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SAMPLING, ANALYSIS, AND DATA VALIDATION OF INDOOR CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

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Abstract

There is an increased concern facing federal and state health officials regarding the risk of public exposure to toxic air contaminants in indoor environments. The immediate interest concerns the indoor exposure to polycyclic aromatic compounds (PAC), many of which are potent carcinogens with known indoor sources. Current outdoor sampling and analytical techniques require collection of a large volume of air using a high volume sampler which is not appropriate for use indoors, since the high sampling flow rates required would substantially alter the indoor environmental conditions and thus introduce a large uncertainty into the assessment of the actual indoor concentrations. Thus, the California Air Resources Board has commissioned research to develop an indoor sampling and analysis method for airborne PAC. We developed a new sampler for measuring particulate and gas phase PAC in indoor environments. The sampler consists of a fan cooled acoustically insulated pump which draws air through a sampling cassette composed of a 47 mm TIGF filter followed by a sorbent cartridge packed with XAD-4 resin. It is relatively unobtrusive with a noise level comparable to a personal computer or refrigerator. The flow rate of the sampler in the field tests was set to approximately 34 liters per minute so that a 25 m^3 sample volume could be collected in a 12-hour period. The 25 m^3 sample volume is necessary to achieve the desired ng/m^3 detection limit for PAC without significantly impacting the indoor concentrations.

A sampling and analytical method for gas-phase polycyclic aromatic hydrocarbons (PAH) was developed specifically for use in indoor air. Samples were collected on sorbent samplers containing two sections of XAD-4 resin, each weighing 2.5 g. The XAD-4 resin was extracted in dichloromethane in an ultrasonic bath, concentrated, and 14 PAH were analyzed for by electron impact gas chromatography-mass spectrometry. Perdeuterated internal standards for quantitation were added to the extracts immediately prior to the analyses. The limit of detection for compounds without measurable blank values was estimated to be ~0.1 ng/m^3 for a sample volume of 25 m^3. We also developed an analytical method for gas-phase nitro polycyclic aromatic hydrocarbons (nitro-PAH) in samples of indoor air. This method was used for the analysis of 1-nitronaphthalene and 2-nitronaphthalene in extracts of the front sections of sorbent samplers used to collect gas-phase PAH. An extraction and analysis method was developed for determination of particulate-phase PAH in indoor air using using HPLC with gradient elution, flow programming and selective fluorescence detection. Twenty-one semi-volatile and particulate-phase PAH were determined, with levels of detection ranging from 0.28 ng/m^3 for retene to 0.001 ng/m^3 for dibenzo(a,h)pyrene. The detection limit for benzo(a)pyrene was 0.018 ng/m^3. Two fluorescence programs were devised to determine closely-eluting and co-eluting pairs in two injections per sample.

The precision of this newly developed indoor PAC sampler was evaluated in a pilot field study conducted in three residences and two commercial buildings. The PAC sample pumps performed quietly and reliably throughout the PAC pilot field study. The indoor concentrations of gas-phase PAH were generally higher indoors than outdoors which is consistent with the presence of known indoor PAH sources in this study. In one residence without any indoor combustion sources, there were many gas-phase PAH with significantly higher indoor concentrations suggesting the presence of indoor sources not directly combustion related. The concentrations of particulate-phase PAH were not as different from the outdoor concentrations as were the gas-phase PAH. From this pilot PAC field study we have concluded that the indoor PAC sampler and analytical methods are ready for deployment in a larger field study for most of the gas-phase PAH measured in this study but not for the particulate-phase PAH or the gas-phase nitro-PAH. The analytical methods for these compounds will require some further development to improve measurement precision before deployment in a large indoor field study.

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The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

Alkyl-PAH	Alkylated polycyclic aromatic hydrocarbons
ATN	Attenuation (optical)
Aza-arenes	PAH containing a nitrogen atom
CARB	California Air Resources Board
CH_2Cl_2	Dichloromethane, methylene chloride
CH_3OH	Methanol
DCM	Dichloromethane, methylene chloride
DMSO	Dimethyl sulfoxide
DOAS	Differential optical absorbtion spectroscopy
EPA	U.S.Environmental Protection Agency
GC	Gas chromatography
GC/FID	Gas chromatography/flame ionization dection
GC/MS	Combined gas chromatography/mass spectrometry
GC/MS/MID	GC/MS operating in the multiple ion detection mode
GC/MS/SIM	GC/MS operating in the selective ion detection mode
GF	Glass fiber (filters)
Hg	Mercury
Hi-vol	High-volume sampler
HPLC	High performance liquid chromatography
LLD	Lower limit of detection
LOQ	Lower limit of qualtification
M	Molar
mol	mole (6.022×10^{23} molecules)
MS	Mass spectrometry
MSD	Mass selective detector
M.W.	Molecular weight
m/z	Mass to charge ratio
NBS-SRM	Standard Reference Material supplied by the National Bureau of Standards (now National Institute of Standards and Technology)
ng	Nanogram (10^{-9} gram)
nm	Nanometer
Nitroarene	PAH containing nitro (NO_2) group(s)
NPAH	Nitro polycyclic aromatic hydrocarbons
O.D.	Optical density
OH	Hydroxyl radical

Open column	Liquid chromatography technique, used for compound chromatographic separation or purification.
PAC	Polycyclic aromatic compounds
PAH	Polycyclic aromatic hydrocarbons
PASH	PAH containing a sulfur atom
pg	Picogram (10^{-12}gram)
ppb	Part per billion
ppt	Part per trillion
PCI	Positive chemical ionization
PST	Pacific standard time
PTFE	Teflon material
PUF	Polyurethane foam
SCFM	Standard cubic feet per minute
Semi-prep column	Semi-preparative scale column used for compound separation or purification by HPLC
SIM	Selective ion monitoring
SF_6	Sulfur hexafluoride gas
SIM	Selective ion monitoring
SRM 1647	NBS-SRM priority pollutant polynuclear aromatic hydrocarbons
SRM 1649	NBS-SRM urban dust/organics
SSI	Size selective inlet
Tenax-GC	Adsorbent polymer of 2,6-diphenyl-p-phenylene oxide
TIC	Total ion chromatogram
TIGF	Teflon impregnated glass fiber (filters)
Torr	Pressure unit equivalent to 1 mm Hg
TSP	Total suspended particulate
μg	Microgram (10^{-6})
μL	Microliter (10^{-6})
μm	Micrometer (10^{-6})
μmol	Micromole (10^{-6})
UV	Ultraviolet
uv/vis	Ultraviolet/visible
W	Watt
XAD	styrene-divinylbenzene polymeric resin

Gas-Phase PAH Abbreviations

NAPH	Naphthalene
2NAPH	2-Methylnaphthalene
1NAPH	1-Methylnaphthalene
BiPHE	Biphenyl
ACNPY	Acenaphthylene
ACNPE	Acenaphthalene
FLRN	Fluorene
PYREN	Pyrene
PHEN	Phenanthrene
ANTH	Anthracene
2ANTH	2-Methylanthracene
9ANTH	9-Methylanthracene
FLUOR	Fluoranthene
CHRYS	Chrysene

Gas-Phase Nitro-PAH Abbreviations

9-NA	9-Nitroanthracene
1-NN	1-Nitronaphthalene
2-NN	2-Nitronaphthalene

Particulate-Phase PAH Abbreviations

Phen	Phenanthrene
Anth	Anthracene
Fluor	Fluoranthrene
Pyr	Pyrene
BaA	Benzo(a)anthracene
Chry	Chrysene
5-MC	5-Methylchyrsene
Ret	Retene
BeP	Benzo(e)pyrene
BbF	Benzo(B)fluoranthene
BkF	Benzo(B)fluoranthene
dBacA	Dibenz(a,c)anthracene
BaP	Benzo(a)pyrene
dBalP	Dibenzo(a,l)pyrene
dBahA	Dibenzo(a,h)anthracene
BghiP	Benzo(g,h,i)perylene
IcdP	Indeno(1,2,3-cd)pyrene
dBaeP	Dibenzo(a,e)pyrene
Cor	Coronene
dBaiP	Dibenzo(a,i,)pyrene
dBahP	Dibenzo(a,h)pyrene

I. PROJECT SUMMARY AND CONCLUSIONS

A. PROJECT SUMMARY

There is an increased concern facing federal and state health officials regarding the risk of public exposure to toxic air contaminants. Recent investigations of indoor air quality have disclosed large differences between indoor and outdoor contaminant concentrations. These differences arise from the presence of indoor contaminant sources and sinks. To date most risk assessments have assumed that the indoor and outdoor concentrations are the same. This assumption and the uncertainty associated with it, due to the fact that people spend an average of 90% of their time indoors, has made consideration of both indoor and outdoor contaminant exposures important. For the most part outdoor exposures are estimable from outdoor concentration measurements conducted by both federal and state agencies. However, with respect to indoor exposures, there have been relatively few measurements of toxic air contaminants.

The California Health and Safety Code Section 39660.5 *et seq.* (Assembly Bill 3052, Tanner) effective January 1, 1987, requires the California Air Resources Board to consider indoor exposures in assessing the risk to public health posed by toxic air contaminants. The immediate interest concerns the indoor exposure to polycyclic aromatic compounds (PAC), many of which are potent carcinogens.

Outdoor measurements have recently been made in California with sampling and analytical techniques which require collection of the PAC from a large volume of air using a high-volume sampler (Atkinson et al., 1988, Arey et al., 1989, Zielinska et al., 1989). These methods are inappropriate for use indoors since the high sampling flow rates required would substantially alter the indoor environmental conditions and thus introduce a large uncertainty into the assessment of the actual indoor concentrations. In addition, little is known regarding the collection of distinctly indoor PAC such as those contained in tobacco smoke, and wood stove, gas range, and unvented space-heater emissions.

Thus, the California Air Resources Board has commissioned research to develop an indoor sampling and analysis method for airborne PAC. This research is the subject of this report.

Criteria for an Indoor PAC Sampler

The following design criteria were proposed for an indoor sampler for PAC. PAC exist in indoor and outdoor air as both gases and particles. A PAC sampler should thus be able to separately collect the PAC vapor and particulate phases. The proposed sampler is designed to separately collect gas and particulate phase PAC utilizing a motor driven air pump to draw air first through a filter medium to collect particulate phase PAC and then through a sorbent bed to collect the gas phase PAC.

Sample Flow Rate. The sample flow rate for the proposed sampler is constrained by several criteria. The lower limit for the sample flow rate is determined by the minimum air volume required by the analytical method to quantify the indoor PAC concentrations at levels consistent with the risk assessment associated with each species of PAC and the length of the proposed sampling period. The upper limit for the sample flow rate is limited by considerations for the impact of the air sampler on the indoor concentrations of PAC.

Sample Flow Control. The sample flow rate should be controlled to maintain a constant sampling rate throughout the measurement period in indoor environments with elevated concentrations of particulate matter such as may be encountered where tobacco smoking is present.

Filter Type. The filter medium should be able to efficiently collect a particulate sample for the measurement period with a minimal increase in pressure drop. Additionally the filter medium should be constructed of materials which minimize artifact formation.

Sorbent Type. The type of sorbent used to collect the gas phase PAC should efficiently collect a broad range of PAC with a minimal pressure drop and minimum break through over the measurement period. The amount of sorbent material is constrained in several ways. Large amounts of sorbent material require more solvent to extract the collected PAC and contribute to higher background contamination which increases the minimum analytical detection limit. From this perspective it is desirable to collect the PAC onto a small amount of sorbent material. The minimum amount of sorbent material is determined by the required contact time for the sampled gas phase PAC to be collected without breakthrough. In addition consideration must be given to the capacity of the absorbent so that a sample may be efficiently collected throughout the measurement period.

Pump Type. The selection of the type of air pump for the sampler is another important consideration since some types of pumps may introduce undesirable contaminants into the sampler exhaust air and subsequently into the indoor air where they may then be collected by the sampler. The air pump must also be able to provide reliable performance over anticipated 12-hour sampling periods.

Acoustics. Since this sampler is intended for deployment in indoor environments including residences, an important criterion is the level of noise created by the sampler. Acoustic shielding of the motor and muffling of the air discharged from the sampler are important considerations in achieving an acceptable noise level. For residences a Noise Criterion (NC) value of 35 is suggested as an appropriate design goal.

Criteria for an Indoor PAC Method of Analysis

The analysis to be developed and validated must provide for the analysis of two classes of PAC, PAH and nitro-PAH, in both vapor and particulate phases, and allow for further development for measurement of aza-arenes. Thus, the scheme of analysis will necessarily be more complex than if only a single class, e.g., particulate-phase PAH, were to be analyzed. Within this context, there are a number of criteria which should be met as fully as possible.

Minimal Number of Procedures. The analytical method to be developed and validated should involve a minimal number of procedures (e.g. separations, reductions). This will maximize recoveries and the precision of the analysis, will minimize the possibilities of losses and contamination, and will help to keep the cost of analysis within acceptable limits.

Specificity. The method developed should minimize interferences from other compounds which might be present in any sample.

Limits of Detection. The method to be developed must be sufficiently sensitive to be used for analysis of small samples, i.e., samples of a size that will have a minimal impact on indoor concentrations. This has been estimated to be a sample of about 25 m^3 collected over a 12-hour period.

Routine Analysis. The method to be developed must be suitable for routine analysis of large numbers of samples which might be collected in a field study. Furthermore, it should be readily transferable to other laboratories. Methods which are highly complex or are quite new and therefore not sufficiently well characterized for a variety of sample matrices, e.g., supercritical fluid extraction, should be avoided. Similarly, methods which require highly specialized instrumentation are not practical.

Instrumentation. The instrumentation to be used should be commercially available, require relatively little maintenance and be so widely used that any problems which might arise can be readily resolved. Instrumentation which has just come into the market and has not been sufficiently tested in a number of laboratories should be avoided. If possible, less costly instrumentation should be used so that it is feasible to have more than one instrument available in a laboratory to handle large sample loads.

Internal Standards. Internal standards should be used to correct for losses during extraction, solvent reduction and/or solvent exchange and class separations.

Validation. The method to be developed should be validated by the analysis of "real world" samples. Routine analysis of positive controls (i.e. NBS Standard Reference Materials) and negative controls (blanks) should be incorporated into the method.

Limits of Detection and Risk Assessment. The analytical scheme to be developed should be sufficiently sensitive so that benzo(a)pyrene, the classical indicator compound for PAH, can be detected at a concentration of 0.3 ng/m^3. This is the concentration for which it has been estimated that the risk of cancer for lifetime exposure is less than 1×10^{-6}. Limits of detection for other carcinogenic compound classes, e.g., nitro-PAH, should reflect their potency as carcinogens in animals, relative to benzo(a)pyrene. For a 25 m^3 indoor air sample, the most sensitive method of analysis and the only one which meets the required 0.3 ng/m^3 lower limit of detection for particulate compounds is high pressure liquid chromatography with fluorescence detection (HPLC/fluorescence). The other methods would require larger air volumes to be sampled to quantitate benzo(a)pyrene at this concentration.

Development of the Indoor PAC Sampler

We have developed a new sampler for measuring particulate and gas phase PAC in indoor environments. The sampler consists of a sampling cassette with a filter followed by a sorbent cartridge and a fan cooled acoustically insulated pump. The pump enclosure with pump weighs 40 kg and has outside dimensions of 76.2 cm x 38.1 cm x 40.6 cm. It is relatively unobtrusive with a Noise Criteria level of 45 (i.e. similar to noise from a personal computer or refrigerator) and can be plugged in to any 110 volt, 5 amp outlet. The flowrate of the sampler is manually adjustable with a union bonnet valve from 4.7 and 47.2 Lpm and once set, will remain constant (i.e. less than 5% variation) throughout the sampling period for most indoor and outdoor environments. A sampler holder and tripod-stand suspend the sampling cassette in the breathing zone. Elapsed time and sampling cassette pressure drop are indicated on the control panel. The sampling cassette consists of a 47 mm Teflon impregnated glass fiber (TIGF) filter in a polycarbonate cassette holder for collection of particulate phase PAC followed by two sections of XAD-4 resin in a stainless steel and glass cartridge for collection of gas phase PAC.

The flow rate of the sampler in the pilot field tests was set to approximately 34 liters per minute so that a 25 m^3 sample volume could be collected in a 12-hour period. The 25 m^3 sample volume is necessary to achieve the desired ng/m^3 detection limit for PAC. The impact of the PAC sampler was estimated using a computer simulation of the indoor PAC concentrations with and without a PAC sampler operating. We concluded from these simulations that the 34 liter per minute sampling rate represents a small reduction of less than five percent of the indoor PAC concentration at most indoor residential or commercial sampling locations.

We designed an acoustical enclosure that draws air from the surrounding environment across the pump head and keeps the pump from overheating. Our field tests were run under various conditions up to ambient temperatures as high as 30 ^{o}C with no occurrence of pump overheating.

We measured the stability of the sample flow rate over 12-hour sampling periods in the pilot field study described in Chapter VI. These tests indicated that for filter loadings up to 6 mg of particulate matter, the pressure drop across the filter increases linearly with loading and that the flow rate through the pump varies inversely with increasing filter pressure drop. A 6 mg particulate load collected in a 25 m^3 sample represents an average particulate

concentration of 240 $\mu g/m^3$. Typical indoor residential and commercial particulate concentrations range from 20 - 100 $\mu g/m^3$. Thus the prototype sampler without a compensating flow controller may be expected to collect 25 m^3 samples in residential and commercial buildings with less than a 10% reduction in the sample flow rate. Furthermore since the filter pressure drop increases and associated sample flow rate decreases are expected to be linear within the 6 mg of total filter load, the average sample flow rate may be computed as the arithmetic average of the initial and final sample flow rate measurements.

Development of an Analytical Method for Measuring Gas-Phase PAH.

A sampling and analytical method for semi-volatile gas phase polycyclic aromatic hydrocarbons (PAH) was successfully developed and validated by this study. Samples are collected on sorbent samplers containing two sections of XAD-4 resin, each weighing 2.5 g. This method has sufficient selectivity, sensitivity, and precision for analysis of vapor phase PAH in small air volumes (i.e. 25 m^3) collected from indoor environments containing a variety of potential sources of PAH. A significant achievement was the highly precise analysis of PAH in environments dominated by cigarette smoke, since this source results in a much more chemically complex matrix than is encountered in studies of outdoor air. The method described in this study is relatively simple and utilizes instrumentation which is available in many environmental laboratories. It is well suited and ready for use in a large scale survey of residential indoor air quality.

For analysis, the front and back sections of each sampler are separately extracted with dichloromethane in an ultrasonic bath. The extracts are concentrated to 500 µL and solvent exchanged to benzene. The extracts are analyzed by electron impact gas chromatography-mass spectrometry (GC-MS). The molecular ions of the PAH are selectively monitored. Two separate analyses are performed. The 500-µL extracts of both the front and back sections of each sample are analyzed for naphthalene, 1- and 2-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene and fluorene. The extract of the front section is further concentrated to 50-75 µL and is analyzed for phenanthrene, anthracene, 2- and 9-methylanthracenes, fluoranthene, pyrene and chrysene. Perdeuterated surrogate compounds for determination of analyte recoveries are spiked onto the samplers prior to sample collection. Perdeuterated internal standards for quantitation are added to the extracts immediately prior to the analyses.

Compounds are identified using retention indices based on their GC retention times relative to the retention times of the perdeuterated surrogate compounds. Compounds are quantified by comparing their integrated ion-current responses to the responses of the internal standard compounds. The recoveries of the surrogate compounds are determined for each field sample. Sorbent blank values are determined from the analysis of blank samples returned from the field. Breakthrough of the most volatile compounds in each field sample is determined from the analysis of the back section of the sorbent sampler. The masses of compounds in a sample are corrected for recovery of a closely related surrogate (perdeuterated PAH) compound, for a sorbent blank value if any, and for breakthrough if any.

The method was evaluated in a pilot field study conducted in three houses and two office buildings. Nineteen samples were collected indoors, and 16 samples were collected outdoors in the near vicinity of the buildings. The sample set contained 11 pairs of duplicate samples.

Only naphthalene and biphenyl exhibited breakthrough from the front to the back section of the sampler in excess of one percent in any sample. The breakthrough of naphthalene occurred in eight of the samples with a maximum loss of ten percent. Biphenyl exhibited some breakthrough in most samples with an average loss of four percent. Six of the compounds had measurable sorbent blanks. Only naphthalene and biphenyl had blank values which exceeded two percent of typical masses in outdoor samples. A contaminant compound which interfered with the analysis of phenanthrene, and to a lesser extent anthracene, was detected in some indoor samples. The source of this compound was not identified.

The limit of detection for the method for compounds without measurable blank values was estimated to be 1.5 ng for a sample volume of 25 m^3 (~0.1 ng m^{-3}). Only the methylanthracenes and chrysene had values at or below the limit of detection in some of the field samples.

Analytical precisions were estimated for eight of the compounds from duplicate analyses of four sample extracts. The analytical precisions for naphthalene and the methylnaphthalenes, expressed as relative 95-percent confidence intervals, were better than three percent. The relative precisions of the other compounds ranged from six to 24%.

The method measurement precision was estimated using the pairs of duplicate samples. The relative precision of the gas phase PAH analyses for the combination of indoor and outdoor samples ranged from 4.8% for acenapthylene to 160% for 9-methylanthracene. The high relative imprecision percentage for 9-methylanthracene was a result of both its low concentration (i.e. close to the analytical detection limit) and the low number of replicate pairs for this compound (i.e only 3). The pooled relative precision for the 12 gas phase PAH compounds with mean concentrations greater than 1 ng/m^3 range from 4.8% to 25.3% except for biphenyl, phenanthrene, and anthracene which have relative precisions of 35.6%, 113% and 80.3% respectively.

The overall measurement uncertainty of the calculated sample masses was estimated by propagating the uncertainties of the individual independent variables for a representative gas-phase compound through the data reduction scheme. Using typical values for volumes, weighed masses and peak-area responses, the total uncertainty, expressed as a relative 95-percent confidence interval, was estimated to be 20 percent. This estimated measurement uncertainty agrees well with the method measurement precision computed from the pairs of duplicate samples for most of the gas-phase PAH.

Development of an Analytical Method for Measuring Gas-Phase Nitro-PAH.

Development of an analytical method for gas-phase nitro-PAH was less successful due to time constraints. These compounds were expected to be present in indoor air at very low concentrations (i.e. several nanograms per cubic meter of air and less). Therefore. a highly sensitive method based on high-performance liquid chromatography (HPLC) with fluorescence detection was selected for development and evaluation. A procedure for sample clean up using solid-phase extraction was incorporated. The method was demonstrated to have sufficient sensitivity. However, significant sample matrix problems were encountered, particularly for samples from indoor environments with tobacco smoke. Despite these problems, the method produced encouraging results. It was concluded that the method would require some further development and evaluation before it would be ready for use in a large-scale filed study of indoor air quality.

This method was used for the analysis of 1-nitronaphthalene (1-NN) and 2-nitronaphthalene (2-NN) in extracts of the front sections of sorbent samplers used to collect gas-phase PAH. A total of 12 composited samples representing indoor and outdoor locations at five collection sites were analyzed.

The composite sample extracts were first fractionated in an attempt to isolate the nitro-PAH (NPAH) from the PAH and other components of the samples. A simple cleanup procedure was attempted which employed solid-phase extraction of the samples with Sep-Pak silica cartridges. Nearly complete recovery of 1- and 2-NN added to the Sep-Pak cartridges as standards was achieved. However, recovery of 1- and 2-NN added to representative sample extracts which were then fractionated was only approximately 60%. An internal standard, 9-nitroanthracene (9-NA), which was added to the Sep-Pak cartridges along with the analytes could not be adequately recovered presumably due to reactive losses.

Analysis of the extract fractions containing NPAH was by HPLC with on-line reduction of the nitro-PAH to the corresponding amino-PAH followed by fluorescence detection. A microbore, reversed phase C-18 column was used for chromatographic separation. This was followed by a reducer column packed with a mixture of zinc dust and silica. Buffered methanol and water were used as solvents.

The analytes were identified on the basis of their chromatographic retention times. They were quantified using peak-height responses and response factors calculated relative to 9-NA which was added the extracts just prior to analysis. Limits of quantitation were estimated to be approximately 3 pg/m^3.

Significant problems were encountered in the analysis of the composite sample extracts. These were: (1) inadequate resolution of chromatographic peaks; (2) lack of an appropriate, non-reactive, internal standard; and (3) insufficient cleanup of sample extracts. Despite these difficulties, it was still possible to quantify 1- and 2-NN in most of the sample extracts. The airborne concentrations of 1-NN were consistently higher than the concentrations of 2-NN. Indoor concentrations were higher than outdoor concentrations, and the indoor site with both cigarette smoke and a wood stove as sources had the highest concentrations.

It was concluded that the method requires some further development before it can be reliably used in any large-scale survey of indoor air quality. Specific recommendations for improving the method are presented.

Development of an Analytical Method for Measuring Particulate-Phase PAH.

An extraction and analysis method has been developed for determination of particulate phase PAH in indoor air. The method development used half of each filter sample so that a second determination could be made if necessary. Twenty-one semi-volatile and particulate-phase PAH were determined, with limits of detection ranging from 0.28 ng/m^3 for retene to 0.001 ng/m^3 for dibenzo(a,h)pyrene. The detection limit for benzo(a)pyrene was 0.018 ng/m^3. PAH were determined using HPLC with gradient elution, flow programming and selective fluorescence detection. Two fluorescence programs were devised to determine closely-eluting and co-eluting pairs in two injections per sample. The two fluorescence programs also provided additional evidence of the identities of PAH which did not co-elute through peak height ratios.

Extraction techniques (sonciation and micro-Soxhlet) and extraction solvents (dichloromethane and a benzene-methanol 1:1, v:v mixture) were compared for filter samples of indoor woodsmoke. Sonication and micro-Soxhlet extraction were found to be equivalent in recovery of PAH on average. However, sonication was chosen for extraction of field samples because it was less subject to evaporation losses, and was faster and less labor intensive than micro-Soxhlet extraction. The benzene-methanol mixture gave better recovery of the whole range of PAH, but dichloromethane had somewhat better recovery of the highest molecular weight particulate-phase PAH. On the other hand, dichloromethane extracts had lower concentrations of semi-volatile PAH than benzene-methanol extracts. The benzene-methanol mixture was used to extract the field samples.

Recovery of PAH from NBS SRM 1649 (urban dust-organics) averaged 105 ± 27 % of reported values for sonication of 3 mg aliquots in the benzene-methanol mixture. Results for comparison of extraction methods and solvents were similar to those reported for extraction of indoor woodsmoke. Recovery of fluoranthene-d_{10}, an internal standard for recovery of semi-volatile PAH, varied with extraction method and was not necessarily related to recovery of higher molecular weight particulate-phase PAH such as benzo(a)pyrene or coronene. Recovery was better for sonication than micro-Soxhlet extraction, and better for benzene-methanol than dichloromethane. An average of 81% ± 11% of fluoranthene-d_{10} added to blanks at the time of extraction was recovered; 68% ± 18% was recovered from loaded field samples.

Complex indoor samples, those containing cigarette smoke or wood smoke, frequently showed evidence of interfering compounds which did not reproduce in chromatographic retention time. When interferences co-eluted with benzo(e)pyrene-d_{12}, the internal standard for quantitation, replicate analyses yielded large coefficients of variation. When complex samples were excluded from calculation of the pooled standard deviation of replicates, coefficients of variation averaged 34%.

Based on perturbation analysis of measurement uncertainty, approximately 98% of the measurement uncertainties for the analysis of benzo(a)pyrene in simple samples (i.e. not containing cigarette smoke or woodsmoke) were those associated with the peak height measurements in the sample and standard solution. About half of this measurement uncertainty was due to the uncertainty in the peak height measurement of the internal standard for quantitation, benzo(e)pyrene-d_{12}. This analysis does not take into account uncertainties due to interferences in complex samples.

When the indoor and outdoor replicates are considered together the pooled variance analyses result in relative precisions at the 95% confidence level ranging from 25%-30% for benzo(b)fluoranthene and benzo(k)fluoranthene to 210% for benzo(a)pyrene, to over 400% for dibenzo(a,c)anthracene. These large relative imprecisions appear to be the result of two recurrent analytical difficulties: interfering compounds and high fluorescent background. From these precision computations it is apparent that the analytical method for measuring particulate phase PAH requires some further development work before it is acceptable for deployment in a large indoor field study. In particular the particulate phase PAH analyses indicate the need for a sample clean up procedure before HPLC analysis.

PAC Pilot Field Study

The newly developed indoor PAC sampler was evaluated in a pilot PAC field study conducted in three residences and two commercial buildings. The sampler was deployed to collect 25 m^3 indoor and outdoor air samples over 12-hour daytime and nighttime sampling periods. The sample pumps performed quietly and reliably throughout the pilot field study.

We conducted five residential tests including one test with one of each of the following three indoor combustion sources of PAC; tobacco smoke, wood stoves, and gas ranges as well as one site without any of these sources and one site with all three of these sources. Since it was important to expose the samplers to the suspected indoor sources of PAC as part of the validation program, we controlled the activity of the potential indoor sources in order to be assured of the exposure during the days of the test. The control of the indoor sources was coordinated with the participants of the study and a detailed log of the source usage was part of the field record generated for each sampling period.

The indoor concentrations of gas phase PAH were generally higher indoors than outdoors which is consistent with the known presence of significant indoor sources of these compounds. In the one residence without any indoor combustion sources there were many gas phase PAH with concentrations significantly higher indoors than outdoor, suggesting the presence of indoor sources which are not directly combustion related.

The indoor concentrations of the particulate phase PAH were not as different from the outdoor concentrations as those of the gas phase PAH. This is probably due in part to the large uncertainties in the measurement of the particulate phase PAH at this stage in the method development. The concentrations of five of the twenty-one particulate phase PAH were significantly higher indoors than outdoors; anthracene, pyrene, benzo(e)pyrene, dibenzo(a,e)pyrene, and coronene. We note that these concentration differences were associated with those sites with active indoor combustion sources.

Air exchange measurements were made concurrently with the collection of each pair of indoor and outdoor PAC samples using a tracer gas decay technique to compute the local age of air and local ventilation rate. While indoor/outdoor concentration ratios or differences may be computed to indicate the sign of an indoor net emission rate (i.e. positive or negative) use of the air exchange rate data collected concurrently with the concentration measurements allows computation of both the sign and the magnitude of the indoor net emission rate.

The indoor net emission rate describes the combined net rate of indoor source emissions and indoor removal. The net emission rate is computed as the product of the difference between simultaneous indoor and outdoor concentrations and the building air exchange

rate. The indoor net emission rates are useful for estimating the indoor concentrations in other buildings which may have different air exchange rates or different outdoor concentrations. The PAC net indoor emission rates may also be compared on a site-by-site basis along with information regarding the presence and activity of potential indoor sources to obtain indications of the type and amount of PAC emitted by each of the indoor sources.

An indoor net emission rate of 1 ng/m^3-hr for a particular contaminant corresponds to an indoor concentration 1 ng/m^3 higher than the outdoor concentration for a building with an air exchange rate of 1 air change per hour (ach). For a building with a lower air exchange rate of 0.33 ach and the same net indoor emission rate the indoor concentrations will be 3 ng/m^3 higher than the outdoor concentration. An indoor net emission rate with a negative value describes a building where the indoor removal rate for that contaminant is greater than the indoor source emission rate which results in indoor concentrations being less than outdoor concentrations. Where there are no significant indoor source or removal mechanisms the indoor net emission rate will be zero and the indoor and outdoor concentrations will be the same.

Our comparison of the indoor net emission rates for residences with and without specific indoor combustion sources of PAC suggests that the following PAC are associated with the following sources:

<u>Tobacco smoke</u> - Gas phase: naphthalene and phenanthrene

<u>Wood stove</u> - Gas phase: naphthalene , biphenyl, acenaphthylene, and acenaphthalene
- Particulate phase: pyrene, retene.

