,c*]anthracene[a]	0.026	0.0135	**53**	0.0311	**121**
Benzo[*ghi*]perylene	2.09	0.634	**30**	1.74	**83**
Indeno[1,2,3-*cd*]pyrene	0.507	0.095	**19**	0.375	**74**
Total 7 AFP-PAHs	21.8	16.8	**77**	17.0	**78**
Total 18 GS-PAHs	29.1	21.7	**75**	22.6	**78**

[a] Co-eluting PAH compounds; values have to be considered as sum of both compounds.

of their deuterated analogues were between 12 and 72% (Table XI). Owing to the total loss of the B[*a*]P internal standard for the low-PAH carbon black L, benzo[*a*]pyrene could not be quantified (Table XIV). Naphthalene and pyrene returned 65% relative to the FDA for sample L, at recoveries of 62 and 12% for the deuterated analogues.

While deuterated naphthalene is exclusively used as an internal standard for native naphthalene, D_{10}-pyrene is taken for the quantification of the seven AFP-PAHs, and D_{12}-benzo[*a*]pyrene for the remaining 10 higher boiling PAH compounds, in the ZEK/AfPS approach. This approach assumes that all native PAH compounds quantified via these internal standards behave as the deuterated compounds through the internal standard method. However, the IStd-recovery data of Table XI already indicate that this seems not to be the case. If a PAH compound shows a stronger affinity to carbon black than its internal standard, much lower concentration values would result, and vice versa. The impact of this effect can best be seen for the seven AFP-PAHs of sample L and for the higher boiling PAHs in samples H and M. While for sample L the recovery of the internal D_{10}-pyrene standard is 12%, the recovery of the isotopologues of the remaining six AFP-PAHs increases from 16% for D_{10}-fluoranthene to 72% for D_8-acenaphthylene. If the

TABLE XIV
COMPARISON, RELATIVE TO THE FDA, OF THE ZEK/AFPS RESULTS OBTAINED WITH 3 AND 16 INTERNAL STANDARDS FOR THE L SAMPLE

	CB Sample L[a]				
	FDA	ZEK/3 IStds		ZEK/16 IStds	
PAH compound	MC, $n = 3$, mg/kg	MC, $n = 5$, mg/kg	% of FDA results	MC, $n = 5$, mg/kg	% of FDA results
(1)	(2)	(3)	(4)	(5)	(6)
Naphthalene	1.93	1.26	**65**	1.25	**65**
Acenaphthylene	0.232	1.13	**487**	0.245	**106**
Acenaphthene	0.0353	0.144	**408**	0.0266	**75**
Fluorene	0.0071	0.050	**704**	0.0173	**244**
Phenanthrene	0.474	1.07	**226**	0.263	**55**
Anthracene	0.0286	0.0612	**214**	0.0186	**65**
Fluoranthene	0.880	0.667	**76**	0.538	**61**
Pyrene	4.57	2.96	**65**	3.16	**69**
Benzo[*a*]anthracene	0.0086	na	**na**	nc	**nc**
Chrysene	0.0141	na	**na**	nc	**nc**
Benzo[*b/j*]fluoranthene[b]	0.0150	na	**na**	na	**na**
Benzo[*k*]fluoranthene	0.0025	na	**na**	na	**na**
Benzo[*e*]pyrene	0.0428	na	**na**	na	**na**
Benzo[a]pyrene	0.0195	na	**na**	na	**na**
Dibenz[*a,h/a,c*]anthracene[b]	nc	na	**na**	na	**na**
Benzo[*ghi*]perylene	0.0360	na	**na**	na	**na**
Indeno[1,2,3-*cd*]pyrene	0.0050	na	**na**	na	**na**
Total 7 AFP-PAHs	6.23	6.08	**98**	4.27	**69**
Total 18 GS-PAHs	8.30	7.34	**88**	5.52	**67**

