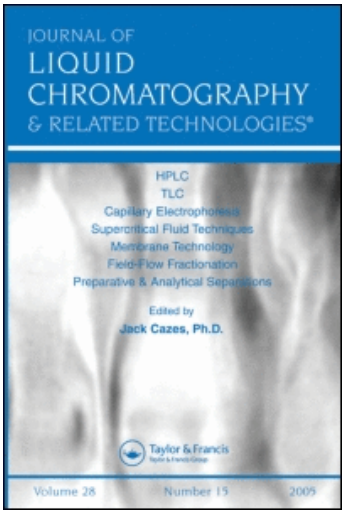

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THE QUANTIFICATION OF 4- TO 6-RING POLYNUCLEAR AROMATIC HYDROCARBONS IN INDOOR AIR SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

A high-performance liquid chromatography (HPLC) method was developed for the quantification of the polynuclear aromatic hydrocarbons (PAHs) chrysene, benzo[b]fluoranthene (B[b]F), benzo[a]pyrene (B[a]P) and benzo[ghi]perylene (B[ghi]P) in the particulate matter of indoor air samples. Samples were collected on 1 μm pore size Fluoropore membrane filters and extracted with acetonitrile (ACN). The PAHs were analyzed on a polymeric octadecylsilane, silica-based column (Vydac 201TP54) with fluorescence detection at selected excitation and emission wavelengths specific to the compounds of interest. A mobile phase gradient of water and ACN was used. The method is reproducible with percent relative standard deviations (%RSD) ranging from 5.0 to 9.6 for the five PAHs. Percent recoveries were *ca.* 100%. Analyses of various samples show that amounts of these five PAHs vary widely in air. A relatively short sampling time (five hours) is required and the procedure is capable of detecting <1 ng m^{-3}.

INTRODUCTION

Sample collection and extraction of PAHs from indoor air containing tobacco smoke have been laborious processes. Salomaa *et al.* used 10 persons to smoke 96 cigarettes over a 6 h period while sampling the air at 66 m^3h^{-1} (1). Particles were

collected on glass fiber filters and vapor-phase PAHs on XAD-2 resin; both of which were extracted in a Soxhlet apparatus for 16 h prior to endpoint determination of 34 PAHs by gas chromatography-mass spectrometry (GC-MS). Chuang *et al.* sampled the air at 230 L min^{-1} in which 25 cigarettes were smoked for 24 h using quartz fiber filters, XAD-2 and XAD-4 resins (2). The filters were not evaluated for PAHs but the XAD resins were extracted in a Soxhlet apparatus for 16 h with dichloromethane followed by an 8 h extraction with ethyl acetate. The vapor-phase PAHs (six) were determined by GC-MS. These techniques, although yielding information on distribution and concentration of PAHs in environmental tobacco smoke (ETS), are time consuming. A more rapid method is described which analyzes for PAH's of 4 rings or greater. It has been suggested by researchers on automobile exhaust that PAHs of 4 rings or greater are of most importance to biological activity (3, 4, 5). These larger PAHs are associated with particles and at least 90% are trapped by filters (6, 7).

This paper describes an HPLC method for the determination of the 4-ring PAH chrysene, 5 ring PAHs B[b]F, B[k]F and B[a]P and the 6-ring PAH B[ghi]P. The analytes are collected with the particulate phase of ETS after as few as eight cigarettes are smoked in an average size room on a filter at a flow rate of *ca.* 16 L min^{-1} for 5-6 h. The filter is extracted with ACN (no cleanup required) and an aliquot is subjected to gradient, reverse-phase chromatography with selective fluorescence detection. This procedure is appropriate for these same PAHs suspended in air from many sources; not just ETS.

MATERIALS AND METHODS

Equipment

HPLC. The HPLC system consisted of two ABI Spectroflow 400 pumps (Applied Biosystems, Inc., Foster City, CA, USA), an 878A autosampler fitted with a 200 μL

sample loop, and a Perkin-Elmer LS-4 Fluorescence Spectrometer (Perkin-Elmer Corp., Norwalk, CT, USA). The pumps and the autosampler were controlled by a DS650 Data System, and data were acquired on a Beckman Computer Automated Laboratory System (Beckman, Waldwick, NJ, USA). Separations were carried out on a Vydac 201TP54, 4.6 x 250 mm, 5 μm particle size, polymeric octadecylsilane on silica (The Separations Group, Hesperia, CA, USA). A 30 x 4.6 mm Brownlee RP-18 Spheri-5MPLC guard refill in a Brownlee 3-cm MPLC holder (Brownlee Labs, Inc., Santa Clara, CA, USA) was placed directly before the analytical column.

Sampling. The sampling train consisted of two Fluoropore 1-μm pore size, 37-mm membrane filters (Millipore Corp., Bedford, MA, USA) contained in cassettes (SKC Inc., Eighty Four, PA, USA) sealed with a 37-mm gasket (Sloan Valve Co., Franklin Park, IL, USA) and connected by 0.635 cm I.D. tubing to a Dawson High Volume Air Sampler (Dawson Assoc., Inc., Lawrenceville, GA, USA) (see Figure 1).

Chemicals

Chrysene, B[b]F, B[k]F, B[a]P and B[ghi]P were obtained from Aldrich (Milwaukee, WI, USA). ACN, distilled in glass, was obtained from Burdick and Jackson (Muskegon, MI, USA).

