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Occupational Exposures to PAHs Measured with UV Derivative Spectroscopy Corrected for Advective and Gaseous Losses

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PAHs (polynuclear aromatic hydrocarbons) are a group of ubiquitous substances that occur in occupational environments as a consequence of the combustion of hydrocarbons and coal, vehicle emissions, etc. Some PAHs are known to be carcinogenic in animal tests, and accordingly, most legislation requires that the air concentration of several of them should be kept at minimum values, implying a model of "no safe threshold" (ACGIH 1985, BChI 1988, DNHST 1991).

An adequate analysis of occupational exposures to PAHs in air should satisfy a number of requisites. The sample must be obtained with a personal portable pump, and should cover a substantial part of the working period (several hours) or a representative part of it. Vapor-phase components should be sampled along with particulates, and it is desirable that those PAHs known to be carcinogenic would be estimated with greater precision than the rest, if a compromise is necessary. Further, for a frequent and effective surveillance, it is convenient that the collection and analytical techniques would require only average trained personnel with the shortest time elapsed between sample collection and producing the results. For several reasons, these simultaneous objectives are sometimes difficult to attain. A portable pump collects a small amount of matter, thus limiting the accuracy that can be achieved during the chemical analysis, and the efficient collection of gaseous forms requires that the air stream would be conveyed through a sufficiently thick pad of adsorptive medium which sets too high a resistance for a long operation of a small pump. Further, the chemical analysis involving gas (GC) or liquid chromatography (LC) normally requires highly trained personnel and preclude the routine processing of many samples as are required for the assessment of the changing exposures in work environments. Under these constraints, the detection limits for individual PAHs in occupational

Table 1. Comparison of results (μg/g) on NBSRM1649 obtained with UV-derivative spectroscopy (UVDS) and other reported techniques.

Certified compound	NBS certif. value	Elsaid (1987)	UVDS
Benzo(a)pyrene	2.9	3.2	4.3
Benzo(ghi)perylene	4.5	6.3	5.7
Fluoranthene	7.1	-	6.8
Benzanthracene	2.6	2.8	1.6
Indo(1,2,3-cd)pyrene	3.3	-	0.2

exposures have been reported to be in the 0.15 - 0.5 μg/m3 range (NIOSH 1985, DFG 1988). In the case of GC, the sensitivity might not be higher than 100 μg/m3 for some PAHs, while LC has a low performance with the PAHs in the higher molecular weight range (Steinegger & Gaus 1981). The analysis with high pressure liquid chromatography (HPLC) and UV-detection poses similar problems (Janssen 1990).

The major limitations of the chromatographic techniques derive from the need to extract and "clean" the sample, i.e., to separate PAHs from other organics that might elute at similar rates and obscure the chromatogram. In the case of an atmosphere containing 0.2 μg/m3 of benzo(a)pyrene (BaP), the mass collected during an 8 hour shift is 0.18 μg at a sampling rate of 1.9 L/min. Assuming a 10% loss during extraction with cyclohexane and the same during subsequent evaporation to 1-2 mL leaves about 0.15 μg. About 10 μL are taken for injection in the chromatograph, resulting in 1 ng of sample in the detector chamber.

If the cleanup and evaporation could be obviated, about 7-10 ng could be delivered to the detector chamber with the corresponding increase in detection accuracy. This purpose has been pursued in this study by extending the use of a newly developed technique of UV-diode array computer enhanced derivative spectroscopy (UVDS) to the analysis of PAHs in particulate samples obtained in the usual way with personal monitors. The results are further corrected for decay-evaporative losses and for gaseous components, using published relations of the rates of these processes and the PAH's molecular weights. The method provides a reliable and conservative estimate of total PAH exposures in occupational environments and has the necessary simplicity to be applied in routine surveillance. The errors in detecting relatively heavy PAHs (i.e. m.w. greater than 200) are lower than in other methods.

