POLYCYCLIC AROMATIC COMPOUNDS

THE ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS IN URBAN AIRBORNE PARTICULATE SAMPLES

By

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ABSTRACT

There are a number of inherent problems associated with the analysis of polycyclic aromatic compounds (PAC) in airborne particulate matter. The compounds of interest constitute a very small fraction of the total sample, but consist of hundreds of different components. Therefore, analytical techniques with very high resolving power are required. To try to address these problems, methods have been developed and improved to isolate, and subsequently profile, and identify the PAC present in typical airborne particulate samples.

Since no single chromatographic technique can provide the desired resolution, a multi-stage clean-up scheme was required prior to analysis. Two methods were investigated in this study. Both methods used a Soxhlet extraction followed by fractionation using an adsorption chromatography step (silica or alumina) and Sephadex LH-20 to isolate the PAC fraction from the other organic constituents.

Another problem associated with the analysis of PAC in airborne particulate matter was because of the method of sample collection. It was believed that there were changes

in the chemical composition of the particulate and hence the PAC, during sample collection using a Hi-Vol sampler. Artifacts were being formed by reaction of gaseous pollutants with the particulate collected on the filter. An experiment was established to show that the addition of a denuder bundle to a Hi-Vol sampler could reduce this artifact formation during sampling by removing the reactive gases prior to the surface of the filter. The value of the denuder bundle was evaluated by comparison of the PAC from the denuder Hi-Vol with a standard Hi-Vol. Normal-phase HPLC coupled with mass spectrometry was shown to be a good method to compare the PAC in these samples. Some differences between standard and denuder Hi-Vol samples were observed in laboratory experiments, while the results from field sampling were inconclusive.

The use of a parallel column gas chromatography-mass spectrometry (GC-MS) (also called third order chromatography) technique was investigated to determine its viability for the identification of the diverse range of PAC present in environmental samples. The PAC in the NBS urban dust sample (SRM 1649) was analyzed to evaluate the method. To aid in data processing, a semi-automated peak detection routine has been developed. This routine used programs to aid in the data processing by simplifying peak detection and

allow calculation of the retention indices of the components. Using the information supplied by the retention indices and the mass spectra, a data base was developed that was applied to a typical airborne particulate sample.

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I am also very grateful for the encouragement and support that my family provided during this time, even when they didn't understand why or what I was doing.

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Special mention goes to Tom Petty, who said it all when he said, "Let me up, -I've had enough".

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

DAD: diode array detector

DCM: dichloromethane

FID: flame ionization detection

FLU: fluorescence detection

GC: gas chromatography

Hi-Vol: high volume

HPLC: high performance liquid chromatography

HRMS: high resolution mass spectrometry

MS: mass spectrometry

n-alkanes: normal alkanes

NBS: National Bureau of Standards

NRC: National Research Council

PAH: polycyclic aromatic hydrocarbons

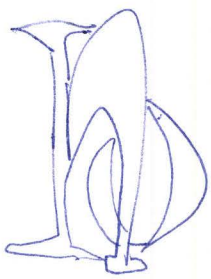
PAC: polycyclic aromatic compounds

RI: retention indices

SPE: solid phase extraction

SRM: standard reference material

UVD: ultraviolet detection



CHAPTER I: INTRODUCTION

The development and application of methods for the isolation and detection of polycyclic aromatic compounds (PAC) in urban airborne particulate matter is the theme of this thesis. In this chapter, the significance of PAC in the environment, and methods for sample collection, fractionation, and analysis will be reviewed. In addition, some of the problems associated with existing methods will be discussed, and the objectives of this study will be presented.

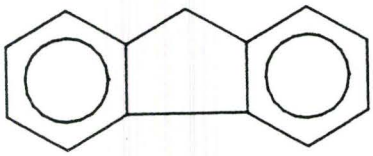
I.1 PAH and PAC

I.1.1 Formation and Occurrence

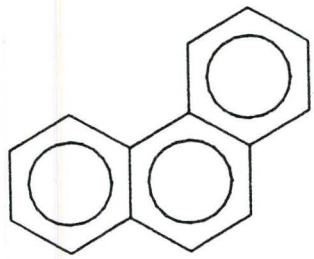
Polycyclic aromatic hydrocarbons (PAH) are ubiquitous compounds that can be formed from natural or anthropogenic sources. The natural sources include combustion due to forest fires and volcanos, and synthesis from biological material. PAH are also formed from man-made sources usually due to incomplete combustion of organic material. The major sources of PAH are coke production, coal-fired power plants, automobile exhaust and commercial

incinerators (1, 2, 3). PAH have been identified in a large number of diverse environmental samples. They include water (4), diesel particulate, sediments (1, 2), and urban airborne particulate matter (1, 2, 5, 6). The structures of typical PAH found in most environmental samples are presented in Figure 1-1. Interest in the analysis of PAH has arisen because many of these compounds are either known or suspected to be carcinogenic and/or mutagenic (7, 8).

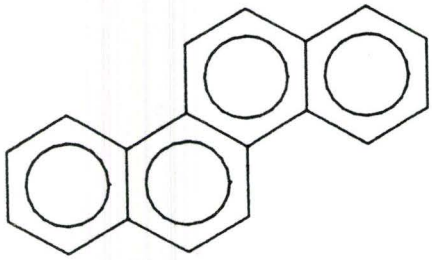
Polycyclic aromatic compounds (PAC) encompass a very large and diverse range of compounds, of which PAH are the parent hydrocarbon class. In addition to the parent PAH, substitution at various positions on the rings by alkyl, nitro and other substituents, or heteroatom substitution in the parent PAH with oxygen, nitrogen or sulfur will produce a variety of different compound classes. A number of these different classes of PAC are represented in Figure 1-2. For simplicity, each different class has been represented by an acronym. For example, polycyclic aromatic ketones have been designated as PAK and heterocyclic PAC where sulfur is the heteroatom have been designated as PASH. It is evident that for all of these different classes of PAC, there are an extremely large number of possible structures, particularly isomeric ones. Carcinogenicity has been shown to be dependent upon structural features of the molecule such as shape, size and steric factors (1). For example,



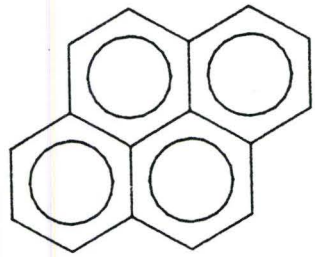
Fluorene



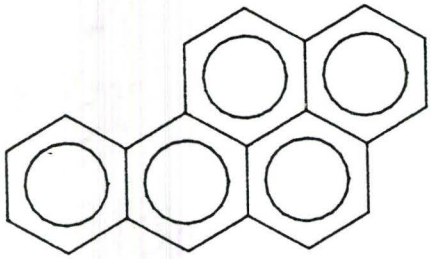
Phenanthrene



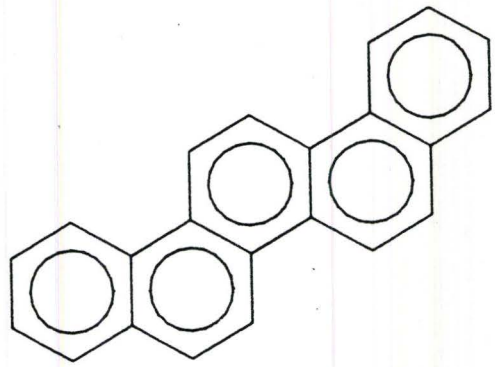
Chrysene



Pyrene



Benzo[a]pyrene



Picene

Figure 1-1: Typical PAH found in most environmental samples.

Figure 1-2: The different classes of PAC (and their acronyms) observed in the environment.

PAH Polycyclic aromatic hydrocarbons

PAOH Polycyclic aromatic oxygen heterocyclics
- PAF Polycyclic aromatic furans
- PAP Polycyclic aromatic pyrans

PASH Polycyclic aromatic sulfur heterocyclics
- PASF Polycyclic aromatic thiofurans
- PASP Polycyclic aromatic thiopyrans

NPAH Nitro polycyclic aromatic hydrocarbons

CPAH Cyano polycyclic aromatic hydrocarbons

PAK Polycyclic aromatic ketones
- PAHK Polycyclic aromatic hydroketones
- PAPK Polycyclic aromatic pyran ketones
- PASPK Polycyclic aromatic thiopyran ketones

PAQ Polycyclic aromatic quinones

ALPAH Polycyclic aromatic aldehydes

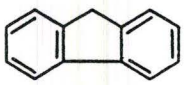
PANH Polycyclic aromatic nitrogen heterocyclics

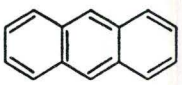
APAH Amino polycyclic aromatic hydrocarbons

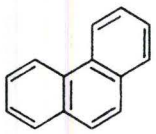
HXPAH Hydoxy polycyclic aromatic hydrocarbons

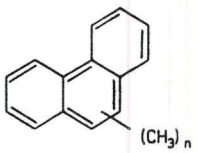
CXPAH Carboxy polycyclic aromatic hydrocarbons

PAH

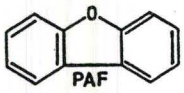


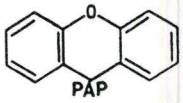




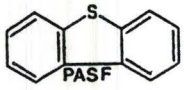


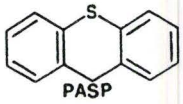
PAOH



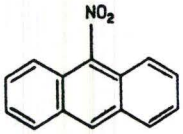


PASH

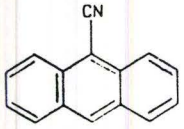




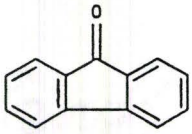
NPAH

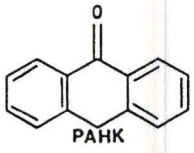


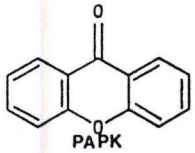
CPAH

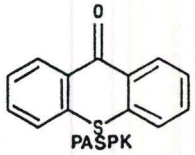


PAK

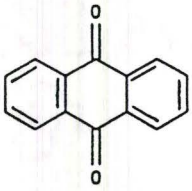




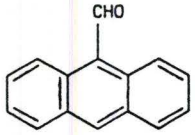




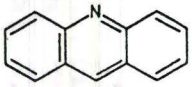
PAQ

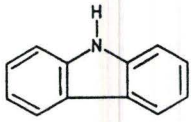


ALPAH

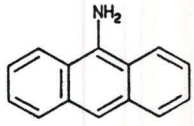


PANH

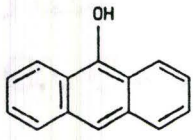




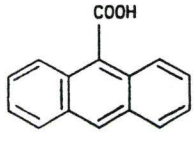
APAH



HXPAH



CXPAH



benzo[a]pyrene, a known carcinogen, has a molecular weight of 252. However, for a PAH with molecular weight 252 and a maximum of one 5-member ring, there are 25 possible isomers (Figure 1-3). The number of possible isomers increases with the addition of alkyl or other substituents. As with the parent PAH, not all of these isomers exhibit carcinogenic or mutagenic activity. Therefore, it is extremely important to have information on the individual PAC in the sample.

I.1.2 Significance

Using the Ames Salmonella mutagenesis assay, organic extracts of airborne particulate matter have been shown to be mutagenic (9, 10, 11, 12). Recent studies have indicated that the bulk of the mutagenic activity associated with the extractable organics present in particulate samples cannot be attributed to the PAH alone (8, 13, 14). Most of this mutagenic activity is of the direct-acting type, that does not require activation by mammalian metabolic enzymes (9, 15, 16). It has been shown that some of this mutagenicity can be attributed to chemical modification of the PAH due to photodecomposition, and by reaction with gaseous pollutants, such as ozone, nitrogen dioxide, and nitric acid. (16, 17, 18, 19). Gibson and others have shown that nitro-PAH can contribute significantly to the mutagenic activity of the sample (20, 21). These derivatives can be formed in situ,

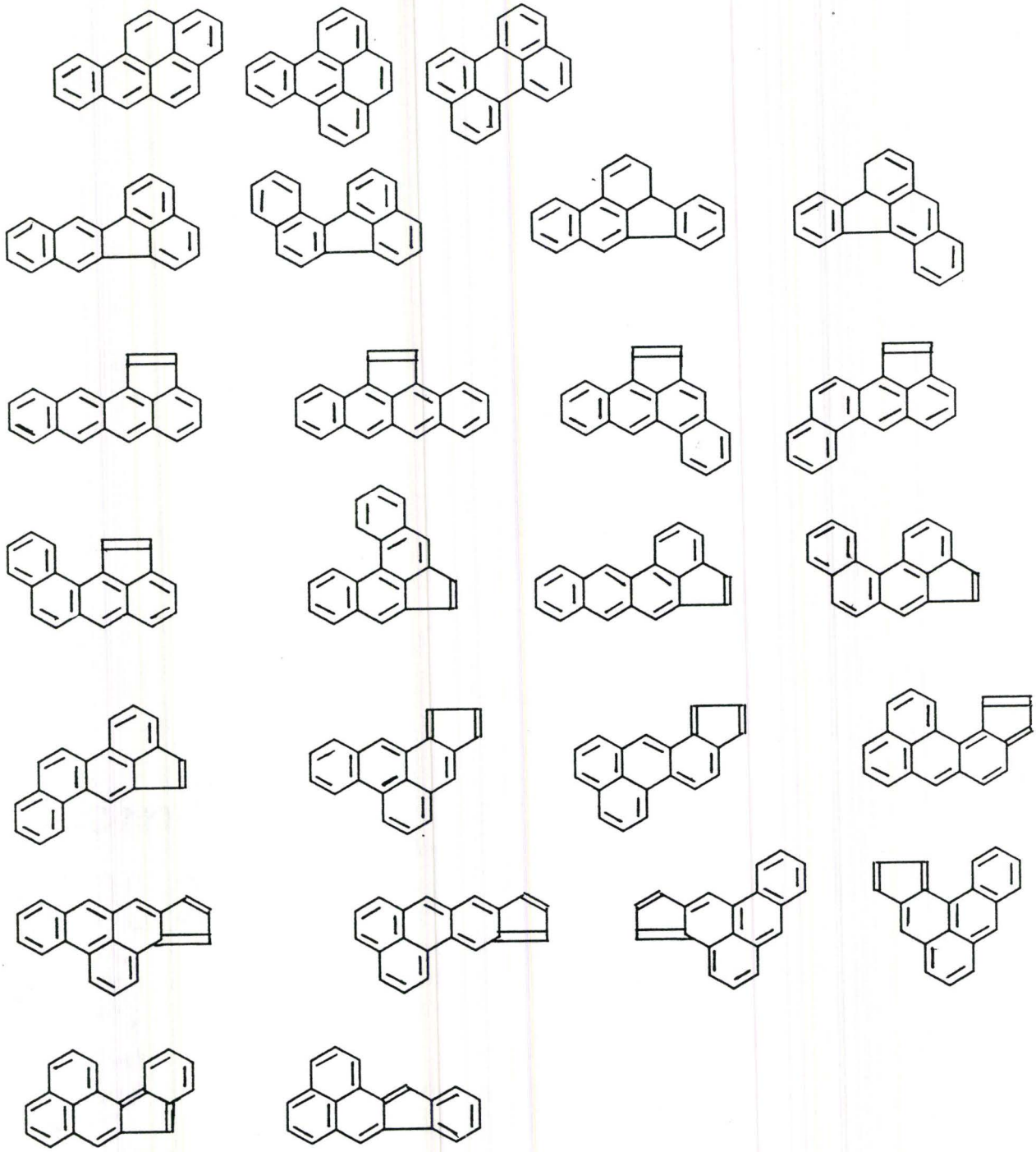


Figure 1-3: The possible isomers for PAH with molecular weight 252 and a maximum of one 5-member ring.

by gas-particle interactions in emission stacks, plumes, and during atmospheric transport (13). Their formation in air are dependent upon many factors, such as, pollutant levels, size of the soot particle, sunlight intensity, and transport time. A number of authors have cited evidence for the transformation of PAH during atmospheric transport (22 and the references cited therein). There is also the possibility that particulate organic matter may change in chemical composition during sample collection, cleanup and analysis. Errors in analysis due to the loss of reactive compounds and/or the formation of artifacts are quite feasible. Sample cleanup and other analysis steps have been shown to introduce interferences or cause transformations of some labile components to occur (23, 24, 25). Therefore care must be taken at each step, from sample collection to detection, to minimize the possibility of artifact formation so that the integrity of the analysis can be maintained. Detection of artifacts formed during sample collection is one of the concerns of this thesis and will be discussed in more detail in the following section.

I.2 Airborne Particulate Matter

I.2.1 Significance

PAC in air results primarily from incomplete combustion of organic matter and can be found in the vapour phase or adsorbed onto particulate matter. Ambient particulates larger than 10 μm in diameter tend to settle out as dust, while those with smaller diameters have much longer residence times (10). Pierce and Katz have shown that the bulk of the PAC are adsorbed onto the smaller particles (26). The mutagenicity and carcinogencity of the organic extracts from these particles have been well-documented by Pitts and others (27, 15). In addition, these particles can be deposited in the lower respiratory tract and are suspected to be a significant aspect of health hazards associated with airborne substances (8 and the references cited therein).

I.2.2 Methods for Sampling

Sampling of airborne particulate matter can be done using methods such as high volume filtration, cascade impaction and electrostatic precipitation (10). Using the last two methods, the particulate can also be sized during collection. Due to the relatively low concentrations of PAC

in air, it is necessary to collect a large air sample in order to be above the detection limit of the analytical method. The most common method for sampling ambient air for particulate matter has been achieved by drawing large volumes of air through a filter using a high volume (Hi-Vol) sampler (28, 29, 30, 31, 32). This method has a very high trapping efficiency for particles with a diameter of less than 20 μm (10).

It has been noted that the chemical composition of the collected aerosol can gradually change upon sampling, due to prolonged exposure of the particulate matter to large volumes of air. This problem is the most serious deficiency in using the Hi-Vol method for sampling. There are two modes by which the composition can change -- volatilization and chemical reactions (13, 18, 33). Changes due to chemical transformation of the filter-collected PAC is of interest in this study.

I.2.3 Chemical Transformations during Hi-Vol Sampling

Chemical reactions can occur on the filter between the deposited PAH and gaseous pollutants. Initial studies have indicated that the filter surface actually catalyzes these reactions (17, 34, 35). For example, it has been shown that benzo[a]pyrene is easily transformed into direct-acting mutagens by reaction with ozone (17), or

nitrogen dioxide and nitric acid (18) on glass fibre filters. The presence of these types of compounds would greatly increase the mutagenic activity of the organic fraction, and, therefore, give a false indication of the mutagenic potential of the air sample.

When using any Hi-Vol sampler, a filter is necessary to collect the particulate matter. The choice of the filter media is dependent upon the efficiency of the filter in collecting particulates and its inertness. The Gelman glass fibre filter and the Pallflex teflon-coated glass fibre filters have been shown to have similar collection efficiencies of particulates (36). The most common choice has been the glass fiber filter (28, 30, 37).

Teflon-coated filters offer a viable alternative due to their high collection efficiency and inertness (29, 36). It is believed that they do not promote artifact reactions. However, Houk and coworkers has show that direct and indirect-acting mutagens are present on "blank" Pallflex teflon-coated glass fibre filters (42). Presence of these mutagens can lead to errors when determining mutagenicity of the particulates by Ames assay. These results are significant for lightly-loaded samples.

Studies have suggested that artifact formation may be promoted on the surface of glass fibre filters (29, 32). For example, Lee has shown that the reactivities of PAH

toward oxidation are dependent upon the chemical and physical nature of the adsorbing surface when the PAH is directly applied to the filter (32). The loss of radio-labeled benzo[a]pyrene is higher on the blank glass fibre filter than on the particulate-laden filter (32). However, the dependence of filter media on decomposition appeared to be negligible when particulate-adsorbed PAH are studied (38, 39). A number of recent studies have indicated that differences in the filter medium may be negligible. Clark and coworkers have shown that under heavy loading of diesel particulates, filter type is unimportant (40). The same result would be expected when sampling airborne particulates. In a recent laboratory experiment, Otson and coworkers generated PAH as vapours and collected them using glass fibre filters (41). No significant degradation of PAH is noted. Therefore the role of the filter type in artifact formation during routine sampling is not clear.

Many laboratory experiments have been performed to test if degradation of PAH occurs on the surface of the filter (17, 18, 32, 34). These experiments did not involve studying actual airborne particulate samples, but filters that had been impregnated with pure PAH such as benzo[a]pyrene. The filters are either coated with the target PAH by evaporation from solution, or a radio-labeled PAH is added to airborne particulate samples and then

exposed to reactive gases. These types of experiments can be placed into two categories: (a) those that monitored a change in the mutagenicity of the total sample (18, 38); or (b) those that detected changes in target PAH that had been added to the system (43). These experiments have proven to be effective in determining the susceptibility of certain PAH to degradation, but they are not representative of actual samples, since the monitored PAH are not naturally-occurring in the particulate sample.

Reactions between PAH adsorbed onto particulate matter and deposited on a filter are extremely complex. They depend upon a number of parameters such as the nature of the carrier, the PAH concentration, gaseous pollutant levels, and exposure time (44 and the references cited therein). The behaviour of PAH adsorbed onto soot or other carrier particles is different from laboratory studies using pure PAH adsorbed onto filters or other substrates such as glass surfaces (19, 43 45, 46). The carrier particle has been shown to have a profound effect on the reactivity of the PAH (32, 43, 47). It has been proven that PAH adsorbed onto particulate matter is much more oxidation-resistant than PAH adsorbed onto the surface of the filter (32, 48, 49). Artifact formation during the sampling of airborne particulate matter using Hi-Vol samplers still has not been conclusively proven.

I.2.4 Denuder Hi-Vol Approach

An alternative method of sampling airborne particulate matter has been proposed by Concord Scientific Corporation. A research program in cooperation with the Ontario Ministry of the Environment and McMaster University, was undertaken to modify the standard Hi-Vol sampler with the addition of denuder tubes (50). The tubes have been used for over thirty years to separate gaseous and particulate matter during air sampling (51, 52 and the references cited therein). However, in the past, design problems with versatile denuder systems have prevented incorporation with Hi-Vol samplers (3). The purpose of the denuder is to minimize, and if possible, eliminate artifact formation on the filter medium by removing ozone and other reactive gases prior to the surface of the filter. As air is drawn through the tubes, the gases diffuse to the sides and are adsorbed or they react with the surface. Particulate-associated PAC will not be affected to any significant degree, and transmission efficiency through the tubes should be almost 100% (53). The goal of this modification is an improved method for the sampling of PAC, that still allows the collection of a sample large enough to facilitate analysis. The denuder Hi-Vol sampler is represented in Figure 1-4. Our contribution to this

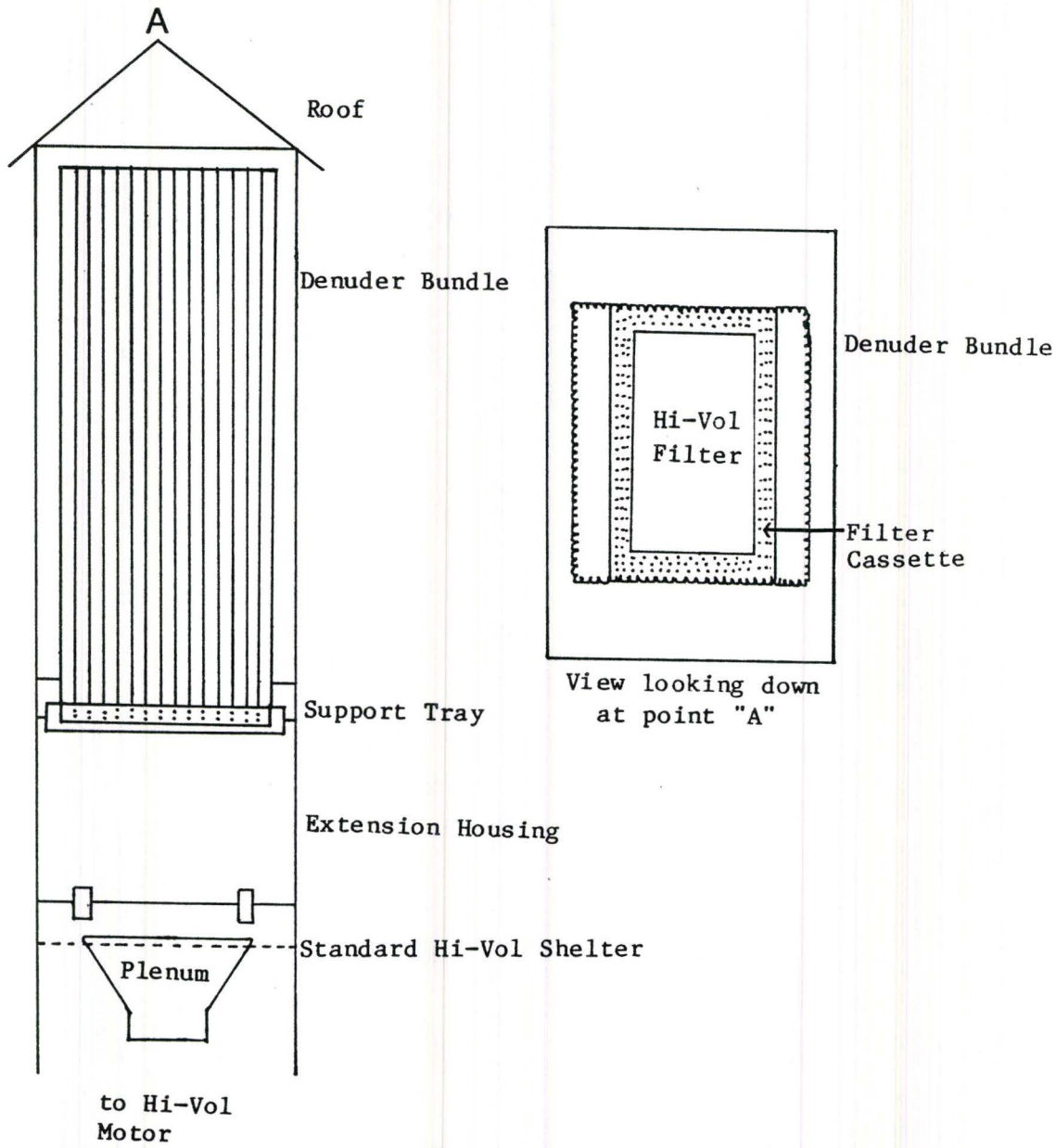


Figure 1-4: Schematic diagram of the denuder Hi-Vol sampler.

research was to evaluate the denuder Hi-Vol in terms of the relative attenuation of PAH and production of PAH derivatives.

I.3 Preparation of Sample for Analysis

The complexity of environmental samples necessitates a selective fractionation or clean-up scheme suitable for the isolation of trace levels of PAC. Removal of as many interferences as possible prior to analysis increases the likelihood of positive identification of a particular component. The method of choice should be developed to include a number of parameters. They are: the origin of sample; the type(s) of compounds being analyzed; and the finishing technique used in the analysis. The origin of the sample, or its matrix, determines the steps required for fractionation. If the method of analysis is very selective such as high performance liquid chromatography (HPLC) with fluorescence detection, a very simple clean-up is possible.

In this study, it was necessary to devise a scheme that would allow isolation of total PAC from airborne particulate matter so that a detailed analysis of the sample components (a "broad spectrum" analysis) could be performed.

I.3.1 Solvent Extraction

PAC are adsorbed onto the surface of the airborne particulate matter. An extraction is therefore required to remove the PAC from the bulk of the sample matrix. Soxhlet extraction and ultrasonication are the popular methods of choice (29, 54, 55, 56). Extraction using high-temperature and supercritical fluids have also been investigated recently for recovery of PAH from particulate samples (57, 58).

Soxhlet extraction was chosen for this study for a number of reasons. The equipment is relatively inexpensive, it requires minimum operator time, and is available. Previous studies in this laboratory have shown that the Soxhlet extraction method is more efficient in extracting organic compounds from particulate samples than ultrasonication (73).

It appears that the extraction efficiency is dependent upon the composition of the particulates (56). For example, the particulate that constitute carbon black has a high content of carbonaceous material. Very poor extraction yields of PAH are obtained using cyclohexane, due to the nature of these particulates (59). The choice of extracting solvent is therefore dependent upon the sample matrix. Although benzene and cyclohexane are popular

solvents (60, 61, 62), it has been shown that they are not very efficient in extracting organic compounds from airborne particulate matter (59, 63). Another disadvantage of benzene is that it is toxic. Thermal degradation of the organic constituents is also a problem that must be considered when performing an extraction. Therefore, low boiling solvents such as dichloromethane (DCM) are preferred (64).

In addition to the nonpolar components, there is also a significant amount of polar organic species present in airborne particulate samples. The solvent of choice should be efficient in extracting both the nonpolar and moderately polar aromatics from the particulates. Both DCM and methanol have proven to be efficient in extracting the organic components present in airborne particulate matter (63, 65, 66). However, there does not appear to be a single extraction solvent that allows efficient extraction of all organic compounds (56). Binary mixtures of polar and non-polar solvents or separate extractions have been shown to yield higher levels of soluble organics (63, 67).

I.3.2 Sample Fractionation

After extraction of the sample, a multi-stage fractionation scheme is required due to the diversity of the urban airborne particulate sample components. This scheme

must be selective enough to effectively isolate the PAC from the other constituents prior to analysis. There are a wide variety of other compounds such as aliphatic and polar components that are usually present in much higher concentrations. These other components would affect the analysis by either masking the PAC or by adversely affecting the efficiency of the chromatographic column used in the finishing method. Also, by reducing the bulk of the sample, better detection limits can be achieved without column overload. In developing an adequate clean-up method, a number of criteria should be followed. The method of choice should be free of potential contamination, quantitative, time-efficient, and require a minimum number of steps. The scheme should also be efficient over a wide molecular weight range for a variety of multi-component mixtures.

I.3.2.1 Methods for Sample Clean-up

Clean-up of environmental samples has been achieved using a variety of methods. The most common methods use either solvent partitioning or column chromatography to isolate the components of interest (54, 68, 69, 1 and references cited therein). Typical clean-up schemes combine simultaneous isolation and fractionation of the PAC and generally require the use of one or more chromatographic techniques (23, 30, 70, 71, 72). The development of

clean-up schemes to effectively isolate the total PAC from the bulk of the sample matrix was one objective of this study. Further fractionation of the PAC into classes (e.g., PAH) and subclasses (e.g., 3-ring PAH) can also performed when more detailed analyses are required.

Clean-up of the extract using open-column chromatography with silica or alumina packing is a popular method of chemical class separation (1, 4, 69 and the references cited therein). It is relatively inexpensive to use and allows simultaneous preparation of numerous samples. One or both of these adsorbents are frequently used as a step in the clean-up of extracts from airborne particulate samples (30, 70, 71, 72). Solid phase extraction (SPE) cartridges with polar bonded stationary phases are a recent innovation that offer the convenience of pre-packed columns and good reproducibility (54, 73).

Lipophilic gels such as Sephadex LH-20 and Bio-Beads SX-12, are becoming more popular in the clean-up and fractionation of PAC in a variety of environmental samples (70, 74, 75, 76, 77). Sephadex LH-20, a propylhydroxylated dextran, offers good reproducibility and the possibility of separation using both steric exclusion and adsorptive modes. The mode is dependent upon the choice of eluent solvents (78). The availability of the ether and hydroxyl groups make the LH-20 a polar gel. Streuti (79) demonstrated that

the gel exhibits the properties of both a soft and a hard acid since adsorption of the electron-rich bases, such as PAC, is achieved by both π electron acceptor sites and hydrogen bonds. When adsorption is the desired mechanism, an alcohol is used as the eluent solvent. Since PAC are poorly solvated with alcohols, there will be more interactions with the stationary phase (78).

Another common method for class separation that has proven to be highly efficient and reproducible is the use of normal-phase HPLC with chemically bonded stationary phases (54, 80, 81, 82). Normal-phase HPLC retention is based on interaction between aromatic π electrons of PAH and the stationary phase. Separation is based on the number of aromatic carbons (55), and therefore, in addition to class fractionation, separation into subclasses according to ring number is also possible (23, 54, 72). Thus, fractionation of the PAC fraction by normal-phase HPLC prior to analysis, according to chemical class or ring number is another means to increase the resolution of the overall method (23, 72, 83, 84, 85). A common semi-preparative fractionation of the PAC into PAH and PAH derivatives can be achieved using normal-phase HPLC with a mixed amino-cyano phase (88). This approach has been used for class fractionation of petroleum crudes (89) and coal derived process solvents (90).

