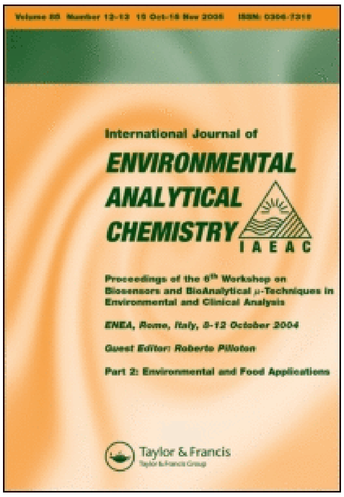

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Polycyclic Aromatic Hydrocarbons (PAH) in Abraded Particles of Brake and Clutch Linings†

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Clutch linings and, in particular, brake linings are subjected to considerable thermal stress. Pyrolytic decomposition of the organic portions of the abraded particles can result from this. The products of such cracking reactions include polycyclic aromatic hydrocarbons (PAH). These substances, some of which are carcinogenic, exhibit distinctly adsorptive properties with respect to chrysotile, which makes up, on average, 30% of brake linings.

The evaluation of the occupational–medical risks to automotive mechanics during the servicing and repairing of braking systems and clutches should take account of synergistic effects between asbestos fibres and PAH.

From the point of view of environmental medicine it should be pointed out that *ca.* 10 t of asbestos fibres are emitted annually in the Federal Republic of Germany as a result of the braking of motorized vehicles.

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It has been possible to determine quantitatively a range of 21 PAH in $n=52$ samples of abraded particles from clutch and brake linings of automobiles and trucks by means of capillary gas chromatography–mass spectrometry. It was found that the PAH concentrations in brake lining abrasions (automobiles $14.4 \pm 20.7\,\mu g/g$; trucks $15.3 \pm 9.9\,\mu g/g$) were appreciably lower than those in clutch lining abrasions (automobiles $32.9 \pm 32.7\,\mu g/g$; trucks $101.5 \pm 194.4\,\mu g/g$). The same trend is apparent for the 5 PAH chosen from the TLV (threshold limit value) list, that have been unequivocally characterized as carcinogenic in animal experiments, which comprised a mean of 24.2% of the total PAH concentration in the samples investigated.

In spite of the relatively low concentrations of PAH, from the point of view of occupational and environmental medicine, the possible combined effect of the asbestos dust and the PAH adsorbed onto it, which is contained in the abraded material from clutch and brake linings, should not be ignored, particularly since animal experiments point to a multiplication of the risks as a result of a stimulation of BaP metabolism by asbestos fibres with an increased formation of DNA/PAH adducts.

KEY WORDS: PAH and asbestos synergism, brake and clutch lining, abraded particles, PAH-analysis.

INTRODUCTION

The composition of the clutch and brake linings of automotive vehicles depends on the stresses to which they are subjected. Normal brake linings contain, on average, 30% chrysotile asbestos along with organic chemical fibres. The necessary strength is obtained by employing binders composed of synthetic resins and/or synthetic rubbers.

Abraded particles are subjected to considerable thermal stresses. Thus, for example, "local" temperatures up to 500°C can occur for short periods during braking. Pyrolytic decomposition reactions of the organic components of the abrasions are thus to be expected.[1] Some of the polycyclic aromatic hydrocarbons (PAH), which are to be expected amongst the products, are proven carcinogens. It has been shown experimentally that chrysotile, in comparison with other types of asbestos or synthetic mineral fibres, possesses a great tendency to adsorb PAH[2].

Occupational–medical experience is available concerning the risks, attendant upon the inhalation of asbestos fibre dust, which automotive mechanics are exposed to when servicing and repairing braking systems and clutches.[3] The practice of blowing out brake drums and clutch housings with compressed air is particularly undesirable from an occupational–medical point of view. Furthermore, the emission of asbestos fibre particles into the environment as a result of braking has also to be taken into account.