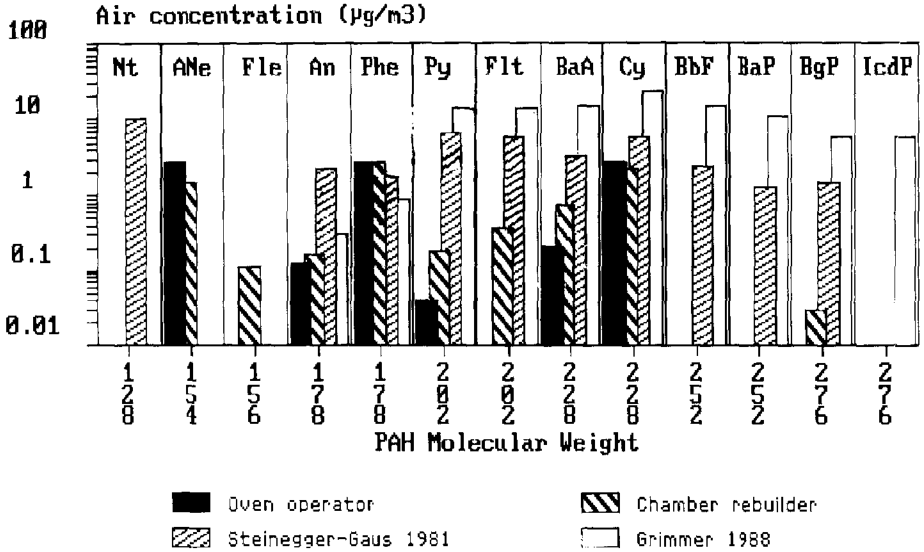

Figure 1. Comparison of exposures to PAHs measured in this study with other results on similar jobs in the same industry. Nt naphthalene; ANe: acenaphthene; Fle: fluorene; An: anthracene; Phe: phenanthrene; Py: pyrene; Flt: fluoranthene; BaA: benzanthracene; Cy: chrysene; BbF: benzo(b)fluoranthene; BaP: benzo(a)pyrene; BgP: benzo(ghi)perylene; IcdP: indo(1,2,3-cd)pyrene.

MATERIALS AND METHODS

Occupational exposures to particulate PAHs were studied at an industrial plant where anodes are produced by mixing calcined petroleum coke and coal tar pitch which are baked prior to their use in an electrolytic process. The anodes are baked in closed ovens and exposure to PAHs arise mainly through environmental dust produced during the transport and handling of unbaked cold ("green") anodes or through minor leaks in the fume transport system within the oven. Two different jobs within the facility were sampled. The oven operator, who controls the operating temperature of the different oven chambers and is exposed to the general environment of the building, and the chamber rebuilder, who works inside the oven chambers after each baking cycle and repairs eventual damages, changes expansion joints, etc. Samples were obtained during normal working periods at air temperatures from 23 °C to 28 °C with SKC Aircheck 224-PCXR7 samplers at 1.8 L/min flow, on a glass fiber (nominal pore size 0.8 μm) filter. The filters were Sohxlet extracted with 25 mL of cyclohexane (SINTORGAN, chromatography grade), and the extract was directly inspected with a UV-diode

