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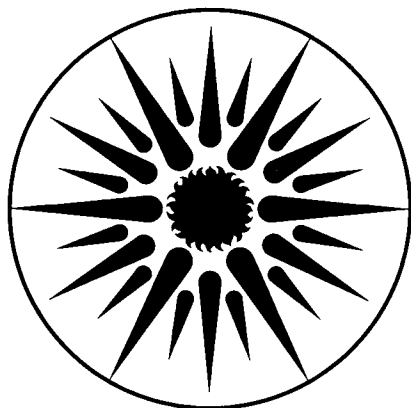
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POLYCYCLIC AROMATIC HYDROCARBONS IN INDOOR AIR AND ENVIRONMENTAL TOBACCO SMOKE MEASURED WITH A NEW INTEGRATED ORGANIC VAPOR-PARTICLE SAMPLER

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ABSTRACT

To avoid sampling artifacts, an integrated organic vapor-particle sampler (IOVPS) has been developed for polycyclic aromatic hydrocarbons (PAH). The IOVPS is based on an XAD-4-coated annular denuder which strips gas phase species from the air stream before collection of particles on a filter. A second denuder downstream of the filter collects species desorbed ("blown off") the particles during sampling. PAH are determined in extracts of both denuders and the filter. For indoor air with no combustion sources, the gas-phase concentrations of several semivolatile PAH measured with the IOVPS averaged about half of those found with a conventional filter-sorbent bed sampler. For environmental tobacco smoke the gas-phase concentrations of the same PAH from the IOVPS averaged 70% of those found with the sorbent bed sampler. Particulate-phase concentrations were correspondingly higher with the IOVPS, but measurable "blow off" semivolatile PAH occurred.

INTRODUCTION

Accurate measurements of phase distributions of polycyclic aromatic hydrocarbons (PAH) in indoor air and environmental tobacco smoke (ETS) are needed in order to assess exposure to carcinogenic compounds, since lung deposition patterns of PAH depend on the distribution of the PAH between the gas and particle phases. Sampling for gas-phase organic polycyclic aromatic hydrocarbons (PAH) has depended on the use of sorbent beds filled with adsorbent resin beads (1,2). Since such beds follow filters, desorption of semivolatile compounds from the filters or collection of gases by the filters can lead to incorrect measurements of gas- and particle-phase concentrations (3). Denuder difference methods have also been used for semivolatile PAH in outdoor air (4), but they require use of paired samplers, and precision suffers from propagation of subtraction errors. To avoid these problems we have developed the integrated organic vapor-particle sampler (IOVPS), based on an XAD-4-coated annular denuder, which strips the gas-phase species from the air stream before collection of the particles on a filter. A denuder or sorbent bed can be used downstream of the filter to correct for "blow off" of semivolatile species from the particles. Likewise, a second filter just downstream of the first filter can also be used to correct for adsorption of gas-phase ("blown off") species by the filter medium. PAH are determined in extracts of the denuders and filters.

The objectives of this presentation are to describe the sampler, validate its operation for sampling PAH in indoor air and environmental tobacco smoke, and compare PAH concentrations obtained with the IOVPS and a filter-sorbent bed sampler.

MATERIALS AND METHODS

Sampling details. The novel aspect of the sampling equipment is the use of ground XAD-4 resin as a coating for annular denuders. Figure 1 shows a schematic diagram of one sampling configuration used for field testing the IOVPS in indoor air and ETS. Commercially available, single-channel glass denuders, 22 cm long, with a 1 mm annulus (University Research Glass, Carrboro, NC, USA) were used with a Teflon-lined aluminum cyclone (cutoff 2.5 microns at 10 L min⁻¹) preceding the first denuder. Three XAD-4-coated denuders were connected in series between the cyclone and a Teflon filter pack which contained a pre-extracted and pre-weighed Teflon-coated glass-fiber filter.

(The three-denuder configuration was used for determining breakthrough of naphthalene and its methyl derivatives as a function of flow rate.) In some experiments, a coated denuder followed the filter pack. The parallel sorbent bed sampler used an aluminum open-face filter holder with a Teflon-coated glass-fiber filter, followed by a glass tube packed with 2.5 g cleaned XAD-4 resin. Flow rates, measured with a dry gas test meter, were 5, 10 and 20 L min⁻¹ for field testing; sampling times varied from 3 to 22 hours. Indoor air with no combustion sources was sampled in an unoccupied room. Diluted sidestream smoke was sampled as a surrogate for ETS in an unventilated 20 m³ chamber at 5 L min⁻¹ for hour-long periods while a single-port smoking machine smoked 3 cigarettes. Ambient temperature varied between 22 and 26°C.