Using a combination of these techniques, the PAH and

the moderately polar PAH derivatives are isolated. These fractions are either examined separately or as the total PAC extract. The choice is dependent upon the resolving power of the finishing technique. One of the objectives of this study was to develop and improve techniques for the isolation of PAC in environmental samples. In this study, two clean-up schemes were developed. The first method, the silica/LH-20 method, is a modified version of a scheme initially developed for the isolation of nitro-PAH in diesel exhaust (73). This method was subsequently improved and modified to isolate the total PAC from the extract of airborne particulate samples. The second method, the alumina/LH-20 method, was a modification of one developed by Lucke and Later for the class fractionation of coal liquids (86, 87). Lucke and Later's fractionation scheme employed a neutral alumina column and a silicic acid column to selectively separate the PAC into subclasses (86). Lee and coworkers have employed similar methodologies using several alumina columns and a Bio-Beads SX-12 column to isolate the PAH and PANH present in air particulates, sediment and fish tissues (70).

I.4 Methods for the Analysis of PAC

Analysis of the PAC in environmental samples has been done using techniques such as mass spectrometry (MS), fluorescence (FLU), and ultraviolet/visible spectroscopy (UVS) (1 and the references cited therein). Generally, the complexity of the PAC fraction necessitates separation of the components prior to detection. Chromatography is an excellent technique for the separation and differentiation of the diverse range of PAC and in particular, the isomers. Methods were developed for the separation and detection of the PAC isolated from airborne particulate samples using a variety of chromatographic methods. Capillary gas chromatography (GC) and reversed-phase high performance liquid chromatography (HPLC) are the most common (55, 72, 83, 91).

I.4.1 Types of Analyses

The different types of analyses can be classified into three categories: (a) target compound; (b) fingerprinting or profiling; and (c) broad spectrum analyses. The most common type of analysis is the quantitative characterization of target PAH by a chromatographic method in combination with a selective

detector, such as reversed-phase HPLC-FLU (55). A profile analysis represents the relative composition of the PAC in a mixture and is used for comparison purposes with similar samples (2). The type and relative amounts of components can vary depending upon the origin of the sample or simply the sampling method. However, in order to detect any new compounds that may be of interest due to their potential carcinogenicity or mutagenicity, a broad spectrum analysis is necessary. Development and improvement of methods for sample profiling and broad spectrum analyses are of interest in this study.

I.4.2 Instrumental Methods

Capillary GC offers good sensitivity, and high resolving power for PAC mixtures. General detectors such as flame ionization (FID) and photoionization (PID) are commonly used for routine analyses. Profile and broad spectrum analyses generally require a method for analyzing the total PAC or selected classes using a general detector. Selective detectors feature an enhanced response to compounds with certain structural features and offer high sensitivity. For example, PAC exhibit a wide range of electron-capturing ability, and hence the electron capture detector (ECD) can be used to distinguish specific compound types. The nitrogen-selective thermionic detector (TSD) can

be utilized in the detection of nitrogen containing compounds and is commonly used in the analysis of nitro-PAH (92, 93, 94). However, there are some inherent problems associated with GC analyses due to the low volatility of the high molecular weight PAC's, and the thermal instability of others.

Reversed-phase HPLC has a much poorer column efficiency than capillary GC, but it offers unique selectivity that can separate isomers not resolved in GC, and is amenable to the higher molecular weight, nonvolatile and thermally labile compounds. The fixed wavelength UV detector operating at 254 nm is considered a general detector for HPLC analyses of PAC. Selectivity can be introduced with variable wavelength detection using a spectrophotometer. Another common and selective method of detection is by fluorescence.

As illustrated in Table 1-1, there are a variety of detectors available for use with these chromatographic methods and they have been categorized as either general or selective. These detectors allow only single-channel monitoring.

Table 1-1: Common types of detectors used in the analysis of PAC in environmental samples (1, 2, 3, 4 and the references cited therein).

Detector Types:	Single channel	Multi-channel
General	Flame Ionization (FID)	Mass Spectrometry
	Photo Ionization (PID)	Ultraviolet/visible Diode array detector (DAD)
	Ultraviolet/visible -(single wavelength) (UVD)	
Selective	Fluorescence (FLU)	Fluorescence (FLU) -(wavelength programming)
	Nitrogen-selective Thermionic (TSD)	
	Electron Capture (ECD)	Mass Spectrometry -(multiple ion detection) (MID)

I.4.3 Multi-channel Detection Systems

Multi-channel detectors have the capability to monitor more than one signal at a time and offer more versatility when determining a diverse range of compounds. For example, the ultraviolet diode array detector (DAD) can provide simultaneous multi-wavelength monitoring coupled with UV spectra acquisition (95). The most popular multi-channel detector is the mass spectrometer. Both of these detectors can be used to provide structural information for compound identification. Examples of common types of detectors used in the detection of PAC are presented in Table 1-1.

The mass spectrometer offers both selective and general detection capabilities. The continuous acquisition of mass spectra can be utilized in the identification of sample components and mass chromatograms can be generated for selective detection. There are a number of different ionization techniques available, electron impact and chemical ionization being the most common (1, 69).

The high resolving power of chromatography coupled with mass spectrometry has proven to be very effective for the separation and identification of PAC (23, 72). The chromatographic system separates the components and provides retention data. The application of a chromatography-mass

spectrometry system provides a great deal of information that can be used in the detection of components in a complex mixture. This type of system is ideal for profiling samples because of the applicability of retention data and mass spectra to the identification of the individual components. In this study, the application of normal-phase HPLC-MS and GC-MS to PAC detection has been examined. The use of reversed-phase HPLC-MS for broad spectrum analyses has also been examined, but will not be discussed here (96, 97).

The use of on-line HPLC-MS for the analysis of PAC is slowly gaining in popularity (95, 98, 99, 100). The problems attributed to interfacing these two techniques have led to its slow development (101). These problems have been discussed in detail elsewhere (100, 101, 102). The most common interfaces use either direct introduction of the HPLC effluent into the mass spectrometer or sample transfer via a moving belt interface (100, 102). Analysis of PAC in this laboratory by HPLC-MS has been limited to the moving belt interface. The process involves spray deposition of the column effluent onto a polyimide belt where the solvent is evaporated. The solute should then be immobilized in a thin film on the belt. Desorption of the solute occurs when it enters the ion source. This type of interface is ideally suited for systems whose solvents are relatively volatile such as those used for normal-phase HPLC. The distribution

of PAC in environmental samples is profiled using normal-phase HPLC-MS in this study.

GC-MS is a powerful analytical tool that has been used extensively in the analysis of PAC (1, 2, 3, 4). GC has a much higher column efficiency than HPLC and therefore the resolution of the mixture is greater.

For the analysis of complex environmental samples, it is quite likely that the recognized peaks in a chromatogram are actually a combination of two or more components (103). The number of observed peaks is not necessarily the same as the number of distinct chemical compounds. Since the retention volume range for a chromatographic system is fixed, as the number of components increases, the probability or severity of the overlap also increases (103). Therefore, a single analysis may not provide sufficient resolution to facilitate identification or quantitation of the individual components. One way to improve the quality of information is to increase the resolution of the system by utilizing multidimensional techniques.

I.5 Multidimensional Techniques for Complex Sample Analysis

A number of different multidimensional techniques can be applied to enhance the resolution of the overall method: (a) the sample can be simplified by extensive

fractionation of the PAC and isolating the fractions of interest prior to analysis; (b) the use of two or more chromatographic columns with different selectivity provides a number of sets of retention data that can aid in the identification of the components; (c) multi-channel detectors, such as mass spectrometry and the DAD, can be used to provide structural information for compound identification; and (d) a combination of two or more of these techniques can also be used.

If only a few fractions are being examined, class fractionation of the PAC is very useful in increasing the resolution of the overall method, by simplifying the sample, and permitting the use of single channel detectors. However, when examining the total PAC, the number of required analyses can increase dramatically and the information gained from these extra analyses may not merit the extra time and effort.

As previously mentioned, coupling the chromatograph to a multi-channel detector provides additional information about the sample that would aid in identification. This type of detector can aid in the resolution of co-eluting components where chromatographic resolution is incomplete.

The combination of multidimensional techniques for the isolation and detection of selected PAC classes is quite common. For example, due to the observed mutagenicity of

PAH derivatives, several studies have isolated and characterized polycyclic aromatic quinones and ketones (37, 84, 104) and nitrated PAH (73, 85, 105, 106, 107, 108) in particulate samples using fractionation and GC-MS. Wise and coworkers separated the PAH fraction into 10 subfractions prior to GC-MS analysis (72). Similarly, Schuetzle and coworkers analyzed the subfractions of PAH derivative region by GC-MS (23). One of the goals of this study was to develop a method for broad spectrum analyses of the total PAC in the airborne particulate samples, without fractionation, using a combination of dual column GC and mass spectrometry (see below).

I.5.1 Dual Column Techniques

The use of two or more GC capillary columns in combination with single channel detectors is one method that has been used to separate the components in a mixture (109, 110, 111). Dual-column GC techniques employ two columns of different selectivity and require either splitting the sample onto two columns in combination with two detectors or transferring a portion of the sample separated on one column to another column (110, 112). If the separation selectivities of the phases are sufficiently distinct, the retention of the components will be different. This difference may aid in the resolution of the components.

More importantly, the retention data obtained from each analysis can be used to identify the PAC. One accepted method for the confirmation of the identity of a particular component is by its retention index on two different stationary phases (112). However, the application of dual column methods to PAC analysis is still not common (2). For extremely complex samples, the use of retention data, even from more than one column, may be insufficient for the unambiguous identification of the components. This problem is due to peak overlap.

I.5.1.1 GC Retention Indices

The major problem associated with PAC analyses is the separation and conclusive identification of individual isomeric compounds. Retention data are very important for PAC analyses because of the vast number of isomers present in the sample. Mass spectral information alone is not sufficient to distinguish between isomers.

Reproducibility of the retention measurements is important. The use of absolute retention times is insufficient since there is a great deal of uncertainty associated with the values. Some of the factors that affect the reproducibility include: chemical reactions (polymerization or catalytic decomposition) and bleeding of the stationary phase during repeated use leading to changes

in thickness and structure; operating temperature; and, temperature programming rate (113).

To be of greatest value for intra- and interlaboratory comparisons, data should be presented in terms of a scale. This scale or index correlates the relative retention of the mixture components to standard reference compounds. These standard reference compounds have assigned indices, and they bracket the components of the chromatogram. The most widely used scheme is the Kovats' retention index scale (114). It has fixed points that are defined by the retention times of normal hydrocarbons (n-alkanes). The Kovats' retention indices indicate the positions of compounds in a chromatogram relative to n-alkane standards. These standards are either co-injected with the sample or analyzed prior to the sample. However, these indices are obtained for isothermal analyses and the results cannot be directly applied to temperature-programmed analyses.

Early studies by van Den Dool and Kratz (115) indicated that reproducibility is improved significantly by using chemically similar bracketing standards during linear temperature programming. A number of retention index systems have been developed for different classes of compounds. These systems are based on a relationship that exist between the structure of the compounds and its

retention on a chromatographic column. To ensure constant elution behaviour among solutes and standards for all operating conditions, chemically similar compounds are used. The indices are more reproducible than the n-alkane system since they are based on chemically similar compounds. They are less sensitive to stationary phase thickness and experimental conditions (113).

Lee and coworkers (113) developed a system for PAH that utilized a series of benzologs as retention standards. The compounds are naphthalene, phenanthrene, chrysene and picene. The selection of these reference compounds is based on a number of considerations. These compounds are readily available as standards, and are soluble in organic solvents. It has been shown that the plot of elution temperature versus retention index is nearly linear under certain temperature programing conditions (113). Due to this relationship between retention and the number of rings, Lee's indices are computed on a linear scale and therefore the best fit line is usually a first order linear interpolation (113). However, this relationship is temperature rate dependent (116). Nonlinearity in the plot can be introduced by changing a number of factors such as different columns, program rates, and irregularities in the oven temperature or in the programming (116, 117). Korhonen (118) has shown differences in the calculated PAC retention

indices for some compounds of -1.58 to 7.50 units, relative to Lee's values. These discrepancies have been explained by differences in the initial temperature and the programming rate, while using a linear interpolation fit of the bracketing standards (118). Lee and coworkers have published a large number of indices for PAC (85, 113, 120, 121). Many other authors have adopted his method of RI calculation (30, 118, 122, 123, 124, 125). With this vast literature database available, it is important to be able to generate comparable values.

The experimental conditions that were used during this study were quite different than Lee's and included a nonlinear temperature program. Therefore, a linear interpolation was not adequate in this case. Halang and coworkers suggested that a cubic spline approximation of the data should be used whenever there is a possibility of a nonlinear response due to any of the aforementioned factors (119). A smooth function going through the data set, should result in more precise values. The cubic spline is a function composed of third-order polynomials connected at the data points (119). They offer a good fit to both linear and nonlinear data sets.

I.5.2 Third Order Chromatography

Ramos (126) has described the combination of two or more chromatographic processes, multichannel detection and multivariate data analysis as third-order chromatography. Data are collected as a function of time, column type and detector channel. For GC-MS, these variables are scan number, column type and m/z ratio. The viability of this method of analysis for the detection of PAC in complex mixtures has been investigated in this study. To be able to handle all the additional information provided by this system, a method of data analysis has been developed.

A thorough and comprehensive way to analyze the results is necessary to be able to maximize the amount of information retrieved from a single analysis and to efficiently utilize it in the detection of the sample components. As mentioned, the problem of co-elution in these types of samples is quite severe. Methods such as searching the total ion chromatogram (TIC) for detectable components (127), are not adequate methods to be able to identify the majority of the PAC. Minor components are easily missed. In a complex sample, this problem becomes more serious since minor components overlap with major components. A great deal of information about the sample components is lost. In addition to missing minor

components, some mass spectra are be very confusing due to co-eluting species (128).

GC-MS generates a vast amount of data in a short period of time. A typical analysis time for one run would be approximately one hour, but data interpretation could require many days of work. Therefore, an effective means of data management is required. A method is needed that minimizes the time required to obtain and interpret the results while utilizing all of the available information.

Attempts have been made to apply chemometric methods to mass spectral interpretation (128 and the references cited therein). These methods are very useful in handling the large amount of data generated by GC-MS. Using pattern recognition methods, Lohninger and coworkers (128) attempted to classify each mass spectrum obtained for a synthetic mixture by the compound's chemical class. However, severe problems result when one compound is a member of several chemical classes. One weakness of pattern recognition methods is the requirement of good chromatographic resolution (128). This prerequisite is difficult to attain in real samples without extensive fractionation of the sample prior to analysis. There have also been many recent developments in computer-based methods for spectral interpretation and structure elucidation (129). Research is now being focused on methods to optimize the speed of

spectral comparisons and to maximize the interpretative nature of the search (130, 131).

However, there are a number of problems that are associated with the use of any of these methods of data interpretation. Errors in identification are still a problem due to peak overlap (103, 132). As the number of components increase, the peak overlap increases, therefore the likelihood of identification using these automatic search techniques decreases. Mass spectra obtained from a GC-MS analysis can contain a large number of extraneous peaks, originating from column bleed and co-eluting species. Therefore, the mass spectra can become very confusing due to presence of these peaks. With the increase in this type of noise, the likelihood of identification decreases significantly.

A method of analysis that utilizes the information provided in mass chromatograms as a means of component detection can be very useful. Mass chromatograms are used for the selective detection of certain compounds or classes of compounds. For example, aliphatic components are detected by monitoring m/z 85 (67). Gallegos has shown that sulfur-containing compounds can be identified by monitoring the CHS^+ fragment ion (133). Phthalic acid esters are monitored using m/z 149. Searching the spectra for isotope clusters of selenium has proven to be a useful method for

obtaining specific information about selenium-containing compounds from a complex GC-MS analysis (134). This method is superior to the others that have been described, since more than one ion is monitored, and these ions must be in a predetermined ratio. When monitoring for specific ions it is important that there are no interferences present in the sample matrix that can influence the analysis. Some clean-up of the sample is therefore necessary. All of these types of compounds have key ions that are distinctive to that particular compound class. Unfortunately, there are not any ions unique to PAC that can be monitored in this fashion.

Few studies have attempted to profile the total PAC in a sample. An ambitious characterization of the NBS air particulate sample (SRM 1648) and the NBS urban dust sample (SRM 1649) by GC-MS has been achieved recently by Wise and coworkers (72). However, only PAH and some of the PASH are identified and quantitated. Schuetzle has applied a variety of chromatographic techniques, in addition to low and high resolution mass spectrometry to identify over one hundred PAH derivatives present in the soluble organic fraction of particulate matter from diesel exhaust (23). The PAH are not considered in this study. Unfortunately, neither Schuetzle nor Wise provided any retention data. This information would have been very useful to aid in the

identification of these components in similar samples without the necessity of such an extensive analysis. Grimmer has characterized over 170 compounds in brown-coal-fired residential stoves by GC-MS, but he did not present any information on the PAH derivatives (77). Tuominen and coworkers have recently established a data base for PAC using retention indices and key fragment ions, but only available standards are used (125).

One goal of the present study was to profile the total PAC in airborne particulate matter by a third order chromatography technique, using several GC columns with different selectivities and a mass spectrometer as the detector. The NBS urban dust sample was extensively studied to determine the applicability of the method. The NBS urban dust sample has been examined by a number of other laboratories to assess the efficiencies of methods that have developed for the extraction and identification of selected PAC in airborne particulate matter (58, 70, 72, 135, 136).

I.6 Summary of Research

The theme of this study was the development and improvement of methods for the detection of PAC in complex mixtures. The emphasis was placed on improvement in the resolution of the overall analysis of airborne particulate

samples by three techniques: (a) the development of multi-stage fractionation schemes to isolate the PAC from the bulk of the matrix; (b) sample profiling based on a chromatographic method coupled with a single or multi-channel detection; and (c) the application of a third order chromatography method combined with retention indices for the detection of the individual species.

It was necessary to devise a fractionation scheme that would allow isolation of total PAC from airborne particulate matter so that a detailed analysis of the sample components (a "broad spectrum" analysis) could be performed. This type of sample required an extraction with a suitable solvent, a subsequent clean-up of the organic extract to separate the PAC from the other components, and possibly further fractionation of the PAC into different compound classes. The PAC in airborne particulate samples were Soxhlet extracted using dichloromethane or using a sequential dichloromethane and methanol extraction. A combination of column chromatographic techniques using classical adsorbents such as silica and alumina, or lipophilic gels, and high performance liquid chromatography (HPLC) with chemically bonded stationary phases were investigated for the isolation of the PAC fraction from the extract. Two clean-up schemes were developed. Each employed an adsorption chromatography step and Sephadex

LH-20. The value of these two methods in the clean-up of airborne particulate samples were evaluated and compared in this study. The first method, the silica/LH-20 method was a procedure that was initially developed for the isolation of nitro-PAH in diesel exhaust (73). It was subsequently improved and modified to isolate the total PAC from the extract of airborne particulate samples. For this method, the PAC fraction was obtained by elution of the extract through a short silica solid phase extraction (SPE) cartridge to remove the very polar compounds, and followed by a Sephadex LH-20 column to remove the aliphatic compounds (Figure 1-5). The alumina/LH-20 method was developed for the isolation of the total PAC in airborne particulates, and utilized a neutral alumina column and a Sephadex LH-20 column (Figure 1-6). Further fractionation of the PAC into PAH and PAH derivatives was achieved using normal-phase HPLC with a mixed amino-cyano phase.

Profiling methods were used to evaluate the denuder Hi-Vol in terms of the relative attenuation of PAH and production of PAH derivatives. The standard Hi-Vol was compared with the denuder in terms of the relative amounts of PAH and PAH derivatives present, using a variety of different methods. Normal-phase HPLC-MS was shown to be the best method to compare the sampling methods. In comparing the denuder Hi-Vol versus the standard Hi-Vol, it was

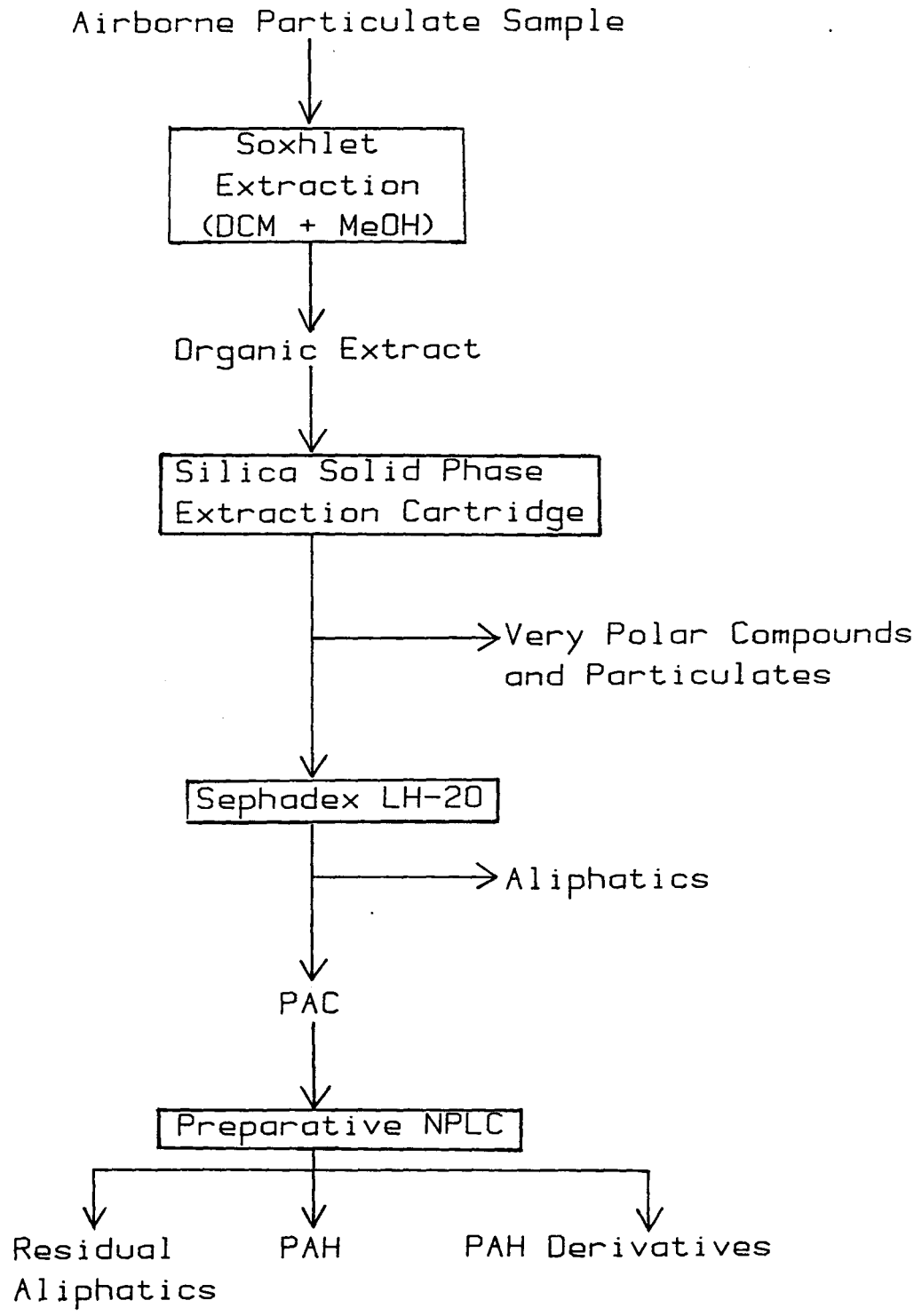


Figure 1-5: The silica/LH-20 clean-up method for the isolation of PAC in environmental samples.

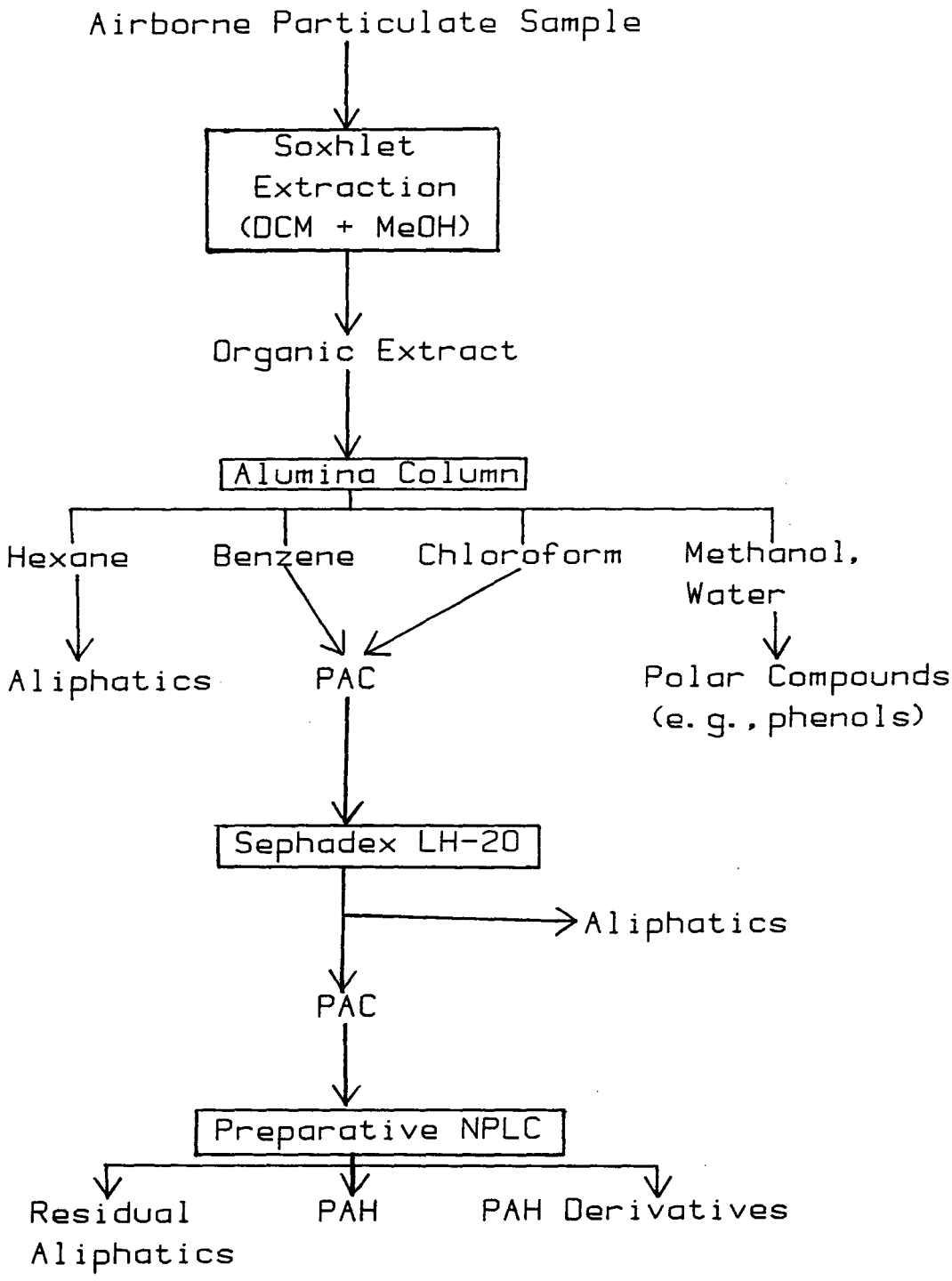


Figure 1-6: The alumina/LH-20 clean-up method for the isolation of PAC in environmental samples.

important to be able to detect surface-promoted artifact formation. Since glass fibre filters are suspected to promote the reaction between the PAC and the pollutant gases, they were chosen for particulate collection in this project.

One goal of the present study was to profile the total PAC in airborne particulate matter by a third order chromatography technique, using several GC columns with different selectivities and a mass spectrometer as the detector. The third order chromatography method required the examination of all individual mass chromatograms as the method of peak detection. In addition to molecular ion information, all of the key fragment ions were detected this way. This data was compiled using a spreadsheet program on a microcomputer (LOTUS 1-2-3). Identification of the PAC was achieved using retention indices (RI), and key fragment ions. Wherever possible, computer programs were written to automate the procedure. This method was designated a semi-automated peak detection routine because of the combination of automated and manual techniques used to identify the components. To aid in the characterization of the components, mass spectral information and the RI of the PAC on each column were obtained using the semi-automated peak detection routine. The advantages of this method over the others was that extensive fractionation was not required

prior to analysis, and complete resolution of the components was not necessary for identification. The NBS urban dust sample was extensively studied to determine the applicability of the method.

Another goal of this study was the establishment of a data base of RI data. The cubic spline interpolation fit was investigated in this study for the calculation of PAC RI. The index values used for the standards were the ones calculated by Lee and coworkers (113). They were used because a close approximation of the literature values was desired for comparison purposes.

I.6.1 Research Objectives

In summary, the objectives of this study are:

A. The development and improvements of techniques for the semi-preparative isolation of polycyclic aromatic hydrocarbons and their derivatives in environmental samples.

B. The use of a number of different profiling methods to evaluate differences in the relative abundances of PAC from a standard Hi-Vol sampler with one equipped with

denuder tubes in conjunction with the Hi-Vol sampler, and the application of normal-phase HPLC-MS for profiling PAC from different environmental sources.

C. Detection and identification of the PAC in a bulk reference sample (NBS urban dust SRM 1649) using a third order chromatography technique and a semi-automated peak detection routine developed for GC-MS.

D. Critical evaluation of this method in the detection of PAC in airborne particulate and application to a typical sample.

E. Establishment of a data base of retention indices that can be used in the detection of PAC in environmental samples.

CHAPTER II: SAMPLE CLEAN-UP

The isolation of PAC from the sample matrix generally requires a solvent extraction and a subsequent fractionation or clean-up of the organic extract. For the samples examined in this study, a Soxhlet extraction was performed using either dichloromethane (DCM) or a sequential combination of DCM and methanol. Two clean-up schemes, the silica/LH-20 method and the alumina/LH-20 method, were investigated for use in isolating the total PAC from urban airborne particulate matter. Each method utilized an adsorption chromatography step to remove the bulk of the polar organic constituents, and a Sephadex LH-20 step to isolate the aromatic compounds from the aliphatic compounds. When necessary, preparative normal-phase HPLC was used to separate the PAC into PAH and PAH derivative fractions. Both methods were relatively fast, easy to use, and each isolated the aromatic components of the sample. Each step in these schemes also provided qualitative information on the nature of the compound classes present in the sample. These methods were critically evaluated and then compared with the other to try to determine whether one of them was superior.

II.1 Soxhlet Extraction

The extracts of the airborne particulate samples, received from Concord Scientific Corporation, were processed by a single DCM Soxhlet extraction. Recent studies by coworkers in this laboratory and elsewhere (137, 63, 67), indicated that a Soxhlet extraction with methanol after a DCM extraction yielded more PAC. Although methanol also extracted inorganic compounds to a certain extent, and thereby complicating the clean-up procedure, it was felt that this approach was worthwhile. Subsequent analyses therefore utilized a sequential DCM-methanol extraction. After the methanol extraction, the extract was evaporated and the residue was extracted into DCM, leaving behind most inorganic constituents.

It was not the purpose of this study to examine, in detail, the extraction efficiencies of various solvents or mixtures of solvents. However, the extraction efficiency of a typical particulate sample, the NBS urban dust sample (SRM 1649), using successive extractions, was determined. A portion of dust was extracted with dichloromethane, followed by a methanol extraction. It was determined that 7% of the dust, by weight, was DCM-extractable while 11% was methanol-extractable, by weight.

II.2 Silica/LH-20 Method

The first clean-up method, silica/LH-20 (Figure 1-5), was a modified version of one initially developed for the isolation of nitro-PAH in diesel exhaust by D'Agostino (73). D'Agostino's clean-up method had been developed primarily as a means of removing the bulk of the sample constituents prior to the preparative normal-phase HPLC step that isolated the nitro-PAH. This method was of interest to this study because of the possibility that it could be adapted to isolate a total PAC fraction with the exclusion of the preparative HPLC step.

The silica/LH-20 method was a three-step clean-up scheme, where the aromatic compounds were effectively isolated from the bulk of the sample. Filtration removed any particulate matter in the extract prior to loading onto the silica solid phase extraction (SPE) cartridge. The silica retained the very polar material in the extract. The aliphatic constituents were removed by the Sephadex LH-20 step.

The SPE cartridges are easy to use, provide reproducible results and are disposable. This step could remove over 50% of the material in the total extract. Dichloromethane was used as the eluting solvent because: (a) it was quite volatile for easy removal; (b) it was a good solvent for PAC; and (c) at this stage the extract was

already in dichloromethane (DCM). The amount of solvent used for eluting the sample from the SPE cartridge was increased to 10 mL DCM from the earlier work on nitrated PAH (3 mL DCM) to ensure that the more polar PAH derivatives, such as the oxygenated PAH, were not retained. Examination of the cut-point using a series of oxygenated PAH standards revealed that less than 1% of these polar PAC were retained on the cartridge. Care must be taken when increasing the cut-point, since this allowed breakthrough of very polar components such as phenolic compounds, that were not of interest in this study. The presence of these components increased the complexity of the mixture, and created interferences in the analytical method. This problem was best illustrated by examination of the NBS urban dust sample (vide infra). Phenolic compounds present in this sample created a serious interference in the PAC analysis. In addition to increasing the complexity of the mixture, these polar compounds also masked the PAC, preventing detection.