[a] Nc, not calculated since not detected at levels above the LOQ; na, not applicable since the recovery of the internal standard D_{12}-B[*a*]P was below the LOQ of 1%.
[b] Co-eluting PAH compounds; values have to be considered as sum of both compounds.

corresponding six native compounds show a similar distribution like their deuterated analogues, quantification via D_{10}-pyrene should lead to falsely high results. Comparison with the 48 h Soxhlet extraction, provided in absolute and relative terms in columns 3 and 4 of Table XIV, clearly indicates that this is the case. The results are higher by a factor of up to seven and cannot be real. This can easily be verified when considering the data of the last two columns in Table XIV, where concentrations and percentages are calculated using the deuterated isotopologue for each of the seven AFP-PAHs. By doing so, mean concentration values in the range of 55 to 106% of the FDA results were obtained, except for fluorene, which showed unreasonably high values not only in these ZEK/AfPS extractions, but also in some subsequent analyses of sample L. These high fluorene values are unrealistic and are most likely due to interfering compounds that could not be separated by the GC column or could not be detected by the low resolution mass spectrometer.

Similar effects were observed for the higher boiling PAHs from benzo[*a*]anthracene to indeno[1,2,3-*cd*]pyrene on samples H and M when quantified via D_{12}-benzo[*a*]pyrene only.

Percentages between one fifth and twice the mean FDA concentrations were obtained (third and fourth columns of Tables XII and XIII). Again, the other internal standards show significantly lower or higher recovery than D_{12}-benzo[*a*]pyrene (Table XI), suggesting a similar behavior of the corresponding native PAHs as well. Thus, quantifying solely via D_{12}-benzo[*a*]pyrene leads to significantly higher or significantly lower values for the larger PAHs. Again, the ZEK/AfPS results for the H and M grades are becoming more in line with the FDA data when using all eight available internal standards for the quantification of the 10 higher boiling PAHs (see columns 5 and 6 of Tables XII and XIII).

As mentioned before, neither the D_{12}-benzo[*a*]pyrene standard nor five of the seven additional standards for the higher boiling PAHs were recovered for the carbon black L. D_{12}-benzo[*a*]anthracene and D_{12}-chrysene were detected at only 2.6 and 3.2% of the amount added, whereas the native analogues were below the LOQs of the method (see Tables XI and XIV). Apparently, the internal standards were fully or nearly totally adsorbed on the surface of this low-PAH carbon black grade.

COMPLEMENTARY TESTS ON THE ZEK/AFPS METHOD

To demonstrate the distribution hypothesis, a series of complementary tests was conducted. Each carbon black sample was again tested against the ZEK/AfPS method but with no addition of the internal standards prior to the extraction. Instead, the 16 deuterated PAHs were added this time to the toluene extract after separation from the carbon black. Table XV summarizes the results relative to the FDA reference. The values and patterns of the native PAHs are similar to those obtained with the original ZEK/AfPS procedure for the 16 internal standards when added prior to the extraction (Tables XII to XIV). This is further highlighted through Table XVI for the seven AFP compounds and the larger PAHs, for which the proportion extracted is comparable to the recovery of the corresponding internal standard. This clearly indicates that the relative distribution of the deuterated and native PAHs between the carbon black surface and the toluene phase are comparable. The data also emphasize the extraction efficiency dependency on the type and the concentration level of the various PAHs and also most likely on the carbon black surface area.