Water was obtained from a Nanopure system, which consisted of a carbor

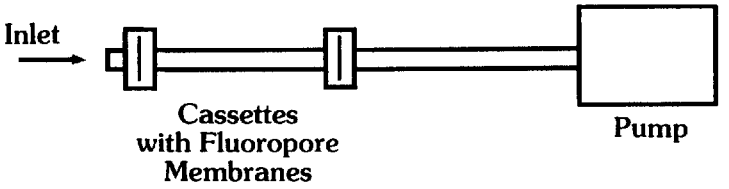

FIGURE 1. Air sample collection apparatus.

cartridge, two high-capacity mixed ion exchange cartridges, and a 0.45-μm filter (Barnstead Co., Div. of Sybron Corp, Dubuque, IA, USA).

Preparation of Standard Solutions

Stock solutions of the five PAHs were prepared in ACN and diluted to the appropriate concentrations with 1:1, ACN:H_2O. The stock solutions were stable at least one month when stored in a refrigerator.

Procedure

All chromatographic separations were performed at room temperature with a mobile phase gradient of water and ACN at a flow rate of 3.0 mL min^{-1}. Figure 2A shows the mobile phase gradient used in the chromatography. The gradient program also includes a ten-minute equilibration delay prior to the next injection. Figure 2B gives the wavelength-time program used for ETS samples. PAHs were quantified based on peak height relative to an external standard.

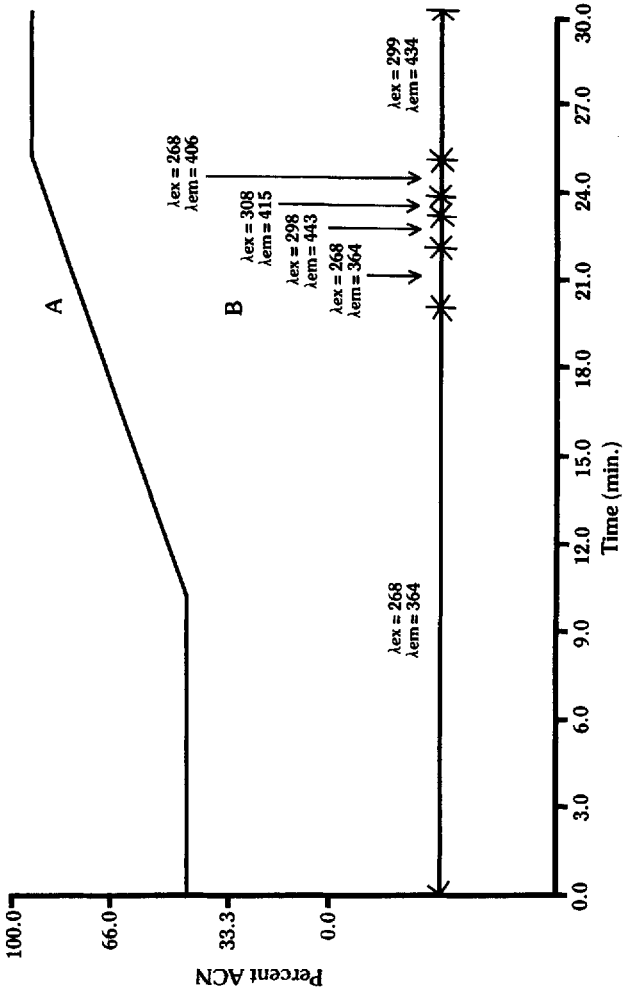

FIGURE 2. Gradient and wavelength program: (A) gradient profile; (B) wavelength program.

Sampling and Sample Preparation. The air sample collection apparatus was precalibrated with a soap film flowmeter (The Gilibrator, Gilian Instrument Corp., Wayne, NJ, USA) at *ca.* 16 L min^{-1} prior to sample collection. After sampling was complete (*ca.* 6 h) the flow was rechecked. Following use, the cassettes were disassembled and the side of the Fluoropore membrane facing the air flow was placed toward the bottom of a 25-mL Erlenmyer flask. ACN (2 mL) was pipetted into the flask which was then stoppered and sonicated 10 min (Ultrasonic Cleaner, Cole-Parmer Instrument Co., Chicago, IL, USA). Water (2 mL) was pipetted into the flask, the solution mixed, and then filtered with the aid of a syringe through a 0.45-μm pore size Acrodisc CR PTFE filter (Gelman Sciences, Ann Arbor, MI, USA) into an autosampler vial.

RESULTS AND DISCUSSION

PAHs Evaluated

Table I lists the PAHs evaluated in this work. Excitation and emission spectra were obtained on 18 PAHs which include the 16 priority pollutant PAHs (8), B[e]P and perylene. Spectral data showed acenaphthene, acenaphthylene, fluoranthene, fluorene and phenanthrene produce very weak emission signals when compared to other PAHs, *e.g.*, anthracene and B[a]P. These were eliminated from further consideration due to their lack of sufficient sensitivity for detection. The more volatile PAHs, naphthalene and anthracene, appeared to be collected only if sampling tubes containing XAD-2 resin were also used, the extract of which gave

Table 1.
PAH Evaluated

Compound, Abbreviation Used in Text	Excitation[a] (nm)	Emission[a] (nm)
acenaphthene	234, 296	326, 342
acenaphthylene	235, 296	330, 344
anthracene	252,360,381	385, 405, 430
benz[a]anthracene, B[a]A	286, 340	390, 412, 436
benzo[b]fluoranthene, B[b]F	298, 352	443
benzo[k]fluoranthene, B[k]F	254, 308, 381, 399	415, 438
benzo[ghi]perylene, B[ghi]P	299, 368, 385	412, 422, 434
benzo[a]pyrene, B[a]P	268, 296, 378	406, 432, 460
benzo[e]pyrene, B[e]P	290, 320	381, 390, 400
chrysene	268, 318	364, 384, 405
dibenz[a,h]anthracene, D[a,h]A	296, 350	400, 424, 448
fluoranthene	284, 358	460
fluorene	265, 296	316
ideno [1,2,3-cd]pyrene, I[1,2,3-cd]P	255, 308, 371	478, 504
naphthalene	220, 278	326, 337
perylene	409, 432	442, 468
phenanthrene	259, 290	354, 370, 390
pyrene	246, 276, 336	379, 398