In this study, the Sephadex LH-20 step was used to separate the aliphatic material from the aromatics. Since adsorption was the desired mechanism, the eluent contained a high percentage of alcohol. Using this mobile phase composition, the aliphatic compounds eluted first in the order of decreasing molecular weight (size-exclusion). Aromatics interacted strongly with the gel and eluted in

order of increasing ring number. However, separation of the PAC by ring size was not required at this stage. The mobile phase composition, dichloromethane/methanol (1:3), initially used in this study was established by D'Agostino (73) for use with diesel exhaust extracts. This system separated the aliphatic and aromatic components in a reasonable length of time. Some of the airborne particulate samples contained a very large amount of aliphatic material, that created a solubility problem when using this mobile phase composition. Addition of hexane to the mobile phase solved the problem and resulted in only a slight change in retention. The mobile phase used in the later stages of the project was hexane/methanol/dichloromethane (1:4:3). The cut-point used in the Sephadex LH-20 step was determined by standard PAC compounds. Confirmation of the cut-point was obtained by examination of the aliphatic region by GC-MS and by reversed-phase HPLC-UVD. No significant levels of PAC were observed in the aliphatic fraction.

The NBS urban dust sample was used to determine the weight distribution of the organic extract in the various fractions using the silica/LH-20 method. The results obtained using this method are presented in Table 2-1. As indicated, one third of the total extract was eluted with DCM on the silica SPE cartridge, and then further fractionated using Sephadex LH-20 to remove the aliphatic

Table 2-1: The weight distribution (% w/w) of the extract residue of the NBS urban dust in fractions collected from the two clean-up methods.

Silica/LH-20 Method

Silica-SPE fractions		*Sephadex LH-20 fractions	
*DCM	33%	Aliphatic	25%
		Aromatic	7%
Methanol	56%		
Retained	(11%)		

Alumina/LH-20 Method

Alumina column fractions		*Sephadex LH-20 fractions	
A1	16%		
*A2/A3	13%	Aliphatic	10%
		Aromatic	1%
A4+A5+A6	49%		
Retained	(22%)		

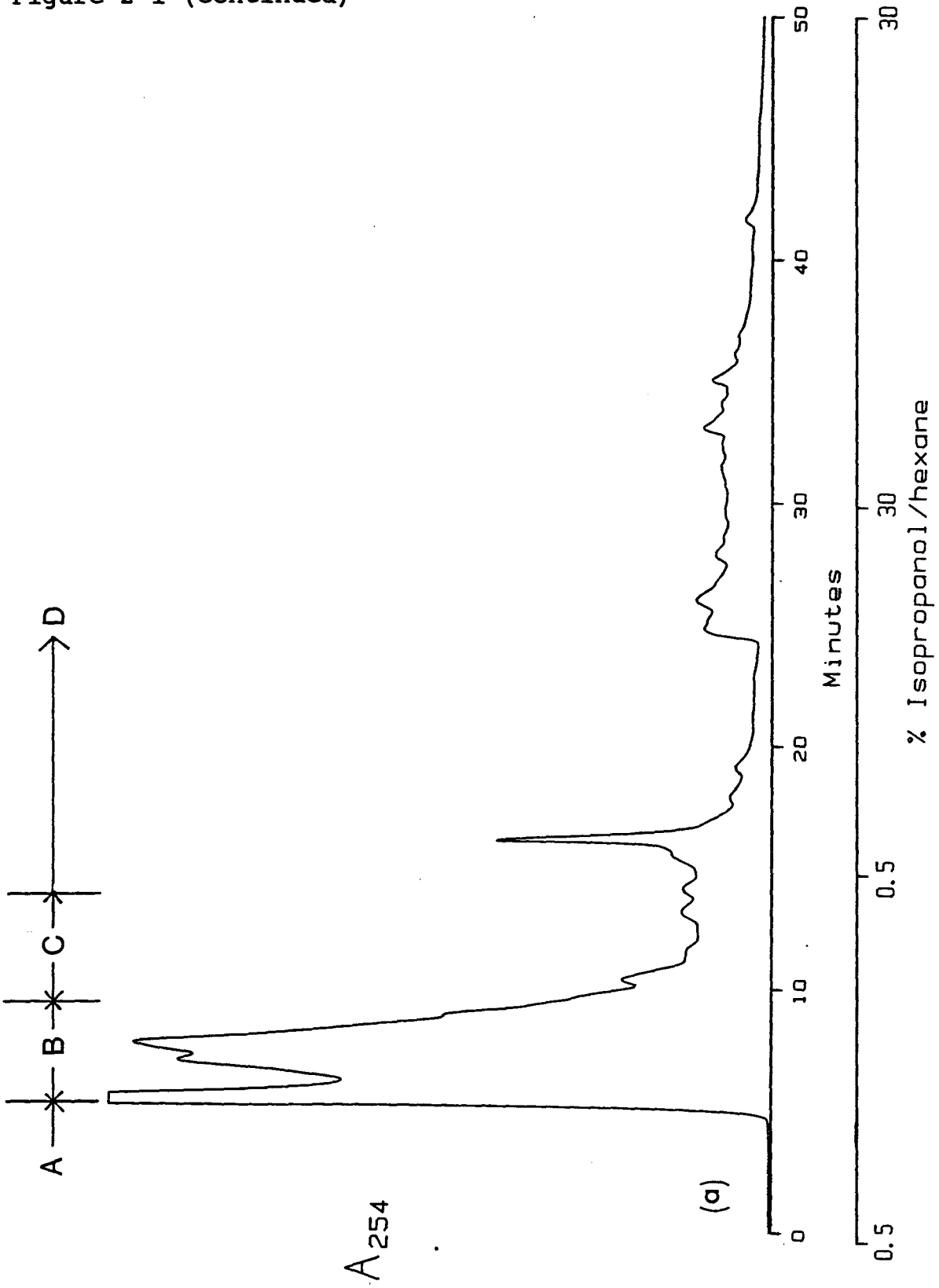
* Indicates the fraction that was collected and further fractionated by Sephadex LH-20.

material. Only 7% of the total extract by weight was collected in the aromatic fraction.

Further fractionation of the PAC into a PAH and a PAH derivative fraction was done by normal-phase HPLC using a mixed amino-cyano phase (88). Choice of this particular column was based on work done by D'Agostino (73) and others in this laboratory. Initially, the mobile phase was a mixture of hexane and isopropanol (conditions listed in experimental chapter). However, this mobile phase provided very poor resolution of the sample components and the cut-point between the PAH and PAH derivative regions was not distinctive (Figure 2-1). Switching to a mixture of hexane and DCM with a non-linear gradient elution provided many advantages. Because the PAC was much more soluble in dichloromethane than in isopropanol, the problem of dissolution of the sample prior to injection was minimized. As illustrated in Figure 2-1, the resolution of the components in the PAH and the PAH derivative regions was dramatically improved. There was some resolution in the PAH region according to the ring size. More importantly, there was a more distinct separation between the PAH and PAH derivative classes. Initial work on fractionation involved using standards to determine the cut-points. The cut-point was now determined using normal-phase HPLC-MS (137). This method provided much more information about the components,

Figure 2-1: Comparison of the differences in separation of the compound classes in the NBS urban dust total PAC (after alumina/LH-20 clean-up) achieved by changing the normal-phase HPLC mobile phase composition and gradient: (a) isopropanol/hexane mobile phase; and (b) dichloromethane/hexane mobile phase. The regions designated with arrows are the following: (A) Residual aliphatic material (not visible to the UV detector); (B) PAH, PASH, PAOH; (C) moderately polar PAH derivatives; and (D) very polar PAH derivatives.

Figure 2-1 (continued)



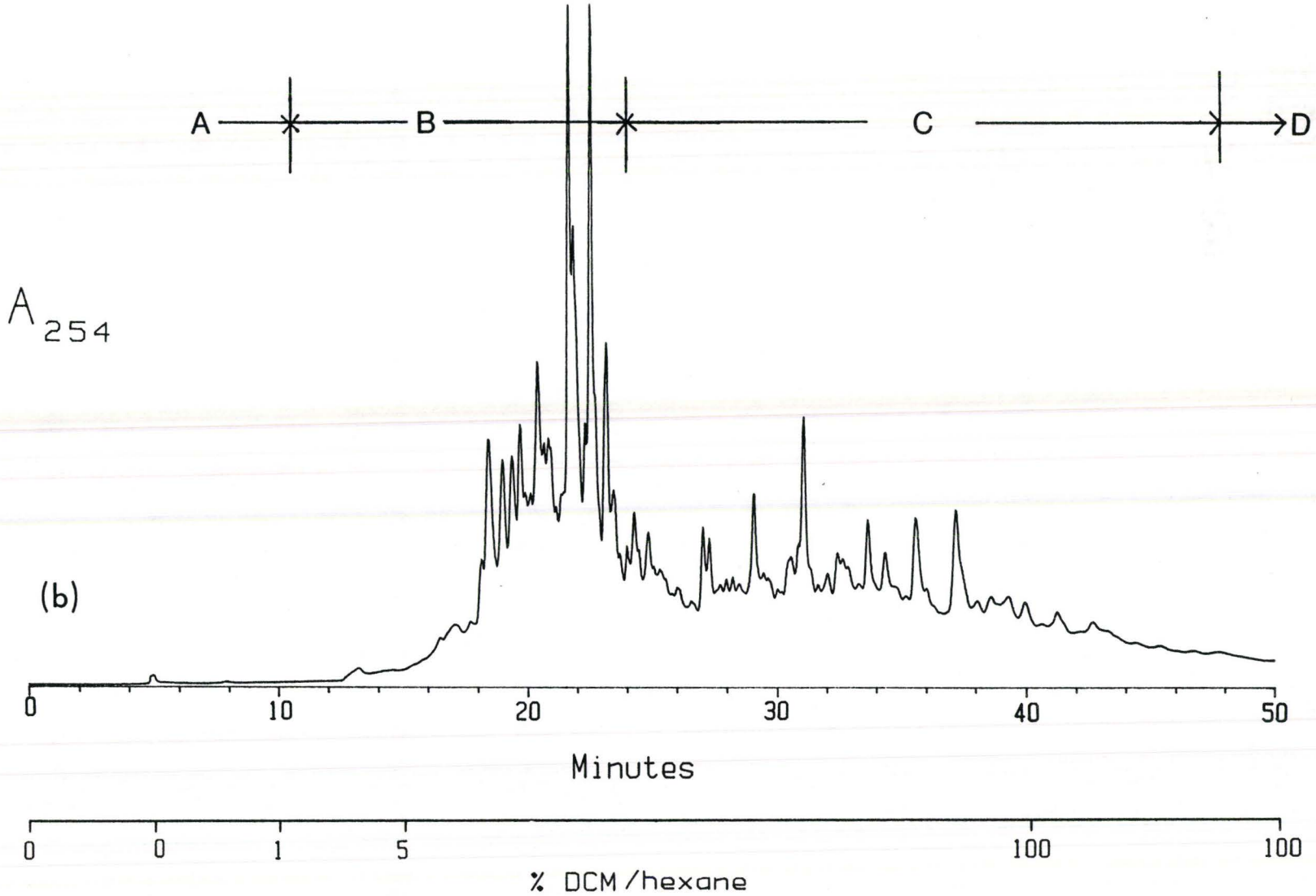


Figure 2-1 (continued)

and gave a precise determination of the point at which the PAH derivatives began to elute. With these improvements in separation, the use of normal-phase HPLC-MS as a profiling method for the aromatics in environmental samples became viable. Applications of this technique will be discussed in Chapter III.

II.3 Alumina/LH-20 Method

In the later stages of this project, a second fractionation method using a neutral alumina column and Sephadex LH-20 was also examined. The alumina/LH-20 method is presented in Figure 1-6.

Common problems when doing adsorption chromatography, were losses because of irreversible adsorption and poor reproducibility. The use of neutral alumina minimized these losses. It could elute a wide range of solutes rapidly and was used to provide reproducible class separations (86). Another disadvantage often cited for classical adsorption chromatography was poor reproducibility. The water content of the alumina was directly related with its activity. It was essential that the adsorbent water content be controlled if reproducible results were to be obtained. The activity of the alumina could even be affected by storage in damp or humid environments. The most common method of ensuring a constant

activity was by calcination of the material followed by addition of known amounts of water to pre-weighed samples (138). Repetition of this procedure each time an alumina column is required, was very tedious and time-consuming. A much simpler method for standardizing adsorbent activity was investigated by Later and coworkers (139). The procedure involved standardizing the moisture content of the alumina by storage in an oven of known temperature. For an optimum separation, using Later's prescribed conditions, the water content should be between 1 to 1.5% (139). Storing the alumina in an oven at 160°C prior to use achieved the desired result. The alumina was allowed to cool in a desicator for fifteen minutes prior to use.

The fractionation of sample components using alumina columns was commonly used for fossil fuels, and was shown to be very effective for this purpose by others (86, 87) and by coworkers in this laboratory (137). The procedures used in this study, were essentially those of Later and coworkers (86, 87), with some important modifications that will be presented. A portion of the extract, containing approximately 100 mg of residue, was coated onto a portion of the alumina and loaded on top of an alumina column. Overloading of the column was not observed to be a problem (the amount used was less than what Later recommends (86)). The fractions were subsequently eluted with solvents of

increasing polarity. The solvents range from hexane to water. In total, six fractions were obtained. The fractions were classified according to this procedure. They were designated by Lee as follows:

A1: aliphatics

A2: PAH

A3: PANH

A4: hydoxy PAH

A5: polar components

A6: polar components

Although the only fractions of interest in the study were A2 and A3, the other fractions were obtained to determine the weight distribution. Examination of the A1, A2, A3 and A4 fractions by GC-MS showed that considerable tailing of the compound classes was occurring. The A1 fraction did contain only aliphatic material, but the A2 and A3 fractions were not clean. Some aliphatic compounds were observed in the A2 fraction and PAH eluted partially in the A3 fraction. Oxy- and nitro- derivatives of PAH were observed in both A2 and A3 fractions. Fractions A2 and A3 were therefore combined and designated A23. Although the compounds classes were not cleanly separated by the alumina column, the results were reproducible. Subsequent fractionation by Sephadex LH-20 revealed that the aromatic fraction contained less than 10% of the total weight of the A23 fraction and only 1% of the

total extract. The weight distribution of the fractions is presented in Table 2-1. When further fractionation was required, it was done by normal-phase HPLC using the method described in the previous section.

It was necessary to determine that no losses of the PAC were occurring because of the cut-points of the analytical methods. The A1 and A4 fractions, and the aliphatic fraction obtained after separation of A23 by Sephadex LH-20 were examined to determine the presence of any PAC by GC-MS and reversed-phase HPLC-UVD. No PAC of interest were found in these fractions thus confirming the integrity of the procedure. The GC-FID chromatogram of the aliphatic region of the A23 fraction is presented in Figure 2-2. The extreme complexity of this fraction illustrated the obvious need to fractionate samples prior to analysis. PAC would clearly be masked by these components.

Analysis of the A4 fraction by GC-MS was difficult, because of the polarity of the components. However, none of the aromatics of interest were detected in this fraction. The reversed-phase HPLC-UVD chromatograms for the A4 fraction and for some PAC standards are presented in Figure 2-3. Analysis by reversed-phase HPLC-UVD showed that the majority of the components in this fraction were very polar. As illustrated, the majority of the components in the A4 fraction eluted before the more polar PAC. Using both of

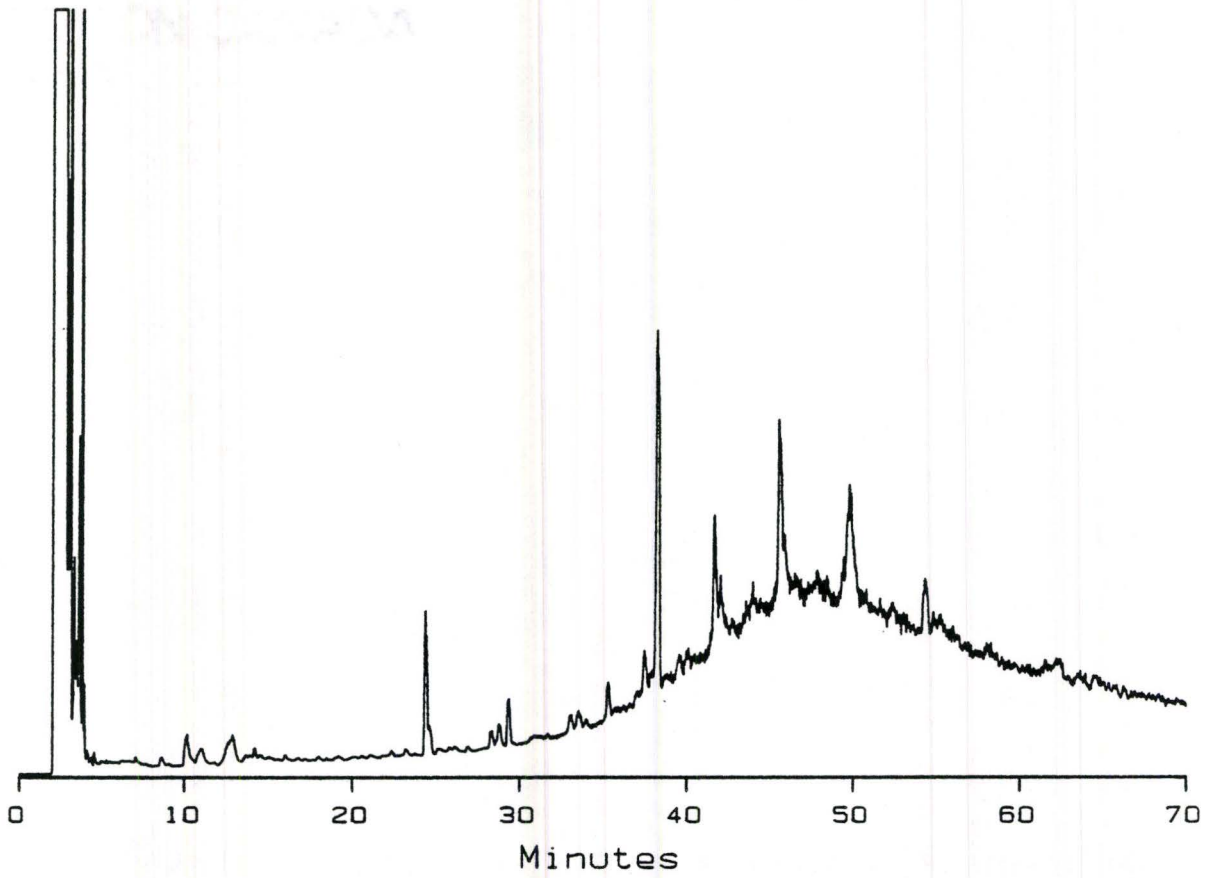


Figure 2-2: The GC-FID chromatogram of the aliphatic fraction obtained from the A23 fraction by separation on a Sephadex LH-20 column.

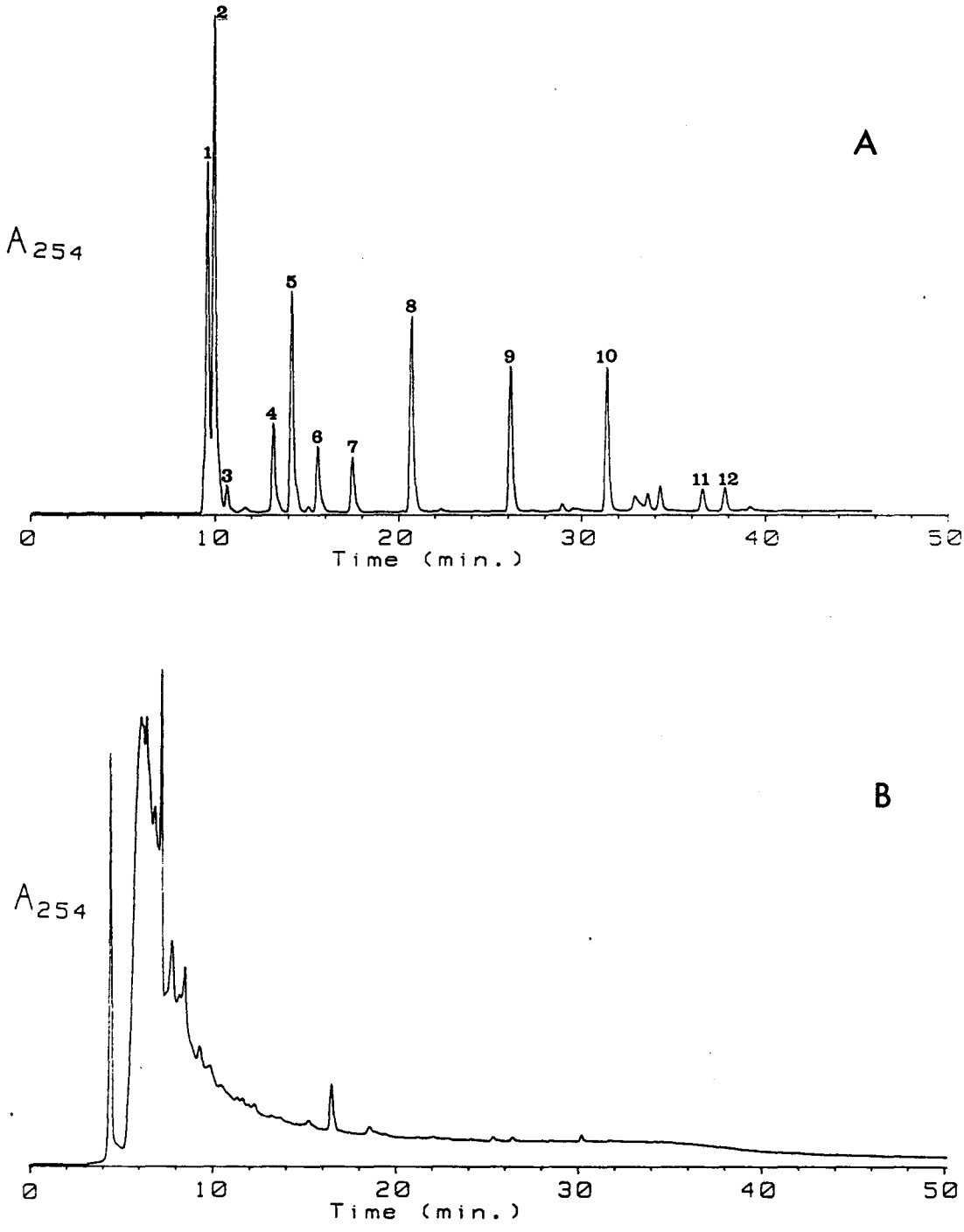


Figure 2-3: Reversed-phase HPLC-UVD chromatogram of (A) some PAC standards: 1=9-fluorenone, 2=anthraquinone, 3=naphthalene, 4=fluorene, 5=phenanthrene, 6=1-nitropyrene, 7=pyrene, 8=chrysene, 9=benzo[a]pyrene, 10=picene, 11=coronene, 12=benzo[rst]pentaphene); and (B) the A4 fraction from the NBS urban dust sample after separation through the alumnia/LH-20 clean-up procedure.

these techniques, a few phenolic compounds were detected. Since this fraction was not of interest in this study, no further analysis was done.

Examination of these results has proven that fractionation using the alumina/LH-20 method, did effectively isolate the aromatic fraction from the aliphatic and polar components that were present in much higher concentration in the extract. The A23 fraction was relatively free of potential interferences that affected the analysis of the PAC by a chromatographic method. The decision to pool fractions A2 and A3 was justified because the alumina column could not cleanly fractionate the various compound classes. As illustrated in Table 2-1, the Sephadex LH-20 step was extremely important in removing the residual aliphatic material that eluted with the aromatic compounds. In addition, the use of normal-phase HPLC to separate the PAC into PAH and PAH derivative fractions was a more reproducible technique than any low resolution open-column method.

II.4 Evaluation of These Methods

These two methods were partially evaluated using the NBS urban dust sample (SRM 1649). This sample was chosen because it is available in bulk, homogeneous, and its matrix is similar to the samples of interest in this study. One

portion of the extract was fractionated using the silica/LH-20 method, while the alumina/LH-20 method was applied to another portion. The results were then compared to determine any differences in the PAC content. The relative weight distribution of the different extract fractions were examined for both fractionation methods to determine the degree of enrichment. In addition, the total aromatics from both methods were compared using GC-MS.

The relative weight distribution of the chemical classes using the two different fractionation methods is presented in Table 2-1. For the silica/LH-20 method, 33% of the extract residue was eluted from the silica SPE cartridge in the DCM fraction. After fractionation with Sephadex LH-20, only 7% of the total extract remained in the aromatic fraction. On the other hand, using the alumina/LH-20 method, 13% of the extract was collected in the A23 fraction. Subsequent fractionation with Sephadex LH-20 resulted in only 1% of the total extract remaining in the aromatic fraction. Thus the total weight of material isolated in the aromatic fraction using this method was significantly different. The total amount of aliphatics isolated using the two methods proved to be very similar (25 to 26%). The weight difference between the two aromatic fractions appeared to be because of the presence of polar components.

The two schemes were then compared by analysis of the total aromatics by GC-FID and GC-MS. The criteria for this comparison was based on: (a) the presence of any discrimination of the adsorbents to the various benzologs and homologs; (b) the total amount of PAH versus the total amount of PAH derivatives; and (c) the presence of any extraneous components, and polar constituents. This experiment was done to obtain qualitative results only. Semi-quantitative data on the relative levels of PAC in each sample was attempted, but poor peak shape, and the lack of an adequate method for area determination using the current version of software on the mass spectral data system hindered the acquisition of any meaningful data.

Initial inspection of the GC-FID chromatograms indicated a tremendous difference in the two methods (Figure 2-4). The chromatogram for the NBS dust aromatics after clean-up using the alumina/LH-20 method was far more complicated than the other one. In the chromatogram of the aromatic fraction where the silica/LH-20 method was used, a few components were present in much higher concentration than the others. Using the GC-MS results, the major components in the aromatic fraction were identified as chlorinated phenolic compounds. They were not of interest in this study. These compounds were retained on the alumina column and elute in the A4 fraction. Examination of the A4

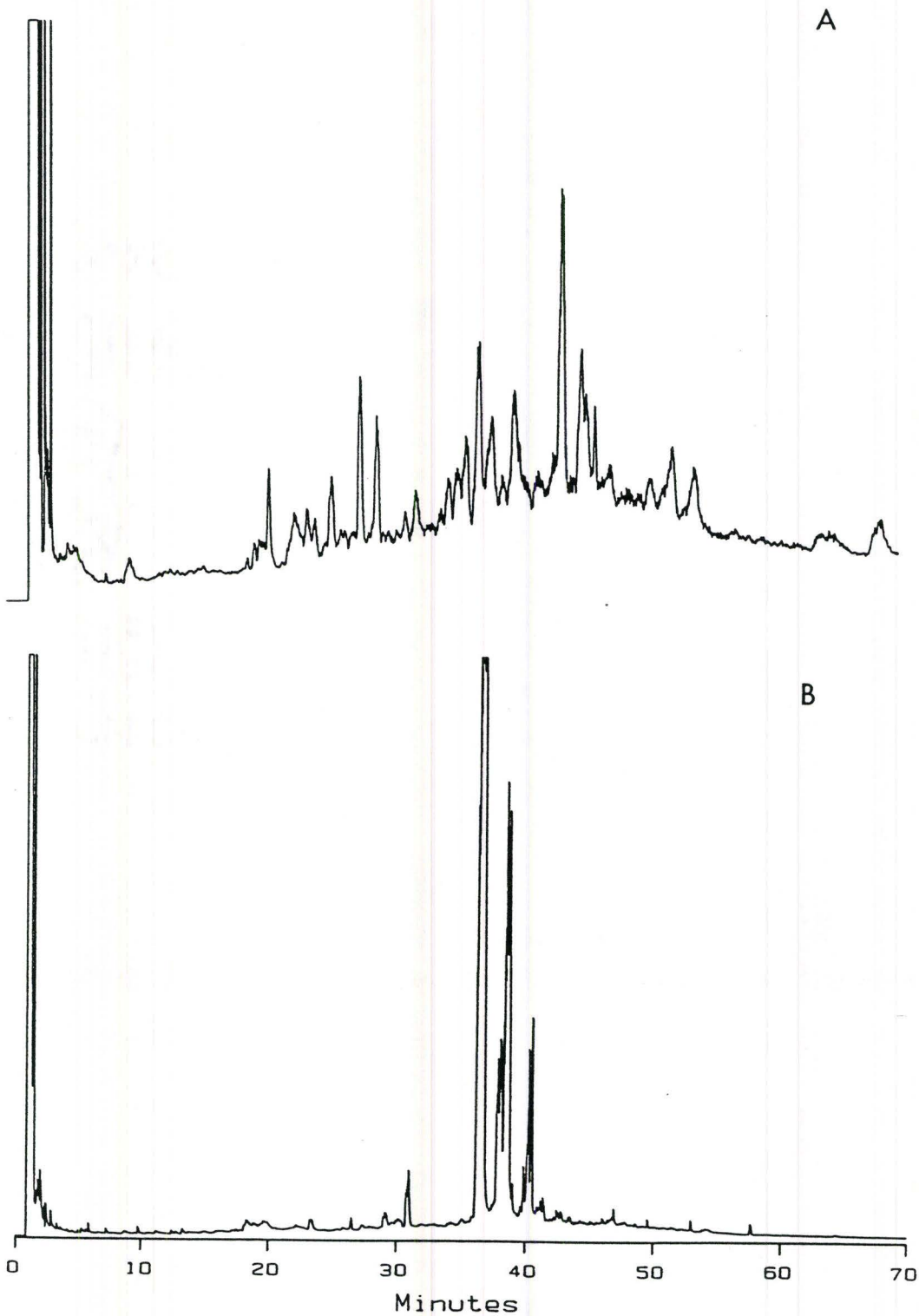


Figure 2-4: Comparison of the GC-FID chromatograms for the total PAC of the NBS urban dust after clean-up using: (A) the alumina/LH-20 method (A23 fraction); and (B) the silica /LH-20 method.

fraction by GC-MS confirms their presence. The major component was tentatively identified as an isomer of [(dihydroxydichloro)diphenyl] methane. The mass spectra is presented in Figure 2-5. This compound, an antiphen, was used as an agricultural fungicide and an antimicrobial. After contacting W.E. May at the National Bureau of Standards, it was discovered that this compound was added to the urban dust sample, but not mentioned in its certificate of analysis. Three other congeners were also tentatively identified in the sample. They were impurities present in the antimicrobial solution.

All of the mass chromatograms for each GC-MS analysis were plotted between m/z 142 and m/z 310. The compounds of interest in this study were represented in this region. Each mass chromatogram was then examined and compared to determine the presence or absence of peaks that were indicative of differences in the two clean-up methods due to discrimination against benzologs or homologs of the PAC based on differences in retention and adsorption during the adsorption chromatography step. Other differences in the sample have been determined and are presented in Table 2-2. These compounds were generally either aliphatic or highly polar and therefore were not of interest in this study. The cut-point for Sephadex LH-20 was determined so that all the aliphatic compounds and most of the benzene

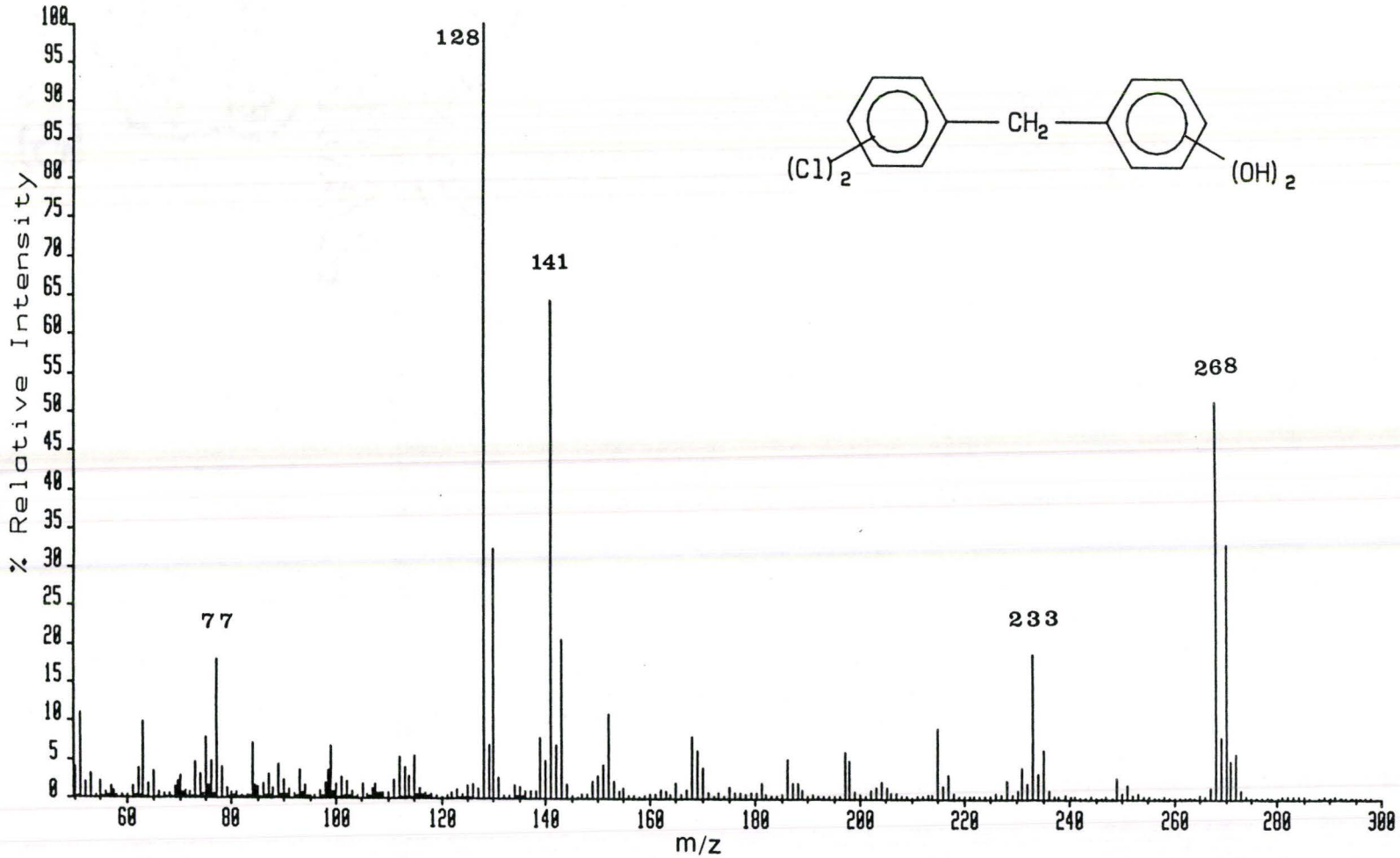


Figure 2-5: The electron ionization mass spectrum of the major component present in the PAC fraction after clean-up using the silica Sep-pak/LH-20 method.