<u>Gas range</u> - Gas phase: biphenyl

B. RECOMMENDATIONS

The following are our recommendations for further development of the indoor PAC sampler and analytical methods.

Indoor PAC Sampler.

We recommend that future work be directed towards reducing the weight and size of the pump box. This could be accomplished by using less material in the support structure and reducing the size of the valve chamber and exhaust chamber. Additional acoustical isolation could be used to further reduce the noise level. We also recommend that a different inlet be incorporated onto the filter cartridge to a assure a more uniform deposition of particulate matter onto the filter. A simple open face filter inlet, perhaps with a stainless steel screen protective cover in front of the filter to prevent tampering, should suffice.

Analytical Method for Measuring Gas-Phase PAH.

This study successfully accomplished its objective of developing and validating a sampling and analytical method for gas-phase PAH for use in a large-scale study of indoor exposures to these compounds. There are, however, several unresolved questions which require additional research. Also, there are ways in which the method either can be improved or made more practical for use in a large-scale study. Finally, experience with the method suggests several quality assurance procedures that should be adopted to help ensure the validity of the data for such a study. These issues are addressed by the following recommendations:

1. Prepare clean XAD-4 resin in large batches and measure the blank value for naphthalene or total extractable hydrocarbons (measurable by FID) prior to preparing sorbent samplers to assure that blank values are at an acceptable level. In addition, storage procedures for clean XAD-4 resin need to be evaluated.

2. Identify the source of the compound which interfered with the analysis of phenanthrene and anthracene in many of the samples of indoor air and, if it is a contaminant or an artifact, make the necessary modifications to eliminate its source.

3. Eliminate the back section of the sorbent sampler. The breakthrough losses of the most volatile compounds, naphthalene and biphenyl, from 2.5 g of XAD-4 were low even in indoor environments with high concentrations of these compounds. Therefore, deletion of the back section would have little effect on the quality of the results and would represent a significant savings in the time required for sample analysis. The number of extractions and concentrations would be decreased by one half, and the number of analyses would be decreased by one third. An additional advantage is that the pressure drop across the sampler would be reduced. This should further reduce potential breakthrough losses and possibly allow the use of a smaller sample pump.

4. Incorporate more internal standards and perdeuterated compounds into the method. Addition of an internal standard which elutes near the end of the first analysis for the most volatile compounds would improve the precisions of the relative retention-time indices for these compounds. The precisions of the quantitative results for individual compounds should be improved by the addition of the corresponding or closely related perdeuterated surrogate compounds either to the samplers or to the sample extracts.

5. Use data-base management software to perform quality control functions and organize the data. Timely quality control is particularly important for a large-scale survey consisting of many samples. Utilization of appropriate data-base management software would greatly reduce the effort required to perform statistical quality control, manipulate the data and prepare reports. A high level of automation should also reduce operator errors and make it easier to perform data audits.

6. Require any laboratory intending to participate in a large-scale study to demonstrate its ability to perform the analyses with acceptable precision and limits of detection prior to initiating the study. This preliminary assessment could be accomplished by the analysis of a number of replicate samples collected from a single location, possibly outdoors. Intercomparison studies conducted among several laboratories would provide an additional measure of uncertainty which was not evaluated in this study.

Analytical Method for Measuring Gas-Phase Nitro-PAH.

This study demonstrated that an analytical method based on HPLC analysis of fractionated extracts with post-column reduction and fluorescence detection can potentially be used for

the analysis of nitro-PAH in indoor air. However, significant problems were encountered due to the complex nature of the samples. Consequently, the method requires further development before it can be reliably used in any large-scale survey of indoor air quality. If the difficulties can not be resolved, it will be necessary to explore alternate methods. One possibility would be to use negative chemical-ionization GC-MS, although this method would probably necessitate the compositing of samples to obtain sufficient analyte masses. The method which is finally selected must be specifically validated for use in indoor air because indoor samples are generally more difficult to analyze than outdoor samples. Finally, an interlaboratory comparison, preferably using different techniques, should be conducted to assess the accuracy of the selected method.

Analytical Method for Measuring Particulate-Phase PAH.

The following are our recommendations for improving the analyses of particulate phase PAC for deployment in a large indoor field study.

1. Sample cleanup (on a Sep-Pak or similar silica column) is recommended for complex samples in order to eliminate interfering compounds.

2. For better recovery of high molecular weight particulate PAH, we recommend extraction in dichloromethane rather than a benzene-methanol mixture. Benzene should be added to the filtered extract before solvent evaporation to reduce loss of semi-volatile compounds.

3. We recommend investigation of the use of a different internal standard for quantitation rather than benzo(e)pyrene-d_{12} or recalibration of samples using the external standard method when the sensitivity of benzo(e)pyrene-d_{12} is more than 30% different than expected from analysis of standards. Fluoranthene-d_{10} might be used for this purpose.

4. For HPLC analyses we recommend use of a 10 microliter injection loop or an automatic injector rather than a 5 microliter loop. This would result in a two fold improvement in detection limits.

5. Installation of sub-ambient temperature control in the column compartment of the HPLC is recommended, to enhance temperature stability and allow better reproducibility of retention times.

6. Two fluorescence detectors in series would allow simultaneous HPLC analysis of an extract using both fluorescence programs. This would cut down on analysis and data reduction time and still allow detection of 22 compounds.

7. Before deployment in a large indoor field study the modified method should be validated on replicate pairs of indoor and outdoor samples.

8. For more rapid sample analysis and data reduction we recommend a single fluorescence program and determination of fewer compounds. An abbreviated list of compounds might include only the particulate PAH which were found in detectable quantities in at least two thirds of the samples in this study and which can be detected with one set of fluorescence conditions. Such a list includes fluoranthene, pyrene (possibly), benzo(a)anthracene or chrysene, 5-methyl chrysene (estimate), benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene, coronene and four dibenzopyrenes (a,l; a,e; a,i and a,h). This list includes many of the particulate PAH carcinogens.

In summary the the indoor PAC sampler and analytical methods are ready for deployment in a larger field study for most of the gas phase PAH but not for the particulate phase PAH or gas phase nitro-PAH contaminants measured in this study. The particulate phase PAH and gas phase nitro-PAH analytical methods will require some further development before deployment in a large indoor filed study. Since the concentrations of the particulate phase PAH and gas phase nitro-PAH were similar in indoor air and since we believe that the existing evidence indicates that the particulate phase PAH are more potent carcinogens than the gas phase nitro-PAH, we recommend that further development of the analytical method for the particulate phase PAH be given a higher priority than that for the gas phase nitro-PAH. The recommended particulate phase PAH development work, which is described in Chapter 5, includes examination of sample clean up procedures and use of an external standard.

II. INTRODUCTION

A. PURPOSE

There is an increased concern facing Federal and State health officials regarding the risk of public exposure to toxic air contaminants. Recent investigations of indoor air quality have disclosed large differences between indoor and outdoor contaminant concentrations. These differences arise from the presence of indoor contaminant sources and sinks. To date most risk assessments have assumed that the indoor and outdoor concentrations are the same. This assumption and the uncertainty associated with it, coupled to the fact that people spend an average of 90% of their time indoors has made consideration of both indoor and outdoor contaminant exposures important. For the most part outdoor exposures are estimable from outdoor concentration measurements conducted by both Federal and State agencies. With respect to indoor exposures, however, there have been relatively few measurements of toxic air contaminants.

The California Health and Safety Code Section 39660.5 *et seq.* (Assembly Bill 3052, Tanner) effective January 1, 1987, requires the California Air Resources Board to consider indoor exposures in assessing the risk to public health posed by toxic air contaminants. The immediate interest concerns the indoor exposure to polycyclic aromatic compounds (PAC), many of which are potent carcinogens. Outdoor measurements have recently been made in California with sampling and analytical techniques which require collection of the contaminant from a large volume of air using a high volume sampler (Atkinson et al., 1988, Arey et al., 1989, Zielinska et al., 1989). These methods are inappropriate for use indoors since the high sampling flow rates required would substantially alter the indoor environmental conditions and thus introduce a large uncertainty into the assessment of the actual indoor concentrations. In addition, little information is known regarding the collection of distinctly indoor PAC such as those contained in tobacco smoke, and wood stove, gas range, and unvented space-heater emissions.

Thus, the California Air Resources Board has commissioned research to develop an indoor sampling and analysis method for airborne PAC. This research is the subject of this report.

The objectives of the research reported here were to:

1. Critically review existing literature on sampling and analysis methods for PAC.

2. Prepare an experimental plan for developing and validating a sampler and analytical methods for selected PAC in indoor air.

3. Develop a sampler for vapor- and particulate-phase PAH in indoor air.

4. Develop and validate analytical methods for vapor- and particulate-phase PAH and nitro-PAH.

5. Field test the sampler and analytical methods in residential and commercial buildings.

6. Make recommendations for applications of the sampler and methods in large field studies.

B. BACKGROUND

During Phase I of this project, a critical review of the literature on sampling and analysis methods for PAH and related compounds was conducted. Existing reviews up to the end of 1984 and reprints of papers on PAH in J.M. Daisey's existing files of papers were compiled and critically reviewed. A search of the literature from 1984 to present, covering sampling and analysis methods and indoor and outdoor concentrations of these compounds in air, provided 580 titles. These were evaluated and 100 abstracts were requested and obtained. Reprints of about 40 of these papers and reports were obtained and critically reviewed with a view toward developing a suitable sampling and analysis method for measuring indoor exposures to this class of compounds. In addition, a number of investigators in the U.S. were contacted for additional information on indoor sampling and analysis methods which might be useful in the development stage. A summary of this review is presented here as the basis for the development of the indoor sample and the analytical methods.

Nature and Sources of Polycyclic Aromatic Compounds

The term polycyclic aromatic compounds (PAC) is generally used to refer to PAH, nitrogen-, sulfur-, and oxygen-heterocyclic analogues of PAH and related PAH derivatives. It is used in this report to refer more specifically to the polycyclic aromatic

hydrocarbons, their nitro-derivatives and nitrogen-heterocyclic PAH (aza-arenes) which are the focus of this work and are depicted in Figure II-1. PAC are ubiquitous in the atmosphere. They are generally produced by combustion of carbonaceous fuels and by certain industrial processes. Fuels containing higher amounts of nitrogen will produce the aza-arenes as well as the PAH. While some of the nitro-PAH are produced by combustion, it is now clear that the many of the mononitro PAH in air are formed from their parent PAH by reactions in the atmosphere (Pitts et al., 1985; Ramdahl et al., 1986).

Major sources of PAC in outdoor air include combustion of gasoline and diesel fuels for transportation and combustion of oil, wood and coal for space heating and power production. In some areas of the U.S., agricultural burning and forest fires can be a significant sources of these compounds at certain times. Industrial processes, such as coke production, petroleum refining, and steel production are also sources of PAC in outdoor air. For indoor air in homes and non-industrial buildings, the principal combustion sources of PAC include cigarette smoking, woodburning, unvented space-heaters, and gas stoves. Infiltration of outdoor air is also a source of PAC in indoor air (Lioy et al., 1988).

Many of the PAH, nitro-PAH and aza-arenes have been shown to be carcinogenic in animals (NAS, 1983). Others are biologically active as tumor promoters and/or co-carcinogens, i.e., they are not carcinogenic but they enhance the activity of other carcinogenic compounds when administered with (co-carcinogens) or after (promoters) such compounds (USDHHS, 1982). More significantly, workers exposed to mixtures of these compounds from industrial processes have been found to have a higher risk of developing lung cancers (NAS, 1983). High exposures to PAH and aza-arenes have recently been reported for a population in China with very high lung cancer rates (Mumford et al., 1987).

Depending upon their molecular weights and vapor pressures, PAC are found in the vapor phase, distributed between vapor and particulate phases, or in the particulate phase (Cautreels and Van Cauwenberghe, 1978, Ligocki and Pankow,1989). The distribution between vapor and particle phases will vary with temperature (Yamasaki et al., 1982). Because PAC are generally produced by combustion, the particulate compounds are found in the respirable (D_{50} = 3.5 um) fraction (Miguel and Friedlander, 1978; Van Vaeck and Van Cauwenberghe, 1985).

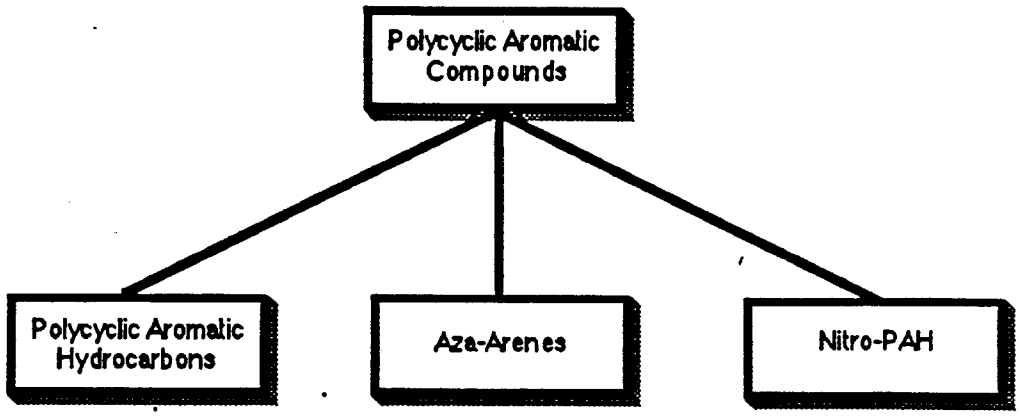


Figure II-1 Depiction of the three different groups of Polycyclic Aromatic Compounds (PAC)

Sampling Methods for PAC

Polycyclic aromatic compounds, and PAH in particular, have been measured in the atmosphere for over 40 years. Most of this sampling and analysis has been done in outdoor air or in industrial environments. Sampling methods for outdoor air have recently been reviewed by Davis et al. (1987). High volume samplers with flow rates in the range of 0.4 to 1.7 m^3/min (15-60 cfm) have been widely used for outdoor air. Samples were generally collected on 8" x 10" glass-fiber filters for 24 hour periods and particulate PAH were measured. In more recent years, a number of investigators have placed a sorbent bed behind the filter to collect the vapor phase PAH as well as any PAH which might volatilize from the particles on the filter during sampling (e.g., Krstulovic et al., 1977; Cautreels and Van Cauwenberghe, 1978; Thrane and Mikalsen, 1981; Yamasaki et al., 1982; You and Bidleman, 1984; Atkinson et al., 1988). Polyurethane foam (PUF), Tenax GC, and XAD resins have been the most commonly used and tested sorbents for vapor phase PAH. However, as Davis et al. (1987) have pointed out, collection efficiencies have not been systematically investigated to quantify relationships between flow rate, linear face velocity, temperature, and retention volumes.

Thrane and Mikalsen (1981) used 5 cm thick PUF plugs placed behind a Hi-Vol filter. They found, on average, that 65 to 70% of the PAH were retained on the first plug and 25

to 30 % on the second plug. Breakthrough to a third plug of PUF was observed mainly for naphthalene and biphenyl. Davis et al. (1987) report comparisons of PUF and XAD-2 resin for collection of volatile PAH using 25 cm thick plugs of PUF or 15 gram beds of XAD-2 sorbent placed behind a Hi-Vol filter. For PUF, less than 5% of the PAH was found on the third plug; similarly, for XAD-2, the third of the three section had less than 9% of the total PAH. Chuang et al. (1986) reported greater than 80% retention of PAC less volatile than quinoline by PUF. However, only 13% of D_8-naphthalene was retained by the PUF; retention for quinoline and isoquinoline were 37% and 50%, respectively. Chuang et al. (1987a), in a field sampling comparison of PUF and XAD-2, reported similar retentions for all PAC except naphthalene, which was more efficiently retained by XAD-2.

In general, PUF sorbent has the lowest resistance to flow but is less efficient at retaining the low molecular weight PAH than are XAD-2 or Tenax GC (Chuang et al., 1987a; Ligocki and Pankow, 1987). Both Tenax GC (poly 2,6-diphenyl-p-phenylene oxide) and XAD-2 (polystyrene-divinylbenzene) retain the lower molecular weight PAH. Tenax GC is typically used to sample for more volatile organic compounds such as toluene and xylenes and is generally thermally desorbed. The XAD-2 resin has been used for sampling the semi-volatile PAH and is solvent extracted for subsequent analysis. XAD-4 differs from XAD-2 in having a higher surface area per gram and smaller diameter pores. Chuang et al. (1987b) have recently reported that XAD-4 has a higher collection efficiency for nicotine, a tracer used for cigarette smoke, than does XAD-2; collection efficiencies for the PAH were similar for the two sorbents.

In industrial environments, high volume samplers have been used for area monitoring and low volume (about 2 liters per minute, Lpm) samplers have been used for personal monitoring (e.g., Bjorseth et al., 1978). In general, particulate phase PAH were collected, although Bjorseth et al. (1978) also collected the vapor phase compounds by using absorption bottles filled with ethanol cooled with dry ice. Leinster and Evans (1986) have recently reviewed certain aspects of sampling for PAH in the industrial workplace. In general, personal samplers do not provide a sufficiently large sample for PAC analysis in non-industrial environments.

Indoor Air Sampling for PAC

There have been many fewer measurements of PAH and related compounds in indoor than outdoor air. Butler and Crossley (1979) collected PAH in three homes of non-smokers in

Birmingham, England on glass fiber filters using Hi-Vol pumps (0.57 m^3/min). Outdoor air samples were also collected at various sites in the area. In this study, indoor and outdoor concentrations of PAH were similar. Alfheim and Ramdahl (1984) examined the impact of various combustion sources on indoor concentrations of PAH in a house in Norway. Woodburning in a stove and in a fireplace and cigarette smoking were investigated. Samples were collected on glass fiber filters backed by XAD-2 resin at a flow rate of 0.133 m^3/min. Knight and Humphreys (1985) sampled PAH in indoor and outdoor air at several woodburning homes. They used an XAD-2 resin bed to collect PAH and sampled for 24 hours at a flow rate of 7 Lpm. Samples were then Soxhlet extracted and analyzed by high pressure liquid chromatography (HPLC) with ultraviolet and fluorescence detectors. Sexton et al. (1986) made paired indoor-outdoor air measurements of particulate PAH at six woodburning homes in Vermont. Samples were collected for 24 hours on quartz filters at a flow rate of 0.424 m^3/min (15 cfm). Concentrations of 9 PAH were measured using gas chromatography-mass spectrometry (GC/MS). The indoor-outdoor ratios of the higher molecular weight compounds were generally greater than one. Daisey et al. (1987) used the same sampler as did Sexton et al. (1986) but collected the samples on a Teflon-coated glass fiber filter to minimize sorption of organic vapors on the filter and filter reactions. Samples were collected in seven homes during woodburning and non-woodburning periods and compared. Concentrations of PAH were 2 to 47 times higher during the woodburning periods.

Wilson et al. (1985) and Chuang et al. (1986) developed and tested a sampler for indoor air which uses a modified EPA medium volume pump with a sampling flow rate of 0.208 m^3/min (7.4 cfm). The sampler was equipped with a quartz filter backed by a PUF sorbent cartridge; however, vapor and particulate phase compounds were not measured separately. The sampler was placed outside the home and the air in the home was pulled through a heavy-walled tube leading from a window port to the sampler head. Samples were collected for eight hours and were Soxhlet extracted and then analyzed using positive chemical ionization GC/MS for PAH and aza-arenes. Nitro-PAH were measured in composited samples using negative chemical ionization GC/MS. No sample clean-up or separation was necessary before the GC/MS analyses although more than one GC/MS injection per sample was probably required because of the order of magnitude differences in the concentrations of some of the PAH. In a later study, Chuang et al. (1987a) modified the sampler to use XAD-2 resin in place of PUF to obtain better collection efficiencies and sample retention. Further work (Chuang et al., 1987b, Wilson and Chuang, 1987) showed that XAD-4 had a better collection efficiency than XAD-2 for nicotine, a tracer for

tobacco smoke. Collection efficiencies for the PAH were similar for the XAD-2 and XAD-4. The acoustic insulation of the sampler was also improved so that the sampler could be placed inside the home (Wilson and Chuang, 1987).

There is, to our knowledge, only one report of measurements of PAH in a number of offices. Turk et al. (1987a,b) collected particle samples with a low flow rate sampler (1.7 Lpm) in 38 office buildings in the Pacific Northwest. Samples with particle loadings greater than 400 μg were extracted and analyzed for seven PAH using HPLC with fluorescence detection. Samples with lower particle loadings were not analyzed because preliminary work had shown that concentrations of PAH were below the limits of of detection. Concentrations of benzo(a)pyrene were generally higher in buildings with smokers than in non-smoking buildings.

For most indoor air sampling for PAH to date, relatively high air flow rates have been used for sampling in homes. These have generally ranged from about 0.57 m^3/min (Butler and Crossley, 1981) to 0.208 m^3/min (Chuang et al., 1985). For a typical 41 m^3 (12'x15'x8') room in a house, sampling at a flow rate of 0.208 m^3/min is equivalent to about 30% of an air change per hour for that room. Concerns about this have recently led investigators in EPA's Integrated Air Cancer Project to begin using a 0.113 m^3/min sampling flow rate for indoor air sampling (J. Lewtas, Personal Communication).

Personal samplers with a flow rate of about 2 Lpm have been used in some indoor air studies. This low sampling flow rate has a negligible effect relative to typical indoor air volumes and air exchange rates. However, while these samplers are suitable for measurements of particulate mass and many trace elements, their application for sampling for organic compounds in indoor environments often results in many samples below the analytical limit of detection. Clearly there is a need for a sampler with a flow rate between the two extremes.

Concentrations of PAC in Outdoor and Indoor Air

Tables II-1 and II-2 present reported ranges of concentrations of the PAH, nitro-PAH and aza-arenes, which are the focus of this report, for outdoor air in California (Atkinson et al.,

Table II-1. Gas Phase Polycyclic Aromatic Compounds Measured in Outdoor and Indoor Air.

Compound [b]	Concentration Ranges (ng/m^3) [a]		
	Outdoor Air [c]	Indoor Air [d]	Indoor Air [e]
Naphthalene	41-6100	750-2200	295-1080
Phenanthrene	BDL-79	49.2-210	30.9-64.5
Anthracene	0.13-21.2	1.5-13.25	0-10.6
1-methylnaphthalene	BDL-500	-	-
2-methylnaphthalene	BDL-1000	-	-
2-methylanthracene	-	-	-
Fluoranthene	0.20-26.2	6.3-26.1*	87.0-211.4
Pyrene	0.09-20.3	3.6-17*	1.0-19.6
Benz(a)anthracene (C)	-	0.00-1.72*	0-5.4
Chrysene (SC)		0.92-4.65*	0
1-Nitronaphthalene	< 0.015-5.7	-	-
2-Nitronaphthalene (C)	0.022-3.1	-	-
2-Nitrofluorene (C)	-	-	-
2,7-Dinitrofluorene (C)	-	-	-
Isoquinoline	-	1.02-620	-
Quinoline (C)	-	0.79-1100	-
Carbazole	-	-	-

a.* = combined vapor and particulate phases, BDL = below detection limit, - = not measured.
b.U.S. Department of Health and Human Services, 1982, animal studies. (C) = carcinogen; (TP/CC) = tumor promoter/co-carcinogen; (SC) = suspected carcinogen.
c. Measured in California with Hi-Vol samplers; Atkinson et al., 1988.
d. Chuang et al., 1986; Wilson and Chuang, 1987a.
e. Knight and Humphreys, 1985.

Table II-2. Particulate Phase Polycyclic Aromatic Compounds Measured in Outdoor and Indoor Air.

Compound [b]	Concentration Ranges (ng/m^3) [a]		
	Outdoor Air [c]	Indoor Air [d]	Indoor Air [e]
Benz(a)anthracene (C)	0.004-18.3	-	-
Fluoranthene (TP/CC)	0.04-29.6	-	0.07-1.18
Pyrene (TP/CC)	0.06-29.8	-	0.02-1.53
Cyclopenta(c,d)pyrene	BDL-11.8	0.18-2.0	-
Chrysene (SC) Triphenylene	0.05-23.6	0.58-7.2	-
Retene	BDL-85.7		
Benzo(b)fluoranthene (C) Benzo(k)fluoranthene (SC) Benzo(j)fluoranthene (SC)	BDL-23.2	0.58-5.1	<0.007-1.22 0.007-0.48 -
Benzo(e)pyrene (TP/CC)	0.005-8.0	0.33-10.0	<0.06-1.36
Benzo(a)pyrene (C)	BDL-12.49	0.28-3.3	<0.009-1.34
Perylene	BDL-2.76	-	-
Indeno(1,2,3-cd)pyrene (C)	BDL-12.31	0.24-3.0	< 0.02-3.54
Benzo(g,h,i)perylene (TP/CC)	0.002-11.35	0.32-3.15	< 0.01-6.20
Dibenz(a,c)anthracene (C) Dibenz(a,h)anthracene	BDL-3.55	-	-
Benzo(c)chrysene	-	-	-
Benzo(b)chrysene	BDL-0.74	-	-
Coronene	BDL-6.63	0.030-2.08	-
2-Nitrofluoranthene	0.006-2.00	0.009-0.16	-
3-Nitrofluoranthene (C)	BDL	-	-
8-Nitrofluoranthene	BDL-0.014	-	-

Table II-2. Continued. Particulate Phase Polycyclic Aromatic Compounds Measured in Outdoor and Indoor Air.

	Concentration Ranges (ng/m^3) [a]		
Compound [b]	Outdoor Air [c]	Indoor Air [d]	Indoor Air [e]
1-Nitropyrene (C)	0.0003-0.045	0.003-0.83	-
2-Nitropyrene	BDL-0.081	-	-
1-Nitronaphthalene	< 0.014-0.077	-	-
Benzacridine Phenanthridine	0.50-1.4 [f]	-	-

a.* = combined vapor and particulate phases.
BDL = below detection limit.
- = not measured.
b.U.S. Department of Health and Human Services, 1982, animal studies.
(C) = carcinogen; (TP/CC) = tumor promoter/co-carcinogen; (SC) = suspected carcinogen.
c. Measured in California with Hi-Vol samplers; Atkinson et al., 1988.
d. Chuang et al., 1986; Wilson and Chuang, 1987.
e. Daisey et al., 1988.
f. Cautreels and Van Cauwenberghe, 1978, samples collected in coal-burning areas of Europe.

1988) and for a few studies of indoor air. Table II-1 presents data for the compounds which are found largely in the gas phase while Table II-2 presents particulate phase compounds. In general, concentrations of the more volatile compounds, (e.g., naphthalene, quinoline), tend to be higher than those of less volatile compounds which are found in the particulate phase, often by orders of magnitude. Certain compounds such as pyrene and fluoranthene are generally found in both phases. The ranges of concentrations of many of the compounds are similar in indoor and outdoor air. However, the indoor measurements that have been made to date suggest that average indoor concentrations of these compounds are considerably higher in homes with sources than in outdoor air.

Sampling for Vapor and Particulate PAC

In order to characterize exposures to PAC, sampling methods which separate and collect vapor and particle phase components and which minimize sampling artifacts are needed. Recently there have been efforts to sample both the gaseous and particulate phases of semi-volatile organic compounds in ambient and indoor air by adding back-up traps containing polyurethane foam (PUF), Tenax-GC or XAD-2 resin to the sampling trains to collect the vapors which pass through the filters (e.g., Cautreels and Van Cauwenberghe, 1978; Yamasaki et al., 1982). Vapor and particulate phases are both separated and collected with this sampling train. However, volatilization losses from the particles on the filter (Appel et al., 1979; Coutant et al., 1988) and condensation of organic vapors on the filter medium (Cadle et al., 1983; Hering et al., in press) can lead to negative and positive artifacts, respectively, for the particles. Positive artifacts (adsorption of organic vapors on quartz filter media) accounted for 15 to 30% of the total carbon collected on particle samples collected in Los Angeles (Hering et al., In Press). Cadle et al. (1983) have reported similar values for quartz and glass fiber filters for samples collected in a rural area of Virginia. Similar experiments have not been done for PAC but it is reasonable to expect adsorption of vapor phase PAC on both glass fiber and quartz filters.

Separating and collecting artifact-free samples of vapor and particulate phases of PAH or other airborne organic compounds is not a trivial sampling problem. Current thinking among many scientists who sample air is that the best way to separate and collect both phases simultaneously would be to use a sampling train with a diffusion denuder followed by a Teflon filter and then by a sorbent. The compounds present in the vapor phase would be removed by the diffusion denuder, and therefore would not adsorb on the particulate phase or on the filter during sampling. The particles would be collected on the filter. The sorbent behind the filter would collect any particulate phase organic compounds which desorbed from the particles during sample collection. However, diffusion denuders have not yet been developed and field tested which would collect PAC or most classes of semi-volatile organic compounds. Thus, the current state-of-the-art for sampling and separating vapor and particle phases is to collect particles on a filter backed by a sorbent bed.

Some recent experiments by Coutant et al. (1988) have shown that at a Hi-Vol filter face velocity of about 33 cm/sec, lower molecular weight PAH, i.e., phenanthrene, anthracene, fluoranthene, pyrene, chrysene and benz(a)anthracene, all displayed some tendency for volatilization losses from the filter. The higher molecular weight PAH, e.g.,

benzo(a)pyrene, were not affected. In principle, the sampler that they developed for these experiments on sampling artifacts could be adapted and used to more accurately measure the vapor and particulate PAH in indoor air. However, this would require 4 rather than 2 analyses for each collected sample since two samplers are used, one with and one without a PAH denuder. The denuder is not analyzed for PAH because there would be very substantial background interferences from the silicone grease which is used to coat the denuder. In summary, although a sampling train consisting of a filter followed by a sorbent bed does not give a 100% accurate separation of vapor and particle phases for all compounds, it will provide a good separation for the very volatile and very non-volatile PAH and a reasonable approximation for PAH of intermediate volatility.

Sampling Artifacts Due to Chemical Reactions

Sampling artifacts associated with filter adsorption and volatilization of PAH have been discussed above. Chemical reactions occurring on filters and sorbents during sample collection are a second class of potential sampling artifacts of concern. Grosjean (1983) investigated the influence of sampling medium on concentrations of 13 particulate PAH measured in the Los Angeles area. Concentrations of PAH were generally higher for samples collected on Teflon filters than for samples collected on quartz or glass fiber. On average, the ratios of concentrations of PAH on glass fiber filters and quartz filters to those collected on Teflon filter ranged from 0.25 for pyrene to 0.80 for coronene. More recently, Ligocki and Pankow (1989) reported that ratios of PAH concentrations on glass fiber filters relative to Teflon filters were one for most of the PAH which they sampled in Portland. However, lower ratios were observed for the lower molecular weight PAH such as phenanthrene. These results suggest that filter reactions may occur on the quartz and glass fiber filters under some conditions and that Teflon or Teflon-coated glass fiber filters are more suitable for sampling PAH.

Over the years there have been many investigations of reactions of particulate PAH with gaseous pollutants such as O_3, NO_2 and SO_2. In general, many of these experiments were conducted under very unrealistic conditions and their relevance to "real world" sampling is questionable. Many experiments involved depositing PAH directly on a filter and then exposing the filter to air or to a gaseous pollutant. Furthermore, many of these experiments utilized extremely high concentrations of the gaseous reactant. In some experiments with NO_2, there were probably traces of nitric acid present. Very high losses were usually

observed under the conditions of these experiments. In some experiments, it was not clear how much of the loss was due to volatilization and how much was due to chemical reactions. It is also now clear that PAH reactions are very dependent upon the nature of the particle with which the PAH are associated (See for example, Behmeyer and Hites, 1985; Daisey and Boone, 1986).