[a] - strongest band underlined, spectra of PAH obtained in 1:1, ACN:H_2O

chromatography problems (see below). B[e]P, D[a,h]A, and I[1, 2, 3-cd]P were below detection limits in the extract of air samples collected on the Fluoropore membrane and were eliminated from further study. Perylene and pyrene were not subjected to analysis since they show no significant potential for biological activity (9, 10). B[a]A was not subjected to analysis since it was not sufficiently resolved from chrysene to perform a change in excitation and emission wavelengths specific for these two compounds (11). The remaining five PAHs, chrysene, B[b]F, B[k]F, B[a]P and B[ghi]P, were chosen based on their collection by a filter, their potential biological activity, suitable chromatographic resolution and spectral properties.

Sampling Volume

Originally, efforts were made to minimize the volume of air sampled to eliminate an extensive sample cleanup and still provide sufficient sensitivity to determine the compounds of interest. This would also minimize sample losses due to excessive (>6 h) sampling time (7). NIOSH procedure 5506 (12), which uses a 2-μm PTFE filter and an XAD-2 sampling tube, recommends lower volumes (200-1000-L) than found elsewhere in the literature (1, 2). Even when as much as 1200 L of air were sampled, in order to obtain a sufficient signal for B[a]P using NIOSH procedure 5506 (200 L greater than the limit for the procedure), the detector noise was so great that it amounted to as much as 75% of the result for B[a]P. Also, other compounds (reported to be constituents of ETS) were found to be below detection limits. This indicated that the sample volume was too low since sufficient sample for quantitative detection was not obtained. Figure 3B shows the noise level to be

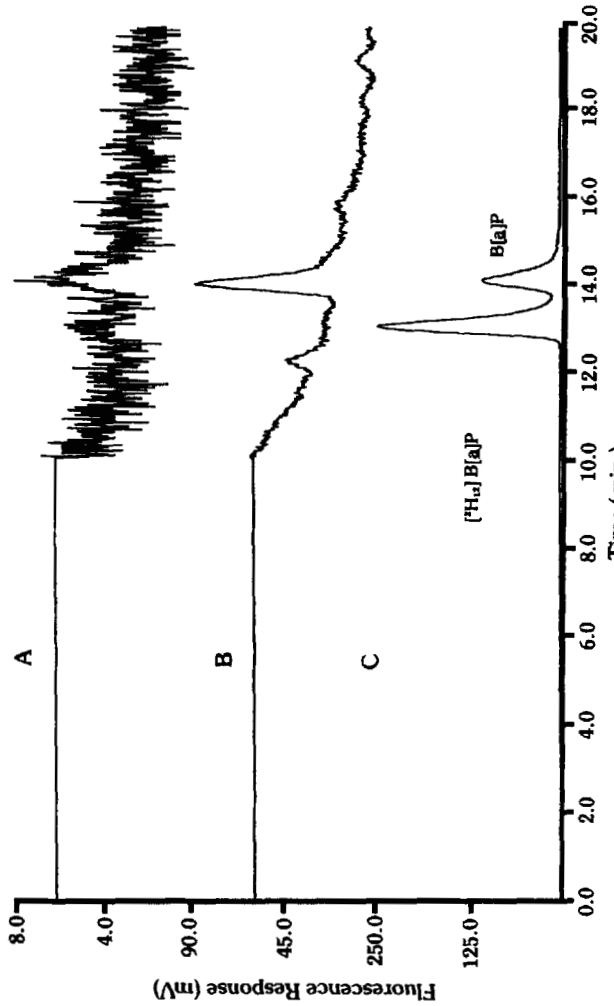

FIGURE 3. Isocratic elution of 1:1, ACN:H_2O extracts (4 mL) for B[a]P: (A) XAD-2 tube; (B) 2-µm PTFE membrane; (C) [$^2H_{12}$]B[a]P-B[a]P standard. Conditions: Vydac 201TP54 (4.6 X 250 mm, 5µ); 90% ACN + 10% H_2O at 1 mL min^{-1}; 200 µL injection volume; fluorescence detection, 378 nm excitation, 406 nm emission. Four cigarettes smoked in 28-m^3 room sampled at 2 L min^{-1} for one hour.

significant when analyzing for B[a]P in ETS. In order to determine if B[a]P is present in ETS without resorting to extensive variations of sampling time and flow rate, cigarettes were smoldered in a 0.06-m^3 box using the 2-μm PTFE filter collection described in NIOSH method 5506. Figure 4 shows that B[a]P is the largest peak in the chromatogram under these sampling conditions and that there are other compounds detected in ETS. Realistically, a compromise had to be found between these two extremes of sampling. An acceptable compromise was achieved using a flow rate of 16 L min^{-1} for five hours. Under these conditions, detector noise was only six percent of the signal for B[a]P.