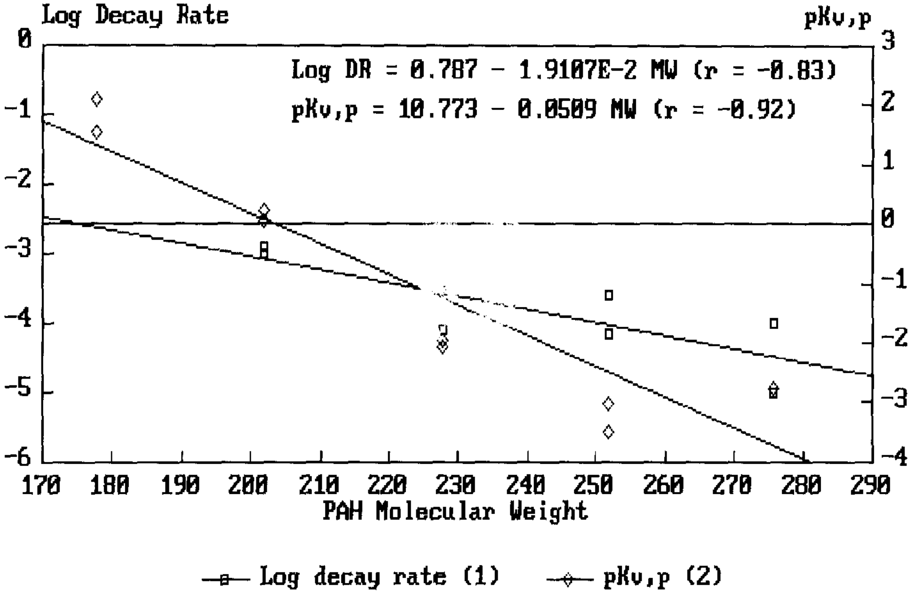

Figure 2. Decay rates of PAHs on glass fiber filters during sampling and 'pK' values of equilibrium of vapor and particulate phase as a function of molecular weight of PAHs in Fig. 1

array spectrometer (HP8452A)in the 220-400 nm range, with 15-sec integration time, with a cyclohexane blank, at 2-nm intervals. The magnetically stored spectra were processed in IBMAT compatible DOS environment with a newly developed software for multicomponent analysis (Ares 1992). The following PAHs were searched: naphthalene (Nt), acenaphthene (ANe), fluorene (Fle), Anthracene (An), phenanthrene (Phe), pyrene (Py), fluoranthene (Flt), benzanthracene (BaA), chrysene (Cy), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), benzo(ghi)perylene (BgP) and indo(1,2,3-cd)pyrene (IcdP). Standards were from CHEMSERVICE West Chester Pa. A sample of NBSRM1649 Urban Dust Organics Reference Material (NBS 1982) was used to check the analytical technique (Table 1).

RESULTS AND DISCUSSION

Figure 1 shows a comparison of the average of 4 samples obtained in each job category inspected in this study with the values reported in similar and other jobs of the same industry. The concentrations observed at intermediate molecular weights are very similar, while some differences exist at the low and high range. These could be caused by varying operating conditions from one plant to another. Also, different jobs and in some

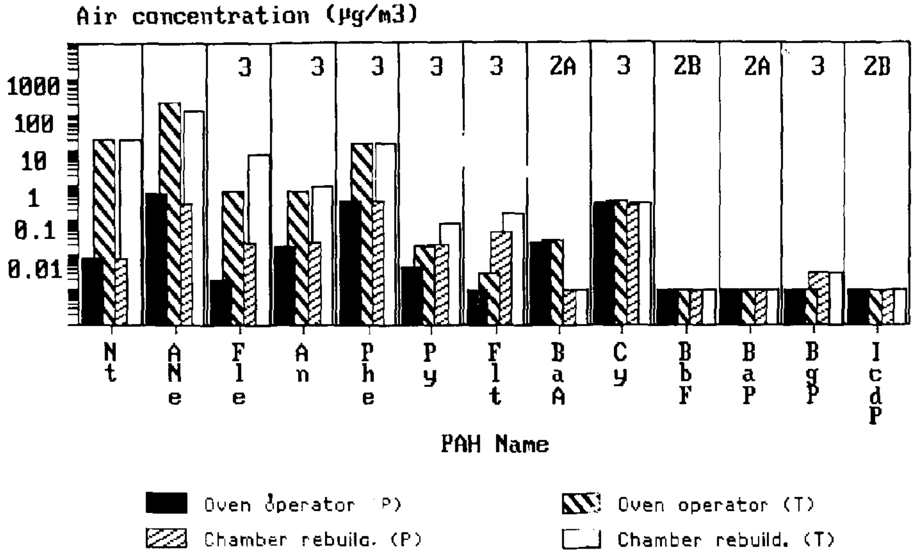

Figure 3. Concentration of PAHs in two job exposures. P: Particulate fraction, corrected for advective loss or detection threshold. T: Total, including gaseous fraction calculated as described in text. IARC's ratings at the top of the figure. Nt: naphthalene; ANe: acenaphthene; Fle: fluorene; An: anthracene; Phe: phenanthrene; Py: pyrene; Flt: fluoranthene; BaA: benzanthracene; Cy: chrysene; BbF: benzo(b)fluoranthene; BaP: benzo(a)pyrene; BgP: benzo(ghi)perylene; IcdP: indo(1,2,3-cd)pyrene.

cases different partial processes in the same industry can generate varying exposures to PAHs. The samples of this study show low values because the workers are exposed to particulate and dust at ambient temperature.