Grosjean et al. (1983) conducted a series of experiments in which benzo(a)pyrene, perylene and 1-nitropyrene were spiked onto pre-collected ambient particulate matter, fly ash, and diesel exhaust on glass fiber and Teflon filters at concentrations within the range of those typically found on filter samples. The samples were then exposed to 100 ppb O_3, 100 ppb SO_2, 100 ppb NO_2 (free of nitric acid) or to filtered ambient air. Samples were exposed for 3 hours at filter face velocities typical of those used for high-volume sampling. Under these conditions, there was no evidence for chemical transformations of PAH irrespective of filter type or particle matrix. An experiment was also done in which benzo(a)pyrene was exposed to higher concentrations of NO_2 (260 ppb) for 8 hours. Nitric acid concentration was less than 0.09 ppb in this experiment. Under this condition, there was no measurable loss of benzo(a)pyrene and no evidence of product formation. When benzo(a)pyrene deposited on diesel exhaust was passively exposed to HNO_3 in a closed chamber for 20 hours, reaction did occur and nitro-PAH derivatives were formed. However, Grosjean does not give the concentration of nitric acid in this experiment. Furthermore, it would be difficult to relate passive exposure to active sampling. These experiments indicate that reactions of filter-collected PAH with the major gaseous pollutants found in the ambient atmosphere, O_3, NO_2, and SO_2, are not significant under typical sampling conditions. It is not clear how important nitric acid reactions might be. Atkinson et al. (1988) have pointed out that reactions of particulate PAH with NO_2, HNO_3, and N_2O_5 are relatively slow under atmospheric conditions. Clearly, more research is needed in this area. Such research must take into account variability in the particle substrate as well as concentrations of gaseous pollutants.

The results of the experiments of Grosjean et al. (1983) have been substantiated for O_3 by Coutant et al. (1988) who compared concentrations of PAH collected on a filter preceded by an ozone denuder to those collected on a filter alone. There was no significant difference in PAH concentrations between the samples. Arey et al. (1988) have investigated the formation of nitro-arenes from parent PAH under high-volume sampling conditions. These investigators spiked particulate-loaded filters with perdeuterated PAH and then exposed the filters to ambient gases for 7 to 10 hours during a period of high NO_2

concentrations. The filters were backed by PUF to collect any PAH or nitro-PAH volatilized from the filter during the experiment. The maximum amount of deuterated nitroarene formed under these conditions was about 0.1% of the spiked perdeuterated perylene. When these investigators took into consideration the amount of PAH volatilized from the filter, they concluded that a maximum of 2-3% of the observed nitropyrene was formed on the filter.

There have been fewer investigations of sampling artifacts for vapor phase PAH collected on sorbents. Zielinska et al. (1986) have reported artifacts resulting from the reaction of fluoranthene with N_2O_5 during sampling on Tenax as well as on filters. Such artifact formation was found to be negligible for PUF sorbent (Sweetman et al., 1986). Zielinska et al. (1986) recommended using perdeuterated PAH spiked onto the Tenax to correct for such artifacts.

For indoor air sampling, XAD-4 appears to be the sorbent of choice since it efficiently collects a wide range of the semi-volatile PAH as well as the alkaloid nicotine, which is being used increasingly as an indicator of environmental tobacco smoke. Research should be done on reactions of XAD-4-adsorbed PAH with NO_2 and possibly O_3. Concentrations of NO_2 are frequently greater in indoor than outdoor air in homes with gas stoves (Dockery et al., 1981) so there is a potential for such reactions be be more significant in such homes. Deuterated compounds spiked on XAD-4 resin prior to sampling can provide information on possible reaction losses in field sampling.

Sample Storage

Chuang et al. (1987a) have investigated the stability of PAH collected on filters, on PUF and on XAD-2 resin. Samples were stored in the dark at room temperature for 0, 10, 20 and 30 days. The PUF and XAD-2 had been spiked with deuterated standards prior to sampling. For the PUF sorbent, there was evidence of losses with storage for both naphthalene and anthracene. The PAH collected on XAD-2, however, were stable for storage of up to 30 days, with the exception of cyclopenta(1,2,3-cd)pyrene. Only trace amounts of this PAH were found on the XAD-2 but the variability in the data at the low levels at which this compound was present prevented any firm conclusions about storage stability. The data for this compound, however, did suggest a trend of decreasing concentration over time.

With the exception of cyclopenta(1,2,3-cd)pyrene, Chuang et.al., (1987a) reported that storage losses of particulate PAH collected on quartz filters were insignificant. Seifert (Institute for Water, Soil and Air Hygiene, Berlin, Personal Communication) has stated that PAH on samples of outdoor particulate matter collected on glass fiber filter were stable for six months when stored in a refrigerator. Since quartz and glass fiber filters are more chemically active than Teflon, storage losses of particulate PAH on Teflon or Teflon-coated glass fiber filters should also be insignificant.

Analysis Methods for PAC

Particulate and vapor phase organic compounds in the atmosphere are a complex mixture of many compound classes with many individual compounds within each class. Analysis for individual compounds within this mixture requires separation of the individual compounds, and in most instances, prior clean-up and/or separation of the compound classes of interest.

Extraction. Samples of vapor phase PAC must first be desorbed thermally or by solvent extraction to recover the collected PAC for analysis. Recoveries of greater than 80% have been reported for PAC less volatile than quinoline, i.e., PAH, nitro-PAH and aza-arenes collected on PUF and Soxhlet extracted with 5% ether in n-hexane (Chuang et al. (1986). Good recoveries (>68%) from PUF have also been reported by Ligocki and Pankow (1985) for PAH of molecular weight greater than that of acenaphthylene using Soxhlet extraction with a mixture of acetone and hexane. Knecht et al. (1987) compared recoveries of 20 PAH from Tenax GC and XAD-2 with cyclohexane, toluene, methanol and ethyl acetate. Virtually complete desorption from Tenax and XAD-2 was reported with toluene. Chuang et al. (1987a) reported recoveries of greater than 70% for several PAH from XAD-2 for Soxhlet extraction with dichloromethane. Chuang et al. (1987b) have recently reported that Soxhlet extraction of PAH from XAD-4 gave generally high recoveries when dichloromethane was used as a solvent but that recovery of nicotine was only 27% with this solvent. Nicotine recoveries of greater than 90% were reported with ethyl acetate but this solvent gave poorer recoveries of acenaphthylene and anthracene than did dichloromethane. These investigators recommended a sequential extraction with dichloromethane followed by ethyl acetate for good recoveries of PAH and nicotine from XAD-4.

For samples of particulate matter, the organic fraction must first be separated from the inorganic components by organic solvent extraction. Extraction is generally accomplished by either Soxhlet or sonication methods. For Soxhlet extraction, the sample is placed in a Soxhlet extraction tube with a siphon on the side; solvent is placed in a round bottomed flask below the Soxhlet tube and a condenser is inserted into the top of the Soxhlet tube. The solvent is heated and vaporized, condensed by the water-cooled condenser and drips down into the Soxhlet tube which holds the sample. When the solvent level in the Soxhlet tube reaches the top of the siphon, the solvent plus the dissolved organics return to the flask. In this way, solvent is cycled repeatedly. Soxhlet extraction has the advantage of many recyclings of redistilled solvent and has been shown to provide good recoveries of PAH by many investigators. Once the Soxhlet apparatus is set up, it can run unattended throughout the day.

Sonication extraction involves placing the sample in solvent and sonicating for a set time, typically 15 to 60 minutes. The solution is then decanted, fresh solvent is added and the process is repeated once or several times more. Extraction time is shorter and extraction temperatures are lower, minimizing volatilization losses of lower molecular weight PAC. Existing data in the literature suggest that the recoveries are generally similar (e.g., Chatot et al., 1971).

The solvent used for extraction appears to be more important than the extraction method. A wide variety of solvents have been investigated with conflicting claims made for efficiency of PAH recovery. Extraction efficiency, however, is very dependent upon the particle matrix. For coal fly ash, benzene and toluene appear to be the solvents which gives the best recovery of PAH (Clement et al., 1984). Chatot et al. (1971) compared extraction efficiencies of ethyl ether, dichloromethane, chloroform, benzene, cyclohexane, acetone and methanol for PAH in outdoor particulate matter. Recoveries of benzo(a)pyrene and total aromatic matter were similar for the first four solvents; the remaining solvents gave lower recoveries. Schuetzle and Perez (1981) have reported that binary solvent mixtures, such as benzene with ethanol, or toluene with isopropanol gave the highest recoveries of benzo(a)pyrene from diesel exhaust samples. Toluene and isopropanol, however, have higher boiling points than most extraction solvents and are consequently, more difficult to evaporate after the extraction and also increase the temperatures to which PAC are exposed in Soxhlet extraction. Grimmer et al. (1982) compared recoveries of PAH from diesel exhaust using cyclohexane, dichloromethane, acetone, methanol or toluene. The samples were boiled in 150 ml of each solvent for 3 hours. Toluene gave the best recoveries from

this sample matrix. D'Agostino et al. (1983) reported an average recovery of 85% for dichloromethane (DCM) extraction and fractionation of 1-nitropyrene in diesel exhaust and airborne particulate matter.

Wise et al. (1982) compared two methods of extraction, clean-up and analysis for PAH using NBS Standard Reference Material 1648, urban particulate matter. Samples analyzed by GC were Soxhlet extracted with a 1:1 (v/v) mixture of benzene and methanol and then subjected to liquid/liquid extraction to remove interfering aliphatic hydrocarbons. Dichloromethane extraction in a Soxhlet, followed by a liquid/liquid extraction, was used for samples to be analyzed by HPLC. Concentrations of PAH determined by the two methods were in good agreement. Miguel and de Andrade (1989) have used acetonitrite for ultrasonic extraction of PAH from Airborne-particles and NBS Standard Reference Material 1648. Recoveries from the SRM were 6 to 20% lower than the NBS values. Currently, dichloromethane (e.g., Nielsen, 1983; Tejada et al., 1986; Daisey et al., 1987; Mumford et al., 1987; Wilson and Chuang, 1987; Coutant et al., 1988) and benzene/methanol, combined or in sequence (Cautreels and Van Cauwenberghe, 1978; Atkinson et al., 1988) are probably the most commonly used solvents for extracting particulate organic compounds. Dichloromethane has a low boiling point and can be easily evaporated during solvent reduction steps. The benzene-methanol mixtures are more polar and will extract more of the polar compounds than does dichloromethane. Depending upon the analytical method and upon the compounds of interest, this can be an advantage (more extracted) or a disadvantage (more interferences in the analysis).

Analysis. Once the organic fraction is extracted from the particulate matter or from the sorbent, individual compounds are generally separated by either capillary gas chromatography or by high pressure liquid chromatography. High pressure liquid chromatography (HPLC), with ultraviolet visible absorbance (UV-VIS) or fluorescence detection, has been very widely used for the analysis of PAH (e.g., Wise et al., 1982; May and Wise, 1984; Greenberg et al., 1985; Daisey et al., 1983; 1987) and for separation of PAH and nitro-PAH fractions. This method has also been used for the analysis of aza-arenes (Yamauchi and Handa, 1987) and nitro-PAH (Nielsen, 1978; Tejada et al.,1986; MacCrehan et al., 1986). Extracts of particulate matter can often be analyzed for PAH without any prior clean-up or with minimal clean-up on commercially available Sep-Paks of silica.

Capillary GC with mass spectrometric (MS) or flame ionization detection (FID) and quantitation is also widely used for separation and analysis of PAC (e.g., Thrane et al., 1985; Jaklin and Krenmayr, 1985; Chuang et al., 1986; Coutant et al., 1987; Atkinson et al., 1988). For electron impact MS or GC/FID analysis of particulate matter, some sample clean-up is required prior to analysis because of the the presence of many other organic compounds in particulate matter which interfere with PAH analysis. Liquid/liquid extraction and column chromatography on silica or HPLC normal phase columns are most commonly used for clean-up (Thrane et al., 1985; Jacklin and Krenmayr, 1985; Atkinson et al., 1988). Selective ion monitoring (SIM) techniques have improved the selectivity and sensitivity of MS analysis by several orders of magnitude. This technique involves monitoring specific ions which are characteristic of the compounds of interest rather than simply the total ion current and is now widely used for GC/MS analysis.

Chuang et al.(1986, 1987a) have recently reported that extracts of particulate and vapor phase PAC can be directly injected and analyzed if positive chemical ionization (PCI) GC/MS with SIM is used. The PCI GC/MS combined with SIM provides selectivity and specificity for the compounds of interest. A second injection of extract is then analyzed for nitro-PAH using negative chemical ionization (NCI) GC/MS. Because of the low concentrations of these compounds in indoor samples, composites samples were used for the latter analysis. These investigators, unfortunately, did not use NBS Standard Reference Material 1648 as a positive control, so it is difficult to compare their results directly to other methods. It should be noted that with selective ion monitoring, only those compounds which are pre-selected for analysis can be analyzed. This is also a feature of HPLC/fluorescence detection, i.e., while selection of excitation and emission wavelengths for each of the compounds in the complex mixture provides a great deal of specificity, compounds which are not pre-selected for analysis may not be detected.

The overall separation efficiency of HPLC columns is not as great as that of capillary GC columns. However, certain isomers which cannot be separated by capillary GC, e.g., chrysene, triphenylene, and the benzofluoranthene isomers, are easily resolved by HPLC. The use of fluorescence detection can provide very good compound specificity and selectivity and can compensate to a large degree for the lower separation efficiency of HPLC. Fluorescence spectroscopy can provide sensitivity comparable or superior to that of GC/MS and can also be used to identify specific compounds. HPLC is often used to pre-fractionate complex environmental mixtures for both GC/MS and HPLC analyses (Schuetzle et.al., 1984; Tomkins et. al., 1984; Stray et.al., 1985; Ruckmick and

Hurtubise, 1985; Atkinson et.al., 1988). The cost of HPLC instrumentation is about one-fourth to one-third that of GC/MS (electron impact) instrumentation. Several investigators have determined that reverse phase HPLC and capillary GC with FID or MS produce essentially equivalent results for the analysis of PAH in extracts of particulate matter (Wise et al., 1982; May and Wise, 1984; Atkinson et al., 1988). Consequently, the choice of method depends on the overall analysis strategy, analysis time, and instrument cost and availability.

Analysis of airborne particulate matter or diesel exhaust for nitro-PAH generally incorporates a preliminary separation and concentration of this class from the extract. Normal phase chromatography, usually HPLC, has been used most commonly for the isolation of the moderately polar nitro-PAH. The nitro-PAH fraction can then be further separated and analyzed for individual compounds by capillary GC coupled with an MS (Schuetzle et al., 1982) or with a nitrogen-selective detector, such as a thermal energy analyzer (Tomkins et al., 1984) or a thermionic nitrogen-phosphorus detector (Paputa-Peck et al., 1983; D'Agostino et al., 1983; Campbell and Lee, 1984). HPLC has also been used. For this approach, the nitro-PAH are reduced to amines for highly sensitive fluorescent detection (Tejada et al., 1986; MacCrehan et al., 1988).

There has been relatively little work done on the development of analytical methods for aza-arenes in airborne particles from non-industrial environments. This is due to the very low concentrations of these compounds compared to PAH in outdoor airborne particulate matter (Dong et al., 1977; Yamauchi and Handa, 1987). Dong et al. (1977) reported outdoor concentrations of particulate quinoline and isoquinoline of 0.022 to 0.18 ng-m^{-3} for New York City. No benzacridine was found for the 100-filter composite samples used in this study. In outdoor air, the chief source of aza-arenes is combustion of nitrogen-containing fuels such as coal. Since very little coal is now burned for space heating in the U.S., outdoor concentrations tend to be about two orders of magnitude lower than those of PAH. In indoor air, environmental tobacco smoke (ETS) is probably the major source of aza-arenes; tobacco contains high concentrations of nitrogen. Dong et al. (1978) reported that vapor-phase quinoline is the aza-arene present in tobacco smoke at the highest concentration. Concentrations of particulate phase aza-arenes in tobacco smoke were reported to be one to two orders of magnitude lower than those of particulate PAH. Quinoline and isoquinoline have been suggested as tracers of ETS (Wilson and Chuang, 1985). However, there may be other sources of these compounds in indoor air (J. Lewtas, personal communication). The volatile aza-arenes, quinoline and iso-quinoline, have been

analyzed directly by positive chemical ionization GC/MS (Chuang et al., 1986; 1987a). Atkinson et al.(1988) investigated electron-impact GC/MS for their analysis. Multi-step clean-up and separation of these polar compounds was required for such analysis. HPLC with fluorescence detection has been used for the higher molecular weight aza-arenes found in particulate matter because these compounds are fairly polar and often difficult to analyze by GC (Dong et al., 1977; Yamauchi and Handa, 1987). Considerable sample clean-up and fractionation is required. Since these compounds are fairly polar, they elute from normal phase chromatographic systems (used for sample fractionation) after the aliphatic hydrocarbons, the PAH and the nitro-PAH and require the use of a polar solvent for recovery. It should also be noted that there are 29 benzacridine isomers and that standards are not commercially available for these compounds (Atkinson et al., 1988).

C. CRITERIA FOR AN INDOOR PAC SAMPLER

The following design criteria are proposed for an indoor sampler for PAC. PAC exist in indoor and outdoor air as both gases and particles. The lower molecular weight PAC exist primarily as gases while the higher molecular weight PAC exist primarily as particles. The dose to the lung from inspired PAC is different for gas and particulate phase PAC thus it is desirable to separately quantify the amount of individual species of PAC present as gases from those present as particles. A PAC sampler should thus be able to separately collect the PAC vapor and particulate phases. The proposed sampler is designed to separately collect gas and particulate phase PAC utilizing a motor driven air pump to draw air first through a filter medium to collect particulate phase PAC and then through a sorbent bed to collect the gas phase PAC.

Sample Flow Rate. The sample flow rate for the proposed sampler is constrained by several criteria. The lower limit for the sample flow rate is determined by the minimum air volume required by the analytical method to quantify the indoor PAC concentrations at levels consistent with the risk assessment associated with each species of PAC and the length of the proposed sampling period. The upper limit for the sample flow rate is limited by considerations for the impact of the air sampler on the indoor concentrations of PAC. The concentrations of any indoor contaminant are determined by the source strength of the contaminant and the total removal rate of the contaminant. For a given source strength the impact of an air sampler on the indoor concentrations may be estimated from a comparison of the total removal rate of PAC from the indoor air with and without the air sampler

running. Thus, for the sampler to have a five percent or less effect upon the indoor concentration, the sample flow rate must not be more then five percent of the total indoor contaminant removal rate which may be estimated as the air exchange rate of the measurement zone. There may be additional indoor removal mechanisms for PAC other than ventilation, however, their presence will make the impact of the air sampler upon the indoor concentrations less than that computed without their consideration.

Sample Flow Control. The sample flow rate should be controlled to maintain a constant sampling rate throughout the measurement period and in indoor environments with elevated concentrations of particulate matter such as may be encountered in indoor environments where tobacco smoking is present. The pressure drop across the sampler filter may be expected to increase as a result of the collected particulate matter restricting the flow passages through the filter. A sample flow rate deviation of less than 10% is considered acceptable and consistent with the expected analytical precision. A constant sample flow rate is desirable so that the time average concentration may be computed.

Filter Type. The filter medium should be able to efficiently collect a particulate sample for the measurement hour period with a minimal increase in pressure drop. Additionally the filter media should be constructed of materials which minimize artifact formation.

Filter Size. The collection area of the filter is constrained by several criteria. Large filter surface areas require more solvent to extract the collected PAC and contribute higher background contaminants which increases the minimum analytical detection limit. From this perspective it is desirable to collect the PAC onto a small amount of filter material. The minimum amount of filter material is determined by the capacity of the filter to collect a sample without exceeding the pressure drop requirements necessary to maintain a constant sample flow rate over a 12 hour period.

Another criterion impacting the selection of the filter size is consideration of an acceptable face velocity. Some of the medium molecular weight semi-volatile PAC exist as a mixture of gas and particulate phases, consequently it is important that the sampling method employed have the ability to accurately quantify the fraction of gas and particle phase PAC without upsetting the relative ratio of gases and particles. This is especially important for the semi-volatile compounds where the collected particle phase may volatilize from the filter during the collection process and be "blown off" the filter. In this respect it is important that the face velocity of the sample stream across the filter is not too high and that the

collection period is not too long. To satisfy this criterion we have decided to design the sampler with a face velocity similar to those of high volume samplers used for sampling outdoor concentrations of PAC. Thus, the selected sample flow rate and face velocity will determine the collection area of the filter.

Filter Holder. The type of filter holder used to hold the filter media in place should ideally be a commercially available size filter and be constructed from inert and non-contaminating materials.

Sorbent Type. The type of sorbent used to collect the gas phase PAC should efficiently collect a broad range of PAC over the measurement period with a minimal pressure drop and minimum break through.

Sorbent Size. The amount of sorbent material is constrained in several ways. Large amounts of sorbent material require more solvent to extract the collected PAC and contribute to higher background contamination which increases the minimum analytical detection limit. From this perspective it is desirable to collect the PAC onto a small amount of sorbent material. The minimum amount of sorbent material is determined by the required contact time for the sampled gas phase PAC to be collected without breakthrough. For a selected sample flow rate, a minimum amount of sorbent material is required to provide the required minimum contact time. In addition consideration must be given to the capacity of the absorbent so that a sample may be efficiently collected throughout the measurement period.

Sorbent Holder. The sorbent holder should be constructed of inert materials which are easy to clean. The inlet and outlet connections should be sized and configured to provide a smooth transition for the sample air stream. The sorbent sampler should also be shielded from light.

Pump Type. The selection of the type of air pump for the sampler is another important consideration since some types of pumps may introduce undesirable contaminants into the sampler exhaust air and subsequently into the indoor air where they may then be collected by the sampler. The air pump must also be able to provide reliable performance over anticipated 12 hour sampling periods.

Acoustics. Since this sampler is intended for deployment in indoor environments including residences an important criterion is the level of noise created by the sampler. Acoustic shielding of the motor and muffling of the air discharged from the sampler will be important considerations in achieving an acceptable noise level. For residences a Noise Criterion (NC) value of 35 is suggested as a appropriate design goal (Harris, 1979).

Power Requirements. The power requirements of the sampler should be as small as possible and not exceed those typically available. A typical residential or commercial electrical outlet is 110 volts AC and provides a maximum of 15 amps of service.

Size. The size of the sampler should be as small as possible to facilitate transport to and from selected field sites. As a practical limit a maximum weight of 40 pounds and outside dimensions of 30 inches (to fit through door ways) is recommended as a design goal.

Cost. The cost of the sampler should be as low as possible so as to be feasible for use in a large scale field study. In this respect a maximum cost of $3500 per unit is recommended as a design goal.

Particle Size Segregation. Particle size segregation is desirable when the health concern is limited to the the smaller inhalable (< 10 μm diameter) or respirable (< 3.5 μm diameter) particles and the contaminant being sampled is present in the larger non-inhalable particles. Segregation of the sampled particles is generally accomplished by providing a size selective inlet (SSI) upstream which separates out the larger non-inhalable particles from the smaller particles which pass through the SSI and are collected upon the filter. Thus the particulate material actually inhaled is collected and the larger particles are excluded.

Gas Phase Denuder. A gas phase denuder is a sampler inlet device which can be used to remove potentially reactive gases such as NO_2 and O_3, and thus minimize reactions of collected PAC on the filter or sorbent bed.

D. CRITERIA FOR AN INDOOR PAC METHOD OF ANALYSIS

The analysis method to be developed and validated must provide for the analysis of two classes of PAC, PAH and nitro-PAH, in both vapor and particulate phases, and allow for further development for measurement of aza-arenes. Thus, the scheme of analysis will

necessarily be more complex than if only a single class, e.g., PAH, were to be analyzed. Within this context, there are a number of criteria which should be met as fully as possible.

Minimal Number of Separations. The analytical method to be developed and validated should involve a minimal number of separations. This will maximize recoveries and the precision of the analysis and will minimize the possibilities of losses and contamination. Extraction of the vapor and particulate phase PAC from the sampling media is a necessary first step in the analysis. The extraction procedure selected should minimize volatilization losses and maximize recoveries of the compounds in all three classes. Sample clean-up and class separations should be minimized; those which are necessary should be selected to minimize losses and contamination.

Specificity. The method developed should minimize interferences from other compounds which might be present in any sample.

Limits of Detection. The method to be developed must be sufficiently sensitive to be used for analysis of small samples, i.e., samples of a size that will have a minimal impact on indoor concentrations. This has been estimated to be a sample of about 25 m^3 collected over a 12 hour period.

Routine Analysis. The method to be developed must be suitable for routine analysis of large numbers of samples which might be collected in a field study. Furthermore, it should be readily transferable to other laboratories. Methods which are highly complex or are quite new and therefore not sufficiently well characterized for a variety of sample matrices, e.g., supercritical fluid extraction, should be avoided. Similarly, methods which require highly specialized instrumentation are not practical.

Instrumentation. The instrumentation to be used should be commercially available, require relatively little maintenance and be so widely used that any problems which might arise can be readily resolved. Instrumentation which has just come into the market and has not been sufficiently tested in a number of laboratories should be avoided. If possible, less costly instrumentation should be used so that it is feasible to have more than one instrument available in a laboratory to handle large sample loads.

Modifications. If possible, the method should be designed so that it could be easily modified in the future, e.g., addition of other compounds within a class or other classes to the analysis scheme.

Internal Standards. Internal standards should be used to correct for losses during extraction, solvent reduction and/or solvent exchange and class separations.

Validation. The method to be developed should be validated by the analysis of "real world" samples. Routine analysis of positive (NBS Standard Reference Materials) and negative controls (blanks) should be incorporated into the method.

Cost. The cost per analysis should be as low as reasonably achievable within the constraints of the desired limits of detection, accuracy and precision.

Documentation. Once the method is developed and standardized, a detailed description of the method should be prepared.

E. LIMITS OF DETECTION AND RISK ASSESSMENT

The analytical scheme to be developed should be sufficiently sensitive that benzo(a)pyrene, the classical indicator compound for PAH, can be detected at a concentration of 0.3 ng/m^3. This is the concentration for which it has been estimated that the risk of cancer for lifetime exposure is less than 1×10^{-6}. Limits of detection for other carcinogenic compound classes, e.g., nitro-PAH, should reflect their potency as carcinogens in animals, relative to benzo(a)pyrene. Unfortunately, there is no consistent body of animal data (i.e., same species, route, dose rate, etc.) for all of the compounds of interest. However, Table II-3 presents a comparison of the carcinogenic potencies of some of the nitro-PAH in mice and rats, relative to that of benzo(a)pyrene. It should be noted that the responses of different species to a given compound can be quite different. Furthermore, the route of exposure can also affect the potency observed. For example, for benzo(a)pyrene in mice, exposures of animals by skin painting induces tumors in 94% of the animals at a dose of only 0.62 mg/kg of body weight. For dietary exposure, doses which are two orders of magnitude greater are required to induce tumors. Nonetheless, this comparison can provide some estimate of the potencies of the nitro-PAH relative to benzo(a)pyrene.

Table II-3. Comparison of the Carcinogenic Potencies of Benzo(a)Pyrene and Some Nitro-PAH in Mice and Rats.

Compound	Animal	Route [a]	Total Lifetime Dose (mg/kg body weight)	Tumor Incidence (% of animals)
Benzo(a)pyrene	mouse [b]	skin	0.15 0.31 0.62	40.0 78.1 93.8
Benzo(a)pyrene	mouse [c]	diet	33	93
1-Nitropyrene	mouse [d]	i p	175 529 1590	21-36 39-43 67-88
1,6-Dinitropyrene	mouse [d]	s.c.	67	50
Benzo(a)pyrene	rat [e]	lung	0.09 0.29 0.86	8.6 31.4 77.1
1-Nitropyrene	rat [d]	s.c.	41.2 82.3	7-10 28-32
1,3-Dinitropyrene	rat [d]	s.c.	13.3	100
1,6-Dinitropyrene	rat [d]	s.c. lung	13.3 0.5	100 82
1,8-Dinitropyrene	rat [d]	s.c.	1.33 0.13	100 90
3-Nitrofluoranthene	rat [f]	s.c.	90	40

a. Routes of exposure: skin = skin painting; diet = diet; i p = intraperitoneal injection; lung=lung implantation; s.c.=sub-cutaneous injection.
b. Grimmer et al., 1983.
c. Gold et al., 1984.
d. Tokiwa and Ohnishi, 1986.
e. Grimmer et al., 1987.
f. Ohgaki et al., 1982.

The data for 1-nitropyrene in mice suggest that it is a less potent carcinogen than is benzo(a)pyrene in the same spec A lifetime dose of 1590 mg/kg is required for a tumor incidence of 67-88% while the benzo(a)pyrene dose which induces tumors in mice at this level is at least two orders of magnitude lower. 1,6-Dinitropyrene appears to be about as potent (diet) or about two orders of magnitude less potent (skin) than is benzo(a)pyrene.

The data for rats shows a similar pattern. A comparison of the rat data for lung implantation of benzo(a)pyrene and 1,6-dinitropyrene suggests that the potencies of these compounds is similar. Exposure by sub-cutaneous injection appears to require a higher dose of 1,6-dinitropyrene to induce tumors in the same percentage of animals than does exposure by lung implantation. However, for this compound, only a single value of 100% is reported rather than a dose-response curve. The potency of 1-nitropyrene, relative to benzo(a)pyrene in rats, is also consistent with that observed for mice. Benzo(a)pyrene is about two orders of magnitude more potent than is 1-nitropyrene. The rat data for the other nitro-PAH suggest that they are either less potent or as potent as benzo(a)pyrene. Tokiwa and Ohnishi (1986) have concluded that the tumorigenic potencies of the dinitropyrenes are very low compared to benzo(a)pyrene.

Grimmer et al. (1987) provide data for a complex mixture which also indicate that the potencies of the nitro-PAH are either similar or lower that that of the PAH. These investigators compared the carcinogenic impact of the nitro-PAH-containing fraction and the PAH-containing fraction of diesel engine exhaust condensate. Animals were exposed to each of the two fractions in proportion to their mass percentages within the mixture, which were similar, 0.7% (nitro-PAH) and 0.8% (PAH fraction) of the extractable organic mass. Tumors were induced in 17% of the animals exposed to the PAH fraction (4 rings or more) and in 3% of the animals exposed to the nitro-PAH-containing fraction. No tumors were induced by the other PAH-containing fractions (< 4 rings).

The animal data for the individual nitro-PAH compounds and for the complex mixture both indicate that the nitro-PAH are equally or less potent than benzo(a)pyrene. Consequently, an acceptable lower limit of detection for this class of compounds should be similar to that of benzo(a)pyrene and the other PAH.

Table II-4 summarizes available data on the lower limits of detection (LLD's) for PAH for various methods of analysis and detection. Appendix A presents more detailed data for

Table II-4. Lower Limits of Detection (LLD) for PAH Using Selected Methods of Analyses and Detection.

Method Sample	Mass Injected (picograms)	Injection Volume (microliters)	Required Sample [a] (nanograms)	LLD - 25 m^3 (ng/m^3)
HPLC/ Fluorescence [b]	0.3-130	20	0.0075-3.25	0.0003-0.13
Capillary GC/FID [c]	50-100	1	25-50	1-2
Capillary GC/MS/SIM [d]	30-300	1	15-150	0.6-6

a. Total Sample Mass Required = $\frac{\text{Mass Injected}}{\text{Injection Volume}}$ x Total Extract Volume (500 µl)
b. Ogan et. al., 1979; Das and Thomas, 1978.
c. Grimmer et al., 1982.
d. Lawrence and Das, 1986

specific compounds. The total mass needed in the sample is calculated based on typical injection volumes and the total solution volume, i.e. 500 µl. The latter is a reasonable volume with which to work, in our experience. With volumes as low as 100 µl, solvent can be easily lost and there can be losses of the more volatile compounds present in the solution, as well. The LLD's (reported as $ng\text{-}m^{-3}$) for HPLC/fluorescence analysis are an order of magnitude or more lower than those for capillary GC/FID or GC/MS/SIM. This is due largely to the fact that a larger volume can be injected onto an HPLC column than onto a capillary GC column. It should also be noted that the reported LLD's (picograms of a standard injected) do not take into account blanks and interferences and thus, are probably somewhat of an underestimate.