Sampling Devices

Three different filters and two different solid sorbents were evaluated for collection of PAHs from ETS either singularly or in combination. The sampling train of a 2-μm PTFE filter followed by a sampling tube filled with XAD-2 proved successful in collecting PAHs (see Figure 5), the nonvolatile being retained on the filter and more volatile on the XAD-2 resin. Figure 3A, however, does show that some B[a]P passes through the 2-μm PTFE filter onto the XAD-2 resin. Because of this result, smaller pore size filters were evaluated. The XAD-2 sampling tubes, even when extracted with ACN, did not efficiently collect the PAHs of 4 rings or greater and therefore its use was abandoned. In addition, the column required cleaning after injection of the extract of these tubes.

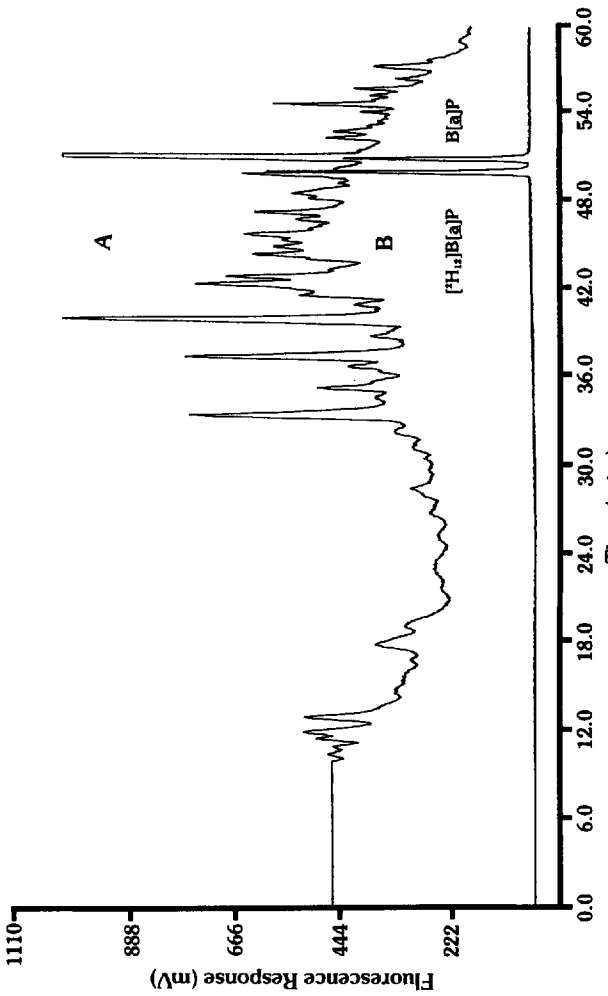

FIGURE 4. Gradient elution of 1:1, ACN:H_2O extract (4 mL) for B[a]P: (A) 2-μm PTFE membrane; (B) [$^2H_{12}$] B[a]P-B[a]P standard. Conditions: same as Figure 3 except gradient of ACN:H_2O, 45:55 initially for 20 minutes to 95:5 over 30 minutes at 1.5 mL min^{-1}. Six cigarettes smoked in 0.06-m^3 box sampled at 2 L min^{-1} for one-half hour.

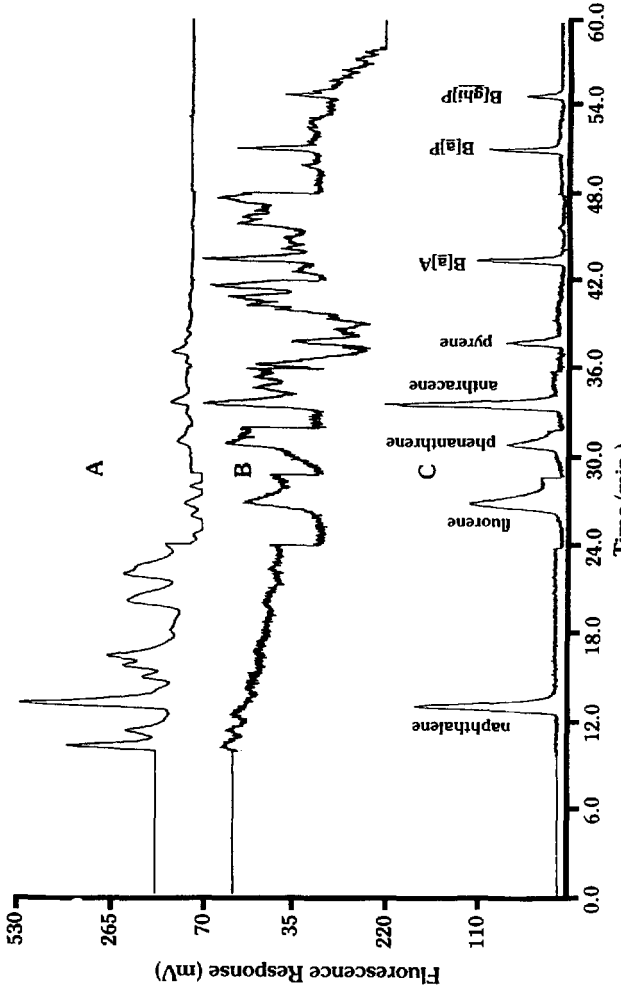

FIGURE 5. Gradient elution of 1:1, ACN:H_2O extract (4 mL) for PAH: (A) XAD-2 tube; (B) 2-µm PTFE membrane; (C) PAH standard. Conditions: same as Figure 4 except wavelength program specific to eight compounds. Four cigarettes smoked in 28-m^3 room sampled at 2 L min^{-1} for one hour.