Extraction. Denuders, filters and sorbent beds were extracted by sonication at 50 °C (capped denuders) or 70 °C (filters) with high purity cyclohexane. Deuterated fluoranthene was added at the time of extraction as an internal standard to correct for any volatility losses during sample preparation. The extracts were passed through silica solid-phase extraction columns, and the solvent was exchanged to acetonitrile. Final sample volume was 500 microL. Two unexposed coated denuders were analyzed as blanks for every field test.

Analysis. For analysis of extracts of the denuders and sorbent beds, the dual-fluorescence method described by Mahanama et al. (5) was adapted for analysis of semi-volatile PAH from naphthalene to chrysene. A Hewlett-Packard high performance liquid chromatograph Model 1090 M was used with a Vydac 201TP52 15 cm column. The gradient program increased the eluent strength from 38% acetonitrile, 2% THF in water, to 95 % acetonitrile, 5% THF over 24 min at 0.5 mL/min. From 25 to 33 minutes the flow increased linearly to 1 mL/min. After 4.5 min the the flow rate returned to 0.5 mL/min, and the mobile phase composition returned to the initial condition during the next two minutes. A 12-minute equilibration at 0.5 mL/min followed. The column was maintained at 30.8 °C.

Each fluorescence detector was independently programmed to change excitation and emission wavelengths to selectively detect the PAH of interest as they eluted from the column. One detector started at (ex, em) 220, 348 nm to detect naphthalene and its 1- and 2-methyl derivatives, acenaphthene and acenaphthylene. At 11.5 min it switched to 245, 434 nm to detect anthracene and the fluoranthenes. At 21.5 min it changed to 263, 371 nm to detect chrysene. The second detector started at 246, 296 nm to detect biphenyl and fluorene; at 11.95 it switched to 245, 359 nm to detect phenanthrene; at 16 min it switched to 245, 391 nm to detect pyrene; and at 21.7 min it changed to 288, 405 nm to detect benz(a)anthracene. These fluorescence programs were developed by studying the excitation and emission spectra of standard compounds to select conditions of both high sensitivity and selectivity. However, during the field testing several modifications were made (results above) to overcome real-world interferences from other PAH and their alkyl derivatives.

Samples were analyzed from 5 microL injections of the denuder and sorbent bed extracts. Standard mixtures were used to quantitate the PAH concentrations. Daily systematic drift of detector response to standards was observed as reported by Mahanama et al. (5), and all samples were drift-corrected. The semivolatile PAH analyzed and their limits of detection (3 times the standard deviation of means observed for blanks), in ng per extract, were naphthalene, 13; 1-methylnaphthalene, 4.8; 2-methylnaphthalene, 19; biphenyl, 69; acenaphthene and acenaphthylene, 4.9; fluorene, 3.9; phenanthrene, 11; anthracene, 0.5; fluoranthene, 0.1; pyrene, 0.1; benz(a)anthracene, 0.1; and chrysene, 1.6. Extracts of filters were treated as described by Mahanama et al. (5), except that 20 microL aliquots were analyzed on the HPLC using a Waters U6K injector.

RESULTS

Summary of field testing results. One measure of the capacity of the IOVPS for volatile PAH is the average recovery of naphthalene and its methyl derivatives on the first of three denuders in series. Table 1 shows the data for indoor air sampling with no combustion sources. The naphthalene concentration varied from 124 to 593 ng m⁻³ in these experiments. The IOVPS collected more than 90% of the naphthalenes when operating at 5 L min⁻¹ for up to 6 hours, but levels of particulate PAH in clean indoor air were below quantitation limits. At 10 L min⁻¹ and 6 hours sampling time, particulate PAH could be detected. For ETS, recovery of the naphthalenes on the first denuder was 98% for one hour of sampling at 5 L min⁻¹, and particulate PAH concentrations were well above quantitation limits. At 10 L min⁻¹, all the semivolatile PAH from phenanthrene to chrysene were recovered on the first of three denuders, within the analytical precision derived from the variance of PAH measured on blank denuders.

Table 1. Percent recovery of naphthalene and its methyl derivatives on the first of three denuders versus flow rate and sampling time.