Table II-5 presents similar data for the nitro-PAH; Appendix B presents data for specific compounds. HPLC/fluorescence is again the most sensitive method for analysis and

Table II-5. Lower Limits of Detection (LLD) for Nitro-PAH Using Selected Methods of Analyses and Detection.

Method Sample	Mass Injected (picograms)	Injection Volume (microliters)	Required Sample [a] (nanograms)	LLD - 25 m^3 (ng/m^3)
HPLC/ Fluorescence [b]	4-80	20	0.1-2.0	0.004-0.08
Capillary GC/Therm. [c]	36-110	1	18-55	0.7-2.2
Capillary GC/MS/SIM [d]	~50	1	~25	1

a. Total Sample Mass Required = $\frac{\text{Mass Injected}}{\text{Injection Volume}}$ x Total Extract Volume (500 µl)
b. Tejada et al., 1986; Nitro-PAH reduced to fluorescent amines.
c. Thermionic detector; White et.al., 1984; Kopczynski, 1987; D'Agostino et al., 1983.
d. Hodgson, A.T., Lawrence Berkeley Laboratory, Personal communication, 1988.

detection. Nitro-PAH analysis by this method, however, requires reduction of the nitro functional group to form the fluorescent amine. Although this can be done on-column, it is a more difficult analysis than is GC/MS/SIM or GC/thermionic detector or analysis for the naturally fluorescent PAH.

Lower limits of detection for the aza-arenes were not found in the literature. For GC/MS/SIM, the LLD's for the vapor phase aza-arenes should be similar to those of the PAH. Quinoline and isoquinoline are not fluorescent. However, they are generally present at very high concentrations and should be readily detectable by HPLC with an ultraviolet/visible absorbance detector as well as by GC/MS/SIM. The higher molecular weight aza-arenes which are present in particulate matter are fluorescent and their detection limits should be similar to those of the PAH.

For a 25 m^3 indoor air sample, the most sensitive method of analysis and the only one which meets the required 0.3 $ng\text{-}m^{-3}$ LLD for particulate compounds is HPLC/fluorescence. The other methods would require larger air volumes to be sampled to quantitate benzo(a)pyrene at this concentration.

III. AN INDOOR PAC SAMPLER

A. INTRODUCTION

The goal of this portion of the study was the development of an indoor air sampler for collecting indoor samples of polycyclic aromatic compounds (PAC) for use in developing a data base of indoor PAC concentrations for public risk assessments. Presently there are no validated samplers that are suitable for sampling PAC in indoor environments. Outdoors sampling PAC are collected using high volume samplers which pull ~ 224 liters per minute (Lpm) of air through a glass fiber filter backed by a cartridge containing a sorbent. These samplers are not suitable for sampling indoors for a number of reasons. First, such a high sampling rate would significantly reduce the indoor PAC concentration and yield data that underestimates the true indoor concentration. The high volume samplers used outdoors are also large and noisy and therefore not suitable for deployment in residential environments.

To quantify air contaminant exposures and population risks, one ideally would put personal monitors on a large number of people, analyze the results and compute the population exposure distribution for each contaminant. However if personal monitors for a contaminant do not exist, we can estimate these exposures by obtaining distributions of indoor and outdoor concentrations and combining these with the distributions of time people spend in those different environments (i.e. time activity data). Because there are no personal PAC monitors this type of macromodeling approach (Traynor, 1987) to exposure computation is needed.

To satisfy the detection limit requirements for a public health risk assessment, a sample volume of ~ 25 m^3 is needed. The chemical analytical approach selected for this study involves extraction and concentration of the extract from the filter or XAD-4 resin and injection of this extract into a GC-MS for gas phase PAC or HPLC-UV for particulate phase PAC. With a 25 m^3 sample size, this approach yields a detection limit of approximately 0.01 - 1 ng/m^3 for most of the gas and particulate species of PAC. While a 25 m^3 volume could be collected in as little as 2-3 hours without significantly decreasing the indoor concentration in a residence, the number of samples that would needed to be analyzed to provide a meaningful average indoor concentration would not be economically feasible for a large indoor air field study.

PAC concentrations are expected to vary significantly with changes in the indoor source emission rate and ventilation rates. A meaningful average indoor concentration requires sampling over a period long enough to average these variances. This means that a minimum sampling time of 12-24 hours is desired to average over the daily activities in residential buildings. For commercial buildings an 8 hour sample period should be sufficient. Because analytical costs are estimated to be significant, the additional cost of repeating short time period samples at the same site to attain a sufficient sampling time would be substantial. For this reason we decided to develop an air sampler which would collect approximately 25 m^3 over an 8-24 hour period. In particular, we planned to use a 12-hour sampling period in our pilot study field verification program in order to examine any diurnal differences in residences. Longer sampling periods may be possible but were not investigated.

B. DESIGN CONSIDERATIONS AND APPROACH.

The following are the design considerations and approach we took during our design of an indoor PAC sampler. PAC exist in indoor and outdoor air as both gases and particles. The lower molecular weight PAC exist primarily as gases while the higher molecular weight PAC exist almost wholly in the particulate phase. Since the deposition of inspired PAC in the lung is different for gas and particulate phase PAC it is desirable to separately quantify the amount of individual species of PAC present as gases from those present in the particle phase. A PAC sampler should thus be able to separately collect the PAC vapor and particulate phases. We designed a sampler that separately collects gas and particulate phase PAC utilizing a motor driven air pump to draw air first through a filter medium to collect particulate phase PAC and then through a sorbent bed to collect the gas phase PAC. We designed the sampler to collect a 25 m^3 sample of air at a constant sampling rate over a 12 hour sampling period.

Sample Flow Rate. There are several constraints on the sample flow rate for such a sampler. The lower limit for the sample flow rate is determined by the minimum air volume required by the analytical method to quantify the indoor PAC concentrations at levels consistent with the risk assessment associated with each species of PAC and the length of the proposed sampling period. The upper limit for the sample flow rate is limited by considerations for the impact of the air sampler on the indoor concentrations of PAC.

Any collection sampling device that is introduced into an indoor environment will reduce the concentrations of the sampled species. For instance a high volume sampling device which collects particulate matter on a filter medium will remove particulate matter from the air being sampled which in turn reduces the concentration of particulate matter in the sampling area. The degree that the sampling device reduces the indoor concentrations of contaminants in question depends on the sampling rate, sampling space volume, source and sink strengths, collection efficiency and ventilation rates.

We calculated the effect that this sampler would have on certain indoor environments using an indoor air quality simulation program, STEP (IEE, 1987). This numerical simulation program uses a mass balance approach to compute the indoor concentrations as a function of time in one or more zones of a building. Among other things the model uses a source menu to program specific activity pattern for indoor sources of contaminants and a ventilation effectiveness factor for describing the distribution of ventilation air within buildings, and allows for transient analyses of indoor contaminant concentrations. For this analysis we used a one minute time resolution and computed the indoor time-averaged concentrations with and without the air sampler operating. The impact of the air sampler was computed as the difference in the time averaged concentrations computed over the sampling period with and without the air sampler operating.

We considered various space volumes, 25 m^3, 100 m^3, and 1000 m^3, with a constant indoor source strength, no indoor removal mechanisms except by the sampler and by ventilation, a ventilation rate of 0.3 air changes per hour and ventilation effectiveness factor of 1.0, and an initial concentration equal to the steady state indoor concentration without the air sampler operating. Higher ventilation rates or other removal mechanisms such as air filtration or surface deposition will cause the actual impacts on the indoor concentrations to be lower than those computed without their consideration. The 25 m^3 space is representative of sampling in a closed bedroom, the 100 m^3 space is representative of sampling in the living room/dining room area of a residence, and the 1000 m^3 space is representative of sampling in a small commercial office space. For larger spaces the computed impacts would be proportionately smaller than the 1000 m^3 projections.

We compared the sampling strategy of 34 Lpm for 12 hours developed in this study, with another proposed PAC sampling strategy (Wilson et. al., 1989) of 224 liters per minute over 2 hours as they impact the air contaminant concentrations for various size indoor environments. The results of these computer simulations are summarized in Table III-1.

Table III-1 Impact of PAC sampler upon the indoor concentrations in various volume environments.

Sampler [a]	Sample Time (minutes)	Sampler Impact [b] %
Indoor air volume=25 m^3		
CARB	721	16.8
EPA	121	33.4
Indoor air volume=100 m^3		
CARB	721	4.8
EPA	121	10.4
Indoor air volume=1000 m^3		
CARB	721	0.5
EPA	121	1.1

a.) The CARB indoor sampler air flow rate was set for 34 Lpm, and the EPA indoor air sampler flow rate was set for 224 Lpm.
b) The impact of the sampler upon indoor concentration was completed as the percentage difference of the time-weighted average indoor concentrations computed with and without the PAC sampler operating.
Indoor time weighted concentrations were computed using STEP (IEE, 1987), a numerical indoor air quality simulation program based upon a mass balance model (Offermann, 1984, IEE,1987). The following assumptions were applied: a constant source strength, 0.3 air changes per hour outside air ventilation and ventilation effectiveness factor of 1.0 . No removal mechanism other than ventilation and that of the sampler.

The reduction of the indoor concentration caused by the 34 Lpm designed air sampler ranged from 16.8% for a small 25 m^3 space to less than 1% for a large 1000 m^3 space. The reduction of the indoor concentration in a typical residential setting with an open indoor air space of approximately 100 m^3 is 4.8%. The reduction caused by the 224 Lpm sampler ranged from 33.4% in the 25 m^3 space to 1.1% in the 1000 m^3 space. The reduction in a typical indoor residential volume of 100 m^3 is computed to be 16.8% which is a factor of 3.5 times higher than the reduction caused by the 34 Lpm sampling strategy. For residential field studies a living room/dining room sampling location is preferable for obtaining a house average concentration with a single indoor sampler. The net air space of a living

room/dining room location including connecting kitchens, hallways and stairways in a typical home is approximately 100 m^3 and hence it is these computations which are representative of the impact of a single sampler in a residential site.

We chose a sample flow rate of 34 Lpm in order to collect a 25 m^3 sample in a 12 hour sampling period. A 12 hour sampling period was selected so as to allow day/night comparisons to be made. A sample size of 25 m^3 was selected to satisfy the detection limit requirements for public health risk assessment. The selected sample flow rate of 34 Lpm will reduce the indoor concentrations in residential and commercial sites by less than 5%.

Sample Flow Control. The sample flow rate should be controlled to maintain a constant sampling rate throughout the measurement period and in environments with elevated concentrations of particulate matter such as may be encountered in indoor environments where tobacco smoking is present. The initial flowrate of air through the sample cassette is expected to decrease as the particulate matter collects on the particulate filter and the filter resistance to air flow increases. A sample flow rate deviation of less than 10% over the sampling period is considered acceptable and consistent with the expected analytical measurement uncertainty. A constant sample flow rate is also desirable so that the time average concentration may be computed.

During the development of the sampler we considered available compensating flow control strategies that would insure a constant sampling rate, should the flowrate reduction associated with filter loading be significant. The two devices considered were a mechanical differential pressure controller and an electronic mass flow controller. Both of these devices, require a substantial pressure drop across them, 260 mm Hg, to operate properly. This pressure drop significantly increases the size of the pump needed for sampling and therefore increases the noise, weight, and size of the sampling system. We decided to evaluate the actual decrease in the sampler air flow rate for a prototype system with a non-compensating flow controller before further pursuing compensating type flow controllers. Subsequent laboratory and field tests indicated that the filter pressure drop increases were small compared to the total system pressure drop and that the sampler flow rate should decrease by less than 5% over a typical indoor 12-hour sampling period without the use of pressure compensating controls.

Non-compensating flow control in the prototype sampler was achieved by using a union bonnet valve with a ball tip stem placed between the vacuum pump and a prototype sampler

cartridge. The pressure drops across each element in the PAC prototype sampling system is depicted in Table III-2. The total pressure drop across the pump is 516 mm Hg at a 34 Lpm sample flow rate. The pressure drop across the valve is sufficient to cause the the flow across the valve to be critical (pressure drop ratio less than 0.53). Thus, the sample flow rate is directly proportional to changes in the upstream pressure and independent of changes in the down stream pressure at the vacuum pump. For a 50% increase in the filter differential pressure drop, the upstream pressure and hence the air flow rate drops just 3.1%.

Sampler Flow Rate Measurement The sample air flow rate should be able to be monitored without disturbing the sampling process. The sample air flow rate during the laboratory and pilot field study was measured with a rotameter which was calibrated with a bubble meter.

Filter Type. The filter medium must be able to efficiently collect particulate matter over a sampling period with a minimal increase in filter differential pressure drop. Additionally, the filter medium should be constructed of materials which minimize artifact formation. The filter medium recommended for collecting the particulate phase PAH is a Teflon impregnated glass fiber medium (TIGF). This medium is capable of collecting a large amount of particulate matter with a minimal pressure drop as compared to membrane filters, and will minimize artifact formation. A minimum particle collection efficiency of 95% is desirable. The particle collection efficiency of fibrous filters increases with increased filter loading and with increased face velocity. The minimum particle collection efficiency has been measured by Liu et. al. (1981) to range from 52% to 98.9% for selected TIGF filter media. We selected a 47 mm Pallflex TX40HI20 TIGF filter which has a collection efficiency of 95.8% and 99.99% for particles in the 0.035 - 1.0 μm diameter particle size range and at face velocities of 30-45 cm/sec (Lui et. al., 1981).

Filter Size. The collection area of the filter is constrained in several ways. Large filter surface areas require more solvent to extract the collected PAC and contribute higher background contaminants which increases the minimum analytical detection limit. From this perspective it is desirable to collect the PAC onto a small amount of filter material. The minimum amount of filter material is determined by the capacity of the filter to collect a sample without exceeding the pressure drop requirements necessary to maintain a constant sample flow rate over a 12 hour period.

Table III-2. Absolute and differential pressures for each component of the indoor PAC sampler.

System component	Absolute pressure [a] Upstream	Downstream	Differential pressure drop[b]	Differential pressure ratio [c]
	mm Hg	mm Hg	mm Hg	
47 mm TIGF filter and cassette	760	730	30	0.96
5 gms XAD-4 sorbent.	730	590	140	0.80
9.5 mm low density polyethylene sample line.	590	550	40	0.93
union bonnett valve.	550	270	280	0.49
muffler	760	786	-26	1.03

a) Absolute pressures measured at a constant sampler flowrate of 34.2 liters per minute and standard temperature and pressure.
b) Pressure drop across filter totals 516 mm Hg.
c) Critical flow occurs when the differential pressure ratio is less than 0.53.

Another factor in the selection of the filter size is consideration of an acceptable face velocity. Some of the medium molecular weight semi-volatile PAC exist as a mixture of gas and particulate phases. Consequently, it is important that the sampling method employed have the ability to quantify the fraction of gas and particle phase PAC without shifting the relative ratio of gases and particles. This is especially important for the semi-volatile particulate compounds where the collected particle may volatilize from the filter during the collection process and be "blown off" the filter. In this respect it is important that the face velocity of the sample stream across the filter be not too high and that the collection period be not too long.

We designed a sampler to operate at a flow rate of 30-40 Lpm and maximum face velocity is 30-40 cm/s. This velocity is comparable with the face velocities used in Hi-Vol sampling of outdoor air. Table III-3 presentss the face velocities used with Hi-Vol samplers during outside air sampling for PAH. At this time we do not know what an acceptable face velocity or collection period is, however, we believe that by selecting a face velocity and collection period similiar to that used with hi-volume samplers that the data collected will be comparable to those generated from hi-volume samplers. The filter size closest to a nominal diameter commercially available filter and with an acceptable face velocity is a 47 mm diameter filter. The face velocity associated with a 30-40 Lpm sample flow rate through this size filter is 34-45 cm/s.

Filter Holder. The type of filter holder used to hold the filter media in place should ideally be a commercially available size filter and be constructed from inert and non-contaminating materials. The filter holder we selected for this study was a standard Nuclepore Swin-lok 47mm diameter in-line filter holder with the inlets of the cap and base machined to a 1/4 inch inside diameter bore with 45° bevels for better air flow and whistle free running. The holder is constructed of clear polycarbonate plastic. Between the cap and the filter membrane is a polycarbonate support grid held in place with a single ethylene-propylene rubber O-ring as shown in Fig. III-2, PAC sample cartridge section. We decided not to run the sampler open face but with the inlet cap so that the filter would be protected from disturbances.

Sorbent Type. The type of sorbent used to collect the gas phase PAC must efficiently collect a broad range of PAC over the measurement period with a minimal pressure drop, minimum break through, and good extraction efficiency. The sorbent used in this study was residue free XAD-4. This sorbent is a polystyrene resin which has the ability to efficiently adsorb a broad range of PAC, over a 12 hour sample period with an acceptable pressure drop and, in addition, will collect nicotine, a tracer of environmental tobacco smoke. Although this was not measured in this study, it may be desirable to do so at a later date.

Table III-3. Characteristics of various samplers used to collect particulate phase PAC.

Type of Collector [a]	Face Velocity (cm/s)	Filter Area/Air Volume (cm^2/m^3)	Investigator (year)
TIGF	46.50	0.50	Atkinson (1988)
TIGF	29.06	0.80	Atkinson (1988)
TIGF	34.88	0.66	Arey (1987)
GF	40.26	0.29	Chuang (1987a)
GF	67.74	0.17	Jacklin (1984)
GF	33.14	0.35	Ligocki (1985)
GF	37.14	0.62	Thrane (1987)
GF	20.53	1.13	Keller (1983)
GF	34.21	0.34	Pyysalo (1987)
GF	32.84	0.35	Yamasaki (1982)

a.) GF = glass fiber filter; TIGF = teflon impregnated glass fiber filter

Sorbent Amount. The amount of sorbent material is constrained in several ways. Large amounts of sorbent material require more solvent to extract the collected PAC and contribute to higher background contamination which increases the minimum analytical detection limit. From this perspective it is desirable to collect the PAC on a small amount of sorbent material. The minimum amount of sorbent material is determined by the required contact time for the sampled gas phase PAC to be collected without significant breakthrough. For a selected sample flow rate, a minimum amount of sorbent material is required to provide the required minimum contact time. In addition consideration must be given to the capacity of the absorbent so that a sample may be efficiently collected throughout the measurement period without contaminant breakthrough.

We initially estimated the amount of XAD-4 sorbent material necessary to efficiently adsorb the gas phase PAH over a 12 hour sampling period to be 5 grams. This estimate was arrived at from consideration of the contact time and contaminant holding capacity of air samplers using XAD-2 during outside sampling for PAH. The contact times for 5 grams of XAD-4 sorbent exposed to a 30-40 Lpm sample flow rate is 0.02-0.04 seconds which is

consistent with the 0.02-0.04 seconds used for air samplers for gas phase PAC in outdoor air. Table III-4 depicts the contact times used with air samplers during outside air sampling for PAC. The contaminant holding capacities were estimated from the ratio of the sorbent volume (or mass) to the volume of air sampled during outside sampling for PAC.

Table III-4 depicts the sorbent volume to air volume ratio for various outdoor samplers. For the proposed 25 m^3 sample size of the indoor sampler, the 5 grams of sorbent material represents 0.57cm^3 of sorbent in the front section per m^3 of air sampled. This compares to values of 0.50 cm^3/m^3 used by Chuang and 0.26 cm^3/m^3 used by Pyysalo for high volume ambient samplers using XAD-2. We measured the actual bulk density of dry XAD-4 to be 0.35 gms/cm^3. Thus from the literature we have concluded that a 5 gram section of XAD-4 should be sufficient for a 25 m^3 indoor air sample. During subsequent development with a prototype sampler it was decided from breakthrough tests using deuterated PAC spiked on to the inlet side of the sorbent material that only 2.5 grams section of XAD-4 would be necessary for a 25 m^3 sample. For the method development portion of this study we decided upon a 2.5 gram front section followed buy a 2.5 gram back section for our indoor PAC sampler. Contaminant collection efficiency and breakthrough were examined in the pilot field study.

Sorbent Cartridge. The sorbent holder must be constructed of inert materials which are easy to clean. The inlet and outlet connections should be sized and configured to provide a smooth transition for the sample air stream. The geometry of the sorbent holder should be such that there is a minimum length to diameter ratio of 1. With ratios smaller than this there is a risk of the sample flow will not be uniformly distributed across the sorbent. With ratios much higher, air flow distribution is assured at the expense of higher pressure drops and air velocity.

We designed the sorbent cartridge to hold 5 grams of XAD-4 in two 2.5 gram sections within a stainless steel, Teflon and glass cartridge assembly as shown in Figure III-1. Each section of sorbent is separated from each other by 0.5 centimeters of glass wool and a stainless steel glass screen. There is an additional 0.5 cm of glass wool at each end of the 2.5 cm Pyrex glass tube. Stainless steel 2.5 cm male connectors with Teflon ferrules fit over the tube ends. A Teflon washer is inserted to prevent the glass from cracking against the stainless steel seat of the compression fitting during insertion. A 1.0 cm -1.9 cm pipe stainless steel union was used to join the sorbent cartridge to the filter holder. A 1.9 cm - 1.0 cm compression fitting connects the sorbent to the pump sampling line.

Table III-4. Characteristics of Various Samplers Used to Collect Gas Phase PAC.

Type of Collector	Contact Time (second)	Sorbent Volume/Air Volume Ratio [a] (cm^3/m^3)	Investigator (year)
XAD-2	0.04	0.50	Chuang (1987a)
XAD-2	0.02	0.26	Pyysalo (1987)
PUF	0.03	1.75	Atkinson (1988)
PUF	0.11	1.25	Chuang (1987)
PUF	0.02	0.24	Jacklin (1984)
PUF	0.06	0.72	Ligocki (1985)
PUF	0.02	0.52	Arey (1987)
PUF	0.09	1.98	Thrane (1987)
PUF	0.04	1.01	Keller (1983)
PUF	0.03	0.34	Yamasaki (1982)
Tenax-GC	0.08	1.75	Atkinson (1988)
Tenax-GC	0.05	1.09	Atkinson (1988)
Tenax-GC	0.07	1.52	Arey (1987)
Tenax-GC	8.55	98.96	Ligocki (1985)
Tenax-GC	0.57	6.60	Ligocki (1985)

a.) Sorbent Volume/Air Volume ratio calculated as the cm^3 of sorbent divided by the m^3 of air sampled.

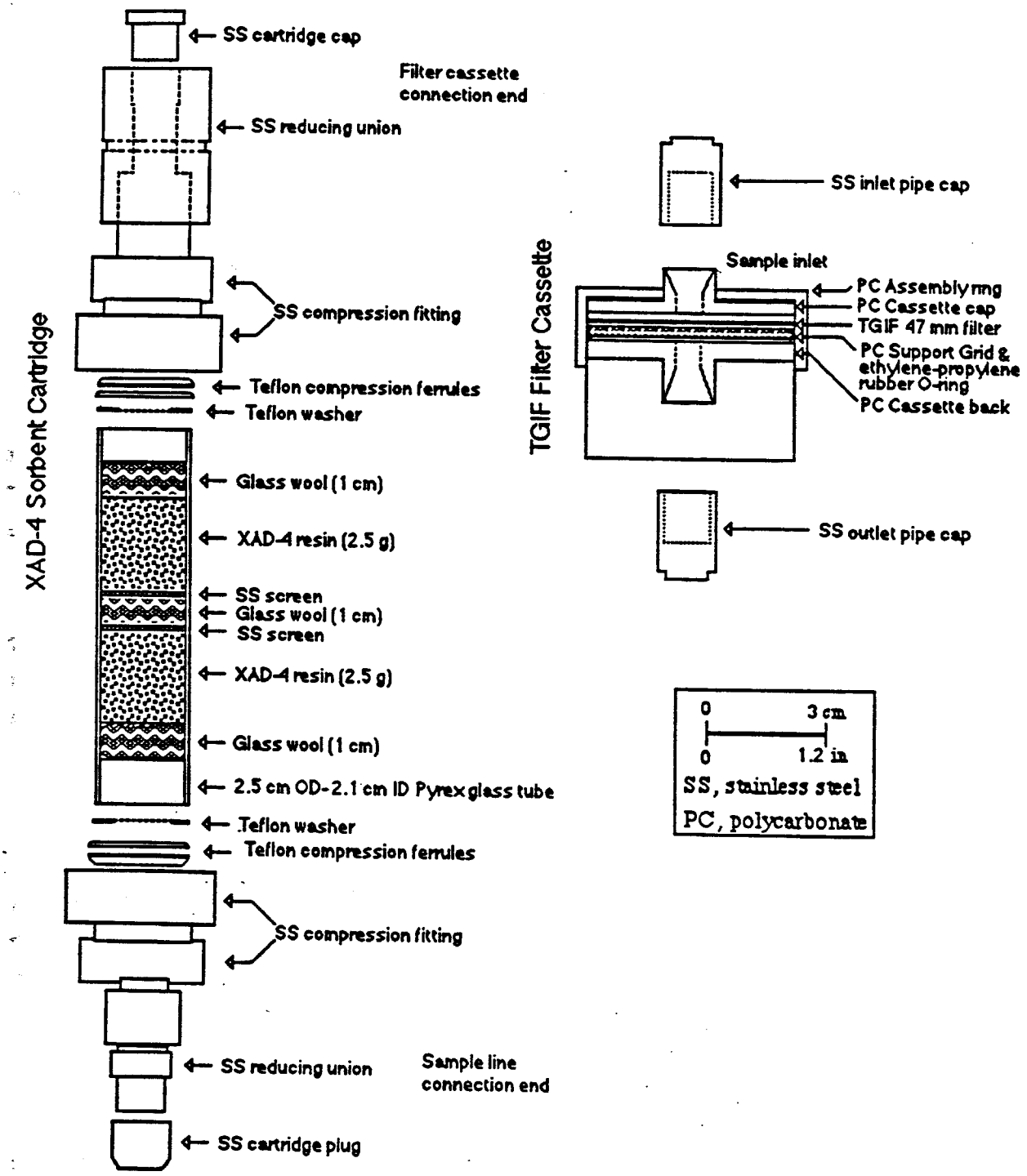


Figure III-1 PAC sampling cartridge assembly depicted components and materials for gas and particulate phase sample cartridges

Pump Type. The selection of the type of air pump for the sampler is another important consideration since some types of pumps may introduce undesirable contaminants into the sampler exhaust air and subsequently into the indoor air that is being sampled. Although a sampling pump placed outside the sampling area or one that is vented outside would eliminate this problem, it would be impractical for a large field sample The air pump must also be able to provide reliable performance over 12 hour sampling periods. Several prototype pumps were tried including a diaphragm pump, rotary vane pump, and a liquid ring pump. The oil-less carbon vane air pump is the usual choice for this type of sampler. A Thomas TA-0030-P, 1/4 horsepower (186.5 watt) rotary vane pump was selected as having the most applicable pump curve with the lowest noise level in the smallest package. The vanes in this pump are primarily graphite based, impregnated with phosphate glass and bound by mix of hydrocarbons. The vanes are then heat treated to 2700 °C. According to the manufacturer the bulk of the pump emissions are carbon particles which are removed by the exhaust filter and a trace amount of phosphate oxides. This type of pump is able to provide reliable performance for anticipated filter loads during the 12 hour sampling period and not release oil vapor into the air. It should provide a flow of 2.1 m^3/hr at a 500 mm Hg vacuum. The 1/4 horsepower pump used in our sampler measures 30.5 cm x 16.5 cm x 17.8 cm and weighs 11.1 kg.

Acoustics. Since this sampler is intended for deployment in indoor environments including residences an important criterion is the level of noise created by the sampler. Acoustic shielding of the motor and muffling of the air discharged from the sampler were important considerations in achieving an acceptable noise level. For indoor applications in residences or commercial buildings, a Noise Criterion (NC) value of 35 is suggested as a design goal. This represents the acoustic guideline for office and reception areas (ASHRAE, 1989). We designed an enclosure that would maximize pump noise attenuation and allow for passage of cooling air across the pump head. We constructed an acoustically insulated enclosure of three chambers inside a box as depicted in Figure III-2. We selected materials that would not significantly off gas contaminants into the air being sampled. Each chamber is constructed using 0.6 cm CDX plywood and screwed onto 1.2 cm CDX plywood base. The pump was mounted on this base with elastomer shock mounts and flexible sample inlet and outlet connections designed to eliminate transmission of pump vibration to the enclosure. We insulated the chambers from the trunk walls with 2.5 cm of low binder fiberglass insulation. We used an additional 2.5 cm of low binder fiberglass to line the

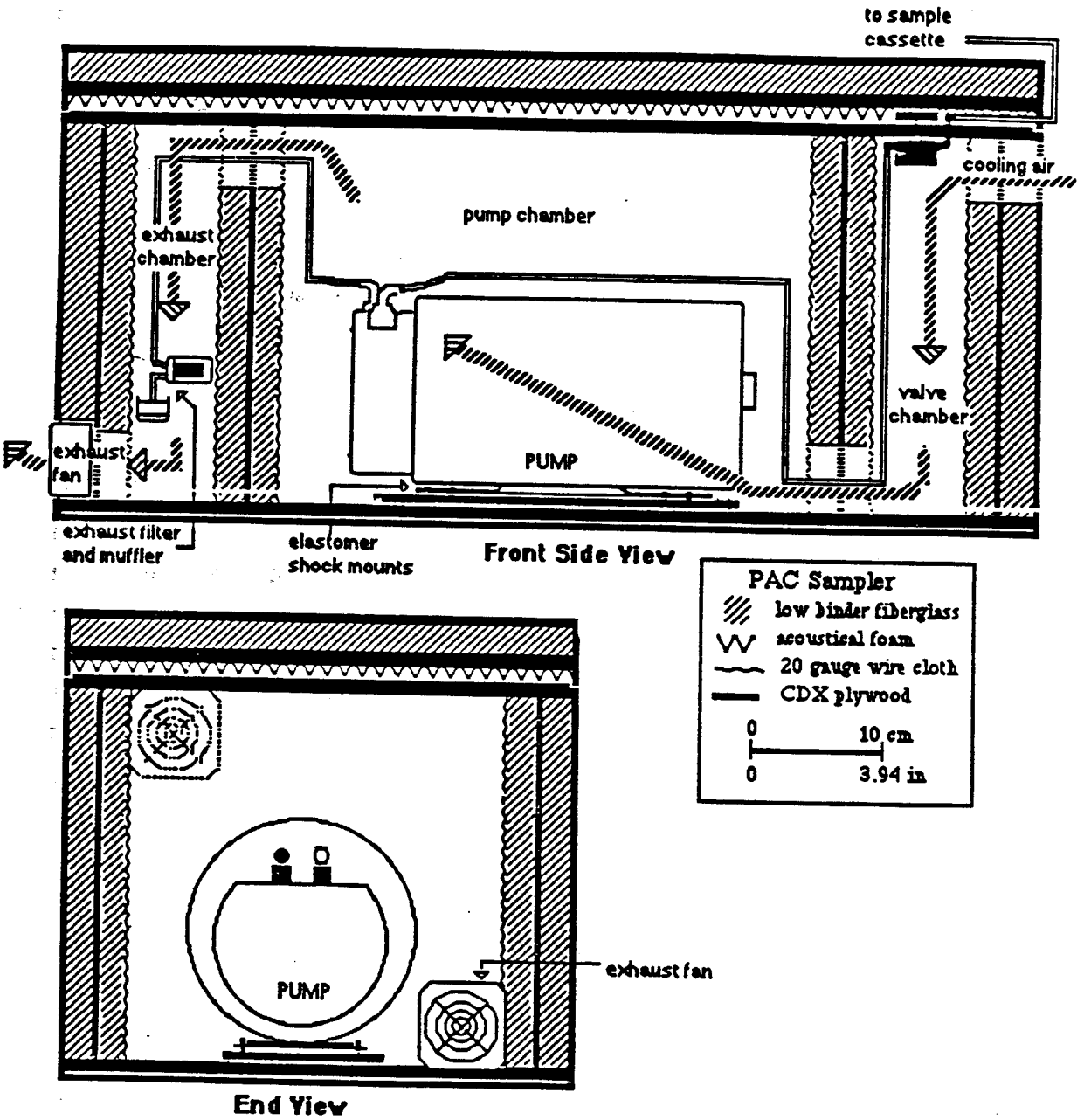


Figure III-2 PAC sampling system pump and acoustic enclosure.

interior of the chambers. The fiberglass is contained inside 6 ml polyethylene bags and kept in place along the pump compartment and all air passageways using 20 gauge galvanized wire screen. The control panel bolts and seals to a gasket on the top of the three chamber enclosure. The control panel is constructed using 1.9 cm CDX plywood covered on the top by black lab top formica mat. The trunk lid is insulated with 2.5 cm of low binder fiberglass insulation and a single sheet of 1.2 cm CDX plywood. We used uncoated acoustical foam to cover the plywood and seal to the control panel. The completed sampling boxes were baked out for 72 hours to off-gas any residual wood or fiberglass odors. The acoustical enclosure weighs 27 kg.To further increase sound attenuation and prevent any carbon particles from being emitted to the sampled air, a muffler and filter system was attached to the sampling pump exhaust. This consisted of a course felt filter within a glass jar followed by a TIGF filter in a modified 47mm Nuclepore filter holder.