The estimation of both the environmental–medical and the occupational–medical risks should take account of the dangers of PAH adsorbed onto asbestos particles. The question to be addressed here is to what extent PAH occur in the particles abraded from clutch linings and, in particular, from brake linings and, thus, to what extent the synergistic effects of chrysotile fibres and PAH need to be considered.

MATERIALS AND METHODS

a) Samples investigated

A total of $n=52$ samples of abraded particles were taken from automotive repair shops. The samples were obtained by brushing out the brakes and clutches that were to be worked on.

The samples were made up as follows:

	Abrasion samples		
Type	Automobile	Truck	Total
Brake	24	10	34
Clutch	11	7	18
Total	35	17	52

b) Sample preparation and analysis

The samples were subjected to multi-stage preparation. A *ca.* 4 h Soxhlet extraction was followed by further sample preparation steps.[4,5]

The qualitative and quantitative analysis of the PAH was performed by capillary gas chromatography. The identification of the individual components was based, on the one hand, on a comparison of gas chromatographic retention times of PAH reference substances and, on the other hand, on mass specific detection of the substance-specific individual masses of the PAH molecules (SIM = selected ion monitoring). This meant that interfering components in the matrix could be largely ignored.

RESULTS

On each occasion it was possible to separate out a total of $n = 21$ PAH from the extracts of the abraded dust from brake and clutch linings, by means of capillary gas chromatography (Figure 1).

The figure illustrates the gas chromatogram of the extract of one abraded dust from one brake lining and one clutch lining coupled with the PAH detected qualitatively by mass spectroscopy. These substances possess differing carcinogenic and mutagenic activities[6-13] (Table I).

The five substances designated with asterisks are listed in the TLV list[14] in chapter III, i.e. they have been unequivocally proven to be carcinogenic in animal tests. Neither the *j*-isomer of the benzofluoranthene nor chrysene and triphenylene could be separated by gas chromatography. The equal molecular weights and similar fragmentation patterns mean that these isomers cannot be differentiated by mass spectroscopy either. The two groups are therefore reported as the sums of their respective isomeric components.

The toxicologically less relevant anthracene and phenanthrene have not been listed. Because of the relatively large percentage quantities of these present, their inclusion in the general PAH profile can lead to false conclusions.

In Table II there is a comparison of the means and standard deviations ($\bar{x} \pm s$) of the PAH concentrations in the abraded dust from brakes and clutches of various vehicles. The presentation differentiates the total 21 PAH analysed and the 5 of them designated as unequivocally carcinogenic in animal experiments in the TLV list.

By carrying out multiple-analyses of one and the same toluene extract of a brake and clutch lining dust sample it could be excluded, that the wide range of the measured PAH-concentrations in the total 52 samples, are a result of a possible analytical fault (Table III).

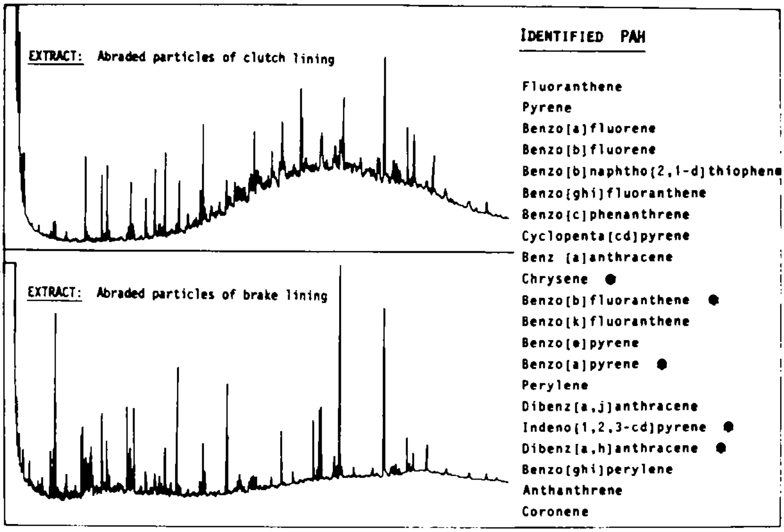

FIGURE 1 Capillary gas chromatogram of worked-up extracts of dust abraded from brake and clutch linings and the individual components of the basic PAH as identified by mass spectroscopy.