Flow rate, L min ⁻¹	Time, hours	% First denuder
5	3	99
5	6	93
10	3	93
10	6	88
20	3	46
20	6	42
20	22	49

Comparison of denuder and sorbent bed results for gas-phase PAH concentrations. Within the limits of analytical precision, the total concentrations of the naphthalenes measured with the IOVPS agreed with those determined from the sorbent bed sampler, except for 20 L min⁻¹ and 22 hours of sampling. However, for indoor air with no combustion sources, the gas-phase concentrations of the semivolatile PAH phenanthrene, anthracene, pyrene and chrysene, measured with the IOVPS, averaged about half of those found with a sorbent bed sampler, as shown in Table 2. For ETS, the gas-phase concentrations of these compounds measured with the IOVPS averaged 70% of those found with the sorbent bed sampler. These data should be considered preliminary, since the blank correction for phenanthrene and pyrene on the sorbent bed sampler introduces considerable uncertainty into the results.

Table 2. Comparison of gas-phase semivolatile PAH concentrations from the IOVPS and a sorbent bed sampler.

Indoor air with no combustion sources, sampled at 20 L min⁻¹

PAH	IOVPS, ng m ⁻³	IOVPS/sorbent
Phenanthrene	42.3	0.95
Anthracene	0.6	0.38
Pyrene	9.7	0.23
Chrysene	2.7	0.49
Average ± std dev		0.51 ± 0.31

ETS (IOVPS, 5 L min⁻¹, sorbent bed sampler at 20 L min⁻¹)

PAH	IOVPS, ng m ⁻³	IOVPS/sorbent
Phenanthrene	151	0.97
Anthracene	26.1	0.71
Pyrene	55.0	0.49
Chrysene	22.1	0.61
Average ± std dev		0.70 ± 0.20

Comparison of particulate-phase PAH concentrations for the two sampler types.

Particulate-phase concentrations of semivolatile PAH were consistently higher for IOVPS filters compared to the filters which preceded the sorbent beds. This observation is consistent with the loss of semivolatile PAH from the latter during sampling. We also found only about 2 % of the total naphthalenes on the post-filter denuder, but substantial "blow off" of the semivolatile PAH was observed.

DISCUSSION

The IOVPS has sufficient capacity for semi-volatile PAH to be useful in indoor air and ETS sampling as long as a sensitive detection method (fluorescence) is used. Since XAD-4 adsorbs a wide range of chemical classes, the IOVPS could be used for other species besides PAH.

Because of the development of a new cleanup technique and the sensitivity of a newly-developed dual fluorescence detector HPLC method, the sampler can be used for determination of the phase distribution of PAH in samples of ETS generated in as little as one hour of sampling using the experimental conditions (number of cigarettes, room size, ventilation rate, etc.) reported here.

Gas-phase semivolatile PAH concentrations obtained with the IOVPS were lower than those measured from sorbent beds, for both indoor air samples and ETS. Particulate-phase semivolatile PAH concentrations showed the reverse. These preliminary results are consistent with "blow off" of PAH from the particles collected in the filter-sorbent bed sampler. Therefore, the IOVPS minimizes sampling artifacts so that more accurate phase distributions of semivolatile PAH are determined.

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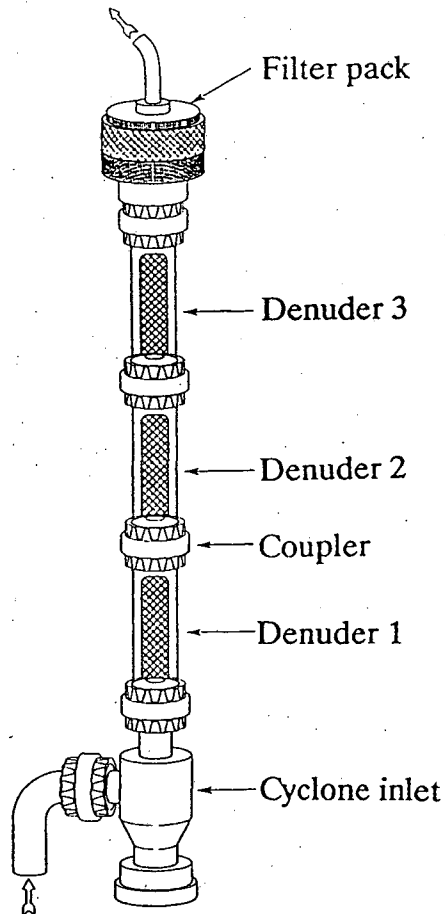


Figure 1. The integrated organic vapor-particle sampler in one field testing configuration. For some experiments the filter pack was placed after the first two denuders. The third denuder followed the filter pack.

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