Pump Cooling Air Design In order to sample for a 12 hour period and maintain operating conditions, heat must be removed from the pump chamber at a constant rate. To achieve this we installed a 1410 Lpm, 5 blade, 1800 RPM axial cooling fan in the exhaust chamber of the sampling box. The fan is mounted between the exhaust chamber and the trunk. It is wired so that it will go on as soon as the sample box is plugged in and stay on after sampling until the sampler is unplugged. Cooling air enters the valve chamber from an opening on the top left side of the sampler and flows through a opening along the bottom of the pump chamber. There it is drawn across the pump and out into the top of the exhaust chamber. The pump cooling air is then mixed with the filtered pump exhaust and drawn down across the exhaust chamber and forced out by the fan. The air pathway throughout the three insulated chambers of the sampler is designed to be acoustically isolating and thermally effective. The sampling pump has an automatic thermal protection circuit that shuts the pump off if the motor temperature exceeds 58 °C.

Control Panel A control panel should be designed to provide at a minimum, an on/off switch and a valve to adjust the air sampling rate.We mounted a valve, elapsed timer, on/off switch, differential pressure gage, and sample line inlet on the control panel. The elapsed timer is an electro-mechanical totalizer and records up to 10,000 minutes including a 1/10 minute digit. At the end of the sampling run the timer can be reset to zero by hand. The toggle on/off switch controls the pump and elapsed timer. The pressure gage is a Minihelic II differential pressure gage and is used to indicate the pressure change at the sampling line inlet. The sampling line inlet is a stainless steel 0.9 cm compression fitting.

indoor and outdoor air are associated with small respirable particles and very little is associated with the larger non-inhalable particles we designed the sampler to be used in an inverted position facing down and either in an open face mode or with a sample cover with an inlet hole. The design of the sampler is such that an SSI may be added at a future date if desired.

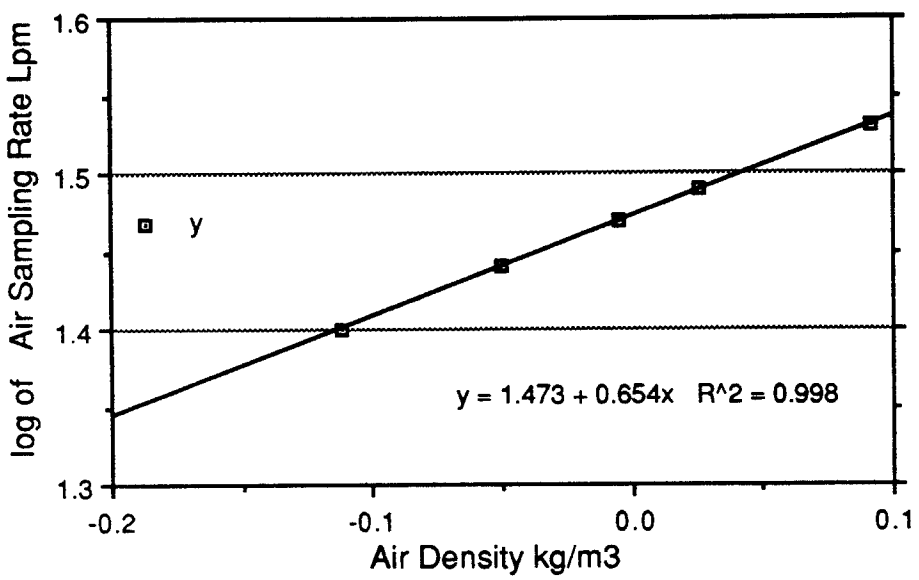
Gas Phase Denuder. A gas phase denuder is a sampler inlet device which can be used to remove potentially reactive gases such as NO_2 and O_3, and thus minimize reactions of collected PAC on the filter or sorbent bed. The need for a denuder needs to be further assessed. At present, there has been only very limited research on the use of denuders for PAC sampling. The design of the sampler is such that a gas phase denuder may be added at a future date if desired.

C. METHODS

We tested the prototype sampler in a series of laboratory and field tests to determine the flow rate stability and noise level of the sampler.

Flow Rate Stability. The flowrate stability of the sampler was investigated by measuring the increase in the filter pressure drop during laboratory and actual field measurements conducted with the sampler set at a constant air sampling rate of 34 Lpm. The sample flow rate was checked using a rotameter at the beginning and the end of each sampling experiment and throughout the sampling period at regular intervals. The flowrate was set at a ball reading of 72.5 (34 Lpm) on the rotameter. The sample air flow rates during the laboratory and pilot field study were measured with a calibrated rotameter (Dwyer, Model RMC-103). The rotameter was connected to the filter inlet and the height of the ball was recorded. The rotameter was calibrated as a function of air density by measuring the airflow rate of standard air (i.e.760 mm Hg, 25°C) with a bubble meter at various rotameter inlet pressures and at a fixed ball height reading of 72 standard cubic feet per hour (scfh). The rotameter inlet was connected through a valve to a large 20 liter bubble meter, and the rotameter outlet was connected to the sampler pump box. We measured the air flow rates through the rotameter at a fixed ball height but with the density air varied by controlling the pressure of air in the rotameter with the valve between the rotameter inlet and the bubble meter. These results were corrected for standard air pressure and temperature. A plot of the rotameter air density calibration along with the equation for computing air density from

temperature, humidity, and pressure are found in Figure III-4. To calculate the flowrate of standard air, the density of the sampled air must be calculated from recorded temperature, humidity, and barometric pressure. The flow rate of standard air is then computed directly



$$\text{density} = 0.02893 * \frac{P}{(T + 273)} * \frac{(1+H)}{(1 + 1.6078 * H)}$$

$$\text{Flow rate} = 1.473 * (\text{density})^{0.654}$$

Flow rate, L/min
T, temperature, C
P, pressure, mm Hg
H, humidity ratio

Figure III-4. Air density calibration of rotometer used to measure the air flowrate through the PAC Sampler.

from the air density calibration equation for the rotameter. During the course of the filter loading experiments as the sample flow rate decreased with increased filter loading the sampler flow control valve was manually adjusted to re-establish a 34 Lpm sampling rate. The filter loadings were calculated from the difference in the filter weight gain as determined from pre- and post- sampling filter weighings made with an electronic microbalance under ambient laboratory humidity conditions. The pressure drop across the TIGF filter was measured with a 2 meter water manometer.

For the 12-hour samples collected in the pilot field study the pressure drops were measured at the beginning and conclusion of the sampling period. The difference between the two pressure drops, final-initial, determine the change in pressure from the loading on the filter.

In addition to the 12-hour data collected during the pilot field study we conducted a test with cigarette smoke to determine the maximum amount of cigarette smoke particles the sampler is capable of collecting. The sampler was exposed in a 34 m^3 test chamber where cigarettes were smoldered to produce an average indoor concentration of approximately 880 $\mu g/m^3$. The filter pressure drop was monitored every 15 minutes until the filter failed after approximately 5 hours of sampling at 34 Lpm.

To further investigate the sampler's capacity on indoor particles other than tobacco smoke particles, we collected a long term indoor sample of over 200 hours in an apartment with a gas stove and no tobacco smoking at a sampling rate of 34 Lpm. The filter pressure drop was monitored with a 2 meter water manometer every few hours.

Noise Level. The Noise Criterion curve was determined for the sampling system at a residential field site using a one third octave band sound meter (B&K). We measured the sound pressure level for each frequency band at a three foot radius around the sampler over a one minute sampling interval.

D. RESULTS

Flow Rate Stability. To determine how much capacity our sampler had to collect particulate matter without reducing the set flow rate by more than 10% we ran a test in a 35 m^3 test room where we used environmental tobacco smoke with a time weighted average concentration of 880 $\mu g/m^3$ to load the TIGF filter at a constant sampling rate and examine

the pressure increases over time. The data from this experiment are presented in Figure III-5. After approximately 200 minutes the pressure drop increase ceased to increase linearly and began increasing exponentially. At approximately 300 minutes the filter pressure drop exceeded the maximum differential pressure measurement range of +/- 70 mm Hg and we stopped the sampling and weighed the filter to determine the total loading. The filter loading was measured to be 10 mg. The flow remained linear up to 200 minutes, which assuming a linear loading would be equal to approximately 6 mg of particulates.

To further investigate the samplers capacity, we collected a long term indoor sample over 200 hours in an apartment with a gas stove and no tobacco smoking. These data are presented in Figure III-6. The flow rate increased linearly over the first 8500 minutes after which it began increasing exponentially. Assuming linear loading the filter load at 8500 minutes is 5.7 grams.

Figure III-7 depicts the differential pressure gain versus the filter weight gain for the 35 indoor and outdoor field samples collected during the pilot field study as well as the 7/19/89 long term indoor sample and the 1/24/89 tobacco smoke overload test. From this figure it is apparent that the differential pressure drop increases are linear up to approximately 6 mg for this type filter. After a loading of approximately 6 mg loading the differential pressure drop begins increasing rapidly. At a 6 mg loading the filter pressure drop is approximately 10 mm Hg over the initial pressure drop of 30 mm Hg. The impact of a 10 mm Hg increase in filter differential pressure drop may be calculated from the difference in the flow rate for the sampling system with and without the 10 mm Hg increase. Figure III-8 is the pump curve for the rotary vane vacuum pump used in the prototype PAC sampler. The prototype sampler has a total pressure drop of 518 mm Hg across the pump with a new filter and at a sample flow rate of 34 Lpm. Note that the flow rate across the pump changes linearly with the total system pressure drop. From this curve we compute that a 10 mm Hg increase in filter pressure drop will reduce the air sampling rate of a sampler set at 34 Lpm to approximately 31.8 Lpm, which represents a 6.5% decrease.

These tests indicated that for loading up to 6 mg of particulate matter, the pressure drop across the filter increases linearly with loading and that the flow rate through the pump varies inversely with increasing filter pressure drop. A 6 mg particulate load collected in a

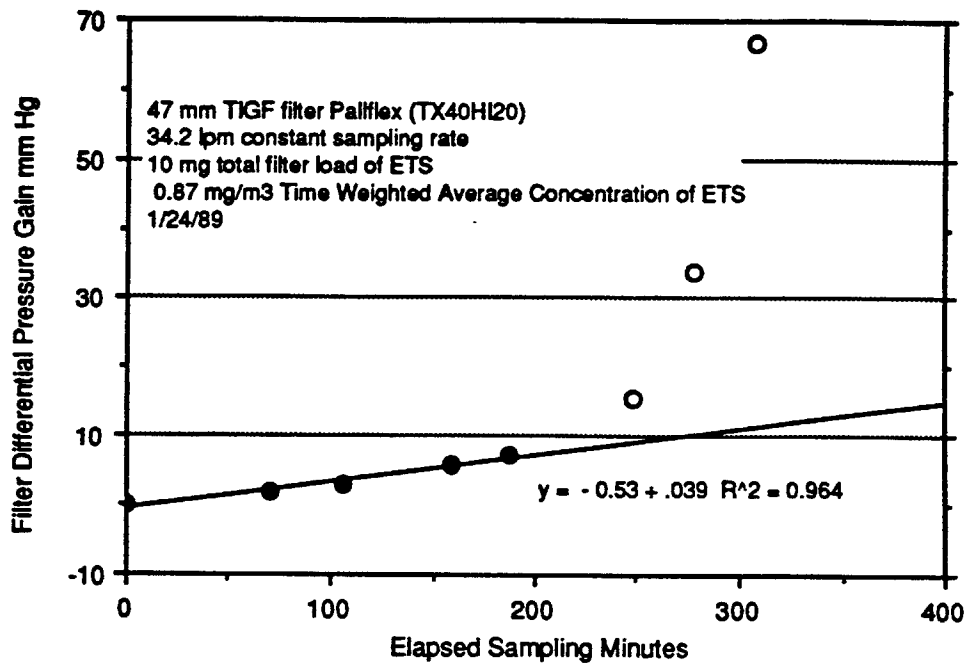


Figure III-5. Environmental Tobacco smoke filter overload tests for a 47 mm Teflon impregnated glass fiber (TGIF) filter.

25 m^3 sample represents an average particulate matter concentration of 240 $\mu g/m^3$. Typical indoor residential and commercial particulate matter concentrations range from 20 - 100 $\mu g/m^3$. Thus the prototype sampler <u>without</u> a compensating flow controller may be expected to collect 25 m^3 samples in residences and commercial buildings with less than a 10% reduction in the sample flow rate. Furthermore since the filter pressure drop increases and associated sample flow rate decreases are expected to be linear within the 6 mg of total filter load, the average sample flow rate may be computed as the arithmetic average of the initial and final sample flow rate measurements.

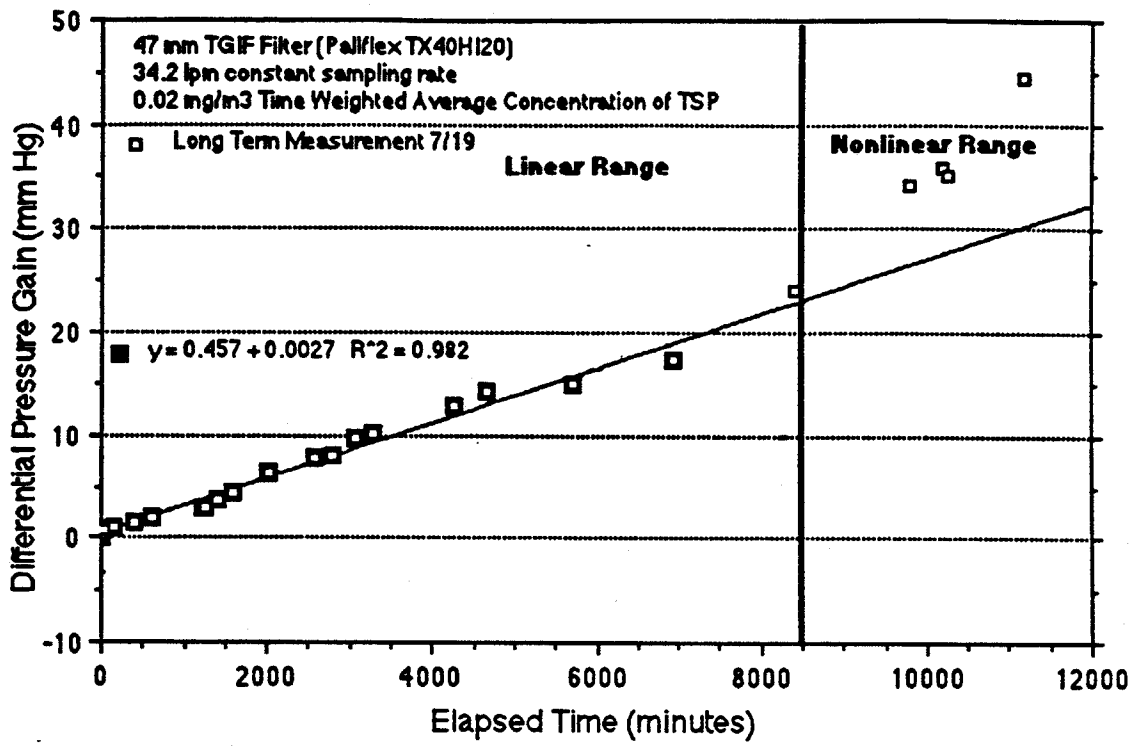


Figure III-6 Filter differential pressure gain for long term testing for a 47 mm Teflon impregnated glass fiber (TIGF) filter.

Air Volume Measurement Uncertainty Calculation

The following measurements are necessary in computing the air volume of the sample; the sample time period, the average rotameter float height, air temperature and humidity, and atmospheric pressure. The estimated observational uncertainties at the 95% confidence limits for each of these variables are presented in Table III-5. The uncertainty in the average air sampling rate is based upon our frequent monitoring of the air sampling rate which included manual corrections using the sampler flow control valve. The measurement uncertainties have been sequentially perturbed in a spread sheet program according to standard error propagation theory to compute the total uncertainty in the computed air sample volume. Briefly the uncertainties are summed in root mean square fashion after weighting each of the variable uncertainties according to the partial derivative of the

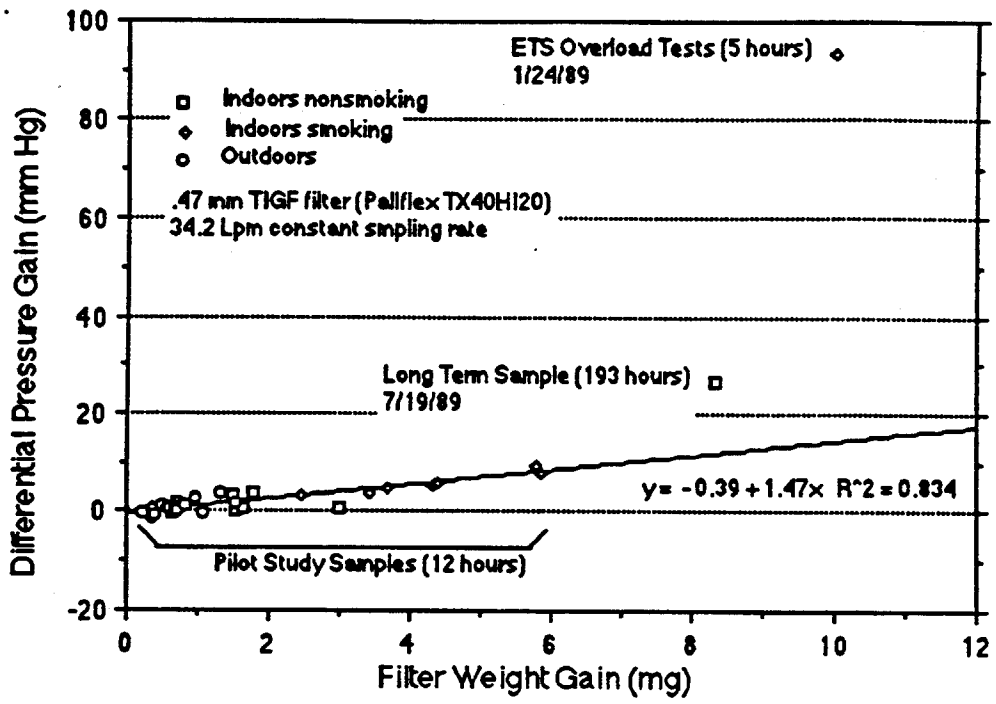


Figure III-7 Filter differential pressure gain as a function of filter weight gain for a 47 mm Teflon imprgnated glass fiber filter (TGIF)

measurement function to that particular variable. The spreadsheet program used for the field data analysis renders itself easily for these computations. The total uncertainty in measuring a 23.95 m^3 air volume is estimated to be absolutely 0.47 m^3 or relatively 2%. As indicated in Table III-5, 77% of the total measurement uncertainty is estimated to be a result of the uncertainty associated with the rotameter ball reading. Field samples collected in a large field study would normally include only initial and final air sampling rate checks and thus the uncertainty in the average air sampling rate will be higher than that estimated for the pilot field study where the sample flow rates were frequently checked and corrected. Assuming that the total particulate load on the filter is less than 6 mg and that the average air sampling rate is computed as the arithmetic average of the initial and final air sampling rate measurements the uncertainty in the volume of air sampled would be more than 2% but still less than 5% which is much less than the anticipated analytical uncertainties.

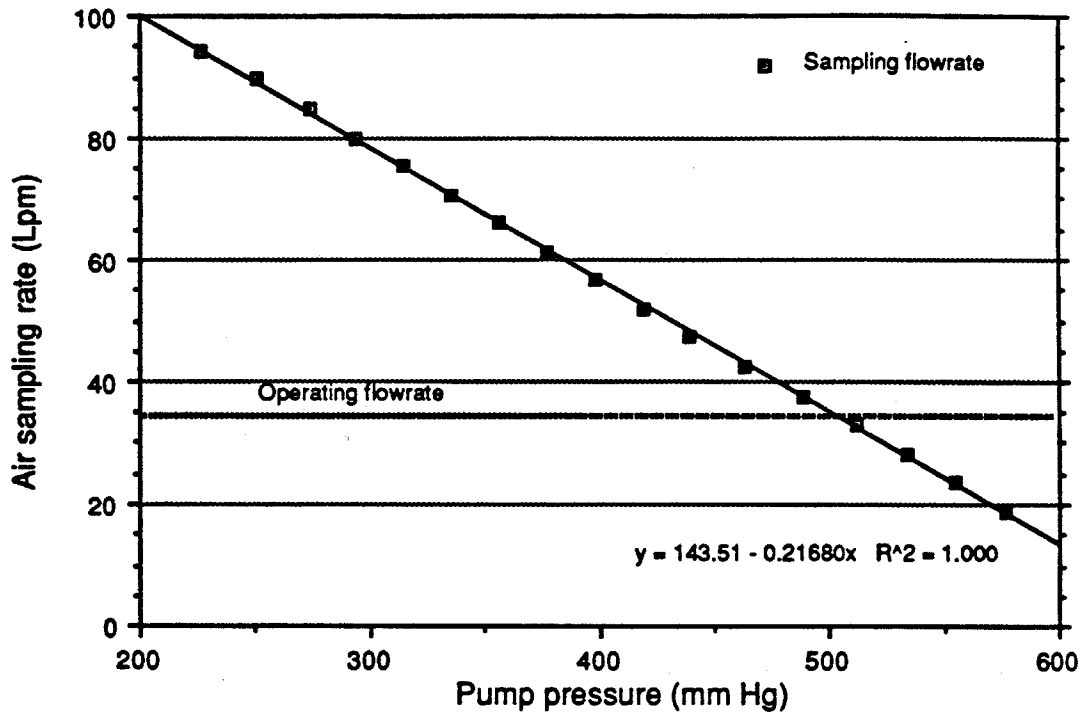


Figure III-8. PAC sampler operational curve.

Acoustics A-weighted sound level tests were performed to identify the relative loudness of the sampler in an indoor environment and the effectiveness of its sound attenuation devices. The A-weighted sound pressure level was found to be 80 dBA without a muffler or the enclosure top lid on. Installing the exhaust muffler reduced the A-weighted sound pressure level to 63 dBA. Bolting on the enclosure top lid further reduced the A-weighted sound

Table III-5. Sampler air volume uncertainty estimate.

Measurement parameter	Units	Value	Abs.[a] Variable Uncert.	Rel.[b] Variable Uncert.	Abs.[c] Variable Perturb.	%[d] of Total Perturb.
On Time	(min)	720	5	0.7	0.0267	12.2
Average Ball Reading	(scfh)	72.5	1.25	1.7	0.1680	77.0
Pressure	(mm Hg)	760	1.3	0.2	0.0005	0.2
Temperature	(C)	21	2.8	13.3	0.0224	10.3
Humidity ratio		0.008	0.002	25.0	0.0005	0.2
Total absolute volume uncertainty [e]	(m^3)	0.467				
Unperturbed volume computation	(m^3)	23.95				
Total relative volume uncertainty	(%)	2.0				

a)Absolute variable uncertainty - estimated 95% confidence limits for data used to compute the volume of air sampled
b) Relative variable uncertainty- calculated as the absolute variable uncertainty divided by the variable value.
c)Absolute variable perturbation - computed as the square of the difference between the volume computed with and without variable perturbation.
d) Percentage of total variable perturbation.
e)Total absolute volume uncertainty calculated as the square root of the sum of the individual variable perturbations.

pressure level to 50 dBA. Additionally, an NC curve was plotted in Figure III-9 to define the octave-band spectrum of the sampler with the enclosure top lid open and closed. The NC is determined by plotting the measured sound pressure levels and determining the frequency band which exceeds the highest noise criteria curve. For the sampler with the muffler on but the top lid of the enclosure off the NC rating at a 3 ft radius from the enclosure was NC 65. The dominant frequency was 8,000 Hz. With the top lid of the enclosure bolted on the NC rating at a 3 ft radius from the enclosure was reduced to NC 45. The dominant frequencies were in the 125-500 Hz range. The blade passage frequency for this type pump is approximately 125 Hz and is suspected as the source of the remaining low frequency noise.

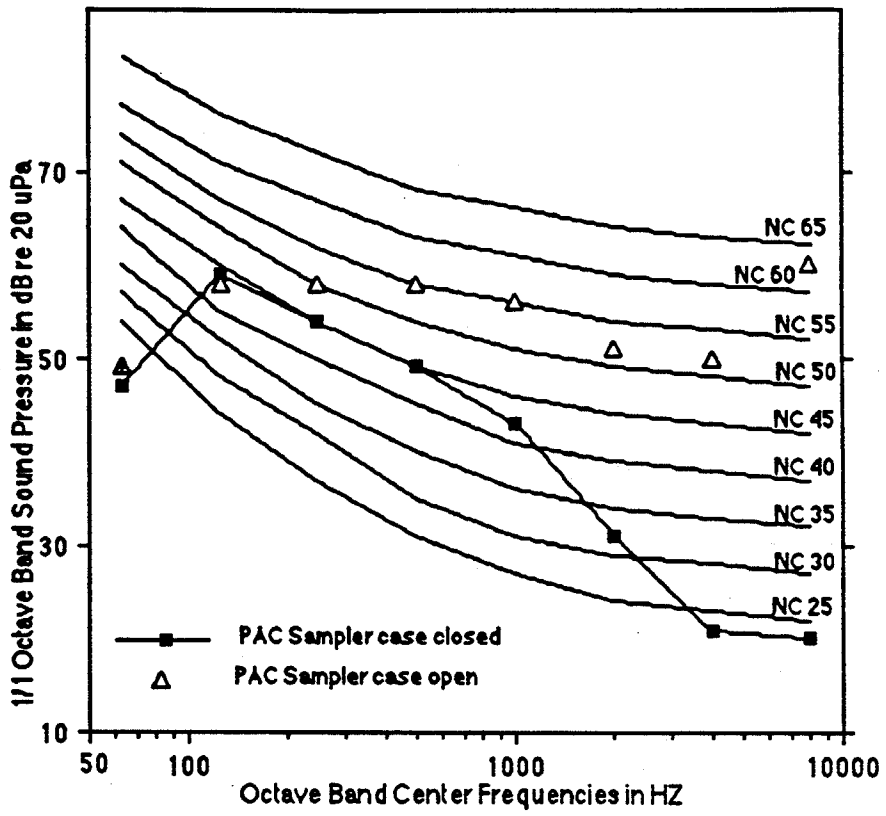


Figure III-9. Noise Criteria Curve for PAC sampling pump.

While we did not achieve our optimistic design goal of NC 35 we were able to mitigate much of the high frequency noise from the pump and achieve an NC 45. The noise level remaining is dominated by frequencies in the 125-500 Hz range and is a little more noisy than a personal computer or a home refrigerator. There were no complaints of noise from the participants in the pilot field study even when two samplers were operated indoors simultaneously.

E. CONCLUSIONS

We developed a new sampler for measuring particulate and gas phase PAC in indoor environments. The sampler consists of a sampling cassette composed of a 47 mm TIGF filter followed by a sorbent cartridge packed with XAD-4 resin and a fan cooled acoustically insulated pump. The pump enclosure with pump weighs 40 kgs and has outside dimensions of 76.2 cm x 38.1 cm x 40.6 cm. It is relatively unobtrusive with a NC level of 45 and can be plugged in to any 110 volt, 5 amp outlet. The flowrate of the sampler is manually adjustable with a union bonnet valve from 4.7 and 47 Lpm and once set, will remain constant (i.e. less than 5%) throughout the sampling period for most indoor and outdoor environments. A sampler holder and tripod-stand suspend the sampling cassette in the breathing zone. Elapsed time and sampling cassette pressure drop are indicated on the control panel. The sampling cassette consists of a 47 mm Teflon impregnated glass fiber (TGIF) filter in a polycarbonate cassette holder for collection of particulate phase PAC followed by two sections of XAD-4 resin in a stainless steel and glass cartridge for collection of gas phase PAC. The flow rate of the sampler in the field tests was set to approximately 34 liters per minute so that a 25 m^3 sample volume may be collected in a 12-hour period. The 25 m^3 sample volume is necessary to achieve the desired ng/m^3 detection limit for PAC. The 34 liter per minute sampling rate represents a small reduction of the indoor PAC concentration at most indoor residential or commercial sampling locations.

We designed an acoustical enclosure that draws air across the pump head and keeps the pump from overheating. Because the cooling air is drawn from the surrounding environment, the temperature of the ambient air can not be too high. Our field tests were run under various conditions up to ambient temperatures as high as 30 ^oC with no occurrence of pump overheating.

We measured the stability of the sample flow rate over 12-hour sampling periods in the pilot field study described in Chapter VI. These tests indicated that for loading up to 6 mg of particulate matter, the pressure drop across the filter increases linearly with loading and that the flow rate through the pump varies inversely with increasing filter pressure drop. A 6 mg particulate load collected in a 25 m^3 sample represents an average particulate concentration of 240 $\mu g/m^3$. Typical indoor residential and commercial particulate concentrations range from 20 - 100 $\mu g/m^3$. Thus the prototype sampler <u>without</u> a compensating flow controller may be expected to collect 25 m^3 samples in residences and commercial buildings with less than a 10% reduction in the sample flow rate. Furthermore

since the filter pressure drop increases and associated sample flow rate decreases are expected to be linear within the 6 mg of total filter load, the average sample flow rate may be computed as the arithmetic average of the initial and final sample flow rate measurements.

We recommend that future work could be directed towards reducing the weight and size of the pump enclosure. This could be accomplished by using less material in the support structure and reducing the size of the valve chamber and exhaust chamber. Additional acoustical isolation could be used to further reduce the noise level.

IV. A SAMPLING AND ANALYTICAL METHOD FOR GAS-PHASE POLYCYCLIC AROMATIC HYDROCARBONS IN INDOOR AIR

A. INTRODUCTION

A number of methods have been developed for collecting and analyzing samples of gas-phase, semi-volatile polycyclic aromatic hydrocarbons (PAH) in ambient outdoor air. However, methods that are suitable for use in indoor environments are not well established. In fact, only recently have there been reports of a sampler and an analytical method designed specifically for this application (Wilson and Chuang, 1987; Wilson et al., 1989). Because of the unique sampling and analytical requirements of indoor air quality studies, considerably more effort is needed to develop and evaluate appropriate methods.