A mixed cellulose ester membrane of 0.8-μm pore size was evaluated since it is completely dissolved by the ACN. This would leave no doubt as to the removal of the PAHs from this filter. However, at least some of the extracted material precipitated when the 2 ml of water was added after sonication. Attempts to filter the extract were successful initially, but upon standing, the extract again became cloudy. Injecting this non-homogeneous mixture would eventually result in clogged tubing. For this reason, the mixed cellulose ester membrane was abandoned.

The C18 Sepak (Waters Assoc., Milford, MA, USA), used by Symons *et al.* (13) to sample refinery effluent, was evaluated for collection of PAHs. This device collected *ca.* one-half the amount collected with 1- and 2-μm pore size membranes.

The 1- μm pore size Fluoropore membrane was chosen for its greater trapping efficiency over the 2-μm pore size filter and because it is currently being used in this laboratory for the determination of respirable suspended particles (14).

Isocratic Versus Gradient Mobile Phase

Isocratic conditions (Figure 3) were used initially to simplify the chromatographic procedure and because B[a]P was the main compound of interest. Previous work had shown that B[a]P could be determined in tobacco smoke 'tar' under isocratic conditions in fewer than 20 minutes (15). However, when working with ETS samples, it became apparent that a column cleaning step

was required in order for the baseline to stabilize. This cleaning increased the total sample run time to 35 minutes. Isocratic conditions were favorable for the separation of B[a]P but there was co-elution and/or insufficient resolution of some PAH pairs, *e.g.*, B[a]A - chrysene, D[a,h]A- B[b]F and perylene - B[k]F. Since there had to be sufficient time between compounds' elution to utilize the detector's wavelength-time feature, isocratic elution conditions were abandoned.

A mobile phase gradient at 1.5 mL min^{-1} flow rate plus selective wavelength detector programming proved more successful than isocratic conditions but required a total run time of 84 minutes (including column equilibration) (Figure 5). This gradient was capable of separating B[a]A from chyrsene (11). The total run time was decreased to 42 minutes by increasing the flow rate to 3.0 mL min^{-1}.

Internal Versus External Standard

Deuterium labeled B[a]P appeared to be an excellent internal standard candidate for simple ETS matrices (see Figure 3). However, a more concentrated ETS sample (Figure 4) showed that interferences may make the use of an internal standard impossible. Because of this and the expense of deuterated PAHs, an external standard quantification was used.

Precision

Table II shows chromatographic precision to be good with relative standard deviations between 5 and 8% Table III gives the overall precision of samples

Table 2.
Chromatographic Precision (n=6)

Compound	Conc. (ng mL^{-1})	$\bar{x}$ (peak height)	σ (peak height)	% RSD
Chrysene	1.45	604.4	32.8	5.43
B[b]F	0.84	95.8	5.2	5.42
B[k]F	0.23	161.8	12.6	7.78
B[a]P	0.68	469.0	25.6	5.46
B[ghi]P	0.46	95.8	7.7	8.04

Table 3.
Overall Precision (n=6) from the Smoking of Eight Cigarettes in a 28-m^3 Room (ng m^{-3})[a]

Compound	$\bar{x}$	σ	% RSD	MDQ
Chrysene	1.10	0.08	7.20	0.04
B[b]F	0.44	0.04	9.09	0.04
B[k]F	0.15	0.01	6.66	0.04
B[a]P	0.54	0.04	7.40	0.08
B[ghi]P	0.46	0.03	6.52	0.12

[a] - Sampled five hours @ 16L min^{-1}

MDQ = minimum detectable quantity, @ 2 x's signal to noise

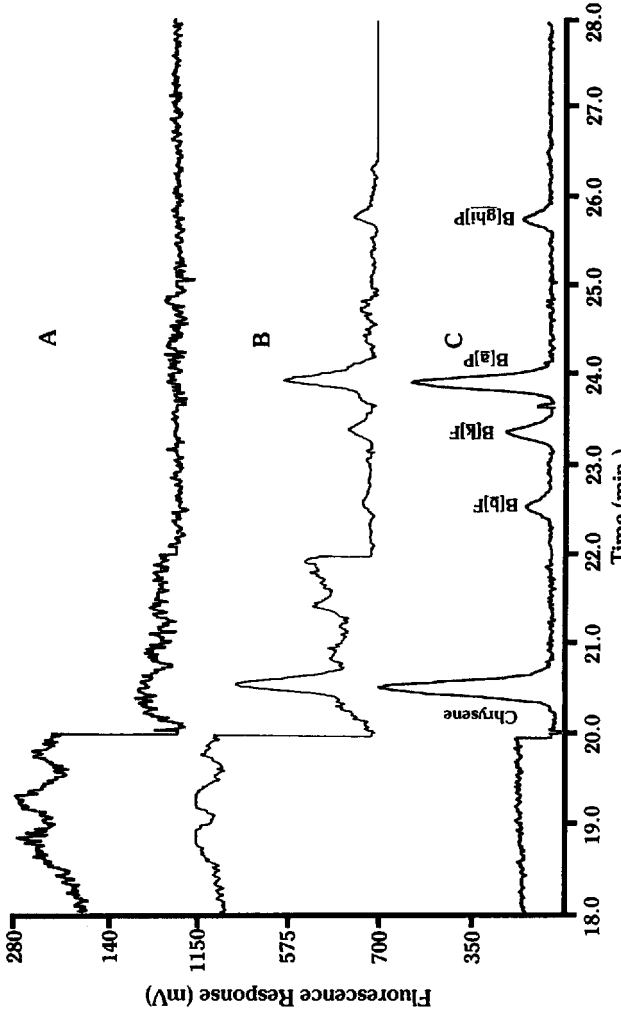

FIGURE 6. Chromatograms from precision study of the smoke from eight cigarettes in 28-m^3 room: (A) backup 1-µm PTFE membrane; (B) sample 1-µm PTFE; (C) PAH standard. Conditions: Vydac 201TP54C (4.6 X 250 mm, 5µ); gradient of ACN:H_2O, 45:55 initially for 10 minutes to 95:5 over 15 minutes at 3.0 mL min^{-1}; 200 µL injection volume; fluorescence detection with wavelength program (see text). Eight cigarettes smoked in 28-m^3 room sampled at 16 L min^{-1} for five hours.