A second series of complementary tests was performed on the carbon black residues obtained through the modified ZEK/AfPS protocol. The three carbon black samples, which have already been extracted through the 1 h sonication treatment, were re-extracted using fresh solvent but with no new addition of internal standards. Assuming that the relative PAH distribution between the two phases is maintained, similar quantitative results should be obtained as long as the IStd-recovery exceeds 1%. To minimize the potential redistribution of the PAHs through readsorption onto the carbon black surface over time, the matrix separation was performed immediately after the sonication treatment for these complementary tests. The extracts were usually allowed to cool down to room temperature prior to the centrifugation step for the other tests. The IStd-recovery rates for these two consecutive extractions are presented in Table XVII. They are somewhat higher than the mean values shown in Table XI with a consistent pattern in decreasing recovery rates as the PAHs get larger. Close to complete loss of the standards is confirmed for the carbon black sample L. The higher recovery rates in the first extraction can probably be attributed to the faster separation from the carbon black matrix, directly after the sonication treatment. The results obtained for the second extraction complement very well those of the first, yielding improved cumulative recovery rates and confirming the PAH distribution patterns for all three carbon black samples. It should be noted that recovery values above 100% are not unreasonable due to a larger uncertainty on the recovery determination compared with the quantification of the native PAHs.

The corresponding concentrations for the 18 native PAHs relative to the FDA reference values are shown in Table XVIII. For the first extraction, the concentrations are similar to those of Tables

TABLE XV
COMPARISON, RELATIVE TO THE FDA, OF THE ZEK/AFPS RESULTS WHEN QUANTIFYING THE PAHS IN THE EXTRACT BY ADDITION OF THE 16 ISTDS AFTER THE EXTRACTION AND MATRIX SEPARATION[a]

PAH compound	CB Sample L, %	CB Sample M, %	CB Sample H, %
Naphthalene	80	72	88
Acenaphthylene	99	66	81
Acenaphthene	100	92	100
Fluorene	314[b]	79	101
Phenanthrene	42	76	77
Anthracene	51	59	67
Fluoranthene	9.4	73	87
Pyrene	6.8	69	84
Benzo(a)anthracene	na	35	29
Chrysene	<71	40	36
Benzo[*b/j*]fluoranthene[c]	<66	19	26
Benzo[*k*]fluoranthene	na	13	14
Benzo[*e*]pyrene	<23	24	32
Benzo[*a*]pyrene	<51	7.2	12
Dibenz[*a,h/a,c*]anthracene[c]	na	<38	na
Benzo[*ghi*]perylene	<28	3.2	7.9
Indeno[1,2,3-*cd*]pyrene	na	2.4	4.8
Total 7 AFP-PAHs	**14**	**71**	**84**
Total 18 GS-PAHs	**29**	**60**	**67**

[a] Na, Not applicable since the LOQ was higher than the concentration detected in the FDA-based analysis; less than sign indicates extraction efficiency lower than the value indicated.
[b] The unreasonable high value of fluorene is most likely caused by one or more compounds interfering in the GC/MS analysis.
[c] Co-eluting PAH compounds.

XII through XIV. Results of comparative magnitude were obtained after the second extraction, supporting the hypothesis that the native and deuterated PAHs have equivalent behavior and affinity toward the carbon black and the solvent phase during the ZEK/AfPS extraction process. The high affinity of the large PAHs for the carbon black surface and their resulting low recovery rates make it almost impossible to quantify these compounds in carbon black using the ZEK/AfPS extraction method.

To get a better understanding of the distribution dynamics of the native and deuterated PAHs between the carbon black surface and toluene, a final series of experiments was performed. Half a gram of the three carbon black samples was suspended in 20 mL toluene with addition of the 16 internal standards. These carbon black suspensions were stored with no ultrasound treatment in a 60 °C water bath for 15 min and allowed to cool down for another 15 min. The subsequent matrix separation and PAH quantification were performed following the same protocol as for the other ZEK/AfPS analyses of this project. Table XIX compiles the results of these tests.