* = Unequivocally demonstrated to be carcinogenic in animal experiments and named in the TLV list.[14]

Chromatographic operating conditions

Glass capillary column

Stationary phase	SE 54, cross-linked
Column length (m)	25
Internal diameter (mm)	0.25
Film thickness (μm)	0.35

Carrier gas (helium)

Flow (ml/min)	0.85–0.87
Temperature program (°C)	120–70–150
	150–2.2–220
	220–10–280

Sample application (on-column injection)

Volume (μl)	1

Detection (FID)

MS: SIM (selected ion monitoring) acquisition

TABLE I

$N = 21$ polycyclic aromatic hydrocarbons (PAH) identified by glass capillary gas chromatography (GCGC/MS) in abraded particles of brake and clutch linings of passenger cars and lorries. Classification of their biological activities in subcutaneous and epicutaneous animal test systems. With the exception of benzo[a]pyrene no adequate data are available on the teratogenicity of the PAH.

Compound	Carcinogenicity (animal studies)	Mutagenicity (Ames test)	References
Fluoranthene	–; CC	+	6, 7, 8
Pyrene	–; CC	–	6, 8, 9, 10
Benzo[a]fluorene	–	–/+	6, 7
Benzo[b]fluorene	–	–	6, 7
Benzo[b]naphtho-[2,1-d]thiophene	–	+	10, 11
Benzo[ghi]fluoranthene	–	–/+	6, 7
Benzo[c]phenanthrene	–; +; + +; TI	+ +; –	6, 9, 11, 13
Cyclopenta[cd]pyrene	±; +; + +; TI	+ + +; –	6, 10, 11
Benz[a]anthracene	±/+; TI	+	6, 7, 9, 12
Chrysene	±/+; TI	+	6, 9, 11, 13
Benzo[b+k]fluoranthene	+/+ +/+ + +; TI	+ +/+ + +	6, 8, 10, 11
Benzo[e]pyrene	–/+	+	6, 10, 11
Benzo[a]pyrene	+ + +/+ + + +; TI	+ + + +	6, 9, 10, 12
Perylene	–	+	7, 9, 13
Dibenz[a,j]anthracene	+ +	+	6, 9, 10, 11, 13
Indeno[1,2,3-cd]pyrene	+/+ +; TI	+ +	6, 9, 10, 12
Dibenz[a,h]anthracene	+ + +/+ + + +; TI	+ +/+ + +	6, 10, 12, 13
Benzo[ghi]perylene	–/+; CC	–/+	9, 11, 12, 13
Anthanthrene	±/+ +	+	9, 10, 13
Coronene	–/+; TI	+	6, 9

Key: – = no evidence for animal carcinogenicity/mutagenicity; ± = very weakly active; + = weakly active; + + = moderate active; + + + – very active; + + + + – extremely active. TI – tumor initiator; CC – carcinogenic with benzo[a]pyrene. The biological activities reported in the literature often differ. In some cases, therefore, several reports are cited (among others 6–13).

The PAH concentrations of brake lining dust are appreciably lower than those of clutch lining dust throughout. There are no significant differences in the PAH loadings of the brake lining abrasion dust from automobiles and trucks. On the other hand, the arithmetic mean of the total PAH content of clutch dust was a factor of 3.4 higher in the dust samples from trucks than in those from automobiles. The same trend can be seen in the case of the five

TABLE II

Mean concentrations of polycyclic aromatic hydrocarbons (PAH) including their standard deviations $\bar{x} \pm s$ in μg/g from dust abraded from the brake and clutch linings of automobiles and trucks, broken down into the concentrations of the individual $n = 21$ PAH, their sums and the sums of the concentrations of the $n = 5$ PAH included in the TLV list[14] (labelled with * in the table).