Table 4.
Linearity of the Analytical Method[a]

Compound	Concentration Range (ng m^{-3})	Sensitivity Range[b] (ng)	Linear Correlation (R^2)	y-intercept (ng m^{-3})
Chrysene	0.29-2.03	0.07-0.49	0.999	0.06
B[b]F	0.18-1.30	0.04-0.31	0.999	0.08
B[k]F	0.05-0.34	0.01-0.08	0.999	0.01
B[a]P	0.14-0.94	0.03-0.22	0.998	0.03
B[ghi]P	0.15-1.07	0.04-0.26	0.999	0.04

[a] - Based on the smoke from eight cigarettes in 28-m^3 room, 4800-L air sample, extracted with 2 mL ACN then diluted with 2 mL H_2O

[b] - 200 µl injection volume

collected from ETS generated by smoking eight cigarettes in a 28-m^3 room. The last column gives the minimum detectable quantity in ng m^{-3} under the sampling conditions used. Figure 6 shows typical chromatograms obtained during precision studies. These results for chrysene, B[a]P and B[ghi]P compare favorably with those of Salomaa *et al.* by GC-MS, when one considers that 96 cigarettes were smoked compared to eight in this work (1).

Linearity

Table IV covers the concentration ranges for the PAHs encountered from ETS in this work. The method is sensitive to concentrations in the sub-nanogram range.

Table 5.
Recovery and Standard Addition[a]

Compound	Amount Added (ng)	Amount Recovered (ng, total)	% Recovery
Chrysene	4.35	9.00	106.8
	8.70	17.39	99.8
	17.40	34.25	96.8, $\bar{x}$ = 101.2

ng m^{-3}: standard addition = 1.52, external standard = 1.43

B[b]F	1.40	3.05	117.8
	2.80	5.71	103.9
	5.60	11.57	106.6, $\bar{x}$ = 109.4

ng m^{-3}: standard addition = 0.51, external standard = 0.50

B[k]F	0.34	0.74	117.6
	0.69	1.41	104.4
	1.38	2.78	101.4, $\bar{x}$ = 107.8

ng m^{-3}: standard addition = 0.15, external standard = 0.14

B[a]P	1.35	2.76	101.4
	2.75	5.56	102.2
	5.40	10.98	103.3, $\bar{x}$ = 103.3

ng m^{-3}: standard addition = 0.54, external standard = 0.53

B[ghi]P	0.92	1.99	116.3
	1.84	3.60	95.6
	3.68	7.16	94.6, $\bar{x}$ = 102.2

ng m^{-3}: standard addition = 0.50, external standard = 0.48

[a] - ETS from eight cigarettes; 2 mL ACN followed by 2 mL H_2O

The responses are linear, R^2 being 0.99 or better. The y-intercept values are zero within experimental error.

Recovery and Standard Addition

Table V shows good recoveries from the 1-μm Fluoropore membrane filter upon addition after sampling. The amounts calculated by standard addition compare favorably with those obtained by external standard quantification.

Extraction Efficiency

To determine if 2 ml of ACN followed by the addition of 2 ml of water is efficient in removing PAHs from the Fluoropore membrane after sampling ETS, the same membrane was sonicated a second time. The amount of chrysene remaining was < 3% of the total collected. The amount of B[a]P was < 2%. B[b]F, B[k]F and B[ghi]P were below detection limits in the second extract indicating that 2 ml of ACN followed by 2 ml of water is sufficient to extract the PAHs.

Breakthrough Study

Two 1-μm Fluoropore membrane filters in series were used in all sampling experiments. The PAHs on the backup membrane were below detection limits in every case (see PAHs from Other Sources). This showed that a single 1-μm Fluoropore membrane filter is sufficient under most sampling conditions for collecting the particulate matter where these compounds are found.

PAHs from Other Sources

To illustrate the utility of the procedure, air samples were taken with PAHs present from various possible sources. Automobile exhaust (Figure 7), smoke from a kerosene lantern (Figure 8), fireplace smoke (Figure 9) and smoke from a gas grill (Figure 10) were sampled. Also shown in these chromatograms is the analysis of the backup Fluoropore membrane where these five PAHs were below