The recovery patterns of the 16 ISTds are slightly different than those found for the ZEK/AfPS extractions with ultrasound treatment. For naphthalene and the seven AFP-PAHs, the recoveries of the appropriate eight ISTds were 3 to 46% lower in absolute terms, whereas the eight ISTds for the higher boiling PAHs showed higher recoveries (3 to 46% in absolute terms). When calculating carbon black related PAH concentrations by using the native and deuterated PAH amounts detected in the toluene phase under this soft extraction in diffusion mode (no sonication treatment),

TABLE XVI
EXTRACTION EFFICIENCY OF THE MODIFIED ZEK/AFPS FOR THE NATIVE GS-PAHS AND THE 16 DEUTERATED INTERNAL STANDARDS

	CB Sample L		CB Sample M		CB Sample H	
Parameter	IStd added after extraction[a]	IStd added before extraction[b]	IStd added after extraction[a]	IStd added before extraction[b]	IStd added after extraction[a]	IStd added before extraction[b]
PAH parameter, %						
Naphthalene[c]	80	62	72	49	88	45
7 AFP-PAHs[c] (range of individual data)	6.8–100[d]	12–72	59–92	60–67	67–101	57–72
Higher boiling GS-PAHs[c] from benzo[*a*]anthracene to indeno[1,2,3-*cd*]pyrene	na to <71	≤4	2.4–40	3.0–47	4.8–36	5–50

[a] Compounds considered when internal standards are added after extraction are native PAHs. Results are given as a percentage of FDA results.
[b] Compounds considered when internal standards are added before extraction are deuterated PAHs. Results are given in terms of mean recovery ($n = 5$).
[c] Native PAH compound or corresponding deuterated internal standard.
[d] With the exception of fluorene, which showed an unrealistic value of 314%, probably due to chromatographic interferences.

TABLE XVII
RECOVERY RATES OF THE 16 INTERNAL STANDARDS FOR TWO CONSECUTIVE ZEK/AFPS EXTRACTIONS

Deuterated internal PAH standard (IStd)	CB Sample L			CB Sample M			CB Sample H		
	First extraction, %[a]	Second extraction, %[b]	Total recovery, %	First extraction, %[a]	Second extraction, %[b]	Total recovery, %	First extraction, %[a]	Second extraction, %[b]	Total recovery, %
D_8-naphthalene[c]	**94**	**19**	**113**	**83**	**2**	**85**	**90**	**9**	**99**
D_8-acenaphtylene	81	11	92	79	2	81	82	7	89
D_{10}-acenaphthene	102	14	116	94	2	96	93	8	101
D_{10}-fluorene	99	15	115	87	3	90	94	8	101
D_{10}-phenanthrene	63	18	81	84	3	87	90	8	97
D_{10}-anthracene	54	19	74	90	4	93	92	8	100
D_{10}-fluoranthene	26	17	43	95	11	106	101	13	114
D_{10}-pyrene[c]	**22**	**15**	**37**	**101**	**13**	**114**	**105**	**15**	**120**
D_{12}-benzo[*a*]anthracene	4	4	8	68	19	87	73	19	92
D_{12}-chrysene	4	4	8	66	18	84	74	17	91
D_{12}-benzo[*b*]fluoranthene	<1	<1	<2	38	21	60	50	21	71
D_{12}-benzo[*k*]fluoranthene	<1	<1	<2	32	19	51	41	19	60
D_{12}-benzo[*a*]pyrene[c]	**<1**	**<1**	**<2**	**18**	**12**	**30**	**30**	**16**	**46**
D_{14}-dibenzo[*a,h*]anthracene	<1	<1	<2	9	6	15	16	7	23
D_{12}-benzo[*ghi*]perylene	<1	<1	<2	6	5	11	11	9	25
D_{12}-indeno[1,2,3-*cd*]pyrene	<1	<1	<2	4	3	7	12	6	18

[a] The 16 internal standards were added prior to the first extraction. Less than symbol indicates recovery of the internal standard below the LOQ indicated.
[b] With no extra addition of internal standards.
[c] Internal standards of the ZEK/AfPS method.