Table 2-2: Compounds found in the aromatic fraction of the NBS urban dust sample (SRM 1649) that were unique to the silica/LH-20 cleanup method.

A: Compounds present due to an error in Sephadex LH-20 cut-point.

Observed Mass	Scan#	Tentative Identity
155	63	Aliphatic compound
156	183	Aliphatic compound
171	323	Aliphatic compound
71[1]	625	Aliphatic compound
71[1]	1076	Aliphatic compound
71[1]	1218	Aliphatic compound
71[1]	1486	Aliphatic compound
71[1]	2192	Aliphatic compound
71[1]	2415	Aliphatic compound
183	146	Benzene homolog
156	207	Benzene homolog
156	229	Benzene homolog
163	259	Benzene homolog
168	287	Benzene homolog
168	300	Benzene homolog
163	546	Benzene homolog

[1] Only the base peak was detected.

.....continued

Table 2-2 (continued)

B: Compounds present in the sample due to an error in the silica SPE cartridge cut-point.

Observed Mass	Scan#	Tentative Identity
172	95	C_7H_5ClOS[2]
186	120	C_8H_7ClOS[2]
270	930	Methyl Ester

Chlorinated phenolic compounds:

282	1283	$C_{14}H_{12}Cl_2O_2$[2]
268	1700	$C_{13}H_{10}Cl_2O_2$[3]
346	1815	$C_{14}H_6Cl_4O_2$[2]
346	1858	$C_{14}H_6Cl_4O$[2]

[2] Tentative identity was assigned after a library search using the VG-11/250 data system on the mass spectrometer.

[3] Refer to Figure 2-5 for structure and mass spectrum.

homologs were eliminated. The silica/LH-20 sample contained a lot more of these compounds. This was expected, since using the alumina/LH-20 method, the bulk of the aliphatic components were eluted prior to fractionation by Sephadex LH-20. The presence of these compounds may be because of an error in the cut-point at the LH-20 step or due to overloading of the column, since the aliphatics were present in much higher concentration at this step in the silica/LH-20 clean-up. The result would be a broadening of the aliphatic region, and therefore this band would overlap into the aromatic fraction.

The original method, developed by D'Agostino (73), was used to isolate the nitro-PAH fraction using the SPE cartridge, Sephadex LH-20, and normal-phase HPLC. It was not designed for isolating the total PAC. Even with the improvements introduced in this study that formed the current silica/LH-20 method, not all sources of interferences were removed. These were shown to affect the analysis of PAC. Polar components, such as phenols, could pass through the silica SPE cartridge. Incomplete separation of the aliphatic and aromatic compounds was another problem in the Sephadex LH-20 fractionation step. However, both of these problems were solved if preparative normal-phase HPLC was used, since these compound classes were isolated in discrete regions. As illustrated in Figure

2-6, the phenolic compounds were now separated from the compounds of interest, and the aliphatic material was eluted prior to the PAH region. Therefore, this method could still be used to isolate the compound classes of interest but an extra step was required.

The alumina/LH-20 method effectively isolated the total aromatics from the bulk of the sample. Extraneous components were minimized. The more polar PAC such as the hydroxy-PAH were excluded. A two-step procedure efficiently removed the aliphatic compounds by elution through the alumina column and subsequent fractionation of the A23 fraction by Sephadex LH-20.

Comparison of these two samples showed that no discrimination of the PAC by the silica or alumina adsorbents were detected, and the relative amounts of PAH and derivatives were the same using either technique. Difficulties in this comparison were encountered since the chlorinated phenolic compounds were present in much higher concentration than the PAC. Since these compounds were not naturally occurring in urban airborne particulates, their exclusion would probably result in two methods of fractionation that were nearly identical. However, their presence did indicate that some phenols could elute in the aromatic fraction, and create potential interferences in the analysis. The use of preparative normal-phase HPLC as the

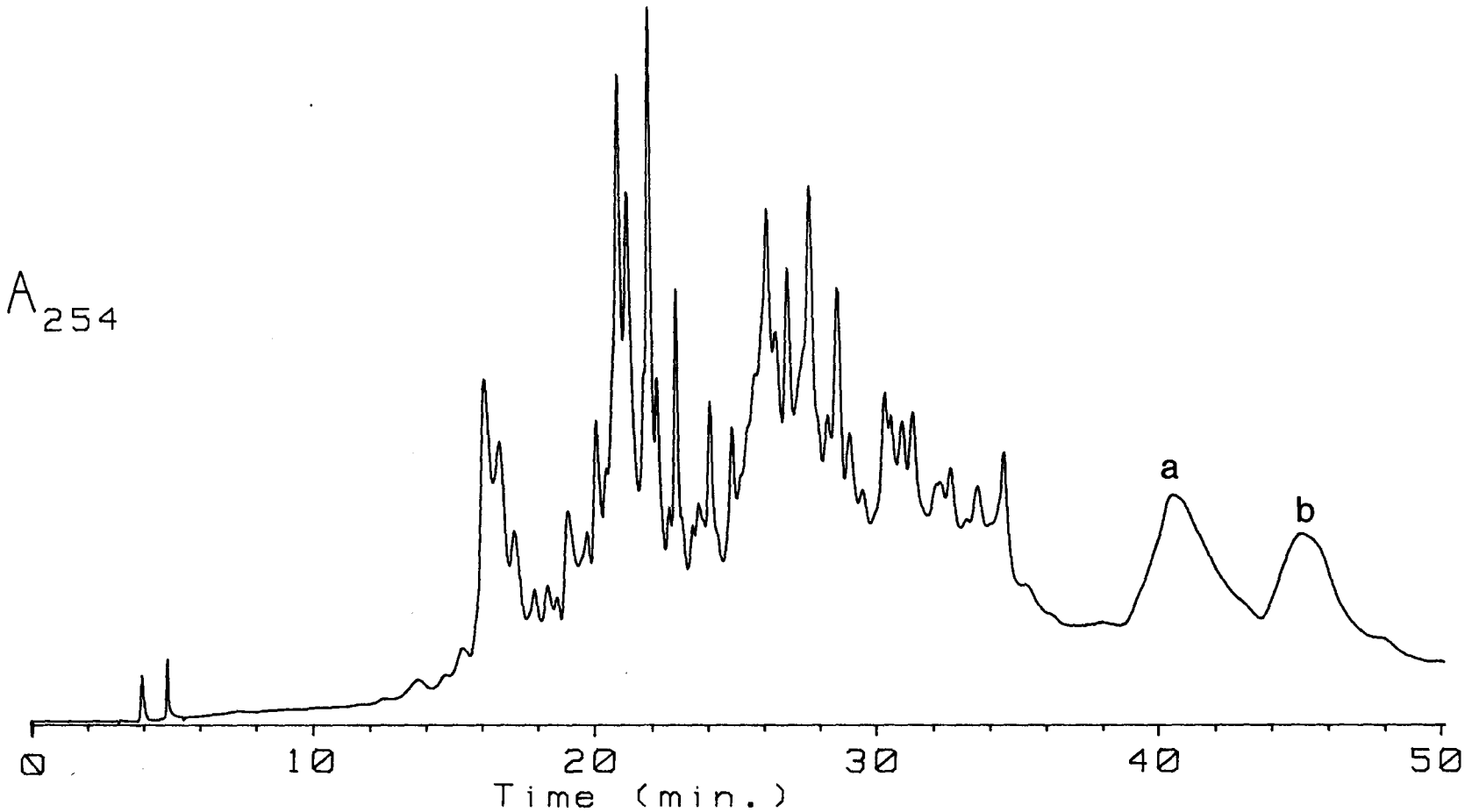


Figure 2-6: The normal-phase HPLC-UVD chromatogram of the PAC in the NBS urban dust sample after clean-up using the silica/LH-20 method. The chlorinated phenolic compounds (peaks a and b) that created problems in the GC analyses are now separated from the PAC of interest.

final clean-up step, effectively isolated the PAC from the other interferences that differentiated these two fractionation methods.

II.5 Handling Precautions and Sample Blanks

Using any clean-up method, contamination of the sample became a serious problem when components were investigated at trace levels. Each step must be critically examined to ensure that the integrity of the analysis was maintained. To verify the method, special handling precautions were taken and blanks were analyzed to discover potential problem areas.

At each stage of the analysis, care was required in handling these samples, since the PAC was present in trace quantities. Therefore, it was important to ensure that no species were introduced during the sampling, clean-up, and analysis steps. Contamination of the sample could have a significant effect on the quality of the results obtained from the analysis. As illustrated by Figure 2-4, these extraneous compounds could effectively mask other components in the sample.

Care was used throughout the procedure to ensure that the sample was not contaminated and only high grade solvents were used. All of the glassware was cleaned by

soaking in an acid bath and then rinsed with copious amounts of water and distilled water to remove any traces of acid. The samples were stored in teflon-capped vials and placed in the freezer. Exposure to ultraviolet light was minimized at each step of the clean-up. After Hi-Vol sampling was complete, the filters were folded in half, wrapped in aluminum foil, and stored in the freezer at -15^{o}C prior to extraction. The samples were extracted shortly after they were obtained. The filters were cut up on a pre-cleaned polyethylene surface. The Soxhlet thimble was made of glass with a glass frit. Glass wool, that was used in the Soxhlet extractor, was pre-extracted with DCM. The Soxhlet apparatus used in the extraction was wrapped in aluminum foil and exposure to UV light was avoided.

Prior to the commencement of this project, three filter types were examined to determine which were suitable for sampling the airborne particulate matter. They were: the Gelman glass fibre filter; the Pallflex teflon-coated glass fibre filter; and a fluorocarbon-coated filter. Concord Scientific Corporation supplied the filters.

It was important to ensure that the filter be as "clean" as possible prior to sample clean-up so that no interferences were introduced into the system. A high filter blank only further complicated this procedure. The filter choice was based mainly on the presence of any

extraneous material that may interfere with the analysis. Examination of a filter blank prior to commencement of sampling also ensured that handling of the filters did not introduce contaminants.

The filter was Soxhlet extracted with DCM and a fraction of the extract was examined by GC-FID. The level of expected interference was then established from the chromatogram. The desired result from this analysis was a blank with a magnitude of response near the detection limit of the method. The chromatogram of the blank showed whether contaminants were present. If they did not co-elute on the column with any peaks of interest in a typical sample, then the blank was acceptable.

The teflon-coated filter and the fluorocarbon-coated filter exhibited very high blank levels and were deemed inadequate for trace analysis. Workers at Concord Scientific attempted to clean the filters prior to use, but their efforts only introduced more contaminants. Other manufacturer's filters were not examined. The extract of a typical blank teflon filter extract, analyzed by GC-FID, is shown in Figure 2-7. As illustrated, there was a large amount of extraneous material. The glass fibre filter was heat-treated, at 400^{o}C for 24 hours prior to use. Heat-treatment not only activated the filter, but it aided in the removal of organic contaminants. The other filter

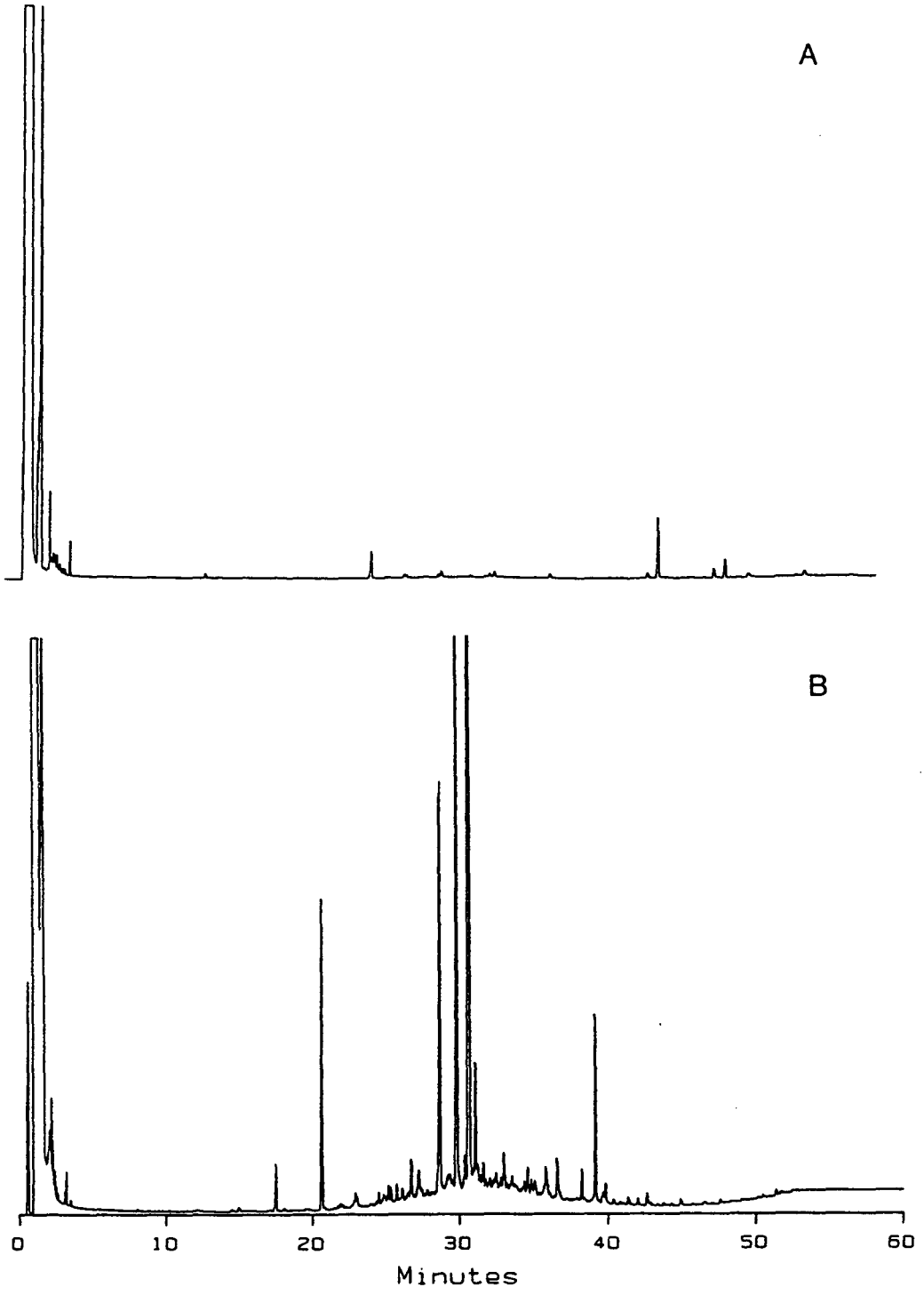


Figure 2-7: GC-FID chromatograms of the DCM extracts of: (A) a glass fibre filter blank; and (B) a teflon filter blank prior to clean-up.

types could not be heated. A typical glass-fibre filter blank is shown in Figure 2-7.

After establishing that the filter blank was acceptable, it was important to determine that the handling of the filters and the clean-up scheme did not introduce contaminants. To determine the combined effect of these factors, blank filters were used. They were handled in the same manner as the samples and put through the clean-up scheme concurrently. The result of putting the blank filters through the clean-up scheme illustrated that no significant contaminants were introduced into the samples. The extract was then examined by GC-FID. An example of a typical chromatogram of a blank filter after clean-up using the silica/LH-20 method, is shown in Figure 2-8. As illustrated, the clean-up process introduced few contaminants, thereby confirming the integrity of the procedure.

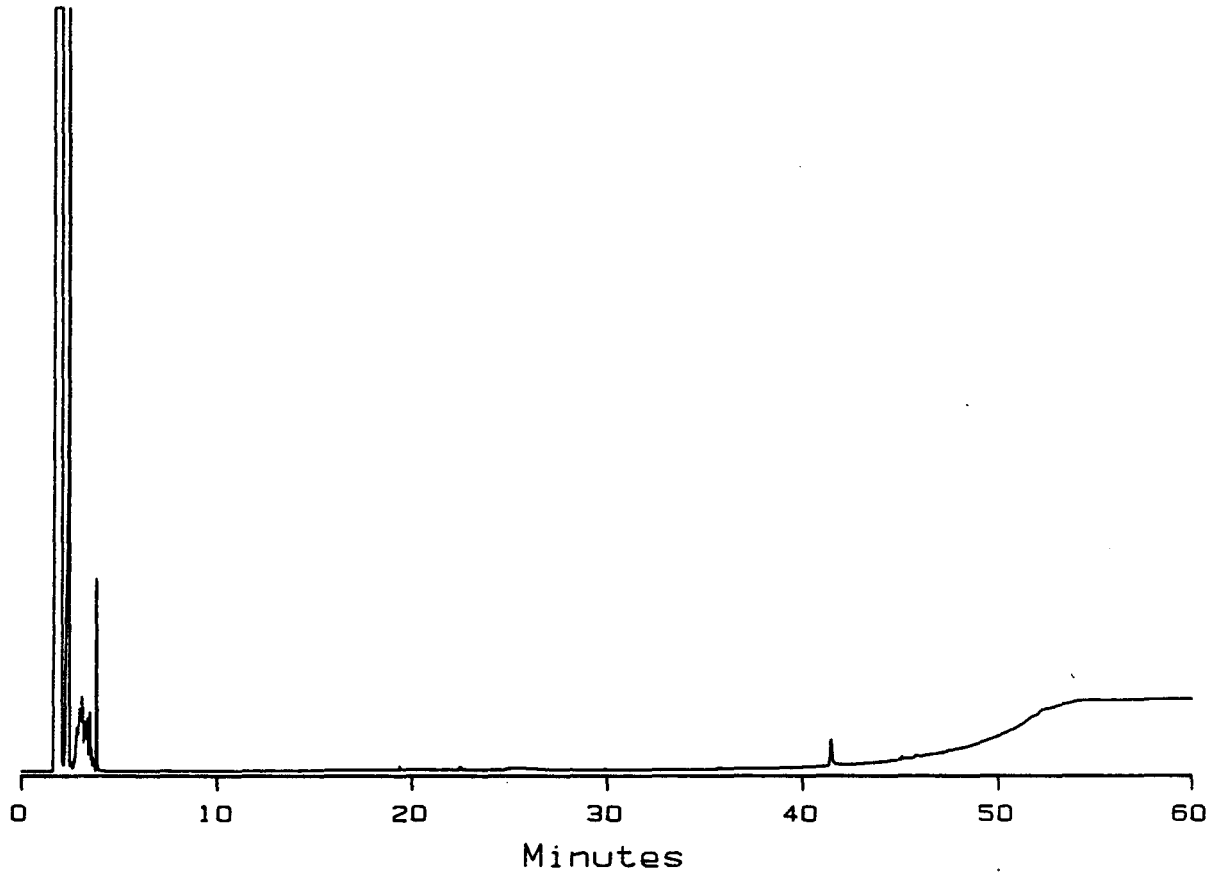


Figure 2-8: GC-FID chromatogram of a glass fibre filter blank after clean-up (using the silica/LH-20 method, PAC fraction).

II.6 Conclusions

Two clean-up methods were developed for the isolation of the total PAC in airborne particulate samples. Using normal-phase HPLC to further separate the PAC into the PAH and PAH derivative fractions, the methods gave identical results. However, the alumina/LH-20 method was shown to be superior for the isolation of a total PAC fraction because it separated out some interfering compounds, such as phenolic compounds.

CHAPTER III: PROFILING METHODS

The applicability of a variety of profiling methods to the determination of the relative levels of PAC in environmental samples was evaluated and the results were presented in this chapter. Methods were developed and improved to analyze samples provided by Concord Scientific Corporation for the determination of the effectiveness of the denuder in the reduction of artifact formation. The PAC samples were examined using chromatographic methods coupled with single or multi-channel detectors.

III.1 Evaluation of Denuder Hi-Vol

Using a Hi-Vol sampler, the airborne particulate matter collected on the filter was continually exposed to large volumes of air containing reactive gases such as ozone. It has been proven that PAH coated on glass fibre filters could react with these gases to form compounds that were mutagenic (13, 18, 32). The problem of artifact formation during Hi-Vol sampling was addressed by Concord Scientific Corporation. A standard Hi-Vol sampler was modified with the addition of a denuder tube bundle, Figure

1-4 (50). Using this design, reactive gases should diffuse to the sides of the tubes and be effectively removed from the airstream. The particulate should be unaffected, and transformations of PAC due to chemical reactions should be minimized.

To try to evaluate the denuder Hi-Vol, Concord Scientific performed a field study and a dynamic exposure laboratory experiment. The filter samples obtained from the denuder Hi-Vol were evaluated by comparison with those obtained from the standard Hi-Vol, in terms of the appearance of different species and the relative amounts of PAH and PAH derivatives present in the sample.

In evaluating the effectiveness of the denuder, it was believed that the expected differences should be readily observed as variations in the chromatograms. These variations would appear in a number of different forms. First of all, if artifact formation occurred in the standard and was prevented in the denuder, then the relative amounts of PAH should be higher and the PAH derivatives should be lower for the denuder Hi-Vol sample. Secondly, reactions between the gases and the PAH could produce PAH derivatives that were unique to the standard Hi-Vol sample.

III.2 Field Study

The samples supplied by Concord Scientific Corporation for analysis were obtained from a sampling site located on the roof of the Hamilton Beach Rescue Unit Association building on Beach Boulevard in eastern Hamilton. The sampling time was twenty-four hours per run. The volume of sampled air was measured, and any pertinent meteorological data was also recorded. The daily ozone concentration range during the sampling period was 40-66 ppb, and 2-5 ppb for nitric acid. Four samplers, two with denuder bundles, were used for each run. The particulate-loaded filters, one from each type of sampler, were paired together, resulting in two sample pairs per run. These pairs were treated exactly the same during the clean-up and analysis steps. In total, five filter pairs were examined. They had been collected over three different sampling periods.

The samples were received from Concord Scientific Corporation after Soxhlet extraction, in the form of a dichloromethane (DCM) extract. Clean-up of the sample was done using the silica/LH-20 method (Figure 1-5). The PAC was further separated into PAH and PAH derivative fractions via normal-phase HPLC. Initial examination of the filter

samples was done using chromatographic methods coupled with single channel detectors, since it was believed that the differences in the pairs would be readily apparent.

III.2.1 Profiling of Field Study Samples

Each filter pair was examined by capillary column gas chromatography coupled with flame ionization or nitrogen-phosphorous detection, and by reversed-phase HPLC, coupled with simultaneous ultraviolet (UVD) and fluorescence detection. Figures 3-1 and 3-2 show respectively the GC-FID chromatograms for the PAH and PAH derivative fractions obtained from a typical sample pair. The chromatograms were normalized according to the volume of air sampled. Normalization allowed comparison of peak heights. As illustrated, there were only very minor differences in the chromatograms that might not be indicative of true changes in the PAC content. Using all of these techniques, no significant differences could be detected in any of the filter pairs. The results from this study were presented in a final report submitted by Concord Scientific Corporation to the Ontario Ministry of the Environment (50). The denuder appeared to have had little impact on the attenuation of the PAC. There were a number of proposed explanations to this discovery: (a) there was little artifact formation occurring during sampling, even with the

Figure 3-1: The GC-FID chromatograms for the PAH fractions obtained for a typical sample pair from the field study. The sample pair consisted of: (A) a filter sample from a standard Hi-Vol; and (B) a filter sample from a denuder Hi-Vol.

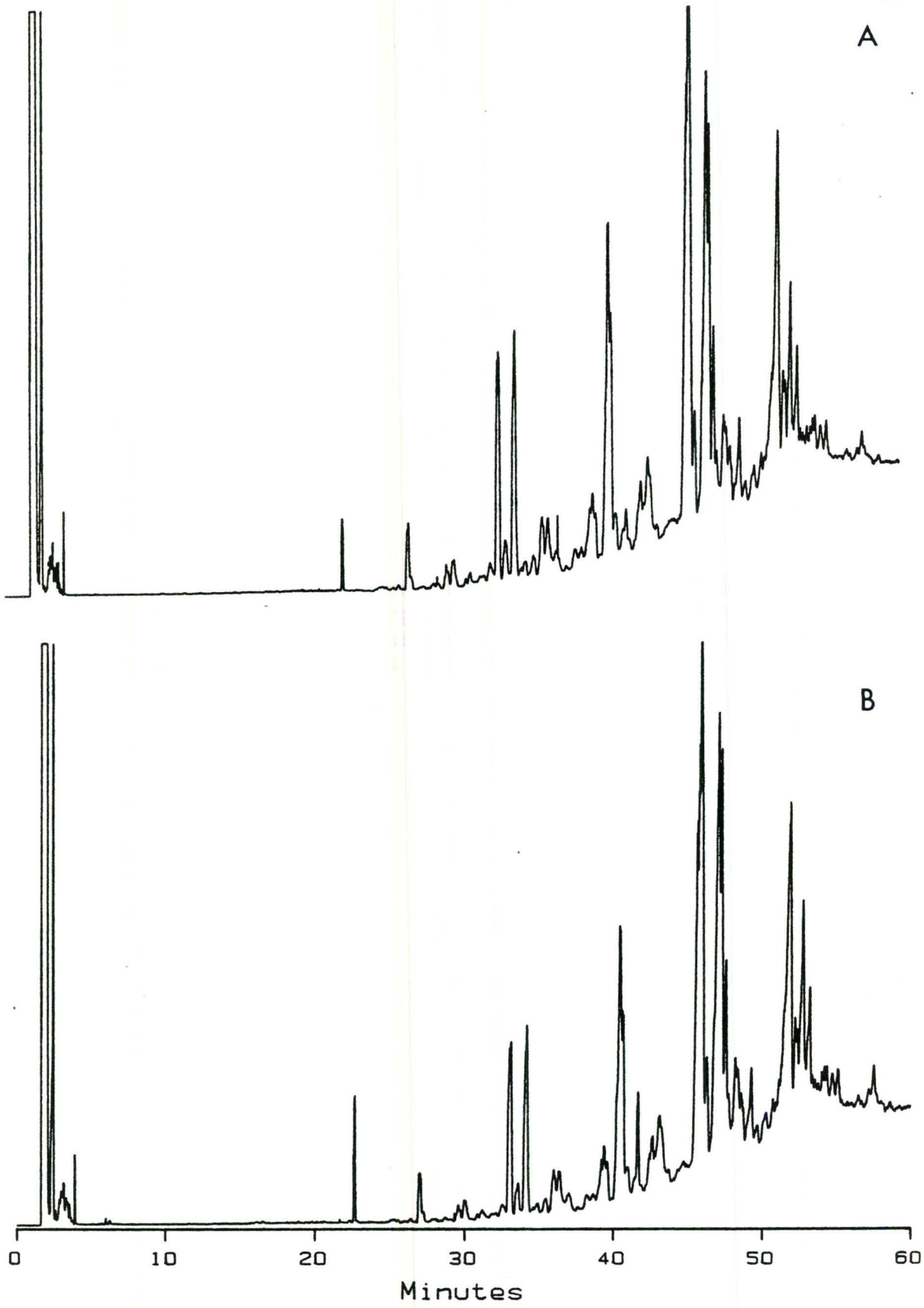
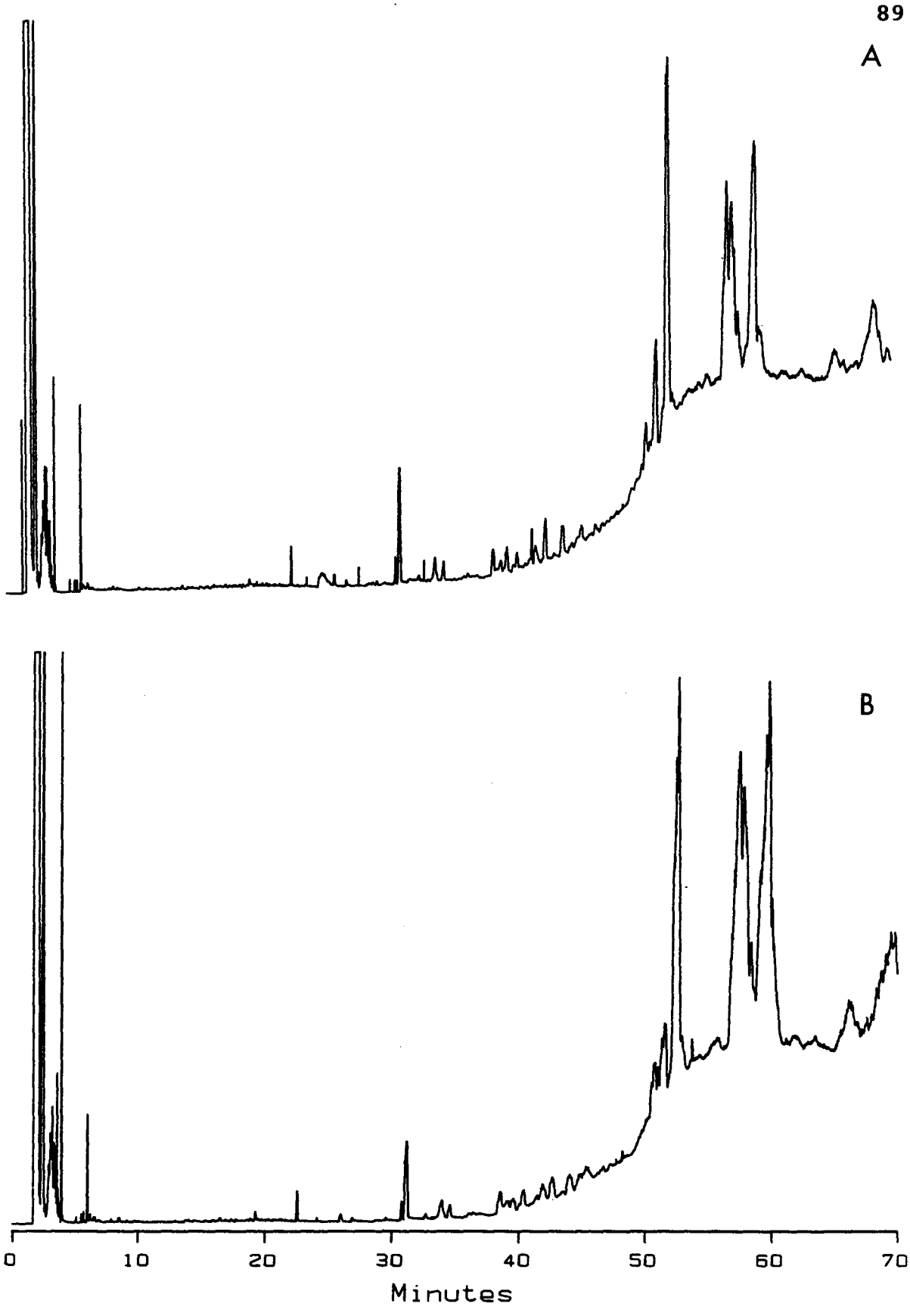

A
B
0
10
20
30
40
50
60
Minutes

Figure 3-2: The GC-FID chromatograms for the PAH derivative fractions obtained for a typical sample pair from the field study. The sample pair consisted of: (A) a filter sample from a standard Hi-Vol; and (B) a filter sample from a denuder Hi-Vol.