Concentration (μg/g) PAH Compound	Abraded particles: Brake linings Automobile ($n=24$)	Brake linings Truck ($n=10$)	Clutch linings Automobile ($n=11$)	Clutch linings Truck ($n=7$)
Fluoranthene	1.2 ± 1.1	1.6 ± 1.3	3.3 ± 3.7	7.0 ± 10.7
Pyrene	1.0 ± 0.9	1.5 ± 1.4	3.5 ± 4.6	6.1 ± 9.8
Benzo[a]fluorene	0.7 ± 1.2	0.8 ± 0.5	1.7 ± 1.5	7.1 ± 14.0
Benzo[b]fluorene	0.8 ± 1.6	0.9 ± 0.7	1.9 ± 1.4	8.6 ± 18.3
Benzo[b]naphtho-[2,1-d]thiophene	0.6 ± 0.9	0.7 ± 0.5	1.0 ± 0.9	6.5 ± 11.8
Benzo[ghi]fluoranthene	0.5 ± 0.6	0.5 ± 0.3	1.0 ± 1.0	3.6 ± 6.5
Benzo[c]phenanthrene	0.4 ± 0.6	0.5 ± 0.3	0.5 ± 0.6	3.5 ± 7.8
Cyclopenta[cd]pyrene	0.4 ± 0.5	0.5 ± 0.3	0.4 ± 0.5	2.4 ± 5.1
Benza[a]anthracene	0.8 ± 1.4	0.8 ± 0.5	3.0 ± 3.3	7.1 ± 12.7
Chrysene *	1.1 ± 1.8	1.0 ± 0.6	2.6 ± 2.3	8.8 ± 12.6
Benzo[b]fluoranthene *	0.8 ± 1.0	0.6 ± 0.4	1.7 ± 1.4	5.9 ± 8.2
Benzo[k]fluoranthene	0.7 ± 1.1	0.6 ± 0.3	1.4 ± 1.2	5.4 ± 8.7
Benzo[e]pyrene	0.7 ± 0.9	0.6 ± 0.3	1.7 ± 1.6	4.5 ± 6.7
Benzo[a]pyrene *	0.6 ± 0.9	0.7 ± 0.4	1.5 ± 1.3	5.0 ± 8.8
Perylene	0.6 ± 1.0	0.6 ± 0.3	1.1 ± 1.2	4.3 ± 8.5
Dibenz[a,j]anthracene	0.5 ± 0.9	0.5 ± 0.2	0.9 ± 0.8	3.6 ± 7.3
Indeno[1,2,3-cd]pyrene *	0.6 ± 0.8	0.6 ± 0.3	1.1 ± 0.9	4.1 ± 6.8
Dibenz[a,h]anthracene *	0.6 ± 1.1	0.5 ± 0.2	0.9 ± 0.7	4.2 ± 8.8
Benzo[ghi]perylene	0.7 ± 0.8	0.6 ± 0.3	1.6 ± 1.4	4.1 ± 6.2
Anthanthrene	0.5 ± 0.9	0.6 ± 0.4	1.0 ± 1.2	5.5 ± 9.8
Coronene	0.6 ± 0.7	0.5 ± 0.3	1.1 ± 1.2	3.2 ± 5.3
Σ 21 PAH	14.4 ± 20.7	15.3 ± 9.9	32.9 ± 32.7	110.5 ± 194.4
Σ 5 PAH*	3.7 ± 5.6	3.4 ± 1.9	7.8 ± 6.6	28.0 ± 45.2

chosen PAH. Here too the sums of their concentrations are 3.6 times higher in the truck samples than in those from automobiles. The five chosen PAH comprise an average of 24.2% of the samples investigated. This corresponds to the numerical ratio of the five chosen to the total 21 PAH.

TABLE III

Mean concentrations of polycyclic aromatic hydrocarbons (PAH) including their standard deviations ($\bar{x} \pm s$) in μg/g of $n=5$ analyses identified by gas chromatography/mass spectroscopy of one and the same toluene extract of a brake and clutch lining dust sample.