The development of a sampling and analytical method for gas-phase PAH in indoor environments is technically challenging. The compounds classified as semi-volatile PAH cover broad ranges of volatility and concentration. Naphthalene, the most volatile PAH, has been reported to be present in indoor air at concentrations ranging up to several thousand nanograms per cubic meter while pyrene, which is considerably less volatile, is typically present in indoor air at levels of 1 to 20 ng/m^3 (Chuang et al., 1987a; Wilson and Chuang, 1987). The most economically efficient solution is to collect this broad range of compounds in a single sample. Consequently, the sampling and analytical method must be capable of retaining naphthalene without significant loss due to breakthrough while providing good recoveries of the PAH present at much lower concentrations.

When collecting samples in occupied residences, the size and noise level of the required sample pump must be kept to a minimum. This restriction necessitates the use of only a small amount of collection media so that the pressure drop across the sampler is small. The sampling flow rate and sample volume are also restricted. The flow rate must be small relative to the air exchange rate of the space being sampled so that the sampling procedure does not significantly reduce the concentrations of the analytes. Since it is desirable to collect samples over time periods that correspond to occupant activity cycles, the volume of air that can be sampled is, therefore, limited. Because of this limitation on sample volume, high analytical sensitivity is required to quantify the compounds that are typically present at low concentrations.

Polyurethane foam (PUF) has been widely used for sampling semi-volatile PAH in outdoor air and has the advantage of a low resistance to air flow. However, it does not effectively retain the more volatile compounds (Chuang et al., 1987b; Atkinson et al., 1988; Arey et al., 1989). To overcome this deficiency, Atkinson and co-workers used three separate sorbent samplers for collecting gas-phase PAH in outdoor air. The least volatile, gas-phase PAH were collected on PUF plugs, and the more volatile compounds were collected on two Tenax-GC cartridges of different size. Tenax-GC is a porous polymer of 2,6-diphenyl-p-phenylene oxide with a surface area of about 35 m^2/g. Naphthalene was collected separately using the smallest Tenax-GC cartridge and a low sample volume to reduce the problem of breakthrough for this compound. Chuang et al. (1987a; 1987b) sampled semi-volatile PAH in indoor and outdoor air using XAD-2 resin which is a non-polar styrene-divinylbenzene polymer with a surface area of 300 m^2/g. The analytes were recovered by solvent extraction of the resin with dichloromethane. In a later study, the investigators (Wilson and Chuang, 1987) switched to XAD-4 resin, which gave better recoveries for PAH and also effectively collected nicotine. This related polymer has a surface area of 725 m^2/g. Based on the acceptable results obtained by these investigators, XAD-4 resin was selected as the sorbent for use in the present study.

The primary goal of this portion of the study was to develop and validate a sampling and analytical method for gas-phase, semi-volatile PAH that would be suitable for use in a proposed, large-scale, field study of PAH concentrations in residential indoor air. The general design objectives for the method were to: 1) provide adequate sensitivity for a broad range of gas-phase PAH in 25-m^3 samples of air collected in indoor environments having a variety of potential sources of these compounds; 2) provide sufficient precision to permit statistical evaluations of concentration differences among environments and sources; 3) incorporate appropriate internal standards to monitor and correct for potential recovery and breakthrough losses of the analytes; and 4) keep the method as simple as possible by involving a minimal number of sample-handling steps prior to analysis. The general approach was to develop and optimize the method based on laboratory and limited field experiments. The method was then used in a pilot field study to quantify 14 semi-volatile PAH in five residences and two commercial buildings. This chapter describes the preparation and analysis of the XAD-4 sorbent samplers and evaluates the performance of the method and the quality of the quantitative results that were obtained in the field study. The sampling apparatus is described and its performance is separately evaluated in Chapter III. The design of the pilot field study and the complete quantitative results for the semi-

volatile PAH are presented and discussed in Chapter VI. Chapter VI also includes a detailed evaluation of the uncertainty inherent in the entire sampling and analytical procedure.

B. METHODS

Preparation and Handling of XAD-4 Sorbent Samplers

Purified XAD-4 resin, 20/60 mesh, obtained from the supplier (Alltech Assoc., Inc., Deerfield, IL), was further cleaned by Soxhlet extraction with methanol followed by dichloromethane (CH_2Cl_2), each for eight hours. The cleaned resin was dried in the extraction thimbles under a stream of nitrogen gas. Residual solvent was removed by transferring the resin to a 2.5-cm O.D. x 50-cm glass tube. Nitrogen gas was introduced at one end of the tube, and the tube was heated with heating tape to ~40°C for four hours. The dry, cleaned resin was stored in sealed glass containers. Glass wool used in the assembly of sorbent samplers was cleaned by Soxhlet extraction following the same procedure. Other components of the samplers were washed with soap and water and rinsed with methanol and CH_2Cl_2 in preparation for use.

The sorbent samplers were assembled as shown in Figure III-2, Chapter III. The glass cartridges were cooled in a freezer and withdrawn just prior to sampler preparation to facilitate loading of the XAD-4 resin which has a static charge. Two sorbent sections, each containing 2.5 g of resin, were directly weighed into each cartridge using a top-loading balance. The front section was then spiked with perdeuterated compounds as described below. The wire screens separating the resin from the center section of glass wool helped reduce the holdup of resin beads on the glass wool when the cartridges were unloaded. Samplers were completely assembled, capped, labeled, wrapped with aluminum foil, and stored in a freezer at -10°C prior to use.

Perdeuterated compounds used as internal standards and surrogates and nondeuterated compounds used as authentic standards for calibration were obtained from a commercial source (Aldrich Chemical Co., Milwaukee, WI). All solvents were high purity HPLC grade (B&J Brand, Baxter Healthcare, Corp., Muskegon, MI). Stock solutions of single or mixed deuterated and nondeuterated standards were made as required by weighing the pure compounds on an electronic microbalance and dissolving them in benzene in 100-ml

volumetric flasks. Calibration standards were made by diluting aliquots of these stock solutions with benzene to the desired concentrations using glass volumetric syringes.

The sorbent samplers were spiked with three perdeuterated compounds at the time of sampler preparation. These compounds served as surrogates for the determination of analyte recovery factors. The additions were made by placing small volumes of stock standard solutions on the XAD-4 resin near the center of the inlet end of the front section prior to inserting the front section of glass wool. The additions made to each sampler were 25 µL of a solution of 2558 ng/µL naphthalene-d_8 (63.95 ug) and 10 µL of a solution of 186.8 ng/ µL phenanthrene-d_{10} (1868 ng) and 79.5 ng/µL pyrene-d_{10} (795 ng).

Sorbent samplers were transported to and from field sites in insulated shipping containers cooled with ice packs. Samples designated as field blanks were handled in the same manner as actual samples. When the samplers were returned to the laboratory, they were stored in a freezer at -10°C for no more than two weeks prior to extraction.

Collection of Samples

The sampling plan for the field portion of the study and the sampling apparatus and procedures that were employed are described in detail in Chapter VI. In brief, there were seven field blanks and 35 field samples. Nineteen of the 35 samples were collected in houses and office buildings, some of which contained combustion sources (cigarette smoke, gas ranges and wood stoves) which can emit gas-phase PAH. The remaining field samples were collected outdoors in the near vicinity of these buildings. The sample set contained 11 pairs of samples, seven pairs collected indoors and four pairs collected outdoors. The members of each pair were simultaneously collected from the same location using identical apparatus and procedures. Results for the paired samples were used to estimate the precision of the method.

Solvent Extraction and Concentration of Samples

The procedure for extraction and concentration of samples for the analysis of gas-phase PAH is presented schematically in Figure IV-1. All glassware used in this procedure was washed with soap and water, solvent rinsed, dried, and then rinsed again with CH_2Cl_2 immediately prior to use.

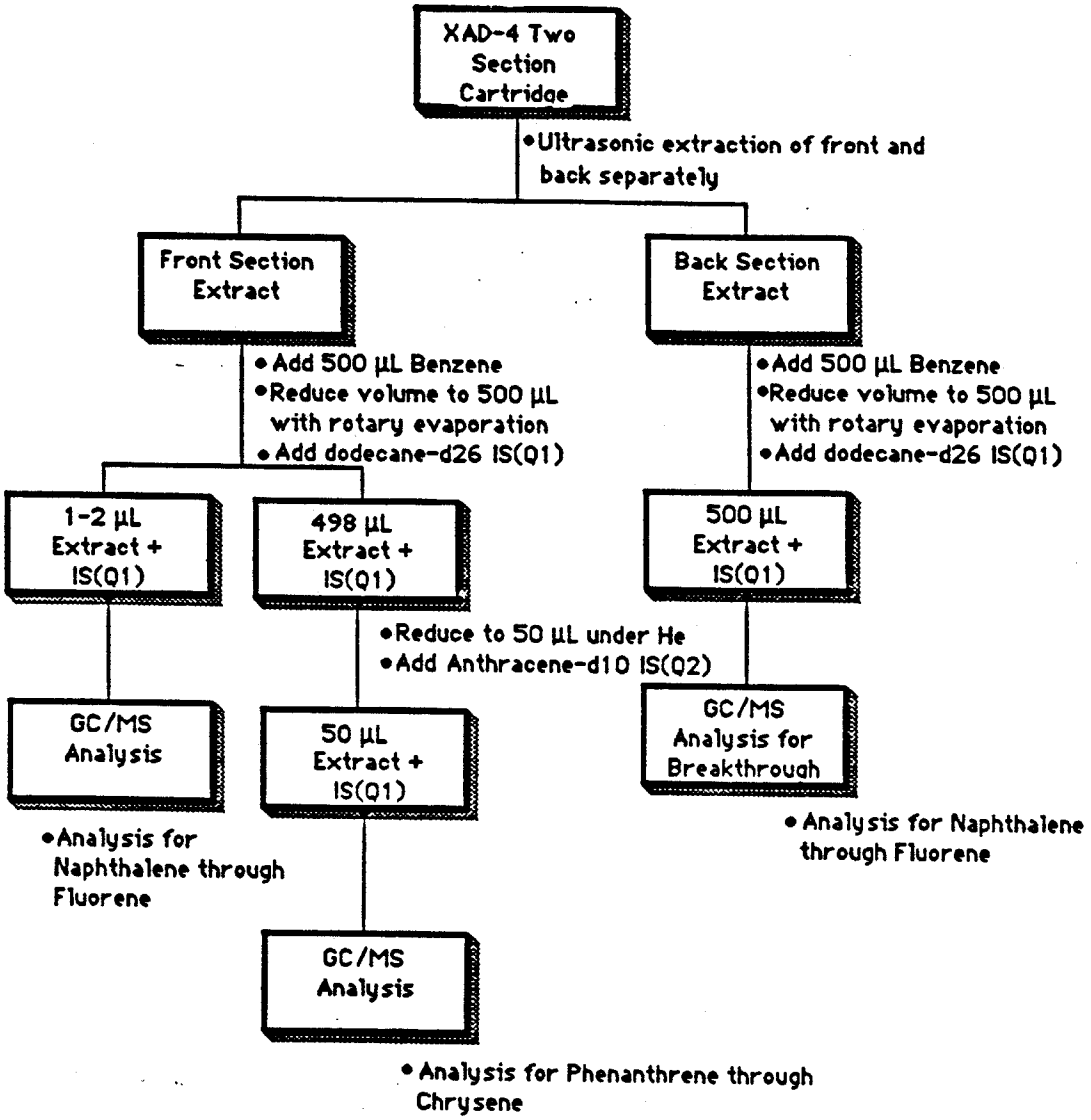


Figure VI-1. Diagram of analytical scheme for vapor-phase PAH.

A sampler was taken from the freezer, and the front and back sections of XAD-4 resin were each transferred to a 100-ml beaker with a watch-glass cover. A 30-ml volume of CH_2Cl_2 was added to each beaker, and the resin was extracted for 30 min in an ultrasonic bath maintained at ~25°C. The back section of resin and solvent were then transferred with two solvent rinses to a glass microanalysis filter holder with a stainless-steel support screen (Model KGS 47, Micro Filtration Systems, Dublin, CA). The base of this apparatus had been modified with a ground glass taper joint to fit a 250-ml vacuum flask. The solvent was filtered through a PTFE membrane filter, 1.0-um pore size, 47-mm diameter (Micro Filtration Systems), and collected in the flask under gentle vacuum. The filter holder and resin were rinsed twice with CH_2Cl_2 during this process. The filtrate was then transferred with two rinses to a 50-ml pear-shaped flask, and 500 µL of benzene was added. The filtration apparatus and filter were rinsed with CH_2Cl_2, and the front section of XAD-4 resin was identically processed using the same apparatus.

The extract was concentrated by rotary evaporation at 20°C under gentle vacuum to 200-300 µL. The extract was transferred with a glass volumetric syringe fitted with a 90° cut needle to a 1-ml cone-shaped vial with a Teflon-lined cap. The pear-shaped flask was then rinsed with a small volume of benzene to bring the total volume of extract to ~500 µL. The extracts were stored in a refrigerator until analysis.

GC-MS Analysis of Sample Extracts

The sample extracts were analyzed by electron impact gas chromatography-mass spectrometry (GC-MS). The analytical instrument consisted of a GC (5790A series, Hewlett Packard Co., Palo Alto, CA) connected via a direct capillary interface to a 5970B series Mass Selective Detector (MSD, Hewlett Packard Co.). The GC was equipped with a 5% phenylmethylsilicone fused-silica capillary column (Phase Rtx-5, 30 m, 0.25-mm I.D., 1.0-um film, Restek Corp., Bellefonte, PA). Manual injections were performed. Injection volumes were 1.0 µL made in the splitless mode. The MSD was operated in the selected ion monitoring mode for the identification and quantitation of the compounds of interest. The molecular ions of the PAH were monitored, and for several compounds, additional ions were monitored either for quantitation (acenaphthene) or as qualifiers for identification. Perdeuterated n-dodecane was quantified using mass (m/z) 50. The ions that were monitored are presented in Table IV-1.

Table IV-1. Fragment ions used for GC-MS selected-ion monitoring of analytes in sample extracts.

COMPOUND	ION (m/z) Quantitative ion	Qualitative ion	QUAL/QUANT [a] (%)
Analysis 1 (10-16 min) [b]			
n-Dodecane-d_{26}	50		
Naphthalene-d_8	136		
Naphthalene	128		
2-Methylnaphthalene	142		
1-Methylnaphthalene	142		
Biphenyl	154	153	45
Acenaphthylene	152		
Acenaphthene	153	154	80
Fluorene	166	165	100
Analysis 2 (20-39 min) [b]			
Phenanthrene-d_{10}	188		
Phenanthrene	178		
Anthracene-d_{10}	188		
Anthracene	178		
2-Methylanthracene	192		
9-Methylanthracene	192		
Fluoranthene	202		
Pyrene-d_{10}	212		
Pyrene	202		
Chrysene	228		

a) QUANT = quantitative ion, QUAL = qualitative ion, QUAL/QUANT = relative abundance.
b) Data acquisition time interval. GC oven temp. program = hold 70oC, 2 min; ramp 15° / min to 130°; ramp 6° /min to 300°; hold.

Two analyses were performed on the extracts using different concentrated volumes. The GC oven temperature program was identical for these two analyses; however, the time intervals for data acquisition were different (Table VI-1). The ~ 500-μL extracts of both the front and back sections of all samples, prepared as described above, were analyzed for naphthalene, 1- and 2-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene (1,2-dihydroacenaphthylene), and fluorene (Analysis 1). The latter four compounds were added to the original list of compounds to be analyzed so that more comparisons could be made with the data obtained by Atkinson et al. (1988) for outdoor air. A 10- or 15-μL volume of a standard solution of 3042-ng/μL n-dodecane-d_{26} (30.42-45.63 ug) was added to each each extract immediately prior to this analysis. The perdeuterated n-dodecane served as the internal standard for quantitation for this analysis. The remaining compounds, phenanthrene, anthracene, 2- and 9-methylanthracene, fluoranthene, pyrene, and chrysene, were analyzed in the extracts of the front sections of the samples only (Analysis 2). Immediately prior to this analysis, the extract was further concentrated by slowly reducing the volume to 50-75 μL under a stream of helium gas. Then, a 10-μL volume of a standard solution of 118.4-ng/μL of anthracene-d_{10} (1184 ng) was added. This compound served as the internal standard for quantitation for this analysis. Some duplicate analyses of both the original and the more highly concentrated extracts were performed to assess the precision of the analytical procedure.

Data Reduction and Analysis

The raw GC-MS instrumental data were acquired and stored using a micro-computer based data system running GC-MS software (59970C series Chemstation, Revision 3.1.1, Hewlett Packard Co.). Backup, archival copies of the data files were stored on magnetic tape. Peak-area responses in the ion-current chromatograms were integrated using the GC-MS software. Peaks with areas less than 10,000 units were arbitrarily rejected to reduce the number of detected peaks. This effectively established a lower limit of detection for the method which was consistent with the uncertainty of distinguishing peaks from background noise (see Results). Since many of the samples contained complex mixtures of compounds, a number of files were manually checked for correct integration of the analyte peaks. The integrated peak-area responses for the analytes in the samples were transcribed into a spreadsheet program running on a PC-computer. The calibrations and all of the other calculations were performed using the spreadsheet program.

Identification and Quantitation of Compounds

Retention-time indices were calculated for all compounds based on the GC retention times of authentic standards relative to the retention times of the perdeuterated surrogate compounds (Table IV-2). Retention indices for phenanthrene, anthracene, methyl-anthracenes, fluoranthene, pyrene, and chrysene were calculated using phenanthrene-d_{10} and pyrene-d_{10} as references according to the following relationship

$$I=100n+\left(\frac{t_{R(substance)}-t_{R(n)}}{t_{R(n+1)}-t_{R(n)}}\right) \qquad (4\text{-}1)$$

where I is the retention index, $t_{R(substance)}$ is the measured retention time of the compound of interest, $t_{R(n)}$ and $t_{R(n+1)}$ are the measured retention times of the bracketing standards that elute before and after the compound, and n is the number of rings of the standard that elutes first. Retention indices for the other compounds were calculated using naphthalene-d_8 as the only reference. The retention indices of the ion current response peaks detected in the samples were compared to expected indices. Generally, if the ion current response peak fell within the 95-percent confidence interval of its expected index and the peak area of the qualifying ion, if any, was present within 20 percent of its expected relative abundance, the identification was considered to be positive. However, some judgment with respect to the retention indices was required since there can be small differences in index values between simple standard mixtures and complex samples.

The compounds were quantified based upon comparisons of their integrated ion-current responses to the ion-current response of the internal standard for quantitation (either n-dodecane-d_{26} or anthracene-d_{10}) which was added at the time of analysis. Calibration response curves were generated for three different concentrations of a standard mixture to evaluate the linearity of the responses. An attempt was made to produce calibration mixtures with concentrations similar to those of the samples being analyzed. Typically, one set of calibration standards was analyzed with and used to quantitate samples analyzed over a two-day period. Relative response factors for the compounds in the standard mixtures were calculated as:

$$RRF_T=\frac{A_T*ng_S}{A_S*ng_T} \qquad (4\text{-}2)$$

Table IV-2. Relative retention-time indices (RTI) for analytes calculated from GC retention times of authentic standards.

COMPOUND	n	RELATIVE RTI [a] MEAN	+/-95% CI
Analysis 1			
n-Dodecane-d_{26}	12	194.17	0.03
Naphthalene-d_8		200.00	
Naphthalene	12	200.56	0.03
2-Methylnaphthalene	12	220.56	0.04
1-Methylnaphthalene	12	224.10	0.03
Biphenyl	12	235.49	0.04
Acenaphthylene	12	250.74	0.06
Acenaphthene	12	257.03	0.05
Fluorene	12	274.76	0.09
Analysis 2			
Phenanthrene-d_{10}		300.00	
Phenanthrene	16	301.57	0.04
Anthracene-d_{10}	16	303.35	0.06
Anthracene	16	304.66	0.04
2-Methylanthracene	16	339.89	0.25
9-Methylanthracene	16	355.52	0.16
Fluoranthene	16	385.24	0.15
Pyrene-d_{10}		400.00	
Pyrene	16	401.25	0.05
Chrysene	16	489.56	0.75

a) GCwas a 5790A series, (Hewlett Packard Co) connected via a direct capillary interface to a 5970B series Mass Selective Detector (Hewlett Packard Co.)

where RRF_T is the relative response factor of the target compound; A_S is the peak area of the quantitation internal standard; A_T is the peak area of the target compound; and ng_S and ng_T are the masses of the internal standard and the target compound in nanograms. The masses of the compounds in the sample extracts were then calculated using the following relationship:

$$ng_T = \frac{A_T * ng_S}{A_S * RRF_T} \qquad (4\text{-}3)$$

Finally, the calculated masses of the compounds in a sample extract were corrected for recovery to produce measures of the actual sample masses. This correction was based upon the recoveries in that sample of the perdeuterated surrogates added at the time of sampler preparation. For naphthalene, the methylnaphthalenes, biphenyl, acenaphthylene, acenaphthene, and fluorene, the masses in a sample extract were divided by the fractional recovery of naphthalene-d_8. The sample masses of phenanthrene and anthracene were determined based upon the recoveries of phenanthrene-d_{10}. The fractional recoveries of pyrene-d_{10} were used to calculate the sample masses of the methylanthracenes, fluoranthene, pyrene, and chrysene.

The sample masses of naphthalene and biphenyl were corrected for breakthrough by adding the masses in the front and back sorbent sections of a sample if breakthrough in that sample was determined to be greater than one percent. If a compound had a sampler blank, the average blank value was subtracted from the sample mass to yield a final corrected sample mass.

Pooled Estimates of Variance

The quantitative results for individual compounds obtained from duplicate analyses of selected sample extracts were used to estimate analytical precisions following the procedure of Ku (1967). To combine several estimates of a common variance into a single estimate, the individually computed variances must be weighted by their respective degrees of freedom. The degrees of freedom for the pooled estimate is the sum of the degrees of freedom of the individual estimates. For the special case where there are k sets of duplicate measurements, the pooled variance, s_p^2, is estimated as:

$$s_p^2 = \frac{1}{2k}\sum_{i}^{k} d_i^2 \qquad (4\text{-}4)$$

where d_i is the difference between duplicate measurements. The pooled estimate of the standard deviation is the square root of the pooled variance. This pooled standard deviation has k degrees of freedom.

Propagation of Uncertainties

When a result is computed from several different variables, each of which is uncertain, the value of the result is uncertain. The most probable value of this uncertainty can be determined by propagating the uncertainties in the individual variables through the data reduction scheme at constant probability using root-sum-square addition (Kline and McClintock, 1953). The fundamental assumption required to justify the root-sum-square propagation is that each of the variables is independent.

The propagated uncertainty in the calculated sample mass of a typical gas-phase compound was estimated by PC-computer using a spreadsheet program. All of the variables used to calculate a sample mass, consisting of independent volume, weighed-mass and peak-area measurements, were combined in a single equation. Representative values were assigned to the variables, and the data were reduced yielding a representative sample mass. A new sample mass was then computed using the same data except that the value of one variable was increased by its uncertainty interval. The difference between the two results represents the uncertainty contribution associated with this variable. This calculation was repeated for each variable. The individual components were then added by the root-sum-square method to obtain an estimate of the uncertainty in the sample mass. In performing these calculations, the uncertainties associated with the various volume measurements were taken to be the manufactures' values for repeatability. The uncertainties associated with the weighed masses were conservatively estimated to be 0.1 percent. The 95-percent confidence intervals for the peak-area measurements were estimated to be +/- 6 percent based on experience with the instrumentation.

C. RESULTS

Relative Response Factors

Response factors for all compounds relative to the calibration standards are presented in Table IV-3. The mean values and 95-percent confidence intervals were calculated using all of the calibrations performed over the course of the study. These relative response factors are specific to the instrument is mass calibrated and with time as the instrument is operated.

Table IV-3. Relative response factors (RF) for analytes calculated from peak-area responses of analytes in standard mixtures.

COMPOUND	n	RELATIVE RF [a] MEAN	+/-95% CI	+/-95% CI MEAN (%)
Analysis 1				
n-Dodecane-d_{26}		1.00		
Naphthalene-d_8	6	2.14	0.49	22.7
Naphthalene	5	2.49	0.38	15.2
2-Methylnaphthalene	5	1.55	0.33	21.0
1-Methylnaphthalene	5	1.62	0.35	21.7
Biphenyl	4	1.99	0.23	11.3
Acenaphthylene	4	1.99	0.13	6.5
Acenaphthene	4	1.78	0.14	8.1
Fluorene	4	1.85	0.09	4.9
Analysis 2				
Anthracene-d_{10}		1.00		
Phenanthrene-d_{10}	5	0.96	0.01	0.8
Phenanthrene	5	1.29	0.19	14.8
Anthracene	5	1.30	0.18	13.7
2-Methylanathracene	5	0.74	0.06	7.9
9-Methylanathracene	5	0.77	0.08	10.7
Flouranthene	5	1.23	0.19	15.7
Pyrene-d_{10}	5	1.03	0.11	11.0
Pyrene	5	1.29	0.21	16.4
Chrysene	5	0.97	0.22	22.2

a) GCwas a 5790A series, (Hewlett Packard Co) connected via a direct capillary interface to a 5970B series Mass Selective Detector (Hewlett Packard Co.)

Other factors contributing to variations in the response factors are errors associated with the measurement of peak areas and with the preparation of primary and diluted standards. The individual response factors typically varied by 10-20 percent over the course of the study as estimated by the ratios of the 95-percent confidence intervals to the means. The effect of temporal variations in instrument sensitivity on the precision of the results was minimized by using response factors for calibration standards analyzed concurrently with groups of sample extracts (typically analyzed over a two-day period) to calculate the masses of compounds in those extracts.

Recovery of Perdeuterated Surrogates

The recoveries of the perdeuterated surrogate compounds, naphthalene-d_8 phenanthrene-d_{10} and pyrene-d_{10}, which were added to the samples at the time of sampler preparation were determined for each sample. These recoveries were used to calculate the masses of the target compounds in the samples from their respective masses measured in the sample extracts. The recoveries of the three compounds for the seven blank samples averaged 70 to 77 percent with 95-percent confidence intervals of +/-15 to 20 percent (Table IV-4). The recoveries of all three compounds were, therefore, approximately equal, indicating that the extraction and concentration methods performed equally well for the entire volatility range of the compounds of interest.

The recoveries of the three surrogates for the field samples are also presented in Table IV-4. These are shown separately for indoor and outdoor samples. The mean recoveries of naphthalene-d_8 were approximately equal and had similar variabilities for indoor, outdoor and blank samples. The mean recoveries of phenanthrene-d_{10} and pyrene-d_{10} for outdoor samples were also approximately equal to their respective recoveries for blank samples. The recoveries of these two compounds for the indoor samples were considerably more variable than the recovery of naphthalene-d_8 for these samples. In addition, many of the indoor samples had low apparent recoveries of phenanthrene-d_{10} and high apparent recoveries of pyrene-d_{10} relative to the outdoor and blank samples. An evaluation of the integrated ion-current chromatograms indicated that the peak-area responses of deuterated and nondeuterated phenanthrene and, to a lesser extent, deuterated and nondeuterated anthracene in the indoor samples were often lower than expected, while the peak-area responses of the other compounds which longer chromatographic retention times were within expected ranges.

In an attempt to identify the cause of the anomalous recoveries in indoor samples, several of the concentrated extracts were analyzed by GC-MS in continuous scanning mode (m/z 33-400) using a split injection (1:50) and the same GC oven temperature program used in the SIM analyses. An outdoor sample had no detectable peaks in the retention-time region of the phenanthrenes, while the two indoor samples analyzed had a peak that eluted at a similar retention time as the phenanthrenes. This peak was quite large in a sample collected

Table IV-4. Recoveries of perdeuterated surrogate compounds for indoor, outdoor and blank samples.

COMPOUND	RECOVERY								
	INDOOR			OUTDOOR			BLANK		
	n	Mean (%)	+/- 95% CI (%)	n	Mean (%)	+/- 95% CI (%)	n	Mean (%)	+/- 95% CI (%)
Naphthalene-d_8	19	72.3	18.6	15	68.9	19.3	7	75.6	20.4
Phenanthrene-d_{10}	19	49.8	48.4	15	70.9	20.7	7	70.5	15.6
Pyrene-d_{10}	18	135.5	70.3	15	73.3	26.9	7	77.4	17.6

in the Truckee residence for which the SIM analysis showed an obvious suppression of the phenanthrene peaks. The peak was relatively small in a sample collected in the Sacramento commercial building for which the SIM analysis appeared normal. The mass spectrum of this compound is shown in Figure IV-2. It was tentatively identified as n-butylbenzenesulfonamide, a plasticizer used with polyamides (nylons). The source of this compound has not been identified, but it was apparently present in such high abundance in many extracts of indoor samples to cause suppression of the ion current responses for the phenanthrenes and, to a lesser extent, for the anthracenes either due to chromatographic or MS detector effects.

Fortunately, the use of multiple surrogates permitted the effect of this background interference to be largely mitigated, at least for compounds other than phenanthrene and anthracene. This was accomplished by using the apparent recoveries of pyrene-d_{10} to calculate the sample masses of the methylanthracenes and the higher molecular weight compounds whose ion current responses appeared to be unaffected by the interference. Considerable uncertainty does exist, however, in the concentrations of phenanthrene and anthracene in the indoor samples as is discussed below.

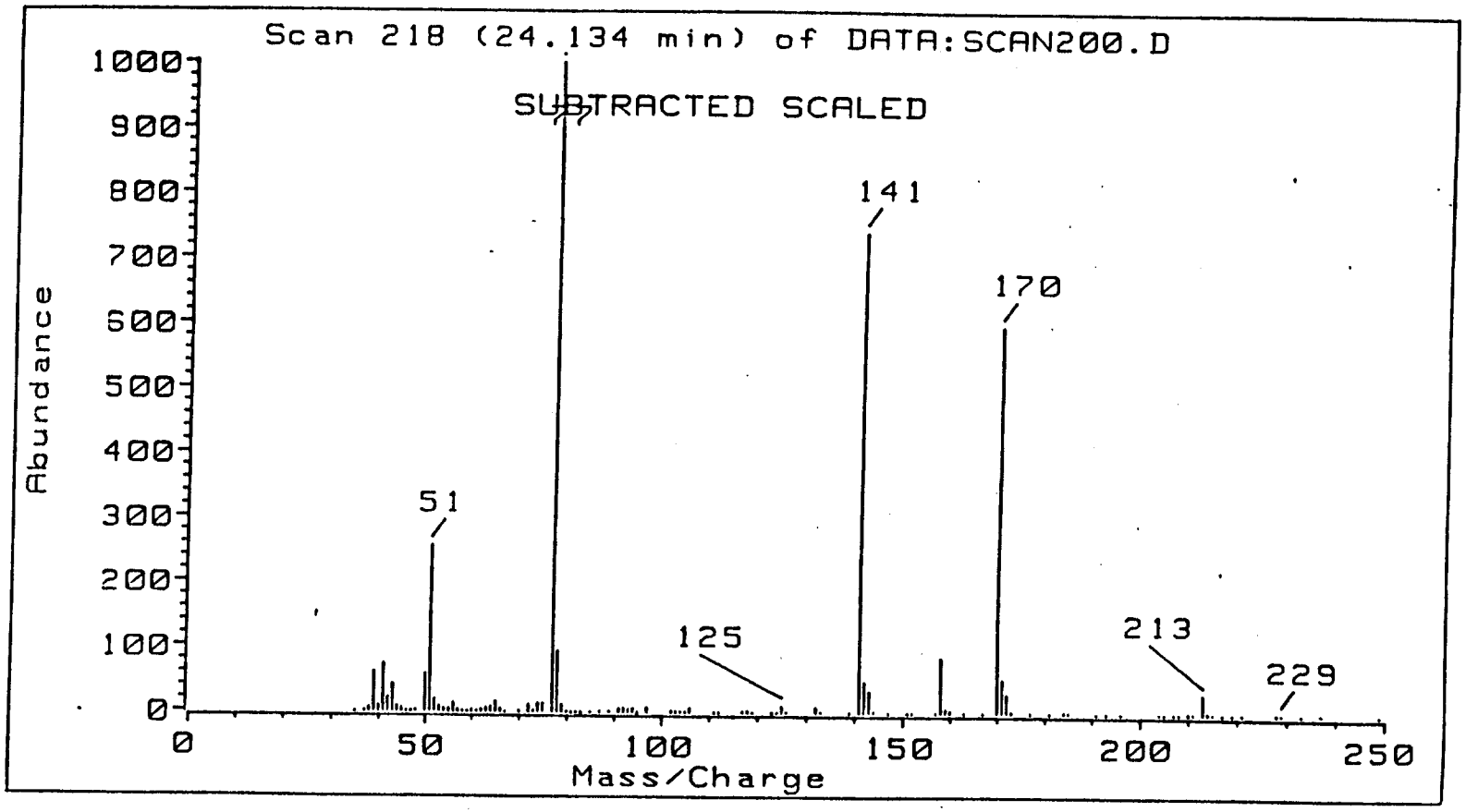


Figure IV-2. Mass spectrum of compound which interfered with analysis of the phenanthrenes in samples of indoor air. Tentatively identified as N-butylbenzenesulfonamide ($C_{10}H_{15}NO_2S$).