TABLE XVIII
COMPARISON, RELATIVE TO THE FDA, OF THE NATIVE PAH RESULTS OBTAINED AFTER A FIRST ZEK/AFPS EXTRACTION AND BY RE-EXTRACTION OF THE RESIDUAL CARBON BLACK WITHOUT NEW INTERNAL STANDARD ADDITION[a]

	CB Sample L		CB Sample M		CB Sample H	
Parameter	First extraction with IStds addition[b]	Re-extraction without standard addition[c]	First extraction with IStds addition[b]	Re-extraction without standard addition[c]	First extraction with IStds addition[b]	Re-extraction without standard addition[c]
Naphthalene	73	96	67	108	75	95
Acenaphthylene	127	164	53	97	70	88
Acenaphthene	104	117	89	391	69	231
Fluorene	394[d]	459[d]	40	158	64	99
Phenanthrene	69	83	62	81	65	80
Anthracene	100	154	50	78	58	79
Fluoranthene	76	78	75	93	85	92
Pyrene	71	77	76	91	79	84
Benzo[*a*]anthracene	<116	<116	50	68	34	30
Chrysene	na	na	57	69	52	72
Benzo[*b/j*]fluoranthene[e]	na	na	62	66	71	77
Benzo[*k*]fluoranthene	na	na	64	66	60	71
Benzo[*e*]pyrene	na	na	165	139	134	103
Benzo[*a*]pyrene	na	na	66	66	66	65
Dibenz[*a,h/a,c*]anthracene[e]	na	na	nc	nc	nd	nd
Benzo[*ghi*]perylene	na	na	86	88	65	75
Indeno[1,2,3-*cd*]pyrene	na	na	86	96	65	83

[a] All extractions were performed in ZEK/AfPS extraction mode using 16 internal standards. All results are given as a percentage of mean FDA result. na, not applicable since the recovery of the internal standard was below the recovery-LOQ of 1%; nc, Not calculated since the LOQ in the ZEK/AfPs analysis was higher than the concentration detected for the FDA method; nd, not detected at levels above the LOQ of the ZEK/AfPS method.
[b] The 16 internal standards were added prior to the first extraction.
[c] With no extra addition of internal standards.
[d] Unrealistic high value, probably due to chromatographic interferences.
[e] Co-eluting PAH compounds.

TABLE XIX
RESULTS AFTER SUSPENDING THE THREE CARBON BLACK GRADES IN TOLUENE FOR 30 MIN WITH NO ULTRASOUND TREATMENT[a]

Native or deuterated PAH compound	CB Sample L			CB Sample M			CB Sample H		
	Concentration, mg/kg[b]	Percentage of FDA result, %[b]	IStd-Recovery, %	Concentration, mg/kg[b]	Percentage of FDA result, %[b]	IStd-Recovery, %[b]	Concentration, mg/kg[b]	Percentage of FDA result, %[b]	IStd-Recovery, %
Naphthalene[c]	**1.09**	**57**	**36**	**0.872**	**57**	**38**	**5.55**	**73**	**9**
Acenaphthylene	0.213	92	32	0.273	40	34	2.60	62	11
Acenaphthene	0.022	63	39	0.010	64	39	<0.01	nc	12
Fluorene	<0.01	nc	35	0.029	21	38	0.015	39	16
Phenanthrene	0.205	43	27	2.41	55	32	3.89	64	26
Anthracene	<0.01	nc	24	0.294	40	33	0.227	57	25
Fluoranthene	0.334	38	21	3.93	69	49	13.2	94	51
Pyrene[c]	**1.71**	**37**	**19**	**7.39**	**73**	**56**	**83.9**	**90**	**68**
Benzo[*a*]anthracene	<0.01	<116	7	0.119	31	65	0.014	29	60
Chrysene	<0.01	<71	7	0.135	36	63	0.020	33	59
Benzo[*b/j*]fluoranthene[d]	na	na	1	0.360	39	47	0.226	55	47
Benzo[*k*]fluoranthene	na	na	1	0.121	33	42	0.027	34	41
Benzo[*e*]pyrene	na	na	<1	0.396	80	na	2.65	105	na
Benzo[*a*]pyrene[c]	**na**	**na**	**<1**	**0.189**	**33**	**30**	**1.05**	**44**	**31**
Dibenz[*a,h/a,c*]anthracene[d]	na	na	<1	nd	nc	17	nd	nc	19
Benzo[*ghi*]perylene	na	na	<1	0.834	40	13	11.9	42	17
Indeno[1,2,3-*cd*]pyrene	na	na	<1	0.160	32	10	1.03	35	15