PAH Compound	Concentration (μg/g) Abraded particles ($n=5$ PAH analyses) Brake linings ($\bar{x} \pm s$)	Clutch linings ($\bar{x} \pm s$)
Fluoranthene	1.56±0.03	1.15±0.01
Pyrene	1.30±0.02	0.66±0.07
Benzo[a]fluorene	0.32±0.001	0.81±0.007
Benzo[b]fluorene	0.29±0.01	0.81±0.01
Benzo[b]naphtho-[2,1-d]thiophene	0.33±0.01	0.42±0.01
Benzo[ghi]fluoranthene	0.79±0.03	1.17±0.02
Benzo[c]phenanthrene	0.28±0.01	0.12±0.01
Cyclopenta[cd]pyrene	0.42±0.09	0.87±0.02
Benz[a]anthracene	0.35±0.01	1.18±0.14
Chrysene *	0.43±0.02	1.32±0.03
Benzo[b]fluoranthene *	0.33±0.01	1.25±0.09
Benzo[k]fluoranthene	0.32±0.006	1.25±0.09
Benzo[e]pyrene	0.32±0.007	1.09±0.02
Benzo[a]pyrene *	0.34±0.005	0.97±0.004
Perylene	0.26±0.007	0.87±0.02
Dibenz[a,j]anthracene	0.21±0.009	0.86±0.03
Indeno[1,2,3-cd]pyrene *	0.30±0.006	1.22±0.03
Dibenz[a,h]anthracene *	0.17±0.007	0.82±0.02
Benzo[ghi]perylene	0.34±0.01	1.32±0.03
Anthanthrene	0.29±0.01	0.83±0.01
Coronene	0.31±0.07	1.53±0.21
∑21 PAH	9.26±0.38	20.52±0.89
∑ 5 PAH *	1.57±0.05	5.58±0.17

DISCUSSION

These results reveal that the dust abraded from brake and clutch linings contains a complex spectrum of adsorbed PAH, some of which have been shown to be carcinogenic in animal experiments.

The mean concentration of PAH in the total of 21 samples analysed was 14.4 to 110.5 $\mu g/g$ abraded dust and for the five chosen PAH the concentration was 3.7–28.0 $\mu g/g$. The variations observed in the clutch abrasion dusts are worthy of particular note.

It is not possible to determine the PAH adsorbed onto isometric particles, on the one hand, and onto asbestos fibres, on the other hand, separately, since there is no adequate method available for separating these fractions. The abrasion dust contains a very high proportion of short chrysotile fibres[15] together with elementary fibrils. A preferential adsorption on these rather than on the other particles is to be expected because of the high specific surface area of these fibres and their high binding affinity for PAH.[2]

The levels of PAH found were relatively low. However, because of the high possibility of a combined carcinogenic effect with the asbestos fibre dust contained in the dust abraded from brake and clutch linings, they should not be ignored in an assessment of the occupational–medical and environmental risks.

For example, the peak concentration in the air breathed by automotive mechanics has been determined to be an average of 6.2×10^6 fibres/m^3 when brake drums are blown out.[16] The mean asbestos concentration in emissions of abraded dust from motor vehicles under realistic conditions is probably of the order of 0.1 to 1.0% by weight.[15,16] The West German environmental authorities [Umweltbundesamt] have, until now, taken an estimated value of 0.25%. On the basis of these results an estimate of 10 t chrysotile-asbestos fibre dust per annum is obtained for emissions during braking in the Federal Republic of Germany.[18]

All the details of the interactive effects of asbestos and PAH have not been investigated. The "carrier hypothesis" has been employed in connection with the epidemiologically demonstrated multiplication of the risks to cigarette smokers of dying of lung cancer, if they are exposed to asbestos dust at their place of work.[19] Mossman *et al.*[20] were able to demonstrate a stimulation of the BaP metabolism of hamster tracheal epithelial cells with an, at times, increased formation of DNA/PAH adducts.

The epidemiological estimation of the risks of the inhalation of asbestos is mainly performed at the moment on the basis of the dose of asbestos dust received. In future the possibility of the synergistic effects of PAH on the dose response relationship under various conditions of exposure should also be taken into account.

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