Sampler Collection Efficiency

The extracts of both the front and back sections of all of the sorbent samplers were analyzed for the most volatile gas-phase PAH to assess the collection efficiency of 2.5 g of XAD-4 resin using a sample volume of 25 m^3. Only three compounds, naphthalene-d_8, naphthalene and biphenyl, exhibited breakthrough from the front to the back section in excess of one percent in any sample. Mean breakthroughs of these compounds for the entire set of field samples are shown in Table IV-5. The mean breakthroughs of naphthalene-d_8 and naphthalene were less than one percent. Breakthrough of naphthalene-d_8 in excess of one percent was observed in only three samples. These samples were from among the first batch of twelve samplers that were prepared. The internal standards were added to these samplers by inserting the syringe needle into the sorbent bed through the inlet section of glass wool. As a result, it was difficult to control the depth at which the standards were added to the sorbent section. If the standards were inadvertently added deep within the section, this could have resulted in premature breakthrough. Subsequent samplers were prepared as described in the Methods section, and the problem of breakthrough of naphthalene-d_8 was eliminated. The collection efficiency for naphthalene on the first sorbent section was less than 99 percent in only eight of the samples with a maximum loss of ten percent. Five of these eight samples had the highest masses of this compound with a median value of 60 ug. The uncertainty in the amount of breakthrough of naphthalene for the sample set, as measured by the 95-percent confidence interval, was about +/-5 percent. This variation was due, in part, to the existence of a sorbent blank for this compound with its own associated uncertainty (see below). Biphenyl exhibited some breakthrough in almost all of the samples in which it was evaluated with an average loss from the front sorbent section of about four percent.

Table IV-5. Breakthrough losses of compounds from front section of sorbent samplers.

COMPOUND	n	BREAKTHROUGH MEAN (%)	+/-95% CI (%)
Naphthalene-d_8	34	0.6	3.3
Naphthalene	34	0.8	5.5
Biphenyl	18	3.7	6.2

Sampler Blank Values

Masses of compounds constituting a sampler blank were determined from analyses of the front and back sorbent sections of the blank samples. Six of the 14 compounds analyzed had measurable sorbent blanks. The mean blank values in nanograms for the six compounds are shown in Table 4-6. The uncertainties in the mean values are indicated by their 95-percent confidence intervals. The mean blank values were subtracted from the total calculated masses of the respective compounds in the field samples indicated in the table to yield blank-corrected sample masses. The blank values of naphthalene and the methylnaphthalenes were separated into two groups because the values for the final batch of field samplers that were prepared were distinctly higher than the values for the previous samplers. It is suspected that this was due to accidental overheating of the XAD-4 resin during the process used to remove residual solvent.

Table IV-6 additionally presents the blank values as percentages of their respective median masses in the 15 outdoor samples which, generally, had lower masses than the indoor samples. This relative comparison shows that only naphthalene and biphenyl had blank values which exceeded two percent of the typical masses in outdoor samples. The blank value for naphthalene in the final batch of samplers, which was excessive, was equal to one third of the typical masses in these samples. Uncertainty in the measurement of blank values which is high relative to their respective sample masses would significantly contribute to uncertainties in estimated amounts of breakthrough and in calculated sample masses. This is particularly true for naphthalene in the final batch of samplers. On the other hand, the blank values for the methylnaphthalenes, phenanthrene and fluoranthene were relatively low, and, therefore, uncertainty in their measurement would have little effect on the uncertainties of the calculated sample masses of these compounds.

Limits of Detection

The probability that the smallest discernible analytical signal can be measured and not be a random fluctuation of the blank signal is dependent upon how many standard deviation units the signal is away from the mean blank signal. Three standard deviation units of the blank signal are recommended so that the chance of error will be small (Winefordner and Long, 1983).

Table IV-6. Masses of compounds measured in blank samples.

COMPOUND	Lab Sample ID[a]	MASS n	MEAN (ng)	+/- 95% CI (ng)	MEAN/ MEDIAN OUTDOOR MASS[b] (%)
Naphthalene	1 - 35	9	374	139	5.5
	36 - 41	4	2268	871	33.5
2-Methylnaphthalene	1 - 35	9	12	7.7	0.3
	36 - 41	4	28	10	0.8
1-Methylnaphthalene	1 - 41	4	27	10	1.7
Biphenyl	1 - 41	12	139	109	5.7
Phenanthrene	1 - 41	7	5.0	5.4	1.2
Fluoranthene	1 - 41	4	1.5	0.6	2.2

[a] Pilot field study.
[b] Mean blank value as a percent of the median mass measured in 15 outdoor samples.

The limits of detection for the compounds with measurable blank values are shown in Table IV-7 using the convention of three standard deviations of the mean blank value. (These values are higher than the 95-percent confidence intervals shown in Table VI-6 which were calculated using the value of Student's t distribution for n-1 degrees of freedom.) The smallest masses of these compounds that were collected in 25 m^3 samples of indoor and outdoor air in this study were well in excess of these estimated limits of detection. Limits of detection for compounds with no measurable blank values were estimated using field sample results for the three compounds, 2- and 9-methylanthracene and chrysene, which had the lowest sample masses. Results for these compounds for which the peak-area responses exceeded but were no more than a factor of five greater than the peak-area reject of 10,000 units were selected from the subset of paired field samples. A total of six pairs of sample masses for the three compounds were, thus, obtained. A pooled estimate of variance was calculated for the six pairs as described in the Methods section. The limit of detection for the method, estimated as three times the pooled standard deviation of these measurements, is 1.5 ng for a sample volume of 25 m^3. This corresponds to a limit of

detection in concentration units of approximately 0.1 ng m^{-3}. Only the methylanthracenes and chrysene had values at or below the limit of detection in some of the field samples.

Table IV-7. Limits of detection (LOD) for compounds with measurable blank values.

COMPOUND	Lab Sample ID[a]	LOD 3 x STD[b] (ng)
Naphthalene	1 - 35	181
	36 - 41	821
2-Methylnaphthalene	1 - 35	10
	36 - 41	9.3
1-Methylnaphthalene	1 - 41	9.2
Biphenyl	1 - 41	149
Phenanthrene	1 - 41	6.6
Fluoranthene	1 - 41	0.5

[a]Pilot field study
[b] Limits of detection (LOD) estimated as 3 x standard deviation of mean blank value.

Precision

Four sample extracts were analyzed in duplicate to obtain estimates of the analytical precisions for individual compounds. Pooled variances were calculated for the compounds as described in the Methods section. Mean values for mass and 95-percent confidence intervals derived from the pooled variances are presented in Table IV-8. To calculate the confidence intervals, pooled standard deviations were multiplied by the value of Student's t distribution for four degrees of freedom (df = number of duplicate analyses). No results are given for biphenyl, acenaphthylene, acenaphthene or fluorene because they were analyzed in duplicate in only two of the four extracts. Chrysene and 9-methylanthracene are omitted because their values were below the limit of detection in two or more of the extracts. Relative precisions are also shown in the table. These were estimated by expressing the 95 percent confidence as percentages of the mean values. Analyses of naphthalene and the

methylnaphthalenes had a high level of precision (better than three percent). The analyses of the other compounds were less precise. Relatively poor precision was obtained for 2-methylanthracene at least, in part, because the masses of this compound in the extracts were low. Two of the four extracts were indoor samples in which there was an apparent interference in the analysis of phenanthrene and, to a lesser extent, anthracene (see above). This interference probably contributed to the imprecision in the analysis of these two compounds.

The uncertainty in the calculated sample masses was estimated by propagation of the uncertainties in the individual variables for a representative gas-phase compound with a sample mass of 1000 ng (equivalent to an air concentration of 40 ng/m^3). Typical values for volumes, weighed masses and peak-area responses were used in this analysis. The results of this analyses is presented in Table IV-8. The 95-percent confidence interval was estimated to be +/-200 ng (+/-20 percent). Of this total uncertainty, 97.5 percent was due to the uncertainty in the various peak-area responses with 65 percent due solely to the peak-area responses of the internal standard for quantitation in both the calibration standards and the sample extract. The overall precision of the method could be improved by either simplifying the data reduction scheme so that fewer peak areas were used in the calculation or by reducing the uncertainty of the peak-area responses. A factor of two improvement in the precision of the peak-area responses would result in about an equivalent improvement in the precision of the overall method.

Applicability to Other Compounds

An attempt was made to incorporate the analysis of the nitroarenes, 1- and 2-nitronaphthalene, into the analysis of the concentrated extracts for phenanthrene and the other higher molecular weight PAH (Analysis 2). The nitronaphthalenes are expected to be present in indoor and outdoor air in low concentrations. Concentrations of these compounds measured at outdoor locations in California were several nanograms per cubic meter or less (Atkinson et al., 1988). Unlike the PAH, for which the molecular ions are the most abundant ions in the spectra, the nitroarenes fragment into several relatively abundant ions. This has the effect of lowering the analytical sensitivity for these compounds.

Table IV-8. Perturbation analyses of variable uncertainties used to calculate the mass of gas phase PAH.

Measurement Parameter	Units	Value	Abs.[a] Variable Uncert.	Rel.[b] Variable Uncert.	Abs.[c] Variable Perturb.	%[d] of Total Perturb.
Vcic- Volume of primary standard mixture	(µL)	100	1	1	0.0001	0.2
Vra- Volume of recovery standard mixture added to sample	(µL)	10	0.1	1	0.0001	0.2
Vrc- Volume of recovery standard mixture for calib standard	(µL)	100	1	1	0.0001	0.2
Vqa- Volume of quantitation standard mixture added to sample	(µL)	10	0.1	1	0.0004	1.0
Vqc- Volume of quantitation standard mixture for calib. standard	(µL)	100	1	1	0.0004	0.9
Vfcl- Volume of flask used to prepare primary standard	(mL)	1.0E+5	100	0.1	0.0000	0.0
Mciw- Mass of compound weighed into flask for primary standard	(mg)	10000	1	0.01	0.0000	0.0
Acis- Area of compound in sample extract	(iu)	1.0E+6	60000	6	0.0036	8.6
Acic- Area of compound in calibration standard	(iu)	1.0E+6	60000	6	0.0032	7.6
Aqs- Area of quantitation standard in sample extract	(iu)	2.5E+7	1.5E+6	6	0.0121	28.8
Ars- Area of recovery standard in sample extract	(iu)	2.0E+7	1.2E+6	6	0.0036	8.6
Arc- Area of recovery standard in calibration sample	(iu)	2.0E+7	1.2E+6	6	0.0032	7.6
Aqc- Area of quantitation standard in calibration sample	(iu)	2.5E+7	1.5E+6	6	0.0153	36.3
Total absolute mass uncertainty [e]	(mg)	0.205				
Unperturbed mass value	(mg)	1				
Total relative mass uncertainty	%	20.5				

a) Absolute variable uncertainty - estimated 95% confidence limits for data used to compute the mass of PAH in a sample extract.
b) Relative variable uncertainty- calculated as the absolute variable uncertainty divided by the variable value..
c) Absolute variable perturbation - computed as the square of the difference between the mass computed with and without variable perturbation.
d) Percentage of total variable perturbation.
e)Total absolute mass uncertainty calculated as the square root of the sum of the individual variable perturbations.

The molecular ion at (m/z) 173, the fragment ion $[M-NO_2]^+$ at 127, and the fragment ion at 115 were selectively monitored for the nitronaphthalenes. The criterion was established that positive identification of a chromatographic peak as one of these compounds would require a correct relative retention time and the correct ratios of the two characteristic ions, 173 and 127.

All of the sample types, both indoor and outdoor, had compounds which eluted in the same retention-time region and which had some of the same fragment ions as the nitronaphthalenes. However, none had the correct ratios of ions 173 and 127. As a result, it was impossible to positively identify any of the chromatographic peaks as the nitronaphthalenes using this method.

D. DISCUSSION

Comparison with Other Methods

Concentrations of PAH in ambient outdoor air have been quantified by many studies with the majority of these studies focusing on PAH associated with particulate matter. Prior to the present study, only one method had been developed and validated for use in indoor environments (Wilson and Chuang, 1987; Chuang et al., 1987b; Wilson et al., 1989). The method described in the present study is similar to this previous method, although there are important distinctions.

In the method developed by Wilson, Chuang and co-workers, samples were collected using a quartz fiber filter backed up by a sorbent bed containing XAD-2 resin. The sample flowrate was 224 L/min collected for up to eight hours, producing a total volume of ~100 m^3. The amount of sorbent material was substantially higher than the amount used by the present method. Although the mass was not given, the volume of XAD-2 resin was 136 cm^3 versus about 6 cm^3 of XAD-4 resin. This large amount of sorbent material was presumably used to prevent breakthrough of the most volatile compounds at the relatively high sample flowrate and volume. The filter and the sorbent material were combined and Soxhlet extracted for 16 hours with CH_2Cl_2. Concentrated extracts were analyzed for PAH by positive chemical ionization GC-MS. The number of individual analyses needed to quantify the range of concentrations of PAH present in combined gas- and particulate-phase

samples was not given. Recoveries of perdeuterated surrogate compounds added to samplers prior to collection of samples of outdoor air were typically 80-90 percent.

The method for analysis of PAH in indoor environments described in the present study has several advantages over the previous method. These advantages are described as follows. The sample flowrate and volume are smaller and more appropriate for use in residences (see Chapter III for a detailed discussion of restrictions on these parameters). Substantially less sorbent material is used which significantly reduces the potential problem of contamination and simplifies sample-handling procedures. By extracting and analyzing filter and sorbent extracts separately, additional information about the partitioning of some compounds between gas- and particulate-phases is obtained. Finally, more laboratories have the capability to perform analyses by electron impact GC-MS than by chemical ionization techniques.

The problem of breakthrough losses of the most volatile PAH was dealt with differently in a method developed recently to quantify gas-phase PAH in outdoor air (Atkinson et al., 1988; Arey et al., 1989). Three different samplers and sample volumes were used for the gas-phase PAH. Two sizes of Tenax-GC cartridges were used. The smallest was packed with only 0.1 g of sorbent material, and the other was packed with 0.6 g of material. Sample flowrates were ~1 and ~10 L/min, respectively. After 12-hour sampling periods, the respective volumes were 0.6 and 6 m^3. The cartridges were eluted with small volumes of diethyl ether which were subsequently solvent exchanged to acetonitrile. Analysis was by electron impact GC-MS. The 0.6 m^3 sample was only analyzed for naphthalene. The 6 m^3 sample was analyzed for the methylnaphthalenes and for compounds with volatilities as low as phenanthrene. Breakthrough of naphthalene was apparent in the 6 m^3 samples. The less volatile gas-phase PAH were sampled using PUF plugs and a sample volume of 430 m^3 collected over 12 hours. The portion of the method employing Tenax-GC cartridges could be used to quantify the more volatile gas-phase PAH in indoor environments. It has the advantage of simplicity since the compounds are recovered by simple elution of the cartridges. The major disadvantages of the method are that separate flow regulation devices are required to collect samples with different volumes and that the less volatile gas-phase compounds are not adequately sampled.

Sample Contaminants and Artifacts

The sorbent material used in the present study, XAD-4 resin, contains organic compounds trapped within the resin structure which, if not adequately removed, can result in sample contamination and high blank values for some compounds. Hunt and Pangaro (1982) showed that the dominant contaminants have structural similarities to the structure of the polymer which suggests that their origin is attributable either to the manufacturing process or to the polymer itself. These investigators were able to extract significant quantities of naphthalene, the methylnaphthalenes and biphenyl, in addition to a number of other compounds, from uncleaned XAD-4 resin. Therefore, it is not surprising that naphthalene and biphenyl were the two compounds with the highest blank values in the present study. They suggested sequential extraction with methanol and CH_2Cl_2 as described in the Methods section, with repetition as needed to achieve acceptable blank values. They also suggested measuring total extractable organic compounds within a boiling point range of 100-300°C as an acceptance criteria for the cleaning procedure.

The high blank value for naphthalene and the increased blank values for the methylnaphthalenes in the last batch of samplers that were prepared for use in this study can probably be explained by thermal decomposition of the resin since this resin was accidentally overheated while removing residual solvent. The acceptable results for the other blank samples suggest that significant decomposition can be prevented by carefully controlling the temperature at 40°C during this procedure. To eliminate the possibility of excessive blank values for naphthalene and other compounds, it should be determined if the resin is acceptably clean prior to preparation of the samplers. This could be accomplished by analyzing the cleaned resin for naphthalene or for total extractable organic compounds as suggested above. For a large-scale study, preparation of large batches of cleaned resin would save time and minimize the number of blank samples to be analyzed. Since it is likely that the cleaned resin would need to be stored for some time, the adequacy of storage procedures needs to be evaluated.

Decomposition products or artifacts can be formed during the collection of gas-phase organic compounds. Indoor concentrations of reactive gases such as nitrogen oxides and sulfur dioxide can be elevated over outdoor concentrations where combustion sources are present. In some circumstances, indoor concentrations of ozone may also be elevated. Even though sorbent materials, such as XAD-4 resin, do not concentrate these inorganic gases,

chemical reactions may occur within the sorbent bed. Only limited research has been conducted on the decomposition products and artifacts resulting from the use of sorbent materials. By using perdeuterated compounds spiked onto sampling cartridges containing Tenax-GC and exposing the cartridges to reactive gases, Pellizzari et al. (1984) clearly demonstrated that oxidants in ambient air can produce reaction products both from the sorbent and from analytes concentrated on the sorbent. Hanson et al. (1981) studied decomposition products of XAD-2 resin formed by reaction with nitrogen dioxide (NO_2) and nitric oxide (NO). Greater decomposition was found with NO_2 than with NO. Most of the XAD-2 decomposition products were oxygenated and many would be expected to have chromatographic retention times near those of gas-phase PAH.

It is suspected that the compound which interfered with the analysis of phenanthrene and anthracene and which was tentatively identified as n-butylbenzenesulfonamide was a contaminant associated with some aspect of sample collection. However, since it was apparently not present in outdoor samples, the source probably was external to the sorbent sampler and not the XAD-4 resin. There is also a possibility that the compound was produced by reaction of a component of the sampler with an inorganic gas present in some of the indoor environments at elevated concentrations. Research is needed to identify and eliminate the source of this compound. If it is found to be a reaction product, it may be necessary to inhibit the chemical reaction. Pellizzari et al. (1984) used sodium thiosulfate impregnated glass fiber filters to quantitatively decompose ozone prior to collection of samples on Tenax-GC cartridges.

Vapor-Particle Partitioning

The PAH exist in air in both the vapor and particle phases. The most common sampling technique, which was also employed by this study, is to pull air through a filter which retains suspended particles followed by a solid sorbent to collect vapors. The ratio between the filter-collected and the sorbent-collected concentrations provides a measure of the partitioning between the two phases. However, the ratio may not truly represent the distribution in the air because of the possibility of either vaporization or condensation during the sampling process. The ratio may overestimate the amount in the vapor phase due to "blowoff" losses of the compounds from particles on the filters. Alternately, the particle mass on the filter may act as a sorbent and artificially remove compounds from the vapor phase.

The volatility of the various PAH as expressed by their liquid-phase vapor pressures is the main factor governing their adsorption to urban air particulate matter (Bidleman et al., 1986). Studies have shown that PAH with two to four rings are predominantly in the vapor phase and that the less volatile of these compounds partition between the two phases. The relative amount of a compound found in the vapor phase will increase with increasing temperature (Yamasaki et al., 1982). This temperature dependence has implications for studies of indoor air quality. The apparent partitioning of the least volatile compounds collected by the sorbent sampler may be significantly affected by temperature differences such as are likely to occur between indoor and outdoor sampling locations. Therefore, it is important to measure both particulate- and gas-phase concentrations for compounds like pyrene and chrysene which typically occur in both phases. In addition, sampling temperatures should be carefully recorded because these may help to explain observed variations in concentrations. Finally, if the sampling apparatus experiences a large rise in temperature during the collection period, compounds may be lost from the particles already collected on the filter, and the gas-phase concentrations may be artificially increased. Protection of outdoor samplers from exposure to direct sunlight is, therefore, essential. The gas-particle partitioning of fluoranthene, pyrene and chrysene that was observed in the pilot field study is discussed in Chapter VI.

Sample Cleanup

The number of sample processing steps in the method described in this study was purposefully keep to a minimum since the more steps that are involved the greater are the chances of loss of the analytes and of contamination. In addition, the cost of added processing is appreciable because sample preparation is labor intensive. The method does not employ sample cleanup procedures and is suitable for the analysis of gas-phase PAH. However, the nitroarenes, 1- and 2-nitronaphthalene, could not be detected even though they were expected to be present in some of the samples in quantities in excess of the detection limits of the method.

Studies which have attempted to measure nitroarenes in outdoor air have generally employed much larger sample volumes and have used extensive sample cleanup procedures to separate the compounds of interest from complex matrices of compounds present at much higher concentrations. In the previously cited method, large-volume samples (430

m^3) were collected using PUF (Atkinson et al., 1988: Arey et al., 1989). The PUF plugs were solvent extracted and the extracts concentrated with procedures similar to those used in this study for the sorbent. The extracts were then fractionated by high-performance liquid chromatography using a silica column and mobile-phase program that employed hexane, CH_2Cl_2 and acetonitrile. A nitroarene-containing fraction was identified, collected, concentrated and analyzed by electron impact GC-MS.

An alternative strategy for the analysis of the nitroarenes that would not require extensive sample cleanup is the use of a selective but more sensitive analytical technique. Wilson and Chuang (1987) quantified nitroarenes in unfractionated extracts obtained in a pilot study of indoor quality using negative chemical ionization GC-MS which is more sensitive than electron impact GC-MS. However, they apparently also had to employ sample volumes of 100 m^3 collected over eight hours to obtain the necessary sensitivity.

These studies suggest that different techniques, such as sample cleanup or negative chemical ionization GC-MS, are required to analyze nitroarenes in samples of indoor air. It also appears that it may be necessary to use larger sample volumes. Since sample flowrates and collection times are restricted in indoor environments, it may be necessary to composite a number of individual samples to obtain adequate volumes.

E. RECOMMENDATIONS

This study successfully accomplished its objective of developing and validating a sampling and analytical method for gas-phase PAH for use in a large-scale study of indoor exposures to these compounds. There are, however, several unresolved questions which require additional research. Also, there are ways in which the method either can be improved or made more practical for use in a large-scale study. Finally, experience with the method suggests several quality assurance procedures that should be adopted to help ensure the validity of the data for such a study. These issues are addressed by the following recommendations:

1. Prepare clean XAD-4 resin in large batches and measure the blank value for naphthalene or total extractable hydrocarbons prior to preparing sorbent samplers to assure that blank

values are at an acceptable level. In addition, storage procedures for clean XAD-4 resin need to be evaluated.

2. Identify the source of the compound which interfered with the analysis of phenanthrene and anthracene in many of the samples of indoor air and, if it is a contaminant or an artifact, make the necessary modifications to eliminate its source.

3. Incorporate more internal standards and perdeuterated compounds into the method. Addition of an internal standard which elutes near the end of the first analysis for the most volatile compounds would improve the precisions of the relative retention-time indices for these compounds. The precisions of the quantitative results for individual compounds should be improved by the addition of the corresponding or closely related perdeuterated surrogate compounds either to the samplers or to the sample extracts.

4. Eliminate the back section of the sorbent sampler. The breakthrough losses of the most volatile compounds, naphthalene and biphenyl, from 2.5 g of XAD-4 were low even in indoor environments with high concentrations of these compounds. Therefore, deletion of the back section would have little effect on the quality of the results and would represent a significant savings in the time required for sample analysis. The number of extractions and concentrations would be decreased by one half, and the number of analyses would be decreased by one third. An additional advantage is that the pressure drop across the sampler would be reduced. This should further reduce potential breakthrough losses and possibly allow the use of a smaller sample pump.

5. Use data-base management software to perform quality control functions and organize the data. Timely quality control is particularly important for a large-scale survey consisting of many samples. Utilization of appropriate data-base management software would greatly reduce the effort required to perform statistical quality control, manipulate the data and prepare reports. A high level of automation should also reduce operator errors and make it easier to perform data audits.

6. Require any laboratory intending to participate in a large-scale study to demonstrate its ability to perform the analyses with acceptable precision and limits of detection prior to initiating the study. This preliminary assessment could be accomplished by the analysis of a number of replicate samples collected from a single location, possibly outdoors.

Intercomparison studies conducted among several laboratories would provide an additional measure of uncertainty which was not evaluated in this study.

V. DEVELOPMENT OF A SEMI-MICRO ANALYTICAL METHOD FOR PARTICULATE POLYCYCLIC AROMATIC HYDROCARBONS

A. INTRODUCTION

The purpose of this phase of the research was to develop an extraction and analysis method for PAH in 25 m^3 - samples of airborne particulate matter collected in buildings. The method had to be applicable for both buildings with no combustion sources (low PAH levels) and buildings with heavy cigarette smoking and other combustion sources (high PAH levels). Additional requirements for an indoor air analytical method include good recoveries of PAH from the particulate matter, minimal sample preparation and clean-up, high specificity for individual PAH and good precision of analysis. The method also had to be suitable for routine analysis of large numbers of samples which might be collected in a large field study.

A secondary purpose of this research was to apply state-of-the-art high pressure liquid chromatography (HPLC) technology (with programmable fluorescence detection and data reduction software) to analysis of PAH. HPLC with fluorescence detection is as much as 1000 times more sensitive than gas chromatography-mass spectrometry for most of the compounds of interest. Thus, an HPLC/fluorescence method of analysis was developed using state-of-the-art HPLC equipment and computer software. The selectivity of the fluorescence detection should make it possible to streamline sample preparation and use no cleanup steps before HPLC analysis for parent PAH compounds.

B. METHODS

Standards and Solvents

A standard mixture of 16 polycyclic aromatic hydrocarbon standards in acetonitrile, Standard Reference Material (SRM) 1647a, was obtained from the National Institute of Standards and Technology [NIST, formerly the National Bureau of Standards (NBS)]. Additional PAH standards were obtained from Aldrich Chemical Co.; from the Commission of European Communities, Community Bureau of Reference (benzofluoranthenes); from the Chemical Repository, Midwest Research Institute

(dibenzopyrenes and 5-methylchrysene) and from Pfaltz and Bauer, Inc. (retene). Perdeuterated fluoranthene and benzo(e)pyrene, used as internal standards, were obtained from MSD Isotopes, Inc. The retene (1-methyl-7-isopropylphenanthrene) was purified by preparative HPLC on a C18 reverse phase column using solvent mixtures of acetonitrile, tetrahydrofuran and water. NBS SRM No. 1649 (Urban particulate matter - organics) was used as a positive control for PAH analyses. Two stock PAH standards were prepared and diluted to various concentrations to prepare HPLC calibrations for use with both high and low wavelength fluorescence programs. Standard A stock solution contained the following PAH, with approximate concentrations in ng/ml: naphthalene - 400, acenaphthylene - 320; acenaphthene - 390, fluorene - 96, phenanthrene - 68, anthracene - 15, fluoranthene-d_{10} - 115, fluoranthene - 150, pyrene - 160, benz(a)anthracene - 75, chrysene - 70, cyclopenta(cd)pyrene - 500, 5-methylchrysene - 100, benzo(e)pyrene-d_{12} - 230, benzo(e)pyrene - 260, benzo(b)fluoranthene - 80, benzo(k)fluoranthene - 90, benzo(a)pyrene - 100, dibenzo(a,l)pyrene - 100, dibenzo(a,h)anthracene - 75, benzo(ghi)perylene - 75, indeno(1,2,3-cd)pyrene - 85, dibenzo(ae)pyrene - 40, coronene - 250, dibenzo(ai)pyrene - 35, and dibenzo(ah)pyrene - 50. Standard B stock solution contained the following PAH, with concentration in ng/ml: phenanthrene - 80, anthracene - 50, fluoranthene-d_{10} - 115, fluoranthene - 80, pyrene - 80, chrysene - 70, retene - 816, benzo(e)pyrene-d_{12} - 170, benzo(j)fluoranthene - 700, perylene - 220, dibenz(ac)anthracene - 360, benzo(a)pyrene - 90, dibenzo(a,l)pyrene - 50, dibenzo(a,h)anthracene - 150, benzo(ghi)perylene - 160, indeno(1,2,3-cd)pyrene - 200, dibenzo(ae)pyrene - 40, coronene - 430, dibenzo(ai)pyrene - 35, and dibenzo(ah)pyrene - 50. A standard solution containing all of the compounds was used to set chromatographic conditions at the beginning of each analysis day.

All organic solvents used were Burdick and Jackson, Inc. distilled-in-glass grade, suitable for HPLC analysis. Before use for HPLC analysis, prepared solvent mixtures were filtered through 0.5 micron pore size Teflon filters under vacuum. All glassware was washed with alcoholic KOH solution and rinsed in deionized water. Immediately prior to use, all glassware was rinsed with distilled-in-glass solvent.

Filter Preparation and Handling

Teflon-coated glass fiber filters (Pallflex TX40HI20WW) were cut into 4.7 cm diameter disks to fit the Swin-lok polycarbonate filter holders. The filters were pre-extracted by

sonication in dichloromethane or benzene for 30 minutes and then for another 30 minutes in methanol. After drying, the filters were weighed, placed in clean Petri dishes and labelled. The filters were loaded into the filter holders less than 48 hours before sampling. Upon return from the field, the filters were weighed and then stored in the freezer at -30°C, in the dark in small Petri dishes. Loaded filters were protected from the light at all times. The sampling apparatus is described in detail in Chapter III.

The sampling plan for the field portion of the study is presented in detail in Chapter VI. In brief, 35 field samples and 7 field blank were collected and analyzed. Nineteen of the field samples were collected in houses and office buildings, some of which contained combustion emissions from cigarette smoke, gas ranges and wood stoves. The remaining field samples were collected outdoors near the buildings while the indoor samples were being collected. The sample set contained 11 duplicate samples, 7 pairs collected indoors and 4 pairs collected outdoors.

Estimation of Optical Attenuation

Before analysis each filter was examined visually to assess homogeneity of loading. The color and odor were recorded. The optical attenuation (Rosen et al., 1978) 'blackness' of each filter was estimated using a Kodak Reflectance Scale. Attenuation is 100 times the optical density shown on or interpolated from the scale. Samples were extracted and analyzed in order of decreasing attenuation, as discussed in the section on HPLC analysis.