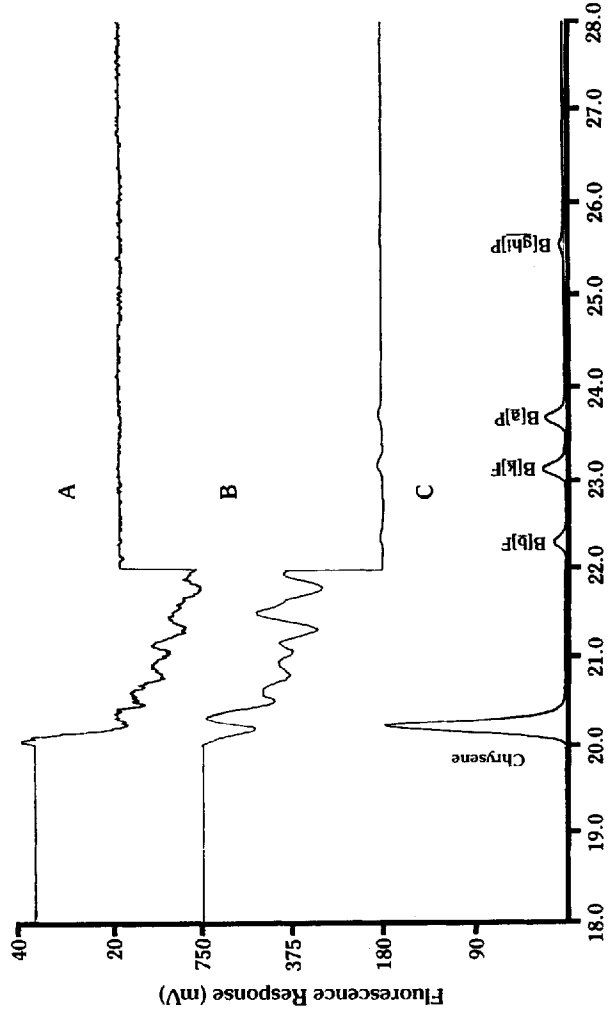

FIGURE 7. Chromatograms of automobile exhaust sampled for two hours at 16 L min^{-1}: (A) backup 1-µm PTFE; (B) sample 1-µm PTFE; (C) PAH standard. Conditions: same as Figure 6.

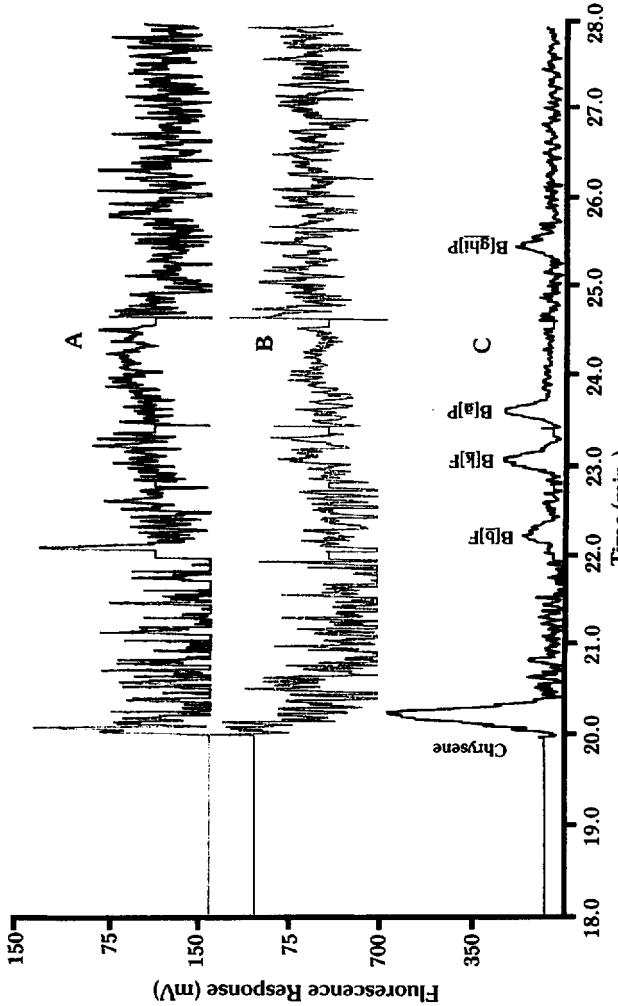

FIGURE 8. Chromatograms of kerosene lantern smoke sampled for five hours at 16 L min^{-1} in 38-m^3 room: (A) backup 1-µm PTFE; (B) sample 1-µm PTFE; (C) PAH standard. Conditions: same as Figure 6.

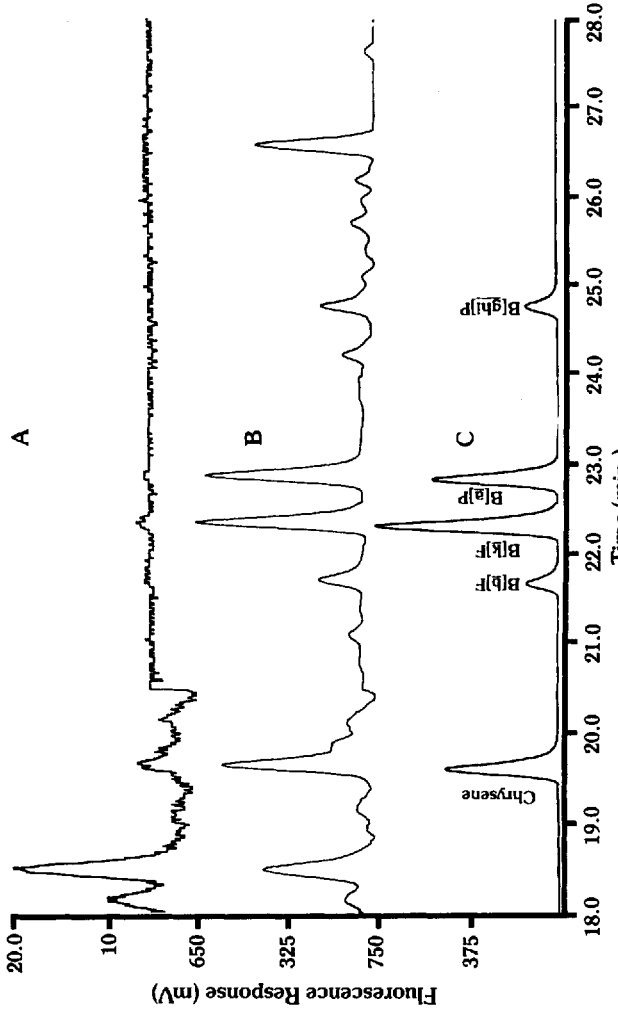

FIGURE 9. Chromatograms of fireplace smoke sampled for two hours at 16 L min^{-1}: (A) backup 1-µm PTFE; (B) sample 1-µm PTFE; (C) PAH standard. Conditions: same as Figure 6.