[a] A quantity of 0.5 g of carbon black was suspended in 20 mL of toluene for 15 min at 60 °C and subsequently cooled down for 15 min prior to filtration and PAH quantification with the 16 internal standards.
[b] Na, not applicable since the LOQ was higher than the concentration for the FDA method; nc, not calculated since the native PAH was not detected at levels above the LOQ; nd, not detected at levels above the LOQ of the ZEK/AfPS method.
[c] Internal standards of the ZEK/AfPS method.
[d] Co-eluting PAH compounds.

percentages in the range of 21 to 94% of the FDA reference values were obtained for naphthalene and the seven AFP-PAHs. For the heavier PAHs, concentration values proved to be generally lower than the FDA results with a few exceptions. As for carbon black sample L, the large PAHs were found to be difficult or impossible to quantify due to a complete loss of the IStds. The concentration and IStd-recovery data of these tests indicate that balanced distribution of the native PAHs and their corresponding IStds between the liquid phase and the carbon black surface has not been achieved as yet under these soft extraction conditions. A significant fraction of the IStds has not been given enough time and energy to be adsorbed on the carbon black surface to the same extent as for the ZEK/AfPS protocol, while a significant fraction of the native PAHs has not been transferred yet to the solvent phase and reached equilibrium.

CONCLUSIONS

Owing to the surface characteristics of carbon black, the determination of PAHs from such a matrix requires specific extraction conditions, different from those applied for conventional environmental matrices. The affinity of PAHs for the carbon black surface requires vigorous extraction conditions. The use of the Soxhlet apparatus with toluene is recommended, as such a system guarantees cycles of fresh solvent to come into contact with the carbon black, compensating for its PAH affinity. The ZEK/AfPS method, established for the PAH analysis of polymers, cannot quantitatively extract PAHs from carbon black for this reason. The extraction efficiency depends on the type of PAHs and their concentration levels in the carbon black; these parameters having an impact on the adsorption strength of the individual PAHs on the carbon black surface. This is especially true for the larger and more toxicologically potent PAHs, which are difficult to extract from the carbon black surface using the ZEK/AfPS extraction conditions. Variation of the ultrasound test conditions for optimization of the PAH extraction efficiency from carbon black was not tested within this study.

Furthermore, applying the minimum of three internal standards as prescribed in the ZEK/AFPS method was proven insufficient for an accurate quantification of the 18 GS-PAHs in carbon black. They can even result, in some cases, in false positives and false negatives. Even if the use of 16 internal standards was shown to improve the quality of the results, the partial or complete loss of the internal standards due to their adsorption on the carbon black surface, combined with a low extraction efficiency for the larger PAHs, make the ZEK/AfPS method unsuitable for carbon black.

Based on our experience, such low internal standard recoveries are usually not observed when testing rubber or plastic materials with the ZEK/AfPS method. This phenomenon could probably be explained by the fact that once incorporated in the rubber or plastics matrix, the carbon black surface is saturated with polymer, making it hardly accessible for the internal standards even under ultrasound vibrations. It would be interesting to evaluate the extraction efficiency of the ZEK/AfPS procedure for the PAHs contributed by the carbon black once embedded in the rubber or plastics matrix.

Close monitoring of the internal standards recovery would be mandatory to make the ZEK/AfPS method more robust. However, such an improved ZEK/AfPS test method would still only be of use as a screening tool for carbon blacks containing medium and high PAH levels, and under no circumstances could be considered for compliance testing of carbon black against regulations.

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