Solvent Extraction and Concentration of Extract

The analytical method developed for particulate PAH in this investigation is shown schematically in Figure V-1. The loaded filter was carefully cut in half. One-half of the filter was cut on a clean aluminum foil surface using a cleaned and solvent-rinsed scalpel. The pieces were transferred with cleaned tweezers to a 5 ml conical-bottom vial with a Teflon-lined cap. Methanol (2.0 ml) and benzene (2.0 ml) and 5.8 ng (10 ul) of fluoranthene-d_{10} were then added to the vial. The fluoranthene-d_{10} was used as an internal standard to trace recoveries of the more volatile PAH through the filtration and concentration steps of the analysis. The vial was then capped and placed in a pre-heated sonicator bath and sonicated for 15 minutes. Bath temperature was maintained at 35°C.

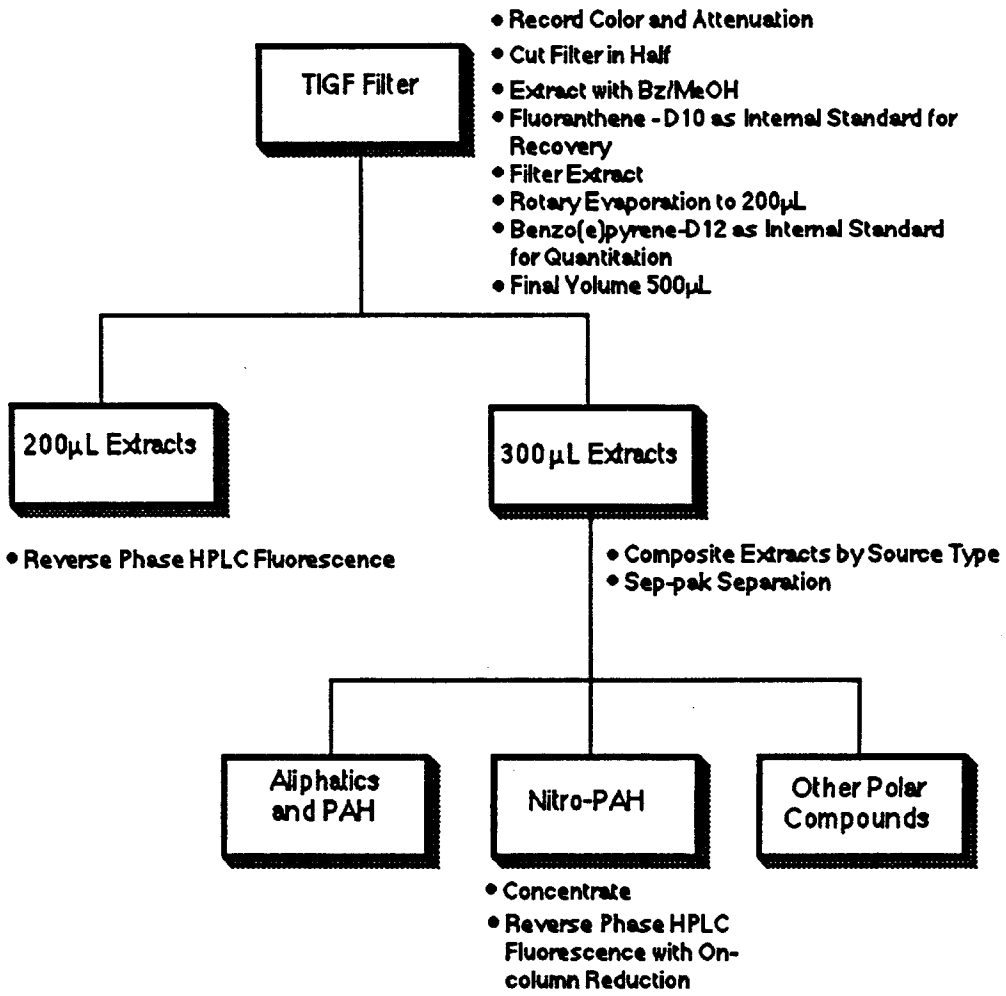


Figure V-1. Schematic diagram of the separation and analysis method for PAH and nitro-PAH in filter samples of particulate matter.

The extract was removed and the sonication repeated with fresh methanol and benzene. In some experiments dichloromethane extracts were prepared. Other experiments used micro-Soxhlet extraction for eight hours in either dichloromethane or a benzene-methanol mixture (1:1, v:v).

The combined extracts were filtered under gentle vacuum through a 47 mm diameter, unlaminated Teflon filter (Millipore Corporation type FHUP, 0.5 micron pore size) using a Millipore all glass micro-filtration apparatus with a 15-ml capacity glass funnel and a 125-ml glass filter flask. The filtrate was collected in an 8-ml amber vial supported inside the filter flask. After filtration the apparatus was rinsed with 2 ml of benzene-methanol (1:1 v:v). The extract and rinsings were transferred to a 30 ml pear-shaped flask with a ground glass neck and stoppered. The extract was reduced in volume to about 200 µl using a rotary evaporator with a water bath held at 38°C. The extract was not allowed to go to dryness. The reduced extract was taken up in a 500 µl gas-tight glass and Teflon syringe, the volume was measured and recorded, and the extract transferred to the same amber vial used previously to collect the filtrate. 100 µl of extraction solvent was carefully added to the flask to rinse the sides and the flask was gently swirled. The rinse was added to the amber vial with the extract; the rinse step was then repeated. An additional 100 µl of solvent was used to rinse the flask and the third rinse was transferred to the amber vial. We then added 38 ng (13 µl) of benzo(e)pyrene-d_{12} to the extract as an internal standard for HPLC quantitation. The extract was then taken up again in the 500 µl syringe and the air ejected. Additional solvent, needed to bring the total volume to about 490 µl was taken up in the syringe. The volume of the solution was measured and recorded, the extract transferred to the amber vial and capped tightly with a Teflon-lined cap, and the vial stored in the freezer at -30°C until analysis. The syringe was cleaned thoroughly before processing the next sample.

Preparation of NBS SRM-1649 for extraction

Six 3 mg aliquots of Standard Reference Material SRM-1649 (urban particulate material-organics, obtained from the National Institute of Standards and Technology, Washington DC) were weighed onto small tared aluminum pans using a Cahn microbalance Model 25. The particles were transferred to a 47 mm diameter unlaminated Teflon filter (0.5 micron pore size, from Millipore Corporation, type FHUP). The filter was wrapped over the particles to make a small package, about 1 cm by 1 cm, and tied loosely with cleaned

narrow gauge nichrome wire. The particles were extracted 3 times in 4 ml benzene-methanol (50:50, v:v) for 15 min at 35° C as described above for filter samples. Three additional 3 mg aliquots were prepared by sonication in dichloromethane and micro-Soxhlet extraction in dichloromethane or a benzene-methanol mixture (1:1, v:v).

HPLC Analysis

Analyses were performed on a Hewlett-Packard Model 1090M high pressure liquid chromatograph with a DR5 solvent delivery system, an HP Model 1046A programmable fluorescence detector with a xenon lamp, and HP Model 799994A LC Workstation software. Aliquots of the extract were chromatographed on a VYDAC 201TP5215 C18 reverse-phase micro bore column, 2.1 mm I.D. x 15 cm, using the solvent program presented in Table V-1. Solvent A consisted of a 47.5:2.5:50 (v:v:v) mixture of acetonitrile, tetrahydrofuran and water, and solvent B was a 95:5 (v:v) mixture of acetonitrile and tetrahydrofuran. Initial flow through the column was 0.5 ml-min^{-1}. The use of the microbore column greatly reduced the volume of waste solvent generated and allowed analysis and equilibration to initial conditions at 40 minute intervals. An external refrigerated bath with a circulating pump was used to maintain the column compartment at 23°C. Table V-2 presents the retention times for the 22 particulate PAH compounds for this solvent program and the two fluorescence wavelength programs. Two different fluorescence wavelength programs (and injections) were used to maximize sensitivity and selectivity for various PAH and to provide data needed to mathematically determine co-eluting PAH. The sensitivities (peak height per nanogram) for each PAH for both fluorescence programs are also given in Table V-2. Peak heights rather than peak areas were measured because they were more reproducible and their use minimized any problems with peak resolution in the samples caused by the software-defined integration limits.

Samples of similar optical attenuation or blackness were analyzed in groups, using standards with the same concentration range, and starting with samples having the highest attenuation values. Previous work by Gundel et al. (1982) showed that PAH concentration was approximately proportional to attenuation for particles collected outdoors. Samples with the heaviest apparent loadings were processed first to enable the analysts to acquire experience in identifying PAH peaks and quantifying them before tackling very lightly loaded samples where the task was expected to be more difficult. Each analysis day began with injection of a mixed standard which contained all the compounds to be determined.

Table V-1. Gradient elution pump control program for HP 1090M liquid chromatograph.

Time [a] (minutes)	Flow rate (mL/min)	Pump 1 (%)	Pump 2 (%)	Function
0.01	0.50	100.0	0.0	Slow increase in elution strength.
1.00	0.50	99.8	0.2	Concave gradient (similar to Waters curve 7)
2.00	0.50	99.1	0.9	
3.00	0.50	97.7	2.3	
4.00	0.50	95.7	4.3	
5.00	0.50	93.0	7.0	
6.00	0.50	89.7	10.3	
7.00	0.50	85.5	14.5	
8.00	0.50	80.6	19.4	
9.00	0.50	74.6	25.4	
10.00	0.50	68.3	31.7	Linear solvent gradient
20.00	0.50	0.0	100.0	
21.00	0.50			Increase flow rate for elution of high MW PAH
26.00	1.00			Decrease flow rate to avoid high pressure
26.05	0.75			
26.10	0.75	0.0	100.0	Reverse solvent composition
28.00	0.75	100.0	0.0	Equilibrate column at initial solvent composition
29.95	0.75			Increase flow rate
32.00	0.85			
38.00	0.85			Decrease flow rate to initial conditions
40.00	0.50			Ready for the next sample

a) Solvent composition and flow rate change linearly between program steps.

PAH	RT Time min	Change min	LOW WAVELENGTH[b] Excit nm	Emis nm	Sensit. pk ht/ng	LOW WAVELENGTH[a] Excit nm	Emis nm	Sensit. pk ht/ng	Quant. Code[c]
Phenanthrene	7.50		230	420	0.88	250	370	2.75	H
Anthracene	8.70	9.0			2.10			8.24	H
Fluoranthene-d_{10}	9.60		230	450	2.46	250	375	0.00	L
Fluoranthene	10.00				2.73			0.00	L
Pyrene	10.70	11.2			0.66			0.84	H
Benzo(a)anthracene	13.60		235	390	3.62	260	365	0.59	L
Chrysene	14.00				1.22			3.85	H
Cyclopenta(cd)pyrene	14.10	14.4			d			0.00	N
5-Methylchrysene	14.80		230	425	0.42	235	375	0.87	C
Retene	14.80				0.01			0.08	C
Benzo(e)pyrene-d_{12}	15.20				0.58			0.49	IS
Benzo(e)pyrene	15.60				0.69			0.50	A
Benzo(j)fluoranthene	15.60				0.00			0.00	N
Benzo(b)fluoranthene	16.10				4.65			0.22	L
Perylene	16.10	16.5			5.05			0.00	N
Benzo(k)fluoranthene	17.00		230	425	26.68	280	370	0.06	C
Dibenzo(ac)anthracene	17.00				0.78			3.26	C
Benzo(a)pyrene	17.40	17.9			4.90			0.19	L
Dibenzo(al)pyrene	18.50		245	485	0.94	290	450	1.80	H
Dibenzo(ah)anthracene	18.70				0.16			0.98	H
Benzo(ghi)perylene	19.30				0.13			0.62	H
Indeno(cd)pyrene	19.80	20.2			1.24			0.18	L
Dibenzo(ae)pyrene	20.70	21.8	230	404	5.14	290	450	0.93	L
Coronene	22.50	23.0	230	445	0.23	290	450	0.48	H
Dibenzo(ai)pyrene	24.20	24.5	230	440	4.96	290	450	1.76	L
Dibenzo(ah)pyrene	25.30		230	455	2.22	290	450	4.28	H

a.) Low wavelength sensitivity data from 4 October 1989. Ex and Em are excitation and emission wavelengths, respectively.
b.) High wavelength sensitivity data from 15 September 1989.
c.) Quantitation code: H= high wavelength; L= low wavelength; C= coeluting pair calculation; A = Average; N = not quantified at these wavelengths; IS = internal standard.
d.) Cyclopenta(cd)pyrene fluoresces at these wavelengths but its sensitivity was not determined.

Table V-2. Separation of PAH using wavelength-programmed fluorescence detection. Retention times, Detector wavelength settings and sensitivities of PAH.

No fluorescence programming was used (Excitation wavelength = 250 nm, all emitted light collected). This chromatogram was immediately used to assign wavelength change times for subsequent analyses using one of the fluorescence programs. Analysis order: Standard A (at appropriate dilution), three sample extracts, standard B, three sample extracts, standard A, and so on, for a total of 14 injections (9 extracts) per nine-hour day. During the equilibration period after every analysis the chromatogram was inspected, and adjustments were made to the wavelength change times. These adjustments were necessary to correct for small systematic drift in retention times (about 1 sec per chromatogram) which may have been caused by small temperature changes or other factors. The next day the same group of standards and samples was analyzed using the other fluorescence program.

Data Reduction

Hewlett-Packard Chemstation foreground-background software was used to integrate already-acquired chromatograms while analyses continued. Chromatogram fluorescence intensities were multiplied by 20, smoothed using a 15 point average and integrated after careful baseline assignment. Peak heights were printed. The sample response to the internal standard benzo(e)pyrene-d_{12} was used to correct for any variation in solution or injection volume between analyses. The response of standards was used to calculate concentrations of PAH in the extracts in pg/ul. Each analysis yielded two ASCII report files (based on standards A and B which bracketed each sample analysis). Terminal emulation software (Optimation Optitalk) transferred the ASCII files to IBM PC-compatible format using null modem software. Final data reduction steps included using SuperCalc 5 (Computer Associates) spreadsheet software to convert the ASCII files to spreadsheet-compatible form for further manipulation. The concentration of each PAH in ng/m^3 was calculated from:

$$C_a = \frac{C_s \cdot V_e}{V_a \cdot f} \qquad (1)$$

where:

C_a = concentration of a given PAH in air in ng/m^3
C_s = concentration in the extract solution in ng/ml
V_e = volume of the extract solution in ml

V_a = air volume of the sample in m^3

f = fraction of the filter which was extracted.

When data reduction was complete for each extract there were four spreadsheet files with the basic chromatographic data and one summary file for the final reported PAH concentrations. For compounds present in both standards A and B, two measurements resulted from calibration with the standards which were injected prior to and after the sample analysis. These two values were averaged for the final summary table. (The Chemstation calibration software could not be used for this.) Table V-2 lists the excitation and emission conditions used to quantitate each compound; i.e., high or low wavelength program or coeluting pair calculation.

C. RESULTS AND DISCUSSION

HPLC Analysis Method Development

The goal of method development was separation and identification of 26 PAH compounds, including 2 internal standards, from the sample matrix by HPLC. Separation depended on programmed gradient elution, with both solvent composition and flow variation, at constant column temperature. Table V-1 presents the gradient elution pump control program which we developed.

The region of gradual change in solvent composition (up to 10 min) gave good separation of semi-volatile PAH [napthalene through pyrene] and the majority of the particulate PAH [benzo(a)anthracene through indeno(1,2,3-c,d)pyrene] eluted as the solvent composition changed linearly from 10 to 20 minutes. The region of linear increase in flow rate caused elution of the most strongly retained compounds [dibenzo(a,e)pyrene through dibenzo(a,h)pyrene] at approximately equal intervals with minimal tailing. The experimental steps necessary to develop this program included:

a) constructing a trial gradient elution program based on earlier work with different HPLC equipment (Gundel et al., 1982 and Daisey et al., 1989a,b)

b) determining elution order for the compounds of interest using solutions of standard compounds

c) adjusting the gradient elution program (initial solvent composition, gradient shape, time and flow rate for each step), and

d) determining factors which control reproducibility of retention times.

Constant column temperature and sufficient equilibration time were crucial factors in control of retention times to within 1.5 sec; even so, during the analytical day a systematic drift of about one second per chromatogram was observed for benzo(a)pyrene.

Selective Fluorescence Detection.

Optimal fluorescence wavelengths were determined in a two step procedure. First, a standard mixture containing all the compounds of interest was analyzed using excitation wavelengths from 210 to 300 nm at 5 nm intervals. The detector monochrometer was set to zero order to collect all emitted light above 305 nm. Peak areas were compared to find the best excitation wavelengths for each compound. In subsequent analyses fluorescence spectra were obtained by isolating each compound in the detector (by stopping the solvent flow) and scanning the emission spectrum at one or two of the best excitation wavelengths to find wavelengths of maximum fluorescence.

Optimally, in the analysis of indoor air extracts or standards, each compound would be detected using excitation and emission wavelengths which give maximum response. These wavelength combinations would be programmed into the detector control, as a function of time, to adjust as each compound eluted from the column. In practice, it was not possible to adjust the detector for each compound and still keep the total analysis time to 40 min per sample, because the detector required several seconds to stabilize after adjustment and because of the limit of about 1.5 sec on reproducibility of retention times. Furthermore, if the adjustment occured as a peak was eluting the baseline of the chromatogram shifted and no quantitation was possible. This limited some of the detector adjustment times to breaks in the chromatogram, i.e., between groups of closely-eluting compounds.

Some compounds co-eluted. To detect both compounds fluorescence must be determined at two different wavelength settings. When possible, detection conditions were found so that one member of the pair could be 'turned on' at one set of wavelengths while the other was 'turned off'. For other co-eluting pairs with similar excitation and emission maxima, total

fluorescence at each of two wavelength settings were apportioned to each compound using simultaneous equations.

Table V-2 presents the two fluorescence detector control programs we devised and the wavelength combinations of maximum sensitivity for each compound. The table presents the compounds in retention order, starting with the earliest to elute. Wavelength combinations used for quantitation are indicated in the column labelled 'Quant Code.' The compounds are grouped according to the wavelength settings within each fluorescence program. The two fluorescence programs are identified as 'low' and 'high' to reflect the fact that all the lower excitation wavelength settings are grouped together in one program, and the higher settings are in the other program. This was done to allow the fluorescence detector to reset faster and reduce background shifts. Sensitivities are listed in units of peak height per nanogram for two analyses of the same standard solutions. (Because of day-to-day variation of the observed sensitivities and dependence on the detector gain other investigators should not use this table for absolute values.) The final choice of excitation and emission wavelengths for the two programs was based on meeting these criteria as well as possible for each group of compounds:

1) Wavelength settings must change at gaps in elution of groups of compounds.

2) The internal standard for quantitation, benzo(e)pyrene-d_{12}, should have good sensitivity in each program.

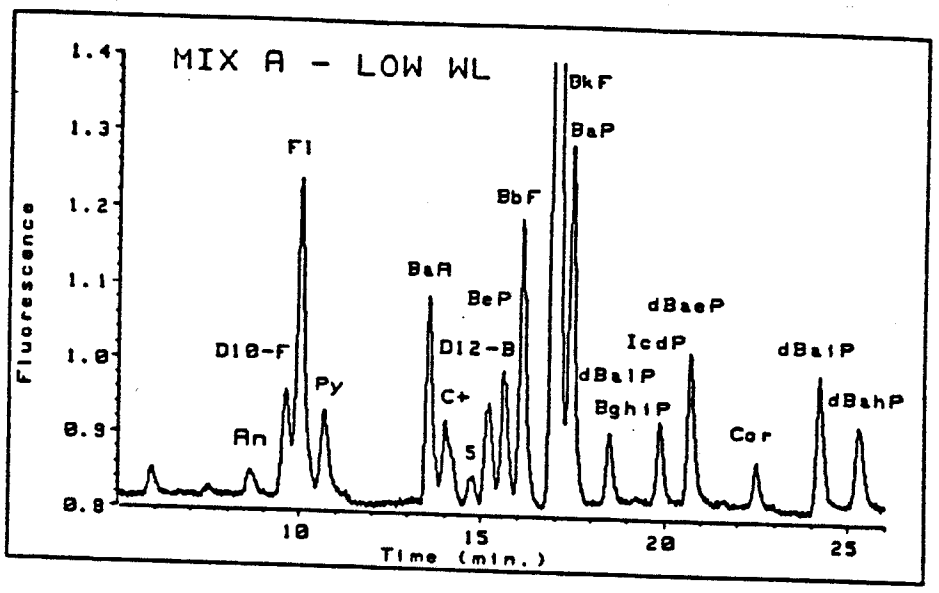
3) All compounds should have maximum sensitivity in one program or the other.

4) Closely-eluting compounds such as benzo(a)anthracene and chrysene should have opposite sensitivity patterns in the two programs.

5) One member of a co-eluting pair should have maximum sensitivity in one program and minimum sensitivity in the other; the other member has the opposite pattern.

6) If criterion 5 could not be met then wavelengths are selected so that each member of the co-eluting pair had measurable fluorescence in each program.

Figures V-2 and V-3 show chromatograms for standards A and B, respectively, for the low (upper) and high (lower) wavelength fluorescence programs. These chromatograms were



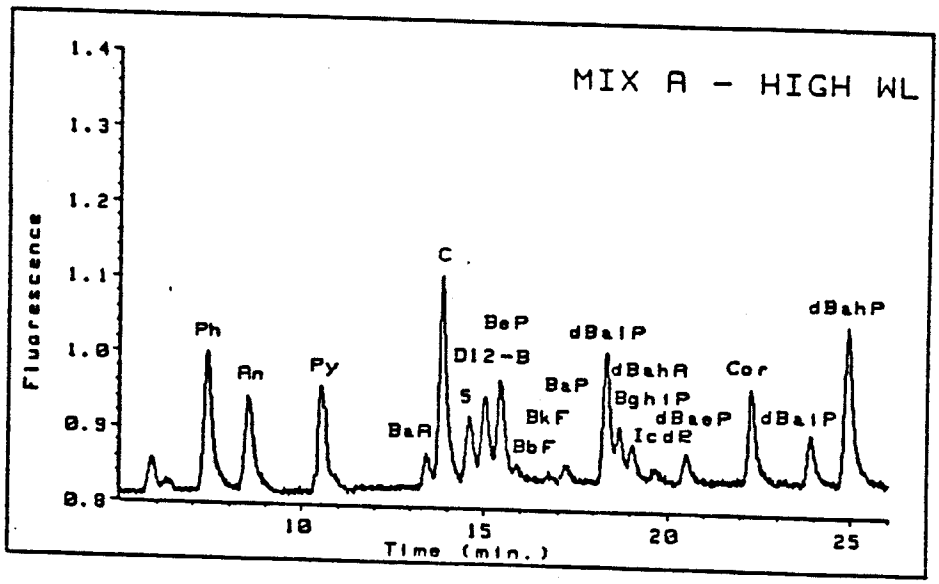


Figure V-2. HPLC chromatogram of PAH standard A for the low (upper figure) and high (lower figure) wavelength fluorescence programs. An = anthracene; D10-F = fluoranthene; Fl = fluoranthene; Py = pyrene; BaA = benz(a)anthracene; C+ = chrysene plus cyclopenta(cd)pyrene; 5 = 5-methylchrysene; D12-B = benzo(e)pyrene - d_{12}; BeP = benzo(e)pyrene; BbF = benzo(b)fluoranthene; BkF = benzo(k)fluoranthene; BaP = benzo(a)pyrene; dBalP = dibenzo(a,l)pyrene; BghiP = benzo(g,h,i)perylene; IcdP = indeno(1,2,3-c,d)pyrene; dBaeP = dibenzo(a,e)pyrene; Cor = coronene; dBaiP = dibenzo(a,i)pyrene; dBahP = dibenzo(a,h)pyrene.

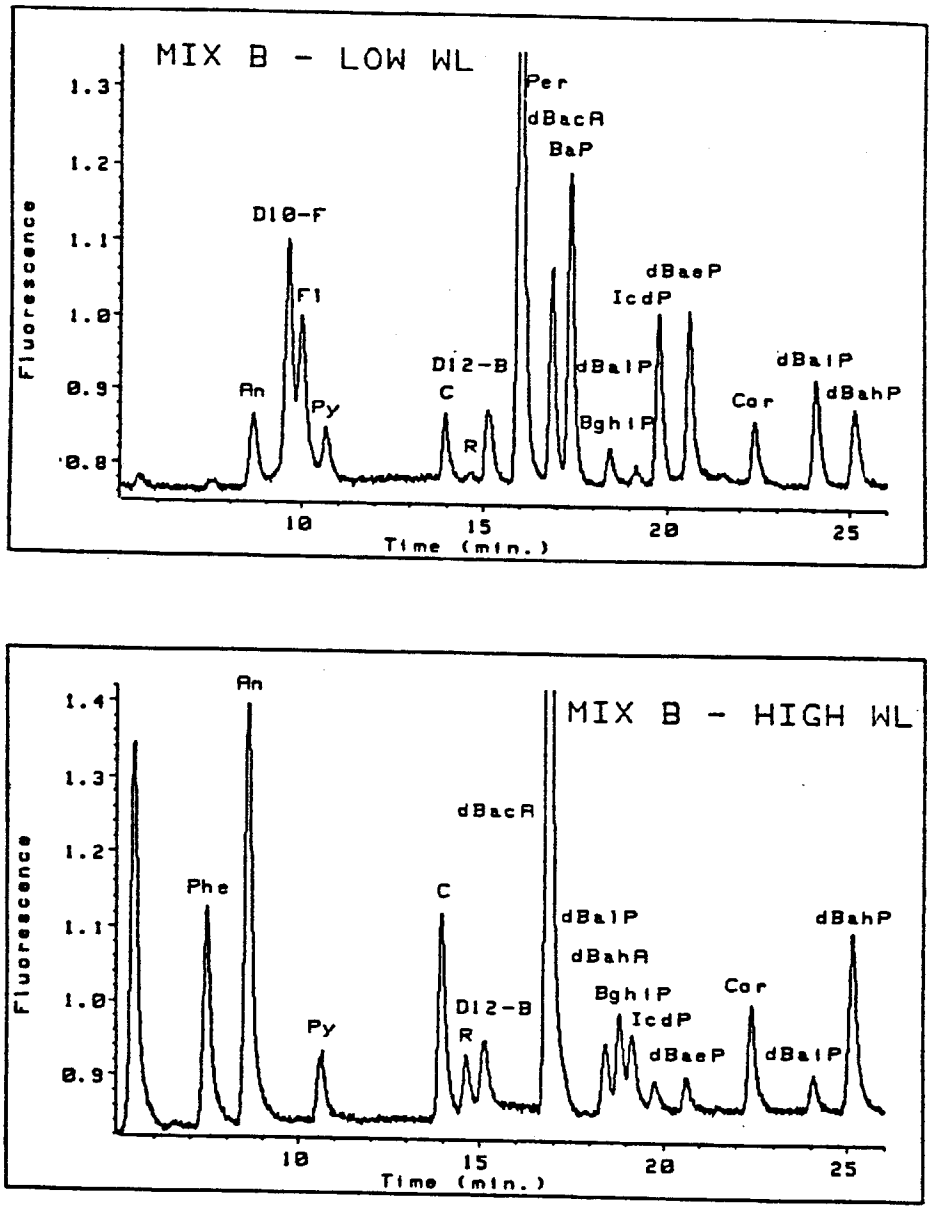


Figure V-3. HPLC chromatogram of PAH standard B for the low (upper figure) and high (lower figure) wavelength fluorescence programs. An = anthracene; D10-F = fluoranthene-d_{10}; Fl = fluoranthene; Py = pyrene; BaA = benz(a)anthracene; C = chrysene; R = retene; D12-B = benzo(e)pyrene - d_{12}; Per = perylene, dBacA = dibenz(a,c)anthracene; BaP = benzo(a)pyrene; dBalP = dibenzo(a,l)pyrene; BghiP = benzo(g,h,i)perylene; IcdP = indeno(1,2,3-c,d)pyrene; dBaeP = dibenzo(a,e)pyrene; Cor = coronene; dBaiP = dibenzo(a,i)pyrene; dBahP = dibenzo(a,h)pyrene.

used to calculate the sensitivities of PAH in Table V-2. There are one closely-eluting pair and four co-eluting pairs of compounds. We tried to find wavelength conditions to satisfy criterion 5 for all five pairs. For benzo(k)fluoranthene and dibenzo(a,c)anthracene this approach worked well. Detection settings for 5-methylchrysene and retene met criterion 6 reasonably well, and simultaneous equations were solved to determine both compounds in complex field samples. Neither criterion 5 or 6 could be met for benzo(e)pyrene and benzo(j)fluoranthene because both programs had to include good response for the internal standard benzo(e)pyrene-d_{12}, and the fluorescence spectra are similar for benzo(e)pyrene and its deuterated analogue. (Benzo(j)fluoranthene fluoresces well at an excitation wavelength of 240 nm and an emission wavelength of 495 nm, but these wavelengths exclude detection of retene and the benzo(e)pyrenes.) Benzo(j)fluoranthene cannot be determined unless a third set of detector settings is used.

For another coeluting pair, (benzo(b)fluoranthene and perylene) neither criterion 5 or 6 was met well enough to give good values for perylene. The sensitivity of benzo(b)fluoranthene at high wavelength is not great enough in the presence of other interfering compounds to permit good estimation of B(b)F, and perylene did not fluoresce at all at the chosen high wavelength setting (Other choices of high wavelength setting did not give good response for the internal standard benzo(e)pyrene.) Reported concentrations for B(b)F may be too high by about 10% because of interference from perylene at low wavelength, based on typical B(b)F to perylene ratios observed in outdoor samples. Cyclopenta(c,d)pyrene could have been determined using simultaneous equations if it had been present in one of the standard solutions without chrysene, so that its sensitivity could have been calculated. This was an oversight.Sensitivity data for cyclopenta(c,d)pyrene can be extracted from the existing chromatograms, but with considerable extra effort. In future work standard B should be prepared with cyclopenta(c,d)pyrene instead of chrysene.

Extraction Methods

Comparison of sonication and microsoxhlet extraction for dichloromethane and a benzene-methanol mixture.

In the early part of the study we compared two extraction methods, sonication and micro-Soxhlet extraction, for three 16 m^3 samples of indoor woodsmoke particles collected in a study of Wisconsin homes (Daisey et al., 1989a). Dichloromethane extracts were analyzed using a Vydac 201TP column (25 cm length, 4.6 mm id, 5 micron particles), Waters

Table V-4. Comparison of extraction methods for NBS SRM-1649 urban dust.

PAH	DCM [a] Soxhlet	DCM [a] Sonication	BzMeOH [b] Soxhlet	BzMeOH [c] Sonication	NBS [d] SRM-1649
Results in µg/gram					
Phenanthrene	1.9	2.9	e	7.9	4.5
Anthracene	0.6	0.6	e	0.5	f
Fluoranthene	e	3.2	6.6	7.3	7.1
Pyrene	3.4	2.7	5.4	7.8	6.3
Benzo(a)anthracene	e	2.5	2.5	3.4	2.6
Chrysene	3.3	2.0	3.5	4.7	3.5
Benzo(e)pyrene	2.6	4.9	2.9	2.6	3.3
Benzo(b)fluoranthene	6.2	5.4	6.2	5.5	6.2
Benzo(k)fluoranthene	1.8	1.6	1.7	1.5	2.0
Benzo(a)pyrene	2.5	2.5	2.0	2.3	2.9
Benzo(ghi)perylene	4.9	4.4	3.8	5.1	4.5
Dibenzo(ae)pyrene	e	1.6	1.1	1.6	e
Coronene	e	7.7	6.1	5.0	e
Fluoranthene-d_{10} [g]	34%	h	99%	92%	h

a.) Extraction with dichloromethane.
b.) Extraction with benzene-methanol (1:1, v:v).
c.) Average of three determinations.
d.) Concentrations provided by NBS (NIST).
e.) Not quantified by data reduction software.
f.) Data not available.
g.) Recovery as percent of added internal standard.
h.) Not added.