A
B
0
10
20
30
40
50
60
70
Minutes

standard Hi-Vol, and all the derivatives were already present in the sample or were formed in the atmosphere before collection; (b) the denuder was ineffective in the prevention of artifact formation; or (c) the differences between the sample compositions were too subtle for the techniques used.

It was not the purpose of this project to investigate the first explanation, but to try to determine whether the denuder was effective. A laboratory experiment was used to try to ascertain an answer. In addition, the methods were improved by going to mass spectral-based techniques in order to have better profiling capability, and the clean-up scheme was simplified by eliminating the normal-phase HPLC fractionation step.

III.3 Laboratory Study: The Dynamic Exposure Experiment

During the sampling of airborne particulate matter, the levels of the reactive gases were continually changing. It was not known at what level, if any, interaction between the gases and the particulate matter would result in artifact formation. Exposure of the sample to high levels of reactive gases was necessary to determine whether the denuder was beneficial. Ozone and nitric acid were chosen because of recent studies on the reactivity of PAH with these gases (17, 19, 140).

Pre-loaded filters were obtained by sampling with a standard Hi-Vol on the roof of the Concord Scientific Corporation building in Toronto. These filters were cut in half and a denuder bundle was placed in front of one of the halves. The two halves were then exposed to airstreams containing either ozone or nitric acid. The experiment was designed by Concord Scientific to mimic field conditions. The conditions were detailed in the experimental section.

The filter samples did not contain very much particulate. It was evident that the amount of PAC in the individual samples was not sufficient for analysis and therefore the samples were combined. The result of these experiments was four pooled samples, a pair of samples for each reactive gas studied. A sample pair consisted of the combined filter halves that had a denuder placed in front of it during exposure, and those that did not.

III.3.1 Analysis of Dynamic Exposure Samples

As previously mentioned, an alternate method of analysis was adopted for these samples. The silica/LH-20 clean-up scheme was still used, but it was evident that even after fractionation of the PAC into two classes, the sample was still too complex for a simple detector. Re-examination of Figures 3-1 and 3-2 exemplifies this problem. Detection of slight changes in the relative amounts of PAC was very

difficult. In addition, the fractionation of these samples was done using gradient elution normal-phase HPLC with hexane and isopropanol as the mobile phase. Using these conditions, the two fractions of interest eluted very quickly and were poorly resolved (Figure 2-1). This step could introduce a large source of error, since the reproducibility of the cut-point was crucial. This was a very serious problem when profiling was done using single channel detectors, since they were not discriminating. Elimination of this step would also significantly decrease clean-up and analysis time.

Gradient elution normal-phase HPLC using hexane and DCM has been shown to greatly enhance the resolution of the PAC (Figure 2-1). The PAH and the PAH derivatives were eluted in two distinct regions. Thus any peak could easily be classified by its location in the chromatogram. Very little resolution of PAH isomers was provided by this method, but, when only the relative levels of PAC were being determined, normal-phase HPLC using an ultraviolet detector or mass spectrometry would be viable methods for profiling.

III.3.2 Normal-phase HPLC-UVD Analyses

An initial survey of the total PAC in the samples by normal-phase HPLC-UVD showed no apparent differences in any of the pairs. Figure 3-3 compares the chromatograms for the ozone exposure samples. The chromatograms for the sample pair exposed to nitric acid is presented in Figure 3-4.

III.3.3 Normal-phase HPLC-MS Analyses

The use of normal-phase HPLC-MS produced more interesting results. The resolution of the system was greatly enhanced by the use of mass chromatograms for the selective detection of various types of PAC. Analysis of the normal-phase HPLC-MS results was done by plotting selected mass chromatograms corresponding to known PAH and PAH derivatives. They were normalized with respect to the 276-PAH, that was arbitrarily chosen as an internal marker, used to correct for volumetric errors. Peak areas from the mass chromatograms of the standard and denuder samples were incorporated into the equation presented at the end of Table 3-1. The result was a "normalized ratio" that was used to compare the samples. If there were no differences between the standard and denuder samples, this ratio should be 1.0.

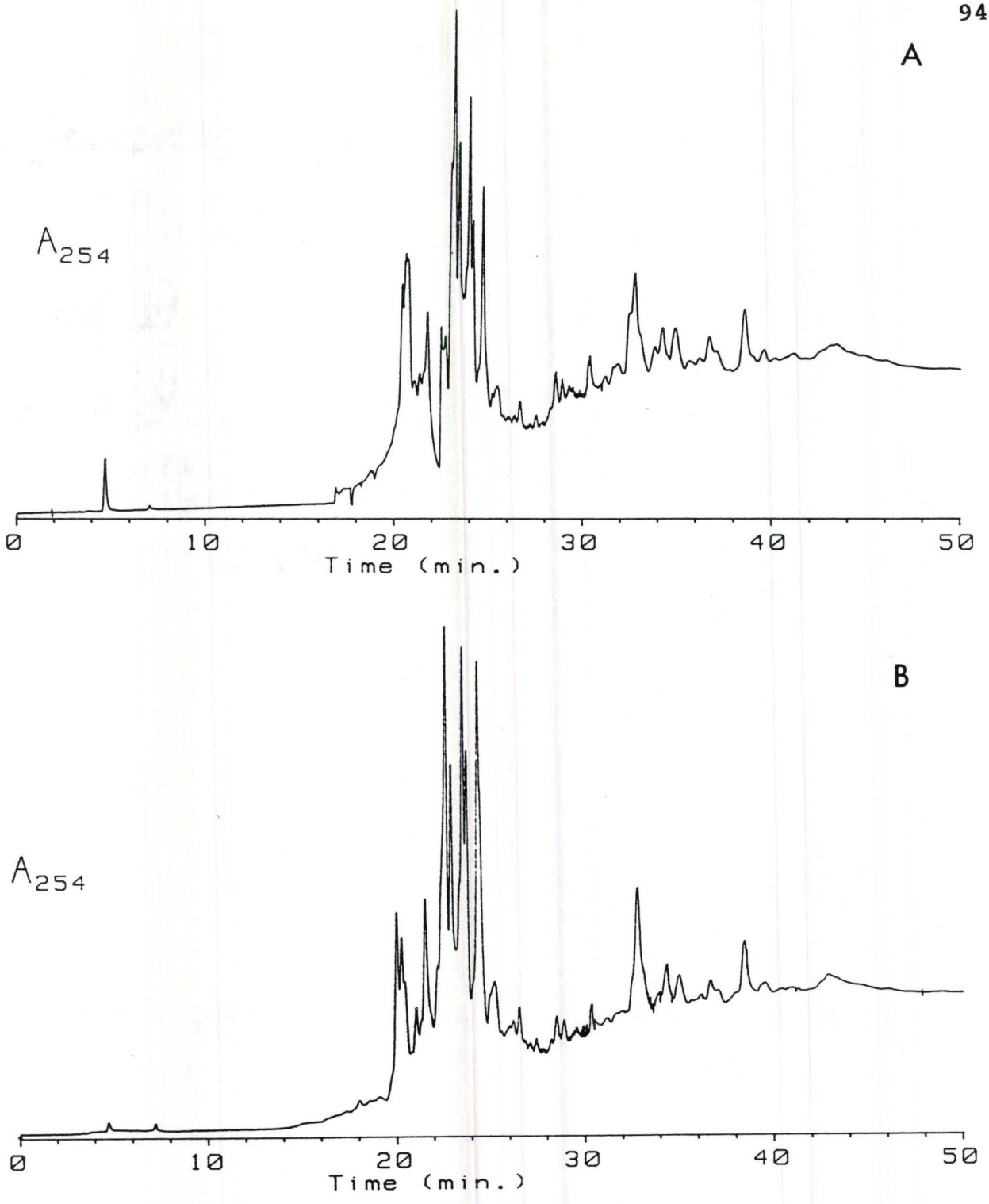


Figure 3-3: The normal-phase HPLC-UVD chromatograms for the dynamic ozone exposure sample pair: (A) filter samples directly exposed to ozone-spiked air; and (B) filter samples exposed to ozone-spiked air that has passed through a denuder bundle.

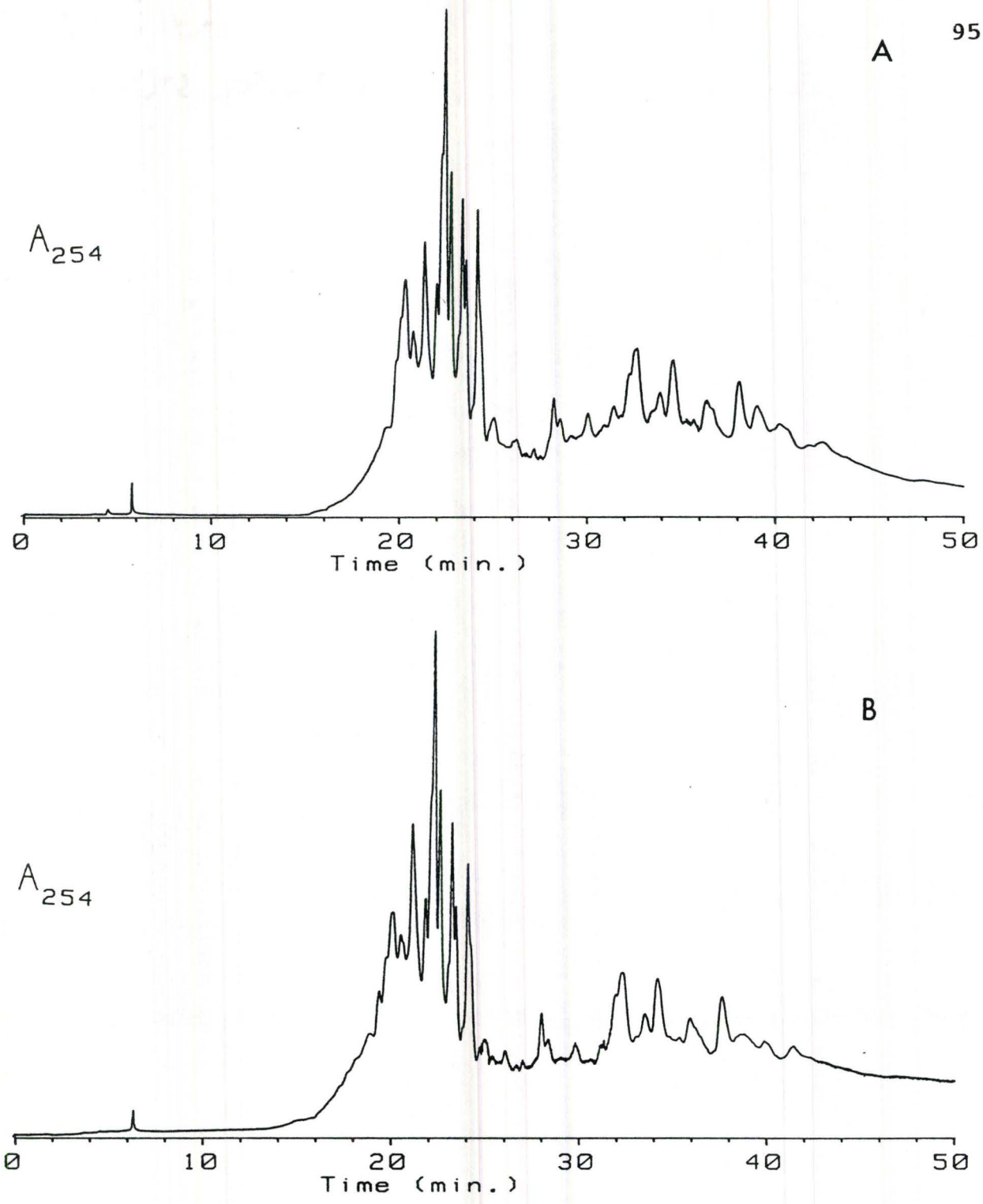


Figure 3-4: The normal-phase HPLC-UVD chromatograms for the dynamic nitric acid exposure sample pair: (A) filter samples directly exposed to nitric acid-spiked air; and (B) filter samples exposed to nitric acid-spiked air that has passed through a denuder bundle.

However, if there were conversion of PAH to PAH derivatives, the ratio for the PAH would be less than 1.0 and the ratio for the derivatives would be greater than 1.0.

III.4 Ozone Exposure Samples

These criteria of determination of the relative differences by ratios were applied to the ozone exposure samples. Examination of the normal-phase HPLC-MS data for these samples, Table 3-1, indicated that dramatic differences were observed in the relative levels of PAC. There was an obvious change in the level of some PAC in the standard sample. Key mass chromatograms normalized against the m/z 276 mass chromatogram (arbitrarily chosen) are presented in Figure 3-5. Compounds in the PAH derivative region (masses 230, 254, 258 and 278) showed normalized ratio values that were significantly greater than 1.00. Therefore they were at a higher concentration in the standard sample than in the denuder sample. The mass spectra of some of these compounds showed losses of 28 mass units from the molecular ion, indicative of ketone and quinone derivatives of PAH. Selected mass spectra are presented in Figure 3-6.

The data in Table 3-1 and Figure 3-5 showed that the concentrations of some PAH were significantly lower in the standard sample. This could be because of reaction of these

Table 3-1: Results from the normal-phase HPLC-MS analyses of the paired dynamic ozone exposure samples.

Compound Identity[1]	Obs. Mass	Scan#	Peak area Standard	Peak area Denuder	Norm.[2] Ratio
PAH:					
Phenanthrene	178	354	3859	20898	0.4
Fluoranthene	202	371	3846	15341	0.5
Pyrene	202	378	5911	23824	0.5
Benzofluorenes	216	378	706	4340	0.4
264-PAH	264	379	194	786	0.6
226-PAH	226	389	1773	6475	0.6
240-PAH	240	397	796	2135	0.8
264-PAH	264	397	542	1052	1.2
Benz[a]anthracene	228	398	7864	25639	0.6
Chrysene	228	402	1987	5605	0.7
240-PAH	240	402	683	1980	0.8
252-PAH	252	413	35443	77576	1.0
264-PAH	264	415	1480	3068	1.1
276-PAH	276	427	33421	75267	1.0
278-PAH	278	429	7464	14301	1.1
PAH Derivatives:					
Anthraquinone	208	557	1929	?[3]	
?	226	667	4438	2229	4.4
216-PAK	230	500	4055	5364	1.7
216-PAK	230	534	1080	1260	1.9
216-PAK	230	618	7628	5862	2.9
216-PAK	230	648	7531	5649	3.0
240-PAK	254	508	746	1323	1.2
240-PAK	254	586	2862	?[3]	
240-PAK	254	608	3365	2824	2.6
240-PAK	254	638	1433	644	5.0
240-PAK	254	677	14787	9821	3.3
228-PAQ	258	536	3556	3394	2.3
228-PAQ	258	600	2357	546	9.7
264-PAK	278	606	5458	4398	2.7
264-PAK	278	628	1197	412	6.5
252-PAQ	282	639	3333	1381	5.4
1-Nitropyrene	247	465	2234	3189	1.5
Nitrofluoranthene	247	476	499	1064	1.0

.....continued

Table 3-1 (continued)

[1] Acronyms for compound types are explained in Figure 1-2.

[2] The 276-PAH peak was used as an internal standard to derive the normalized ratio:

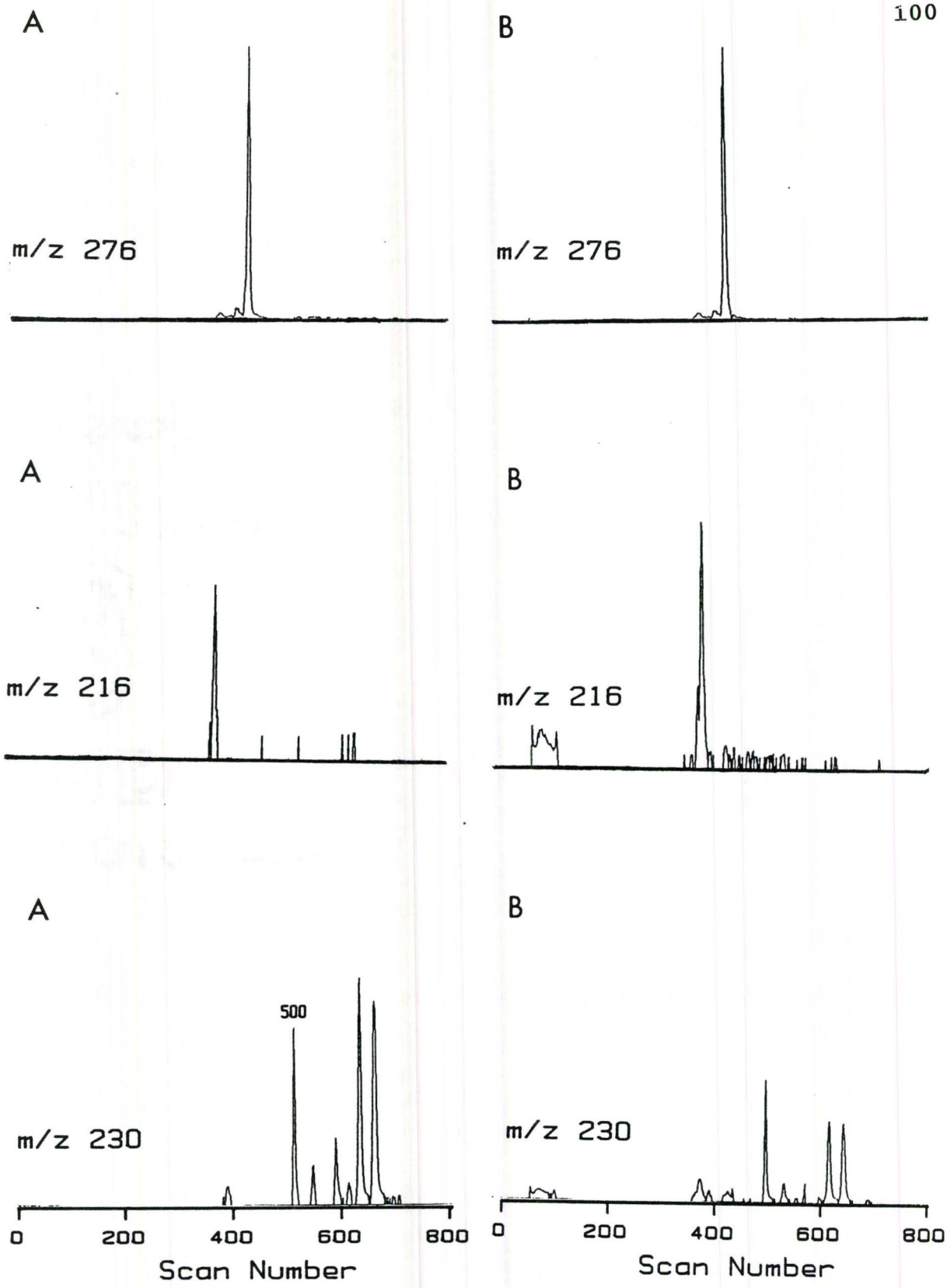
$$\text{Norm. Ratio} = \frac{(A_{s,j}/A_{d,j})}{(A_{d,m}/A_{s,m})}$$

where A = area, s = standard Hi-Vol, d = denuder Hi-Vol, j = peak of interest, and m = 276 PAH.

[3] The area could not be determined.

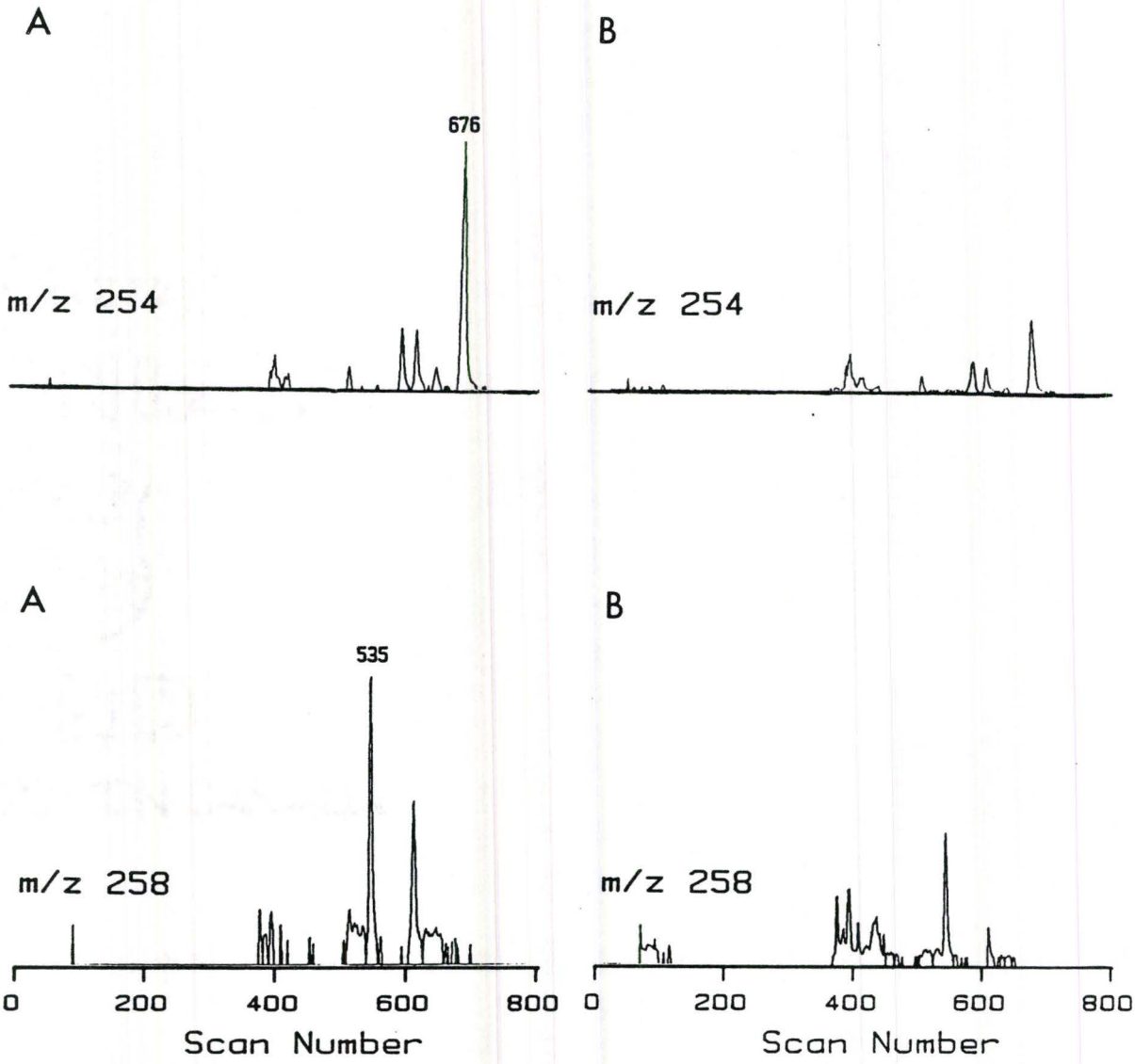
Figure 3-5: Reconstructed mass chromatograms (from a normal-phase HPLC-MS analysis using full scan mode) where differences in the relative levels were noted between: (A) the standard ozone sample; and (B) the denuder ozone sample. They have been normalized against the m/z 276 mass chromatogram.

Figure 3-5 (continued)



A: Standard Ozone Exposure Sample
B: Denuder Ozone Exposure Sample

Figure 3-5 (continued)



A: Standard Ozone Exposure Sample

B: Denuder Ozone Exposure Sample

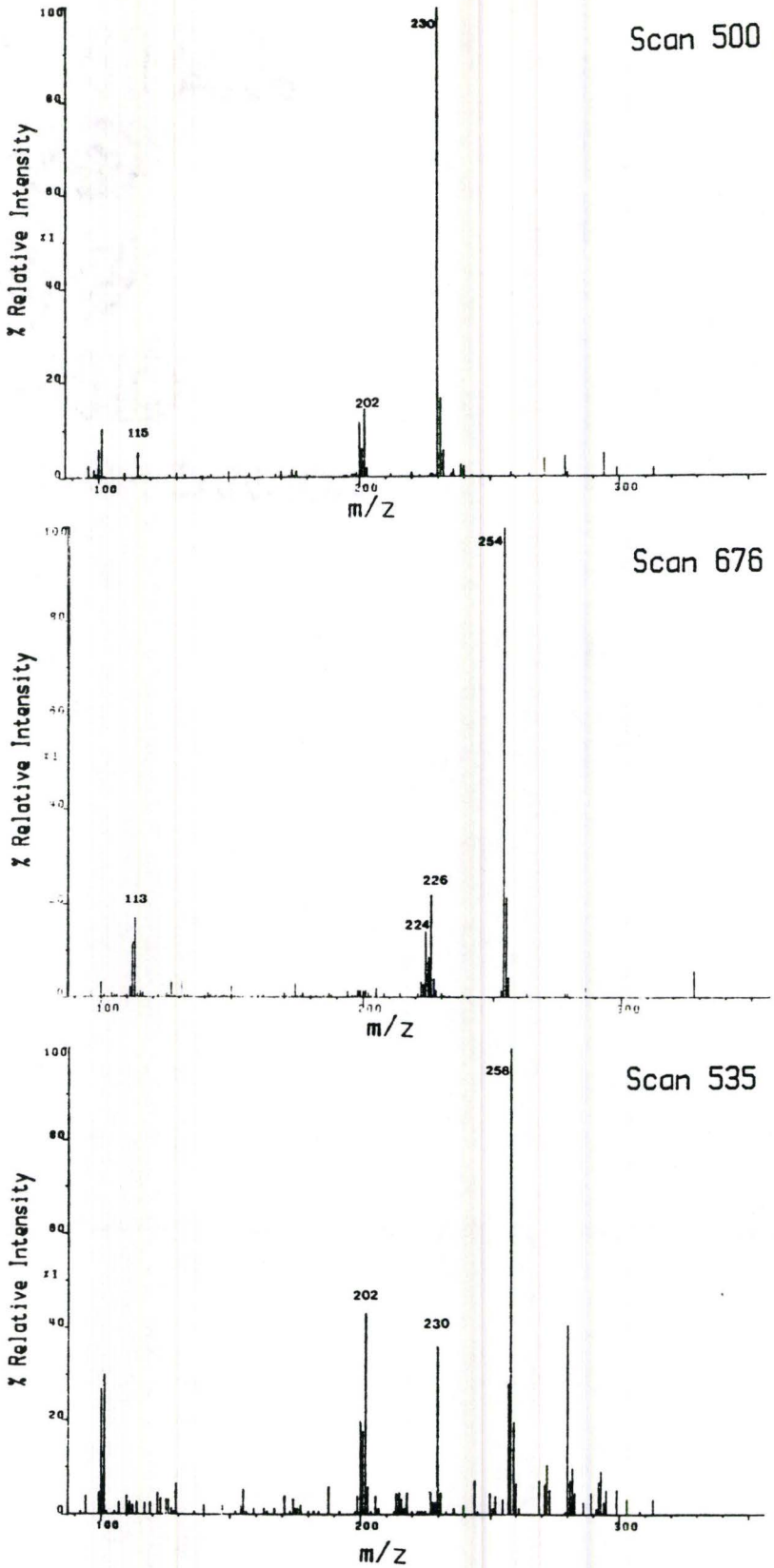


Figure 3-6: The mass spectra of some PAH derivatives whose relative levels increased during dynamic ozone exposure experiment.

PAH to the observed PAH derivatives and possibly other undetected products. There was a possibility that these differences could be because of a higher evaporative loss of more volatile PAH. This seemed unlikely since the same volume of air passed through both samples, and during clean-up, they were handled in the same way.

It appeared that no unique compounds were present in the standard sample. However, there was an increase in the concentration of oxygenated PAH derivatives and a decreased concentration of some PAH when the filter was exposed to ozone without the denuder. The extent of reaction still occurring even with the denuder could not be determined with the present experimental design. It would have been worthwhile to have divided the filters into three and saved the last third as a control for the ozone exposed fractions. However, it was useful to note that the nitric acid exposure experiments showed very similar levels of PAH and PAH derivatives (Table 3-2) to those in the denuder ozone sample. This would tend to support the argument that the denuder did stop most of the oxidation reactions due to the ozone.

III.5 Nitric Acid Exposure Samples

The normal-phase HPLC-MS data from the exposure of nitric acid to the standard and denuder samples did not indicate any significant differences. As illustrated in Table 3-2, the level of oxygenated PAH and nitrated PAH derivatives were virtually the same in both samples. These results could be explained by a number of possibilities: (a) the dynamic exposure conditions were inappropriate to effect nitration; (b) the reactions did occur, but the denuder did not provide additional protection; and (c) nitration reactions occurred prior to the dynamic exposure. No conclusion could be made without further experimentation.

There was one additional observation that could be made about the data in Table 3-1 that should be noted at this time. The concentration of 1-nitropyrene in the standard ozone sample was about 50% higher than in the other sample. The level of 1-nitropyrene did not differ in the nitric acid exposure samples. At first this suggested a problem with the analysis. However, it was possible that high levels of ozone mixed with air with a trace of nitrogen dioxide could produce a nitrating agent, N_2O_5, by the following reaction:

$$O_3 + NO_2 \longrightarrow N_2O_5$$

Table 3-2: Results from the normal-phase HPLC-MS analyses of the paired dynamic nitric acid exposure samples.

Compound Identity[1]	Obs. Mass	Scan#	Peak area Standard	Peak area Denuder	Norm.[2] Ratio
PAH:					
Phenanthrene	178	354	25094	30590	0.7
Fluoranthene	202	371	28140	25788	0.9
Pyrene	202	378	37301	?[3]	
Benzofluorenes	216	378	?[3]	?[3]	
264-PAH	264	379	?[3]	?[3]	
226-PAH	226	389	24101	?[3]	
240-PAH	240	397	?[3]	?[3]	
264-PAH	264	397	?[3]	?[3]	
Benz[a]anthracene	228	398	66726	62832	0.9
Chrysene	228	402	17850	18226	0.8
240-PAH	240	402	?[3]	?[3]	
252-PAH	252	413	140710	153793	0.7
264-PAH	264	415	?[3]	?[3]	
276-PAH	276	427	186938	163050	1.0
278-PAH	278	429	28075	31214	0.7
PAH derivative:					
Anthraquinone	208	557	14339	14374	0.8
?	226	667	9571	7221	1.1
216-PAK	230	500	33364	39760	0.7
216-PAK	230	534	3952	4343	0.7
216-PAK	230	618	41641	48755	0.7
216-PAK	230	648	33061	30413	0.9
240-PAK	254	508	4504	1077	0.9
240-PAK	254	586	7534	6862	0.9
240-PAK	254	608	8396	8952	0.8
240-PAK	254	638	?[3]	?[3]	
240-PAK	254	677	37052	29983	1.0
228-PAQ	258	536	12671	13664	0.8
228-PAQ	258	600	6924	7584	0.7
264-PAK	278	606	13130	13128	0.8
264-PAK	278	628	2686	2558	0.9
252-PAQ	282	639	9420	9280	0.8
1-Nitropyrene	247	465	3288	3505	0.8
Nitrofluoranthene	247	476	2623	3726	0.6

.....continued

Table 3-2 (continued)

[1] Acronyms for compound types are explained in Figure 1-2.

[2] The 276-PAH peak was used as an internal standard to derive the normalized ratio:

$$\text{Norm. Ratio} = \frac{(A_{s,j}/A_{d,j})}{(A_{d,m}/A_{s,m})}$$

where A = area, s = standard Hi-Vol, d = denuder Hi-Vol, j = peak of interest, and m = 276 PAH.

[3] The area could not be determined.

During the course of this work, Pitts and coworkers (141) showed that N_2O_5 is a powerful nitrating agent for pyrene, whereas nitric acid does not appear to react with absorbed pyrene to any extent. Early work by Grosjean and others (19) suggested that nitric acid is a potent nitrating agent, but differences in the nature of the PAH studied, experimental conditions, and pollutant air composition could have a large effect on the results.

III.6 Other Applications of Normal-phase HPLC-MS

The applicability of normal-phase HPLC-MS in profiling PAC in a wider variety of samples was also examined. Another set of archived filters from the field study experiment was studied to determine whether the more discriminating HPLC-MS technique could detect any differences in these samples. Three other samples, the NBS urban dust sample, a typical airborne particulate sample and a marine sediment were also compared.