Grimmer (1988) has shown that the PAH concentration in particulate matter collected with glass fiber filters can be affected by evaporative losses occurring from the filter by the effect of the air stream passing through it, and by decomposition during the sampling time. Also, a fraction of the PAHs of lower molecular weight (below 200) can be in gaseous form at ambient temperature (Valerio & Pala 1990). In Grimmer's study, this was shown by placing a pad of PORAPAK PS adsorbent layer behind the glass fiber filter with respect to the air stream. The pad retained a considerable amount of PAHs which were probably in the gaseous phase during the sampling time, or were removed from the glass fiber filter as a result of volatilization.

A scrutiny of these data shows that a major fraction of the variance of the amounts collected in the gas phase can be explained by the molecular weight of the individual PAHs.

In order to quantify the magnitude of these effects, a model of simple decay (dC/dt = -rC) where C is the air (particulate) concentration and 'r' is a constant of decay for each PAH, was assumed for the advective loss, and fitted to Grimmer's (1988) Table-3 data. The model was solved by iteration at 1 min intervals, until an adequate 'r' value was found which would generate the observed advective loss for each PAH listed. A backward integration of losses computed with this model using the final weighed mass and duration times of the samples in this study yielded an estimate of the mass which would have been collected in the absence of advective loss.

The gaseous component of each PAH in this study was estimated by assuming a model of simple equilibrium between the gaseous and particulate phase, characterized by an equilibrium constant Kv,p = Cv/Cp, where Cv is the air concentration in vapour form and Cp the corresponding in particle form. The p-values (pKv,p = -log Kv,p) of this constant for different PAHs were computed on the basis of Grimmer's (1988) Table-4 data. Figure 2 shows that both the log of decay rates and the pKv,p values are significantly correlated with the molecular weight, which allows the computation of estimated losses for compounds not listed in Grimmer's Table 4.

These corrections should be regarded as approximate and could be affected by differences in the air temperature at which the samples of the different studies were taken. A more accurate correction for advective and gaseous losses should introduce the effect of ambient temperature on the gas-solid phase equilibria. It has not been usual to report the values of ambient temperature along with the results on occupational exposure to PAHs. Variations of some degrees in ambient temperature which could occur in industrial environments can shift the equilibria between gaseous and particulate PAHs (Yamasaki et al. 1982).

Figure 3 shows the corrected values that estimate the total exposure to PAHs of the jobs sampled in this study, including gaseous and particulate forms. For the sake of a conservative estimate, it has been assumed that all PAHs not found in the samples could however be present at a level below the detection limit 0.01 μg/m3. In the case of Nt, this detection error could imply that the compound can still be present at 0.08 μg/m3 in the particulate phase and at 181 μg/m3 in the gaseous form. In the case of BaP, BgP or heavier PAHs, the underestimation is negligible, since the gaseous form is almost absent (<0.00001 μg/m3) and the advective loss is very low. It is important to relate the relative efficiency of these samples in estimating the PAH exposure depending on their molecular weight, with the distribution of IARC's (1987) classes listed at the top of Figure 3. Class 3 refers to compounds where evidence of carcinogenicity is inadequate or limited in animal or short term tests Class 2A refers to sufficient evidence in both cases, while 2B refers to any combination of sufficient inadequate of both. For the PAHs sampled in this study, classes other than 3 occur in the range where PAH exposure is accurately estimated through the collection of particulates in glass fiber filters. The complete estimation of the PAH profile in Figure 3 can be attained in a few minutes after the extraction of the personal monitor filter.

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