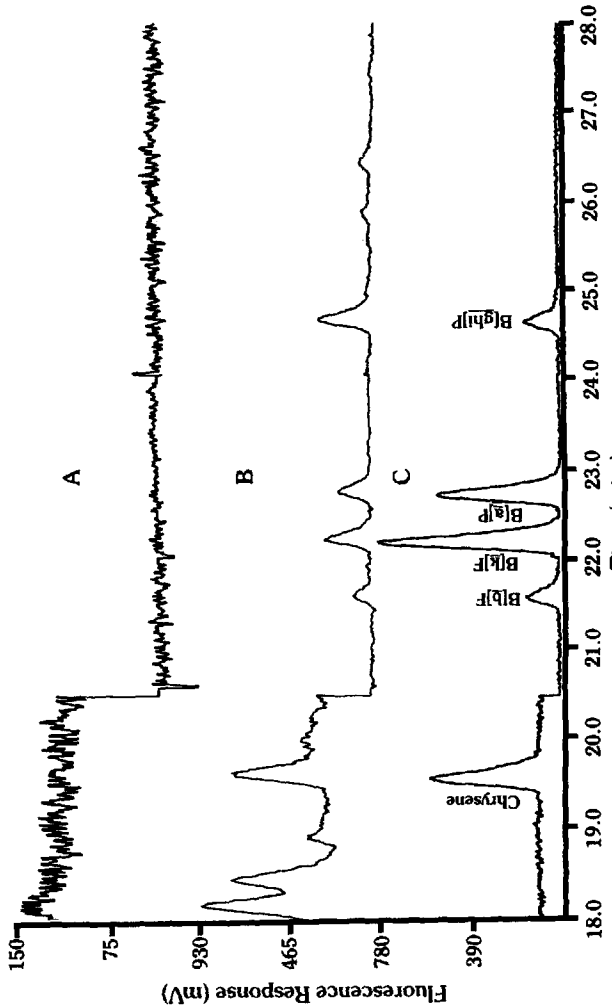

FIGURE 10. Chromatograms of gas grill smoke from cooking hamburgers sampled for 15 minutes at 16 L min^{-1}: (A) backup 1-µm PTFE; (B) sample 1-µm PTFE; (C) PAH standard. Conditions: same as Figure 6.

Table 6.
PAH from Other Sources (ng m^{-3})

Source	Volume of air sampled (L)	Chrysene	B[b]F	B[k]F	B[a]P	B[ghi]P
Fireplace[a]	1840	57.00	61.41	35.32	108.70	59.24
Gas Grill[b]	240	21.12	15.12	5.08	13.25	40.50
Auto Exhaust[c]	2276	13.92	2.81	0.84	1.76	1.01
Eight Cigarettes[d]	4800	1.10	0.44	0.15	0.54	0.46
Kerosene Lantern[d]	4800	<0.09	<0.15	<0.03	<0.07	<0.10

[a] - Sampled in a 45-m^3 room

[b] - Sampled outside while cooking hamburgers, 2 feet above grill lid

detection limits in every sample matrix. The time-wavelength program used for these samples was the same used for ETS samples with the exception of the wavelengths for B[a]P. To minimize interference in the automobile exhaust, fireplace and gas grill samples, an excitation wavelength of 378 nm was used instead of 268 nm even though this resulted in a loss in sensitivity, it is an example of the utility of fluorescence detection when one has a choice of wavelengths for detection to eliminate interferences.

Table VI gives the results of duplicate analyses of the five PAHs from these other sources in decreasing order of B[a]P content. Included in this table are the PAHs from the smoking of eight cigarettes in a 28-m^3 room. Auto exhaust values compare well in magnitude to those values found in urban air by different end point determinations (16, 17). The particles from a kerosene lantern, although

visible on the Fluoropore membrane, yielded PAH values which were below detection limits. Fireplace smoke, which is considered to be a prominent source of PAHs (18), gave the highest results for the five matrices analyzed, equivalent to the ETS of 1600 cigarettes. The results compare well with those obtained by Thairu *et al.* from biomass burning in Kenya (19). A second extraction of the Fluoropore membrane filter used in the fireplace smoke sampling revealed that *ca.* 8% of the PAH remained unextracted. This removal may be improved by (1) increasing the amount of ACN extractant, (2) sonicating for a longer time, and (3) decreasing the total volume of air sampled, since more than a sufficient amount of these analytes was obtained. The smoke from a gas grill contains a significant amount of PAHs. No literature citations were found to compare these results but they are presented here to show the versatility of this method.

CONCLUSIONS

The described HPLC method was developed for the determination of chrysene, B[b]F, B[k]F, B[a]P and B[ghi]P in indoor air. Minimal sampling time and handling, in conjunction with selective detection, enables reliable measurements of these PAHs to be made.

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