III.6.1 Additional Field Study Samples

Since the dynamic exposure experiment showed that the denuder did prevent some artifact formation, it was necessary to re-examine the remaining archived field study samples to determine whether the other profiling methods

have failed to detect the differences in the levels of PAC. A sample pair that was not previously investigated, but collected at the same time as the other field samples, was used. In this case, the method was further improved using an internal standard, perdeuterated pyrene, added to the samples prior to analysis. Normal-phase HPLC-UVD and normal-phase HPLC-MS analyses of a sample pair obtained during the field study were performed to determine whether any differences could be detected using these methods. The normal-phase HPLC-UVD chromatograms for the standard and denuder samples, as shown in Figure 3-7, indicated no apparent differences in the sample pair. Interpretation of the normal-phase HPLC-MS data was done by manual determination of peak heights on the individual mass chromatograms, and calculation of the normalized ratio. The current version of software on the mass spectral data system, lacked an adequate method for area determination. The results of the analysis are presented in Table 3-3. The equation used in the calculation of the ratio is presented at the end of the table. When peak heights were used, peaks that were slightly skewed or tailing may increase the error in the determination. As illustrated, the analytical uncertainty appeared to be quite high. This could be due in part to the difficulties in doing quantitative HPLC-MS experiments. In general, the ratio for all of the PAH and

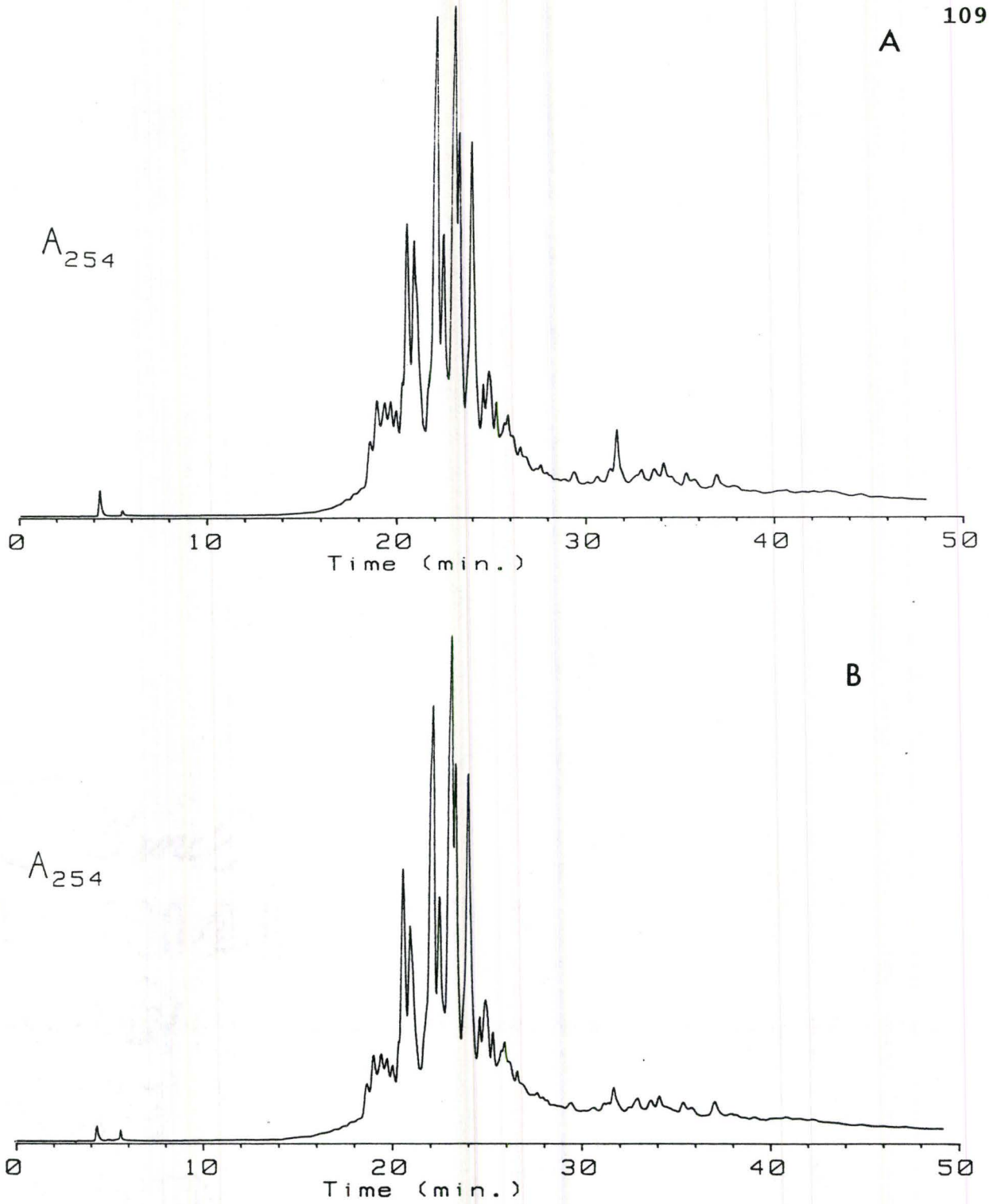


Figure 3-7: The normal-phase HPLC-UVD chromatograms for a sample pair from the field study. The sample pair consisted of: (A) a filter sample from a standard Hi-Vol; and (B) a filter sample from a denuder Hi-Vol.

Table 3-3: The results of the normal-phase HPLC-MS analyses of the denuder and standard Hi-Vol samples from the field study.

Compound[1] Identity	Obs. Mass	Scan#	Peak Heights Standard	Peak Heights Denuder	Norm.[2] Ratio
PAH:					
Phenanthrene	178	457	8888	4478	1.4
Anthracene	178	448	2442	1279	1.4
C1-166-PAH	180	502	962	654	1.0
190-PAH	190	466	674	353	1.4
190-PAH	190	449	1192	583	1.5
C1-166-PASH	198	541	373	258	1.0
C1-166-PASH	198	566	531	373	1.0
C1-166-PASH	198	414	269	218	0.9
C1-166-PASH	198	429	287	123	1.7
Pyrene	202	494	18819	10258	1.3
Fluoranthene	202	510	19692	10960	1.3
C1-190-PAH	204	502	576	452	0.9
C1-190-PAH	204	471	1047	571	1.3
C1-190-PAH	204	486	1282	542	1.7
C2-178-PAH	206	501	874	638	1.0
C2-178-PAH	206	491	702	344	1.5
C2-178-PAH	206	477	3027	1522	1.4
Pyrene-D10	212	501	35828	25547	1.0
216-PAH	216	510	4475	2430	1.3
216-PAH	216	515	5391	3521	1.1
C2-190-PAH	218	487	1455	703	1.5
C2-190-PAH	218	476	1390	664	1.5
C2-190-PAH	218	499	2230	1099	1.4
C2-190-PAH	218	465	3281	1297	1.8
C4-166-PAH	222	565	704	433	1.2
C4-166-PAH	222	586	580	333	1.2
C4-166-PAH	222	571	749	476	1.1
226-PAH	226	530	5101	2726	1.3
228-PAH	228	540	26442	16697	1.1
228-PAH	228	520	3777	1974	1.4
228-PAH	228	549	9118	4442	1.5
C1-216-PAH	230	540	544	430	0.9
C1-216-PAH	230	512	2441	1455	1.2
C1-216-PAH	230	518	2403	1319	1.3
240-PAH	240	537	2925	1784	1.2
240-PAH	240	548	2738	1353	1.4

.....continued

Table 3-3 (continued)

Compound[1] Identity	Obs. Mass	Scan#	Peak Heights Standard	Peak Heights Denuder	Norm.[2] Ratio
PAH:					
C1-228-PAH	242	499	1767	750	1.7
C1-228-PAH	242	544	7173	4758	1.1
C1-228-PAH	242	523	1837	891	1.5
C4-190-PAH	246	589	525	446	0.8
C4-190-PAH	246	491	859	446	1.4
C1-216-PASH	248	586	1475	945	1.1
C1-216-PASH	248	515	2001	1049	1.4
252-PAH	252	571	40224	30814	0.9
252-PAH	252	565	42529	32243	0.9
H2-252-PAH	254	550	1267	773	1.2
H2-252-PAH	254	541	2766	1652	1.2
H2-252-PAH	254	572	1117	826	1.0
H2-252-PAH	254	563	1199	813	1.1
238-PASH	256	544	4243	2583	1.2
C3-216-PAH	258	532	1445	786	1.3
C3-216-PAH	258	518	1474	798	1.3
C3-216-PAH	258	548	1060	480	1.6
C3-216-PAH	258	489	915	448	1.5
266-PAH	266	569	6267	4961	0.9
C2-240-PAH	268	553	3330	2430	1.0
C2-240-PAH	268	558	2293	1260	1.3
C2-240-PAH	268	540	4899	3045	1.1
C3-228-PAH	270	535	1072	603	1.3
C3-228-PAH	270	548	1343	756	1.3
C3-228-PAH	270	590	463	261	1.3
276-PAH	276	590	48383	31755	1.1
278-PAH	278	558	1915	1023	1.3
278-PAH	278	585	16898	10387	1.2
278-PAH	278	564	1998	1279	1.1
C2-252-PAH	280	574	1909	1152	1.2
C2-252-PAH	280	566	2729	1695	1.1
C2-252-PAH	280	556	1385	868	1.1
266-PASH	284	555	1795	1197	1.1
266-PASH	284	566	1486	1108	1.0
290-PAH	290	591	4890	2887	1.2
290-PAH	290	585	4529	2702	1.2
C1-278-PAH	292	583	2706	1689	1.1
C1-278-PAH	292	566	3018	1749	1.2
302-PAH	302	604	12242	6982	1.3

.....continued

Table 3-3 (continued)

Compound[1] Identity	Obs. Mass	Scan#	Peak Heights Standard	Peak Heights Denuder	Norm.[2] Ratio
PAH Derivatives:					
Fluorenone	180	746	1070	334	2.3
178-PAHK	194	757	332	122	1.9
166-PAQ	196	814	306	153	1.4
190-PAK	204	731	536	292	1.3
Anthraquinone	208	763	2388	740	2.3
190-PAQ	220	809	629	325	1.4
C1-178-PAQ	222	756	543	227	1.7
216-PAK	230	670	2515	960	1.9
216-PAK	230	802	2304	1046	1.6
216-PAK	230	846	2515	1190	1.5
216-PAK	230	754	768	294	1.9
240-PAK	254	790	818	493	1.2
240-PAK	254	765	600	373	1.1
240-PAK	254	884	2766	1652	1.2
240-PAK	254	679	627	373	1.2
226-PAQ	256	740	293	178	1.2
228-PAQ	258	713	1438	476	2.2
228-PAQ	258	791	726	460	1.1
240-PAQ	270	840	258	171	1.1
240-PAQ	270	777	417	261	1.1
264-PAK	278	789	583	460	0.9
266-PAK	280	812	494	284	1.2
266-PAK	280	716	323	184	1.3
266-PAK	280	834	726	434	1.2
266-PAK	280	858	645	501	0.9
266-PAK	280	695	538	351	1.1
252-PAQ	282	834	278	157	1.3
C1-240-PAQ	284	754	159	130	0.9

[1] Acronyms for compound types are explained in Figure 1-2.

[2] The perdeuterated pyrene peak was used as an internal standard to derive the normalized ratio:

$$\text{Norm. Ratio} = \frac{(P_{s,j}/P_{d,j})}{(P_{d,m}/P_{s,m})}$$

where P = peak height, s = standard Hi-Vol, d = denuder Hi-Vol, j = peak of interest, and m = 202 PAH-D10 (perdeuterated pyrene).

PAH derivatives was above 1.0. Unlike the results from the dynamic exposure experiment, there were no trends in the data. The results indicated that there were essentially no differences in the sample pair outside of experimental error.

III.6.2 Comparison of Different Environmental Samples

After showing the applicability of the normal-phase HPLC-MS profiling method to the denuder problem, other environmental samples were examined. They were the NBS urban dust sample, a typical airborne particulate sample collected in Hamilton, and the NRC marine sediment sample. These samples came from very different sources, and the distribution of the classes of PAC was quite different. This fact was quite evident in the appearance of the total ion current chromatograms from the normal-phase HPLC-MS analyses for the three samples presented in Figures 3-8 through 3-10 respectively. The relative distribution of PAH to PAH derivatives was different in each of these samples. There were a lot more PAH derivatives in the NBS dust sample than in the other samples. The PAH fractions were very different as well. The sediment sample, taken from Halifax Harbour, appears to have more of the lower molecular weight PAH than the other samples. This would be expected because of the nature of the sample collection. Sampling air for

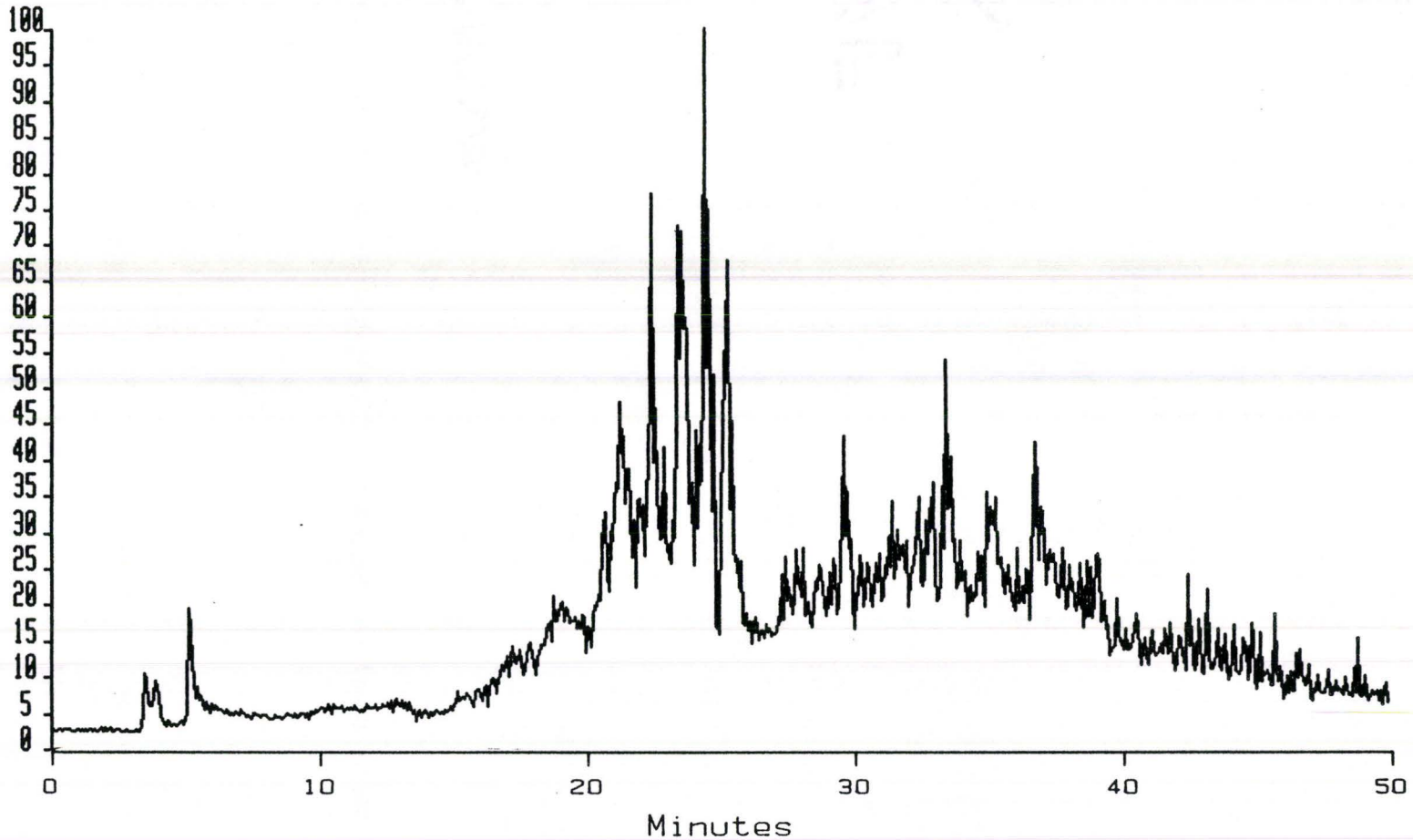


Figure 3-8: The normal-phase HPLC-MS total ion current chromatogram for the NBS urban dust sample.

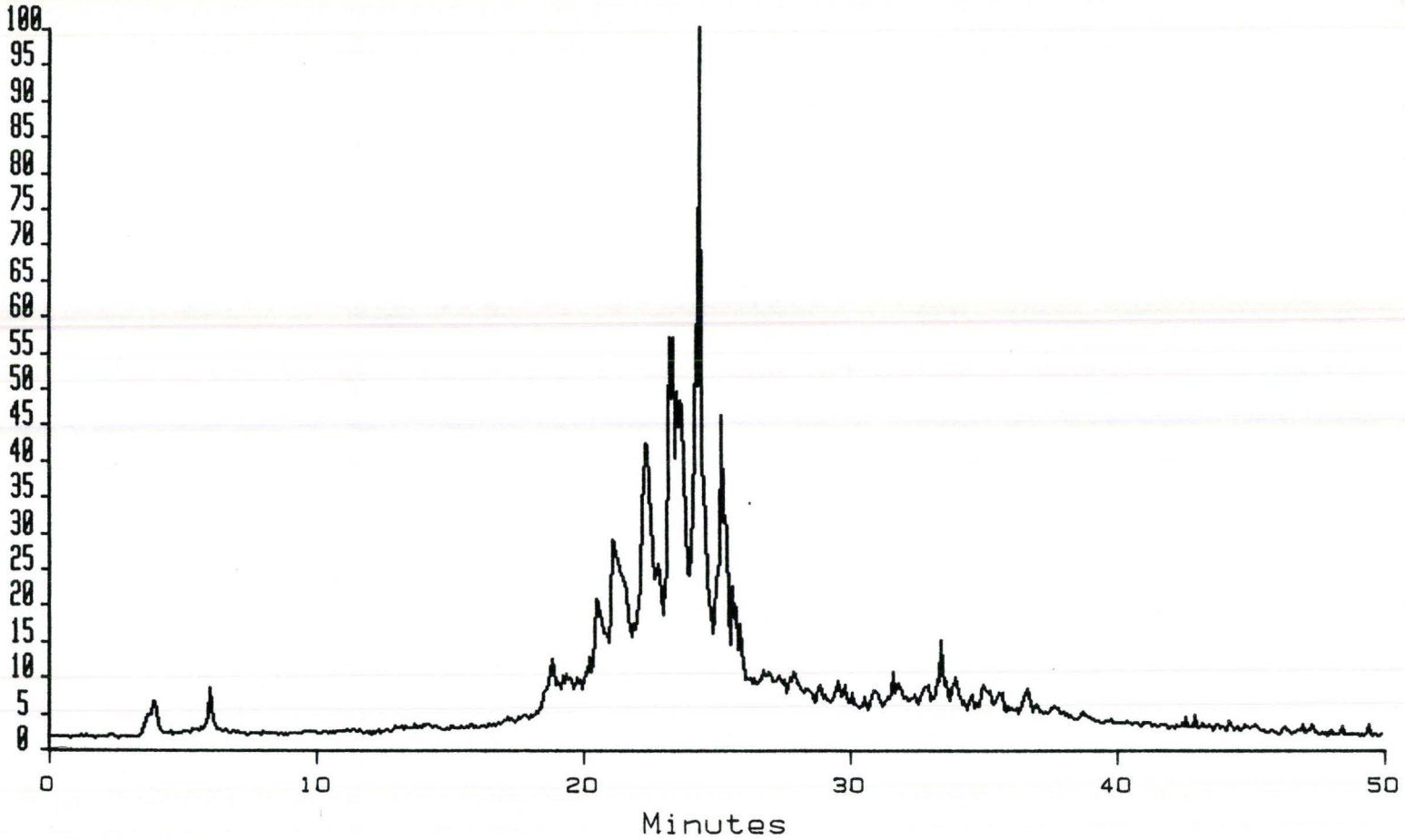


Figure 3-9: The normal-phase HPLC-MS total ion current chromatogram for the Hamilton airborne particulate sample.

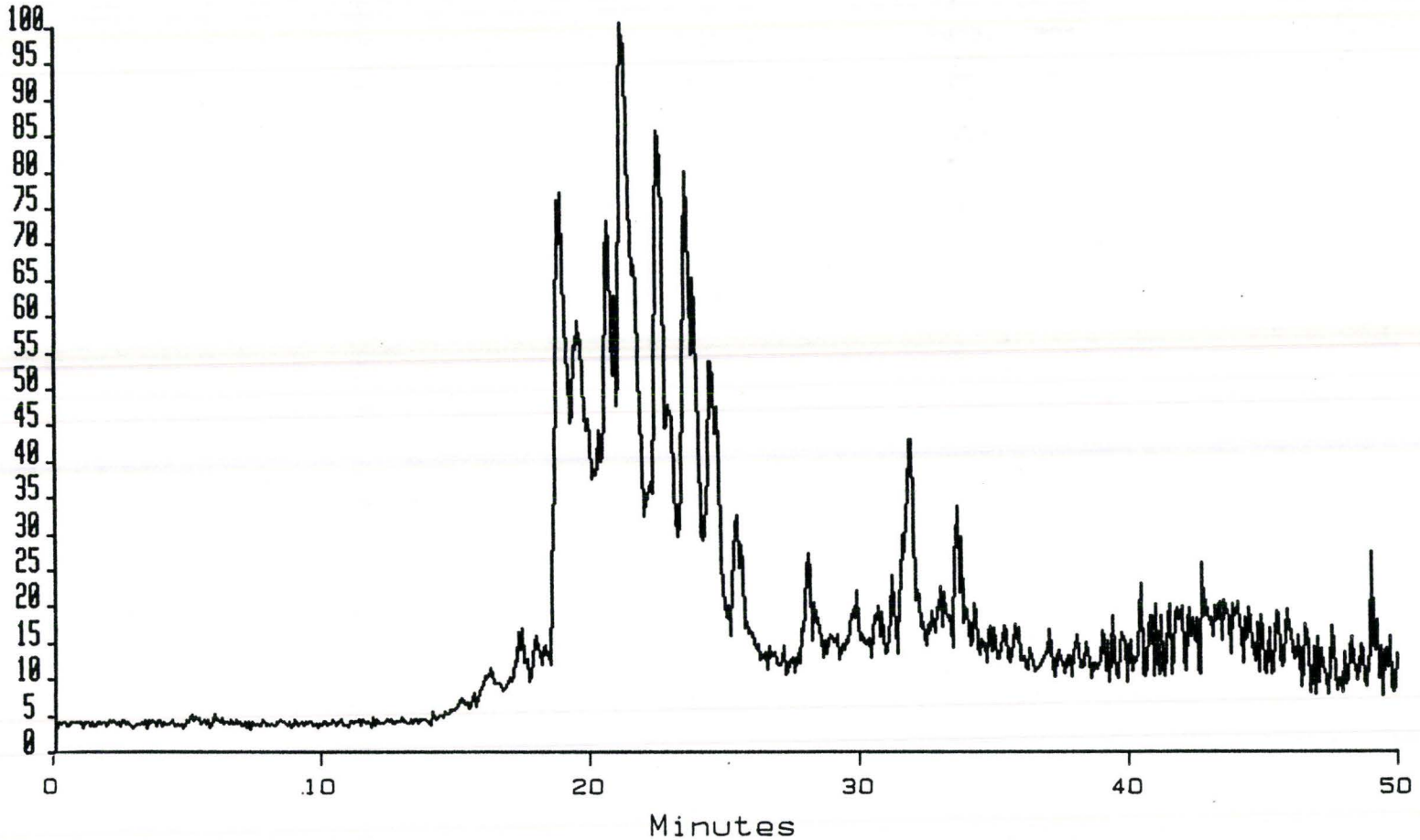


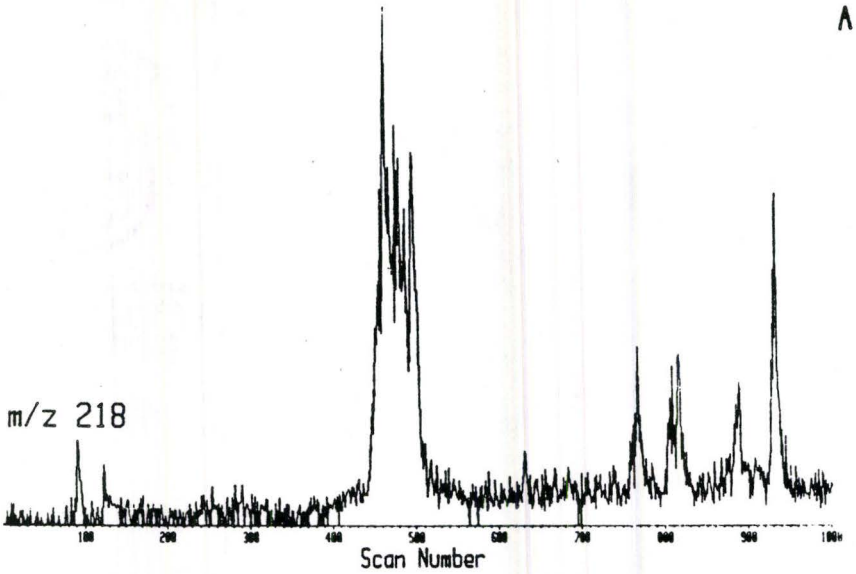
Figure 3-10: The normal-phase HPLC-MS total ion current chromatogram for the NRC sediment sample.

extended periods of time would result in losses in the more volatile PAH. The NBS dust sample was collected over a period of twelve months using a baghouse. There was a very high probability that some the sample components could have oxidized to form other components, such as oxygenated PAH derivatives. The airborne particulate sample was collected over a twenty-four hour period using a Hi-Vol sampler.

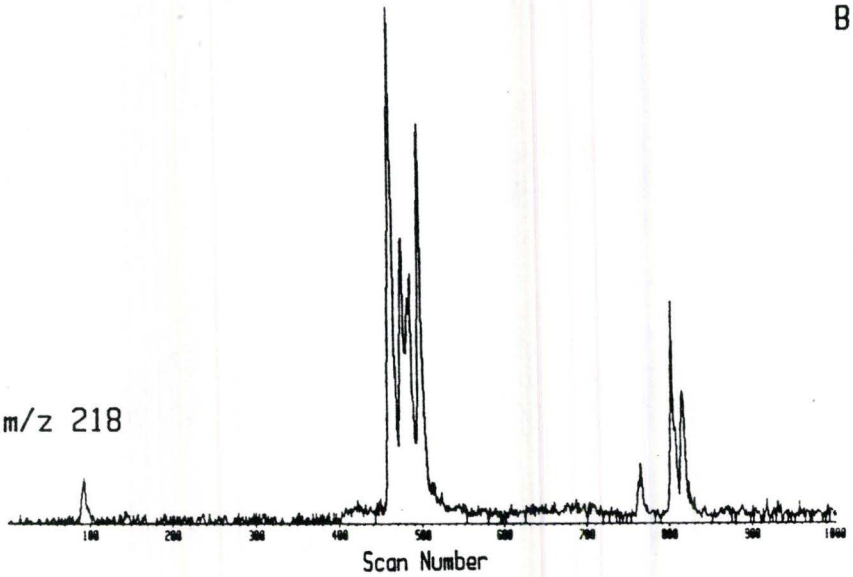
Specific information about the distribution of the sample components could be ascertained by examination of the mass chromatograms. Using normal-phase HPLC, all of the PAH eluted very close together while the PAH derivatives were generally well-separated. The m/z 218 mass chromatograms for these three samples are presented in Figure 3-11. The distribution of the PAH for these samples was very similar. The most common types of PAH with molecular weight 218 are the H2-216-PAH and C2-190-PAH. Typical PAH derivatives that are detected in the m/z 218 mass chromatogram include 202-PAHK and C1-190-PAK. There were many more PAH derivatives in the NBS dust sample. On the other hand, the NRC sample has very few, and they were present in much lower concentration. For the components with m/z 230, the relative abundance of PAH (such as C2-202-PAH) to PAH derivative (such as 216-PAK) was much more evenly distributed in the airborne particulate sample than in the other two (Figure 3-12).

Figure 3-11: The m/z 218 mass chromatograms (from normal-phase HPLC-MS) of the PAC fractions from: (A) the NBS urban dust sample; (B) the Hamilton airborne particulate sample; and (C) the NRC sediment sample.

A NBS Dust



B Hamilton Airborne Particulate



C NRC Sediment

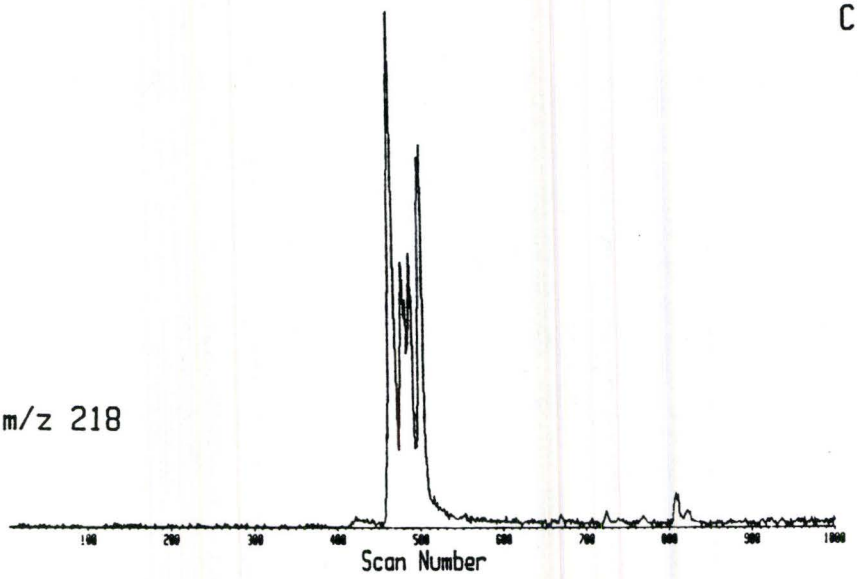
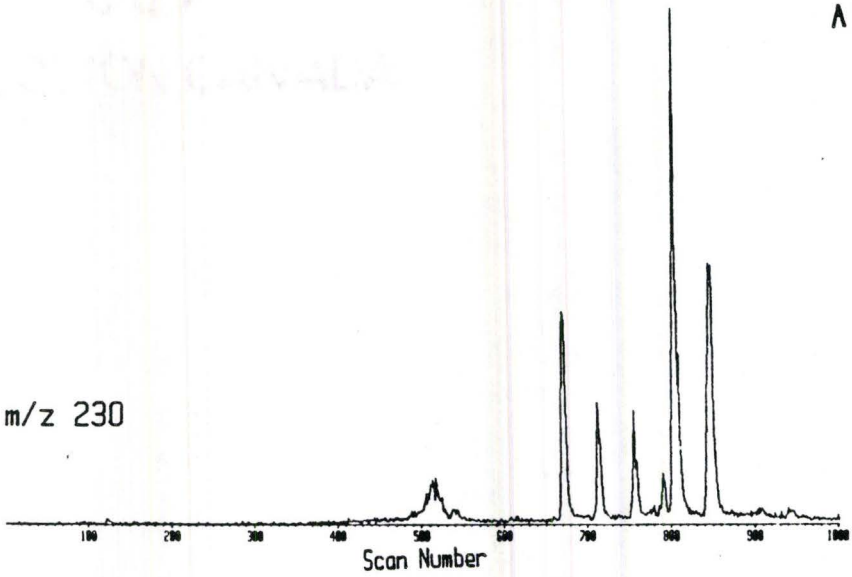
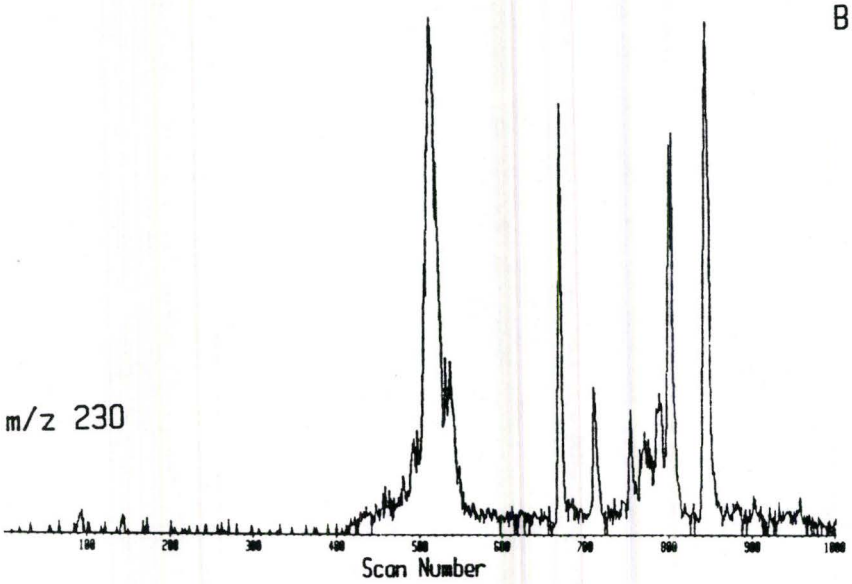


Figure 3-12: The m/z 230 mass chromatograms (from normal-phase HPLC-MS) of the PAC fractions from: (A) the NBS urban dust sample; (B) the Hamilton airborne particulate sample; and C) the NRC sediment sample.

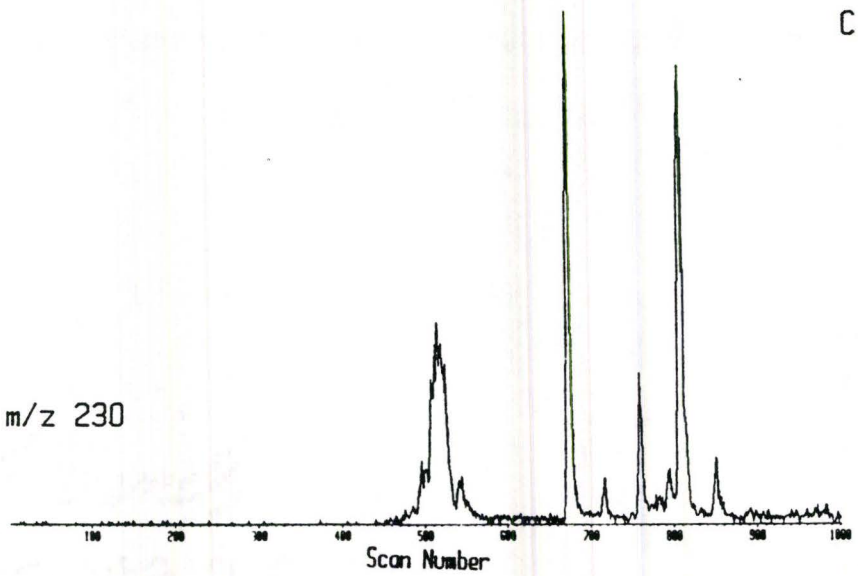
A NBS Dust



B Hamilton Airborne Particulate



C NRC Sediment



III.7 Conclusions

The results from the analyses of the field study samples indicated that the value of the denuder in the reduction of artifact formation was indeterminate at this point. The laboratory tests showed that during the exposure of filters to high levels of ozone, the denuder did appear to reduce the formation of oxygenated PAH derivatives. However, no effect was seen during the laboratory exposure of the samples to nitric acid. From these experiments, no conclusion could be made on the value of the denuder in the reduction of artifact formation under ambient sampling conditions. The results obtained in this study have created more questions than they have solved. Much more work is required in developing experiments to test these sampling methods. Obviously the particular sampling site, and the extent and type of pollution will affect the results.

However, the use of normal-phase HPLC for profiling these samples was shown to be a viable method to determine the relative distribution of PAC. The distribution of the PAC in the PAH and PAH derivative fractions could be easily determined with the application of normal-phase HPLC-MS. Using mass chromatograms as a means of detection, the selectivity of the determination was greatly enhanced. This profiling method could easily be used to examine the

distribution of components in samples, either quantitatively, for the denuder study, or qualitatively, for comparison of different environmental samples.

CHAPTER IV: ANALYSIS OF NBS DUST

In the previous chapter, the samples were profiled to determine the relative abundances of the PAC. However, it was also necessary to be able to identify the individual components. A broad spectrum analysis of the total PAC in an environmental sample required a system with high resolving power, such as GC, and a general detector. The total PAC extract, isolated from the NBS urban dust sample (SRM 1649) by the alumina/LH-20 method, was used for evaluation. This sample was analyzed using capillary GC coupled with either flame ionization detection (FID) or a mass spectrometer. The development of a method that could quickly and efficiently identify the majority of the components in a complex mixture was the goal of this study.

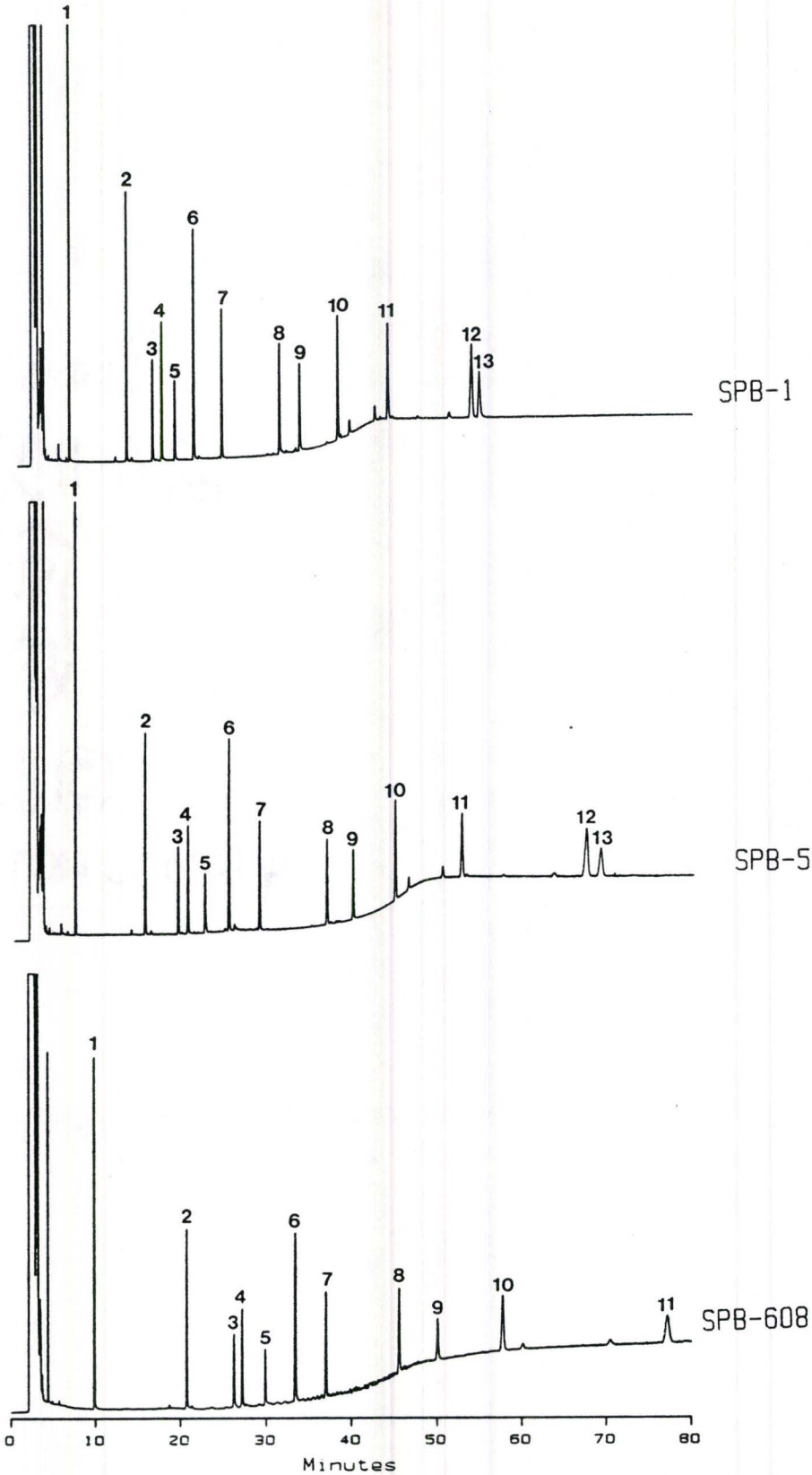
IV.1 GC-FID Analyses

Initial examination of the PAC in the dust was performed using GC-FID. Three different columns were used, each stationary phase had a different polarity and hence a slightly different separation selectivity. The stationary phases are SPB-1 (methyl siloxane), SPB-5 (5% phenyl-methyl

siloxane) and SPB-608 (40% phenyl-methyl siloxane). The SPB-1 column is the least polar while the SPB-608 is the most polar. As illustrated in the GC-FID chromatograms in Figure 4-1, the retention of a standard PAC mixture was quite different on the three columns. This difference in retention should aid in the separation and identification of the PAC in airborne particulate samples.

The GC-FID chromatogram of the PAC fraction from the NBS dust, using the SPB-5 column, is presented in Figure 4-2. It was apparent by inspection of the chromatogram that the sample was very complex. Therefore, the possibility of peak overlap would be quite great. GC-FID chromatograms from the SPB-1 and SPB-608 columns are presented in Figures 4-3 and 4-4 respectively. The differences in the stationary phases' ability to separate the components was evident, either by comparison of the three chromatograms or by the differences in retention of the identified species. One portion of the sample was fractionated using preparative normal-phase HPLC and re-examined using the SPB-5 column. The chromatograms were still quite complex. The GC-FID chromatograms of the PAH and PAH derivative fractions are presented in Figures 4-5 and 4-6 respectively. It was evident that GC-FID could not be used satisfactorily to detect compounds in this sample with any degree of confidence. Further fractionation of the PAC into

Figure 4-1: The GC-FID chromatograms of some PAC standards on the SPB-1 column, the SPB-5 column, and the SPB-608 column. The peak identities are: 1=naphthalene, 2=fluorene, 3=9-fluorenone, 4=phenanthrene, 5=xanthone, 6=anthraquinone, 7=pyrene, 8=chrysene, 9=1-nitropyrene, 10=benzo[a]pyrene, 11=picene, 12=coronene, 13=benzo[rst]pentaphene.


1
2
3
4
5
6
7
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9
10
11
12
13
SPB-1
1
2
3
4
5
6
7
8
9
10
11
12
13
SPB-5
1
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3
4
5
6
7
8
9
10
11
SPB-608
0
10
20
30
40
50
60
70
80
Minutes

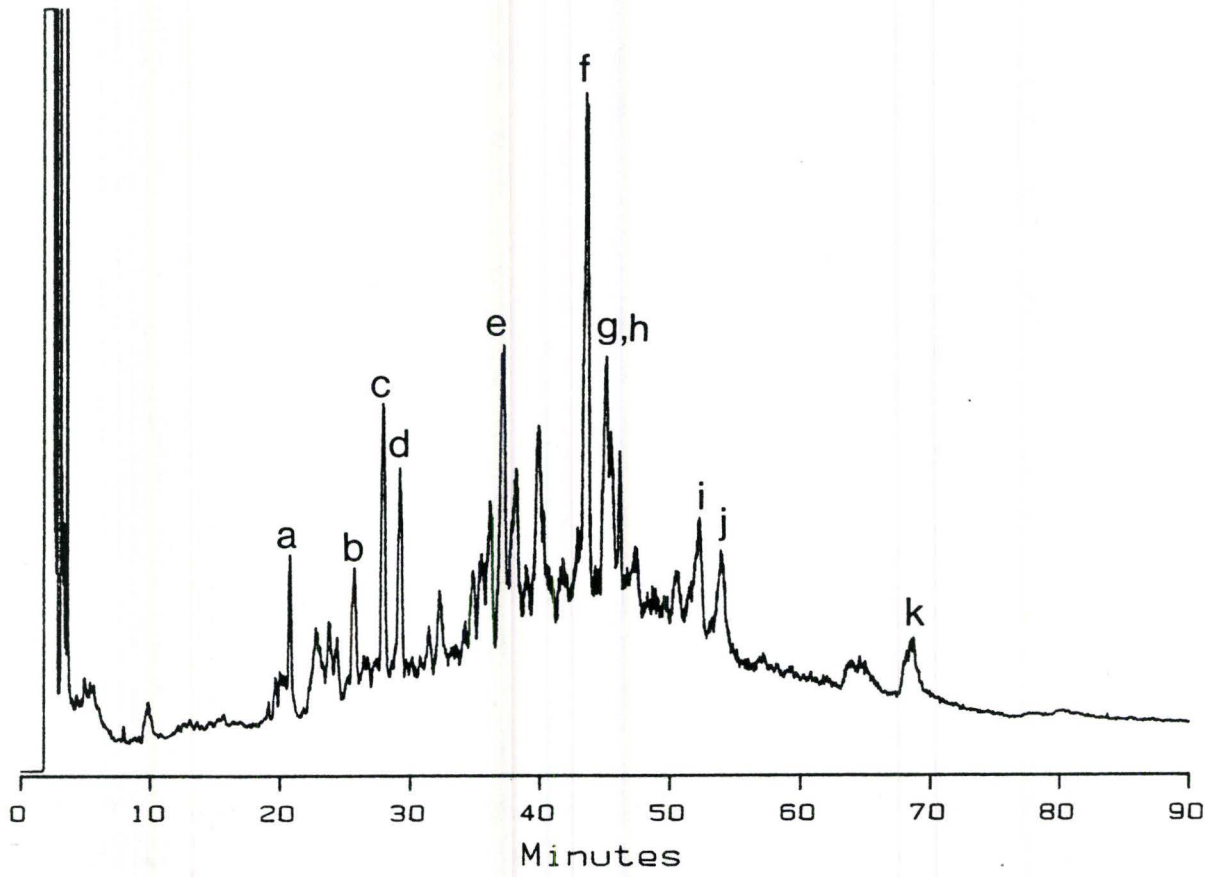


Figure 4-2: The GC-FID chromatogram of the PAC fraction from the NBS urban dust sample using the SPB-5 column. The identified species are: a=phenanthrene, b=anthraquinone, c=fluoranthene, d=pyrene, e=chrysene/triphenylene, f=benzofluoranthene, g=benzo[e]pyrene, h=benzo[a]pyrene, i=276-PAH, j=benzo[ghi]perylene, k=300-PAH.

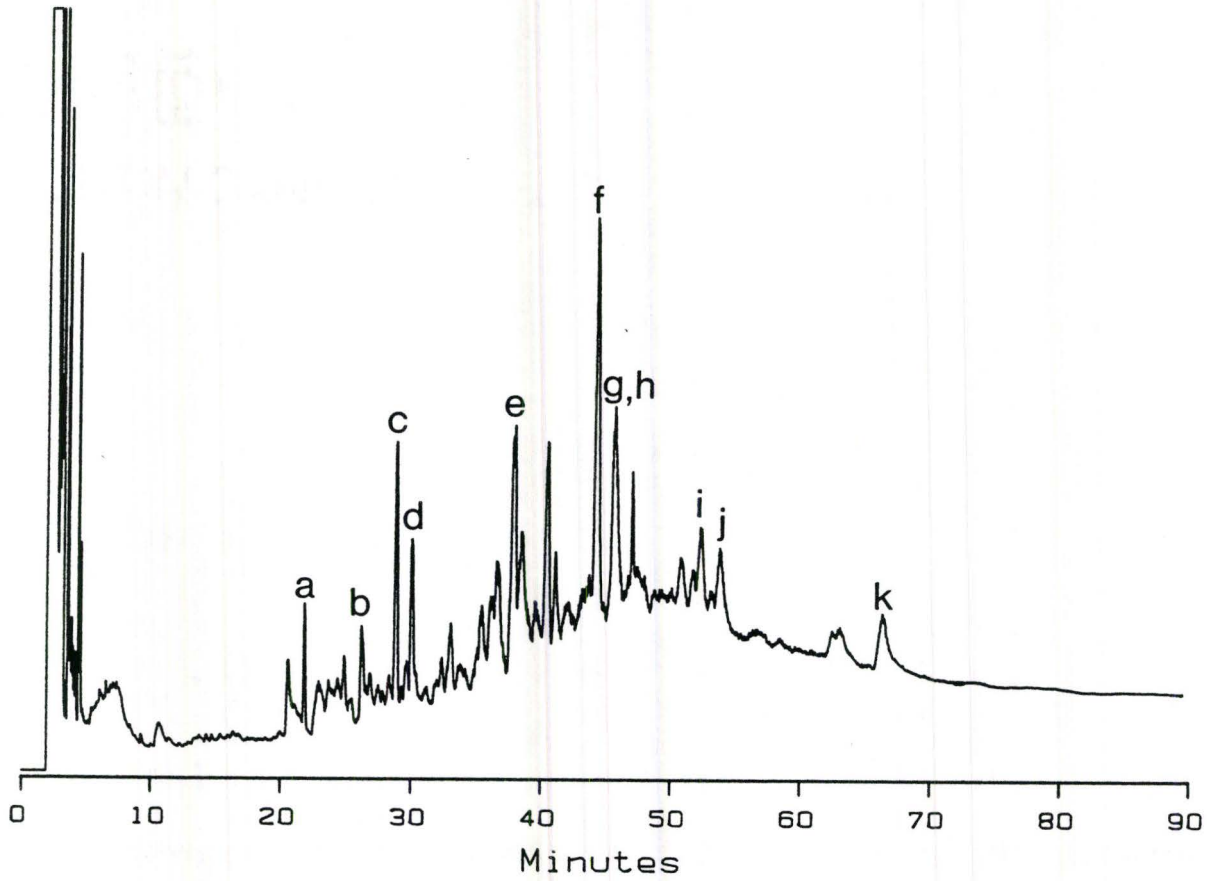


Figure 4-3: The GC-FID chromatogram of the PAC fraction from the NBS urban dust sample using the SPB-1 column. The identified species are: a= phenanthrene, b=anthraquinone, c=fluoranthene, d=pyrene, e= chrysene/triphenylene, f=benzofluoranthene, g=benzo[e]pyrene, h= benzo[a]pyrene, i=276-PAH, j=benzo[ghi]perylene, k=300-PAH.

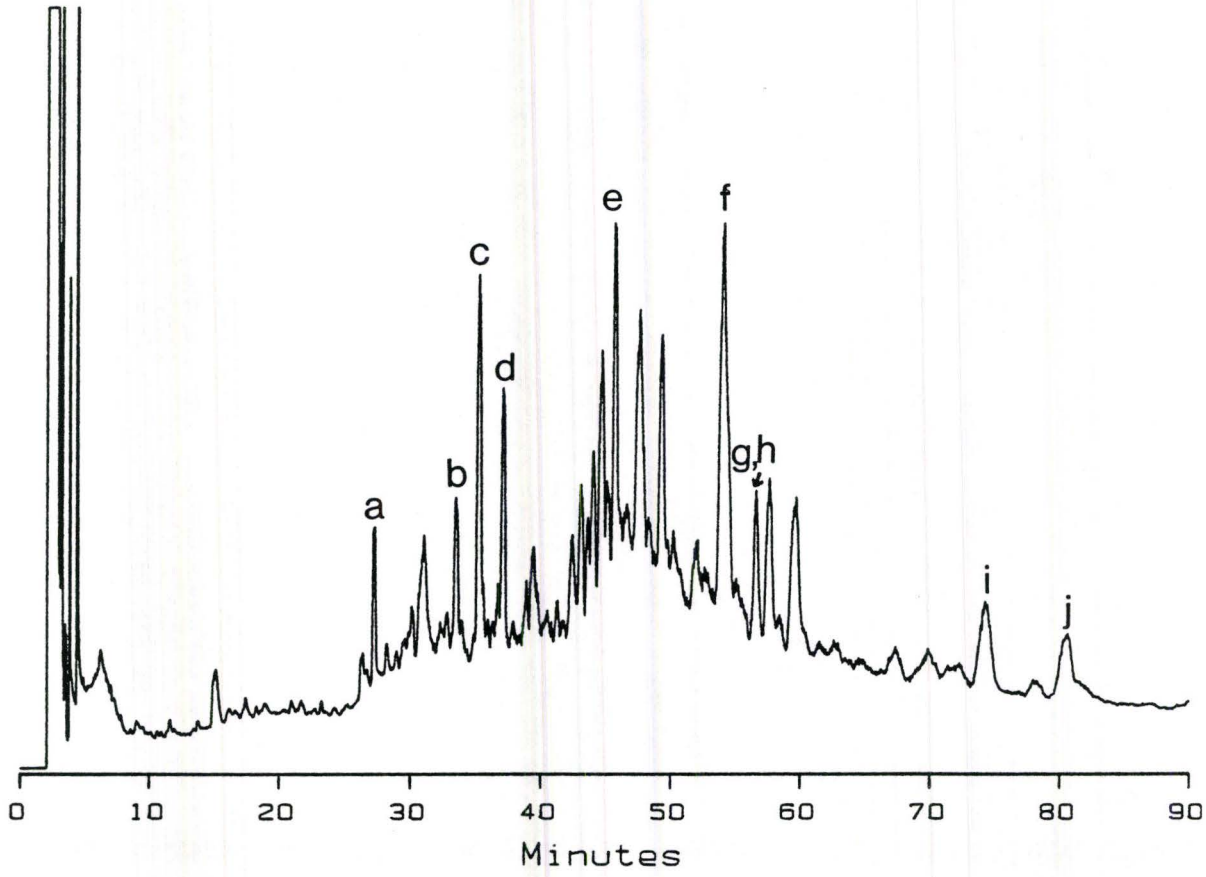


Figure 4-4: The GC-FID chromatogram of the PAC fraction from the NBS urban dust sample using the SPB-608 column. The identified species are: a=phenanthrene, b=anthraquinone, c=fluoranthene, d=pyrene, e=chrysene/triphenylene, f=benzofluoranthene, g=benzo[e]pyrene, h=benzo[a]pyrene, i=276-PAH, j=benzo[ghi]perylene.

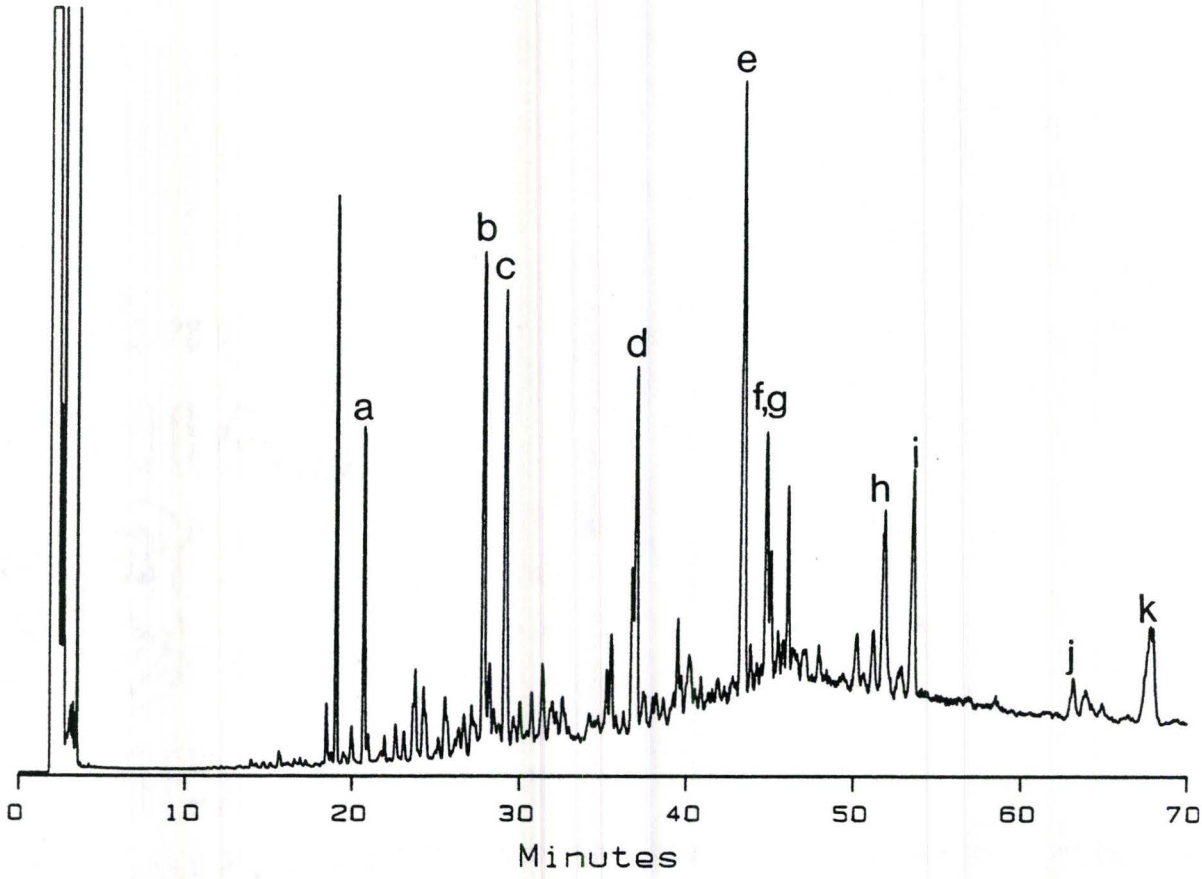


Figure 4-5: The GC-FID chromatogram of the PAH fraction from the NBS urban dust sample using the SPB-5 column. The identified species are: a= phenanthrene, b=fluoranthene, c=pyrene, d=chrysene/triphenylene, e=benzofluoranthene, f=benzo[e]pyrene, g=benzo[a]pyrene, h=276-PAH, i= 276-PAH, j=302-PAH, k=300-PAH.

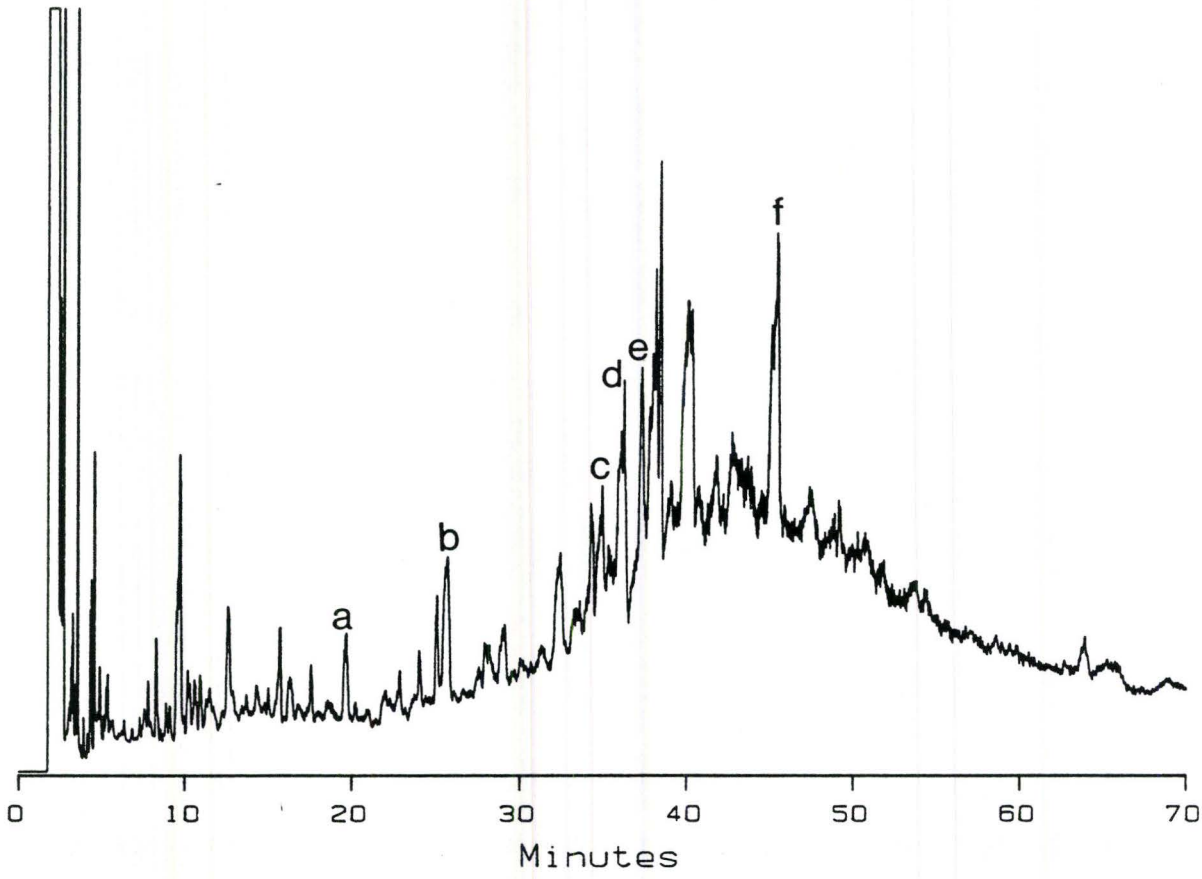


Figure 4-6: The GC-FID chromatogram of the PAH derivative fraction from the NBS urban dust sample using the SPB-5 column. The identified species are: a=fluorenone, b=anthraquinone, c=216-PAK, d=216-PAK, e=C3-140- PANH, f=240-PAK.

subclasses can improve the resolution to some extent. However, the amount of work required for these extra analyses increases significantly and there may not be substantial improvements in compound detection.

IV.2 GC-MS Analyses

Both low resolution and high resolution mass spectrometry (HRMS) were used in conjunction with GC for further analyses. Combining GC with HRMS is a very powerful method, since elemental composition are determined without the need for extensive fractionation prior to analysis. All GC-MS analyses were performed on a ZAB-E mass spectrometer. Electron impact spectra were obtained in the full scan mode.

The GC-MS analyses of the PAC fraction provided much more information about the sample than GC-FID, that could be used to identify the components. A single analysis still might not provide sufficient resolution for the identification of the majority of the components. The third order chromatography method, where data is collected as a function of scan number, column type and m/z ratio, was applied to this problem (126). The three columns used in the GC-FID analyses were evaluated to determine two complementary ones to be used in later analyses. All of the information obtained in these analyses was utilized to identify the components. To be able to efficiently manage

the vast amount of generated data and to expedite the time required for data analysis, a systematic method of data processing was developed, and designated a semi-automated peak detection routine. It used a combination of programs to plot the data in the desired format, manual peak detection, and the LOTUS 1-2-3 spreadsheet program for the organization of the data and calculation of retention indices.

IV.3 The Semi-Automated Peak Detection Method

The semi-automated peak detection method was used to aid in the detection of the sample components and the calculation of retention indices (RI). The information obtained from these analyses was organized with the use of the LOTUS 1-2-3. The process followed these steps:

1. Automated plotting of all mass chromatograms using a program written for this purpose.
2. Manual peak detection and measurement.
3. Entry of the results into Lotus 1-2-3.
4. Sorting of the results according to the scan numbers.
5. Automated plotting of all of the unique spectra.
6. Identification of the molecular ions and the fragment ions.
7. Comparison of results with other columns and correlation of peaks.

8. Calculation of the RI of the components for each column, and assignment of tentative identification of the components.

9. Calculation of the retention increments.

The programs used to plot the data are listed in Appendix 1. They were written to operate on the VG-11/250 data system.

The desired data processing method was one that can be easily automated. Attempts were made to utilize the peak detection routine available on the VG-11/250 data system. The program called "Enhance" implemented the Biller-Biemann algorithm that automatically detected and flagged individual scans in a GC-MS run where the intensities of several masses have maximized simultaneously (142). The mass spectra at these scans could then be examined at a later time. Unfortunately, this algorithm was rather primitive. It did not recognize peak shape, only a sustained signal above a threshold and a maximum signal. It had no capacity for partially resolved isomer sets, that were extremely common in complex samples. Information on minor components was virtually lost in the presence of major ones. This program could not identify the individual components unless they were well-resolved. The requirement of good chromatographic resolution is a weakness of all pattern recognition methods (129). This prerequisite could be difficult to obtain in real samples without extensive fractionation prior to analysis. Because of the problems associated with this

automated method, it was decided that the peak detection would be done manually. At this time, the eye is still the best peak detector, but a program could eventually be developed that is similar to the modern chromatographic data processing systems.

The individual mass chromatograms were examined to identify possible components. Mass chromatograms have been used for the selective detection of certain classes of compounds in a number of other studies (67, 133, 134, 143). All of these compounds had key ions that were distinctive to that particular compound class. Unfortunately, there are not any ions that were unique to PAH that could be monitored in this fashion. The most intense ion in the electron impact spectrum is the molecular ion. However, other PAC do undergo fragmentation indicative of certain compound classes. For example, alkylated PAC are determined by their distinctive $[M-15]^+$ ion. The $[M-28]^+$ ion is characteristic of polycyclic aromatic ketones or quinones. An additional loss of 28 mass units is indicative of a quinone type of compound.

Upon completion of peak detection, the results were entered into a LOTUS 1-2-3 spreadsheet and sorted by scan number. Unique scan numbers were obtained and entered into another program on the VG-11/250 data system used for plotting the mass spectra. The molecular and fragment ion

information was originally obtained from the mass chromatograms, and the mass spectrum was simply used for confirmation. Interpretation of the mass spectrum was extremely difficult in situations where a large number of components co-eluted.

After the molecular ions were assigned, peak matching was used to correlate the results with those obtained from the other columns. The spreadsheet results, individual mass chromatograms and mass spectra were all used to correlate these peaks. All of this additional information was then entered into the spreadsheet.

Retention indices (RI) were calculated using a modified version (vide infra) of the method developed by Lee (113). A template in LOTUS 1-2-3 was developed to perform the calculation of the RI. The template and the formula used in the calculation were described in Appendix 3.

At this time, the spreadsheet consisted of columns that contain key fragment ions, and the RI of each component on the three columns (Appendix 2). Using these results, tentative identities were now assigned. Depending upon the available information, it was also possible to confirm the identities of some of the components.

The difference in the retention of the compounds on different columns, the retention increment, was another possible source of information about the nature of the

components. The calculation of retention increment was done by taking the difference between the RI of a component on the SPB-5 column and its RI on another column.

The programs written for the VG-11/250 data system significantly reduced the time required to process the results. The programs were run overnight when the computer was not needed to operate the mass spectrometer. The use of LOTUS 1-2-3 greatly facilitated data management. It was useful as a simple spreadsheet, but also had the ability to be efficient in the calculation of the retention indices. The capability to sort the data was also necessary to be able to detect trends in the results. In conclusion, the semi-automated peak detection routine had proven to be quite flexible. It could be easily adapted to any analysis using a chromatographic system coupled to a mass spectrometer.

IV.4 The NBS Urban Dust Sample

To determine the applicability of the third order chromatography method and the peak detection routine, a detailed analysis was performed on the total PAC fraction in the NBS urban dust sample. The use of this particular sample had a number of distinct advantages. It has a similar composition and matrix to urban airborne particulate matter and is available in bulk quantities. Therefore, a new sample is not required for each analysis, and other

laboratories can analyze the same sample by alternate methods to verify these results. Confirmation of any quantitative work is also possible, since some of the species in this sample are certified. The NBS dust sample was used to obtain a detailed profile of typical PAC present in airborne particulate samples. This information was very useful when examining similar samples. Retention indices from three different GC capillary columns, characteristic fragment ions, and the accurate mass of some of the components were all used to aid in detection of the PAC in the sample and to establish a database.

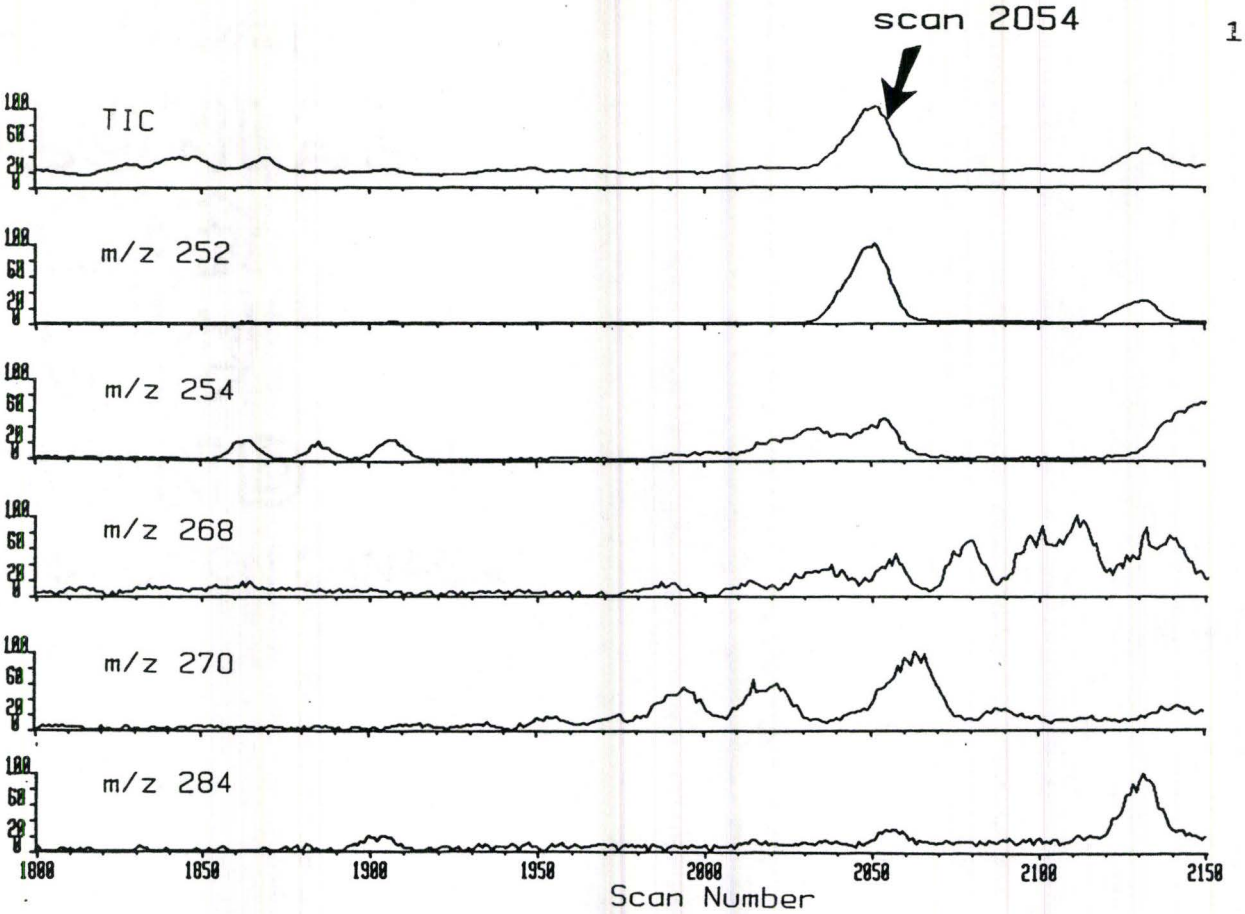
IV.4.1 Analysis of the Total PAC Extract

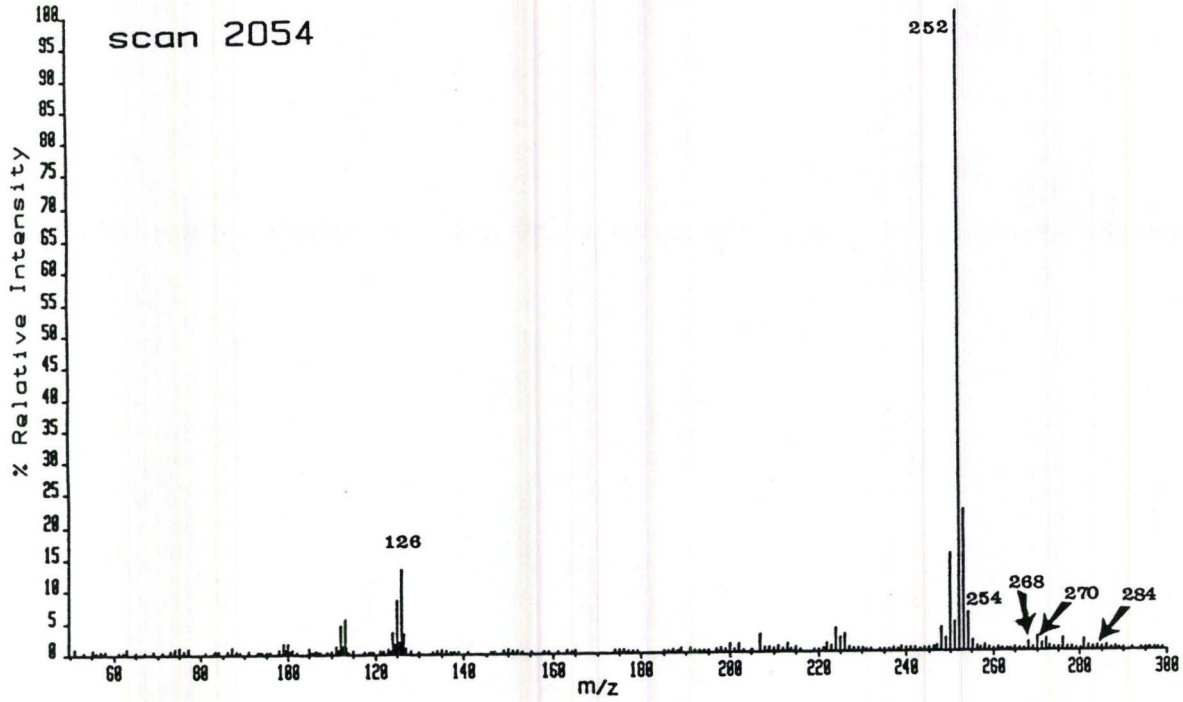
The first GC-MS analysis of the total PAC was done using the SPB-5 column. The stationary phase in this column (5% phenyl-methyl silicone) is intermediate in polarity, and therefore correlation of results with those obtained from the other columns was easier. The results obtained from the spreadsheet showed that the problem of peak overlap was very severe. In most regions in the chromatograms, each peak consisted of several different components. Peak detection using mass chromatograms was much easier because, in general, the mass spectra were very confusing due to overlapping components.

Although the manual method of peak detection was

rather tedious, it proved to be very powerful in detecting components not separated by the column. Ideally, the mass spectrum should contain information about one particular component that could then be used to aid in its identification. Unfortunately, it was rare to be able to glean any additional information from the mass spectrum because of the large number of components that co-eluted. There were numerous occasions where compounds would not have been detected by simply examining the mass spectrum obtained at the top of a peak in the total ion current chromatogram. In one example, five different components all reached their maxima in less than six seconds on the SPB-5 column. The major peak, a component with molecular weight 252, was actually an unresolved mixture of three isomers of benzofluoranthene and was present in much higher concentration than the other components. As illustrated in Figure 4-7, initial inspection of the mass spectrum at the apex of the peak at scan 2054 in the total ion current chromatogram indicated that there was only one component eluting in this region. The other components were present but barely detectable in the mass spectrum. Using the peak detection routine, all the components were detected. Therefore, the combination of the spreadsheet results, the mass chromatograms, and the mass spectra were all essential to aid in the detection of the sample components.

Figure 4-7: Comparison of the information obtained from the mass chromatograms and the mass spectrum at scan 2054. When only the mass spectrum is examined, the detection of the minor components (with molecular weights of 254, 268, 270, and 284) was very difficult in the presence of the major component, an unresolved mixture of the three isomers of benzofluoranthene (molecular weight =252).


scan 2054
TIC
m/z 252
m/z 254
m/z 268
m/z 270
m/z 284
1800
1850
1900
1950
2000
2050
2100
2150
Scan Number


scan 2054
% Relative Intensity
252
126
254
268
270
284
m/z

The peaks detected from the GC-MS analysis using the SPB-5 column, were correlated with those from the other columns. Peak matching was rather difficult in some cases. Some peaks were broadened, and resolution between others were actually lost on the SPB-1 column. Conversely, there was enhanced separation of some of the components using the SPB-608 column. The difficulties in peak assignments are illustrated in Appendix 2 for components that were separated by the SPB-608 but could not be correlated with the results obtained from the other columns. They are indicated by the symbol "?", beside their molecular weight.

The differences in retention of the components using the different stationary phases is illustrated in Table 4-1. For a common PAC, such as anthraquinone, its retention and hence its RI was different on all three columns. Therefore the co-eluting species were also different. Table 4-1 illustrates the types of compounds that co-eluted with anthraquinone on the three columns. It was interesting to note that on each column, anthraquinone co-eluted with a different 212 molecular weight compound.

The large amount of data obtained from the GC-MS analyses of the NBS dust sample is tabulated, and is presented in Appendix 2. This Appendix contains information on the molecular weight of the components, fragment ions, the region where the compound eluted on the normal-phase

Table 4-1: Comparison of the types of compounds that co-eluted with anthraquinone on the three different columns.

A: Data sorted by SPB-1 RI

Cmpd[1] No.	Type[2]	Observed Mass	Retention Indices SPB-1	SPB-5	SPB-608	Tentative Identity[3]
418	DERIV	270	327.4	320.3	---	240-PAQ
125	PAH	212	328.5	327.1	321.3	C2-166-PASH
3	PAH	"149"[4]	328.5	326.8	317.3	phthlate
174	DERIV	223	328.6	326.8	317.1	C4-166-PANH
115	**DERIV**	**208**	**328.7**	**330.1**	**332.5**	**Anthraquinone**
98	PAH	204	330.2	329.5	325.8	C1-190-PAH

B: Data sorted by SPB-5 RI

Cmpd No.	Type	Observed Mass	Retention Indices SPB-1	**SPB-5**	SPB-608	Tentative Identity
125	PAH	212	328.5	327.1	321.3	C2-166-PASH
90	PAH	198	331.8	329.4	330.9	C1-166-PASH
98	PAH	204	330.2	329.5	325.8	C1-190-PAH
115	**DERIV**	**208**	**328.7**	**330.1**	**332.5**	**Anthraquinone**
126	PAH	212	331.8	330.3	324.0	C2-166-PASH
105	PAH	206	333.7	332.1	325.5	C2-178-PAH

C: Data sorted by SPB-608 RI

Cmpd No.	Type	Observed Mass	Retention Indices SPB-1	SPB-5	**SPB-608**	Tentative Identity
90	PAH	198	331.8	329.4	330.9	C1-166-PASH
282	PAH	244	335.1	334.6	331.9	C3-202-PAH
115	**DERIV**	**208**	**328.7**	**330.1**	**332.5**	**Anthraquinone**
109	PAH	206	340.8	339.0	332.5	C2-178-PAH
175	PAH	226	342.3	340.5	332.9	226-PAH,
131	PAH	212	340.3	339.1	332.9	C2-166-PASH
230	PAH	236	347.3	344.5	333.1	C2-190-PASH

.....continued

Table 4-1 (continued)

[1] Cmpd No.: corresponds to the assigned numbers for the compounds listed in Appendix 2.

[2] Type: indicates the fraction (PAH or PAH derivative) where the component was detected.

[3] Tentative Identity: Acronyms are explained in Figure 1-2.

[4] "149": The molecular weight for the phthlate ester could not be determined, only the base peak, 149, was detected.

HPLC column, and the accurate mass of some components. In addition, it lists all the retention data and tentative identification of the PAC. In total, over 500 PAC were detected using the third order chromatography method and the peak detection routine. Table 4-2 summarizes some of the compounds whose identity have been positively confirmed using a number of techniques.

IV.4.2 Evaluation of the Third Order Chromatography Method for PAC Analysis

It was necessary to determine whether analysis of the PAC fraction by the third order chromatography method would be a viable method for environmental samples. A portion of the PAC extract was separated by preparative normal-phase HPLC into a PAH fraction and a PAH derivative fraction. The fractions were then analyzed using the SPB-5 column and compared with the original results. With the enhanced resolution, it was now possible to determine whether there were any co-eluting species in the GC analysis of the total PAC sample. This experiment was also used to detect any compounds not separated on all three columns, that adversely affected identification. All of this information was used to determine whether further fractionation of the PAC was necessary for routine analyses. In addition, the regions where potential problems in

Table 4-2: Compounds identified in the NBS urban dust sample (SRM 1649).

Observed Mass (Error (mmu))	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[1] (1-5)	ΔRI[2] (5-608)	Identity	Literature[3] RI(SPB-5)	Comments[4]
166	268.2	268.2	268.2	0.0	0.0	Fluorene	268.17	a,b
167.073(-2)	----	----	----	----	----	Carbazole[5]		
168	----	----	----	----	----	Dibenzofuran[5]		
178	300.0	300.0	300.0	0.0	0.0	Phenanthrene	300.00	a,b
178	301.7	301.7	----	0.0	----	Anthracene	301.69	a,b
180.057(-.7)	292.5	293.6	295.4	-1.0	-1.8	Fluorenone	294.79	
184	295.3	295.7	296.3	-0.4	-0.7	Naphtho[1,2-b]thiophene	295.80	
190	321.8	321.5	320.2	0.3	1.4	4H-Cyclopenta[def]phenanthrene	322.08	a,b
202	344.0	343.5	341.5	0.5	2.0	Fluoranthene	344.01	a,b
202	351.2	351.2	351.2	0.0	0.0	Pyrene	351.20	a,b
208.052(-7)	328.7	330.1	332.5	-1.4	-2.4	Anthraquinone	329.23	b
208	348.4	348.7	349.4	-0.3	-0.7	Phenanthro[4,5-bcd]thiophene	348.80	
216	372.9	371.9	369.5	1.0	2.4	11H-Benzo[b]fluorene	369.39	a,b
226	391.1	390.4	389.3	0.7	1.0	Benzo[ghi]fluoranthene	389.60	
228	400.0	398.5	396.5	1.5	2.0	Benz[a]anthracene	398.50	a,b
228	400.0	400.0	400.0	0.0	-0.0	Triphenylene	400.00	a,b
228	400.0	400.0	400.0	0.0	-0.0	Chrysene	400.00	a,b
230	----	----	----	----	----	Benzo[b]fluorenone[6]		a,b
230.073(2)	406.7	406.7	410.7	-0.0	-4.0	7-Benz[de]anthrone	406.50	a,b
252	444.1	443.9	442.9	-0.2	1.0	Benzofluoranthenes		
252	----	----	----	----	----	Benzo[j]fluoranthene[6]		a,b
252	----	----	----	----	----	Benzo[b]fluoranthene[6]		a,b
252	----	----	----	----	----	Benzo[k]fluoranthene[6]		a,b
252	----	----	----	----	----	Benzo[e]pyrene[6]		a,b
252	453.4	453.4	453.4	0.0	0.0	Benzo[a]pyrene	453.40	a,b

.....continued

Table 4-2 (continued)

Observed Mass (Error (mmu))	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[1] (1-5)	ΔRI[2] (5-608)	Identity	Literature[3] RI(SPB-5)	Comments[4]
254	----	----	----	----	----	Ketocyclopenta[mno]chrysene[6]		a,b
258	----	----	----	----	----	Benzo[a]anthraquinone[6]		a,b
258	----	----	----	----	----	Benzo[b]anthraquinone[6]		a,b
276	486.4	484.7	482.5	1.7	2.2	Indeno[1,2,3-cd]pyrene	481.87	a,b
276	500.3	----	----	----	----	Benzo[ghi]perylene[6]		a,b
278	----	----	----	----	----	Benzo[b]chrysene[6]		a,b
278	----	----	----	----	----	Dibenz[a,h]anthracene[6]		a,b
278	496.0	495.4	494.5	0.7	0.9	Dibenz[a,c]anthracene	495.00	a,b
278	500.0	500.0	500.0	0.0	0.0	Picene	500.00	a,b
300	----	----	----	----	----	Coronene[6]		a,b

RI: Retention index

1 RI(SPB-1) - RI(SPB-5)

2 RI(SPB-5) - RI(SPB-608)

3 Literature values obtained from Lee's work (113, 120, 121, 85)

4 a: Confirmed by reversed-phase HPLC retention index
b: Confirmed by DAD uv-vis spectra

5 No retention data available, compounds eluted before first standard

6 Specific isomer confirmed by DAD uv-vis spectrum only

detection would occur, if the total PAC was analyzed, were identified. It was also important to critically examine this loss in relation to the time required to do the additional fractionation and analyses. The components in the total extract was assigned a label indicating whether they were present in the PAH or the PAH derivative fraction (Appendix 2). This information was also useful in identifying the components.

The PAC fraction from the NBS dust sample was extremely complicated. Unlike most airborne particulate samples, there were a large, diverse number of PAH derivatives present at relatively high concentrations. This sample was actually much more complicated than any of the other samples that were examined in this study. The diversity in sample components was probably due to the fact that NBS dust sample was collected over a twelve month period in a baghouse, instead of 24 hours on a Hi-Vol sampler, and therefore the dust was probably heavily oxidized.

Since very little information was available on the PAH derivatives in NBS dust, this fraction was also examined by GC-HRMS (high resolution mass spectrometry). A program was written to list all the high resolution data for the detected components. The program is included in Appendix 1 and the results are tabulated and are included in Appendix

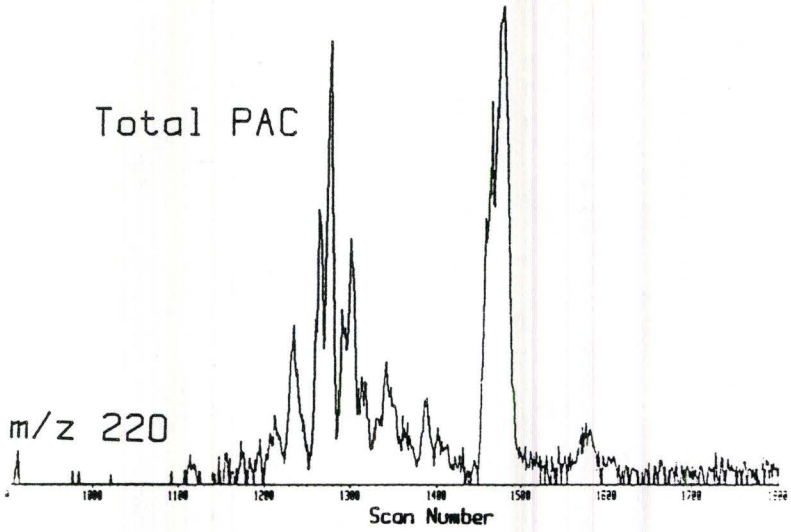
2.

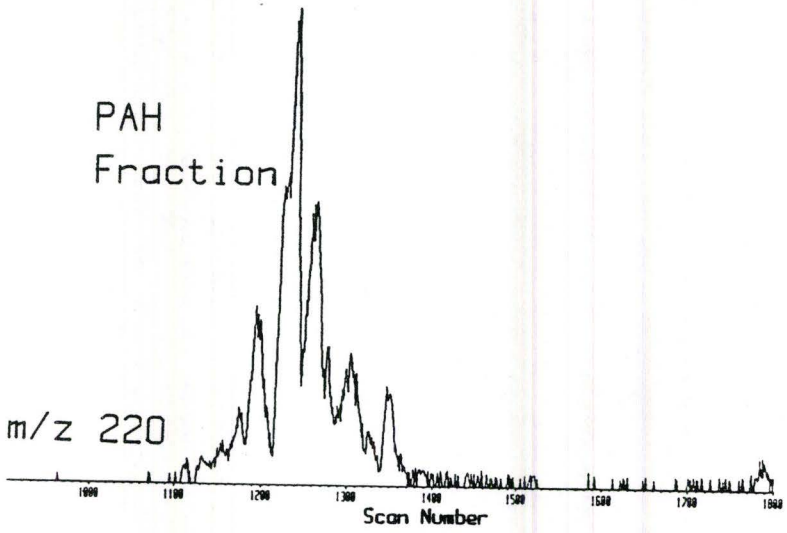
For the analysis of the total PAC, the ideal case, for easy peak detection, was when the PAH and PAH derivatives with the same molecular weight were well-separated. Figure 4-8 shows the m/z 220 mass chromatogram fraction before and after fractionation of the PAC. The PAH eluted much earlier than the PAH derivatives and peak assignment was very easy.

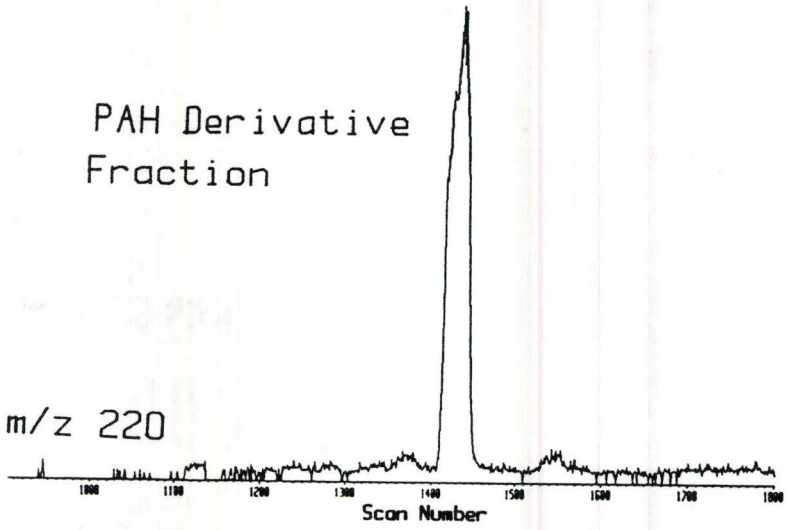
After careful examination of the data obtained from the analysis of the PAH and PAH derivative fractions, it became evident that a number of poor assignments had been made. Nearly ninety compounds had not been identified in the PAC extract analysis. One-third of the missing components not found in the total extract, were present in such low concentrations that additional fractionation was required before they can be detected. These compounds are included in the final table listed in Appendix 2 and are indicated by the letters "ND". The remaining two-thirds could not be detected because of the complexity of the sample. The problems with detection were generally due to poor resolution of these components. Co-elution was a much more serious problem than originally suspected.

In a number of cases, the PAH and derivatives with the same molecular weight co-eluted on the GC column. Peaks detected in the mass chromatogram of the total extract

Figure 4-8: The m/z 220 mass chromatograms of the NBS urban dust illustrating the distribution of the peaks in the total PAC fraction in relation to the PAH and PAH derivative fractions. In this case, the two fractions were well-separated in the total PAC fraction.


Total PAC
m/z 220
Scan Number

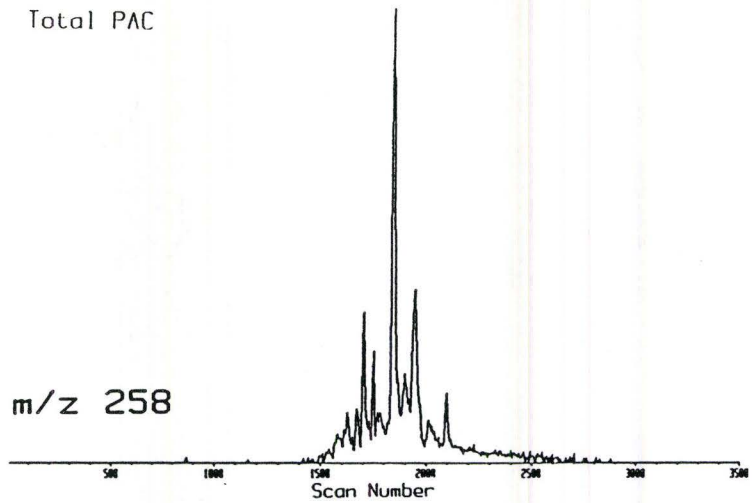

PAH
Fraction
m/z 220
Scan Number

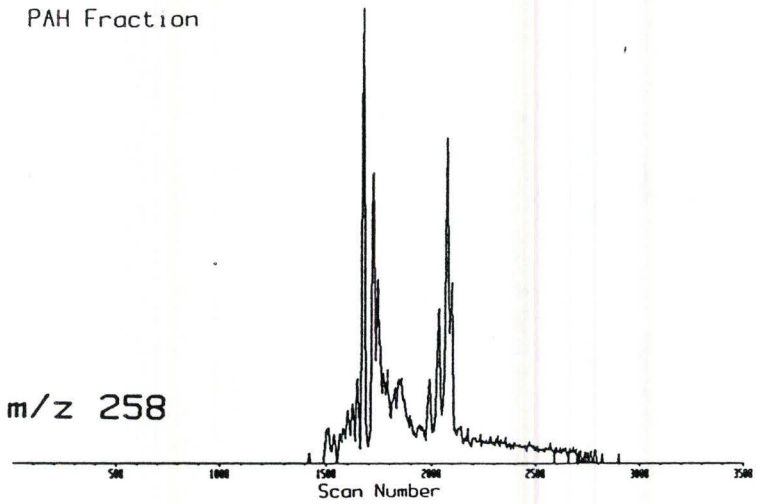

PAH Derivative
Fraction
m/z 220
Scan Number

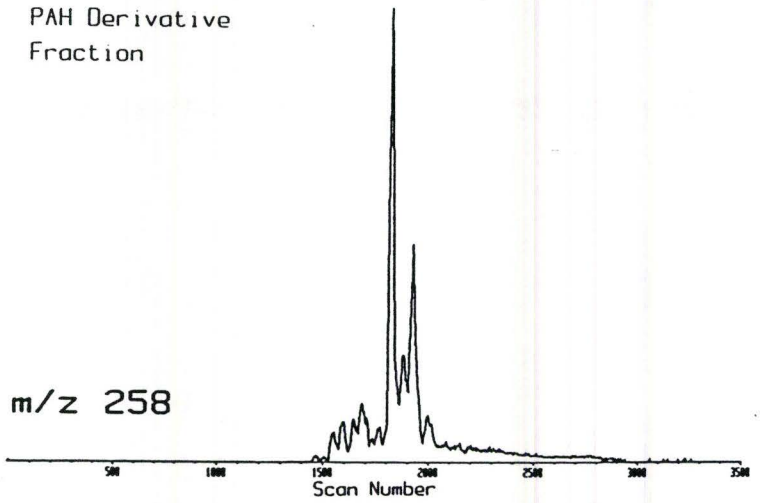
were discovered to be a combination of PAH and PAH derivatives with the same molecular weight. These peaks were erroneously identified on all three columns as a single component. Fractionation was necessary to be able to resolve these PAH from the PAH derivatives. Additional peaks were detected after fractionation for components with the molecular weights 194, 244, 258, 268, 270, 272, and 280. In Appendix 2, the components marked with an asterisk were originally identified as a single species in the mass chromatograms in the PAC analysis. Components that were separated by fractionation but could not be correlated with peaks in the total extract are indicated by "CT" in Appendix 2. For example, Figure 4-9 shows the m/z 258 mass chromatograms of the PAC before and after fractionation. It was evident that there were actually many more components present than can be originally detected. Some of the peaks were actually a combination of components.

A similar problem was also noted in cases where the PAH or the PAH derivatives at a particular m/z value were present in much lower concentration than the other. Therefore detection was difficult. This was another example of a situation where the PAH and the PAH derivatives co-eluted. PAH derivatives with molecular weights 230, 256, 270, and 272 were discovered to have effectively overwhelmed the PAH with the same molecular weight, and made their

Figure 4-9: The m/z 258 mass chromatograms of the NBS urban dust illustrating the distribution of the peaks in the total PAC fraction in relation to the PAH and PAH derivative fractions. In this case, the two fractions co-eluted and determination of the individual species in the PAC fraction was difficult.


Total PAC
m/z 258
Scan Number


PAH Fraction
m/z 258
Scan Number


PAH Derivative
Fraction
m/z 258
Scan Number

detection difficult. Similarly, some of the PAH with molecular weights 244, 252, 256, and 268 were present in much higher concentration than the PAH derivatives. These components are also indicated by "CT" in Appendix 2. In cases where PAC with the same molecular weight co-eluted, information was lost without fractionation.

An identification problem was also noted for some components whose molecular ion was an odd mass number. There were a number of cases where molecular ions were initially missed due to the presence of fragment or isotopic ions from other species that were much more intense, or simply because the mass chromatogram was so complicated that peak assignments were difficult. These missed species included compounds with molecular weights 179, 203, 211, 217, 229, and 247, and are indicated by "CT" in Appendix 2. For example, species with molecular weight 179 could not be detected due to the intense $[M+1]^+$ ion from the 178-PAH, which are present in much higher concentration. As illustrated in Figure 4-10, the 179-PANH could not be determined without fractionation.

Another interesting aspect of the analysis of the NBS dust sample was the enhanced resolution of some PAH after fractionation. As illustrated in Figure 4-11, more PAH with the molecular weight 252 are resolved after fractionation. This separation problem was probably due to

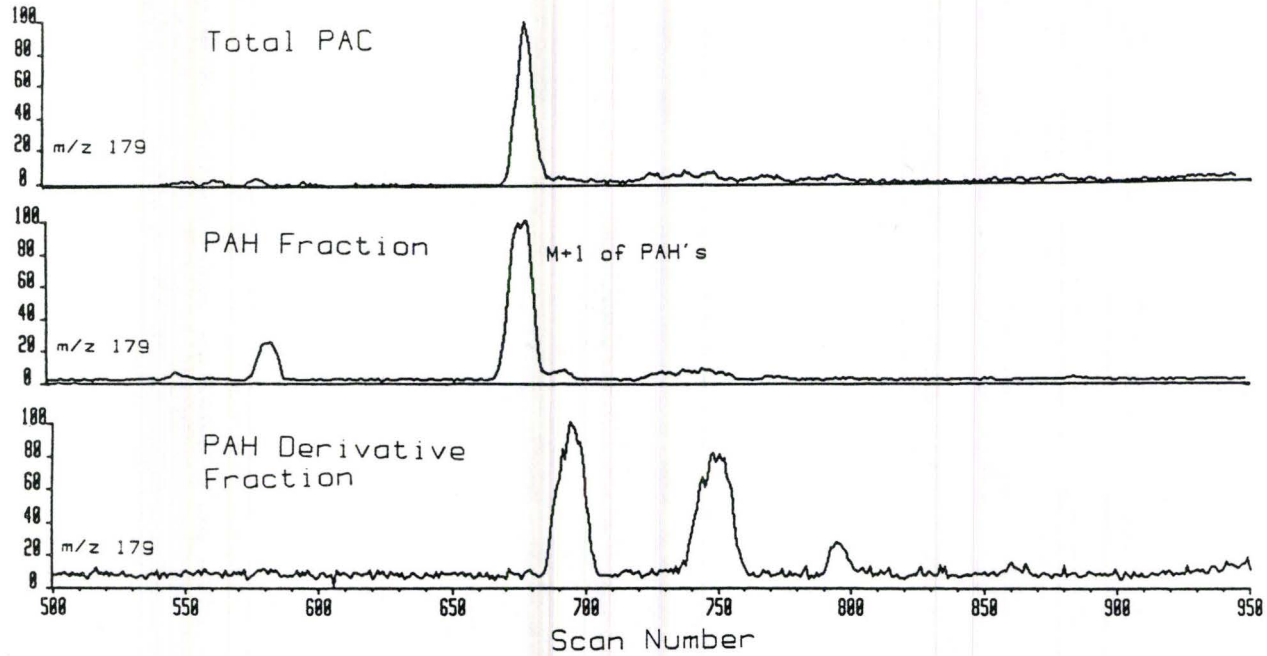
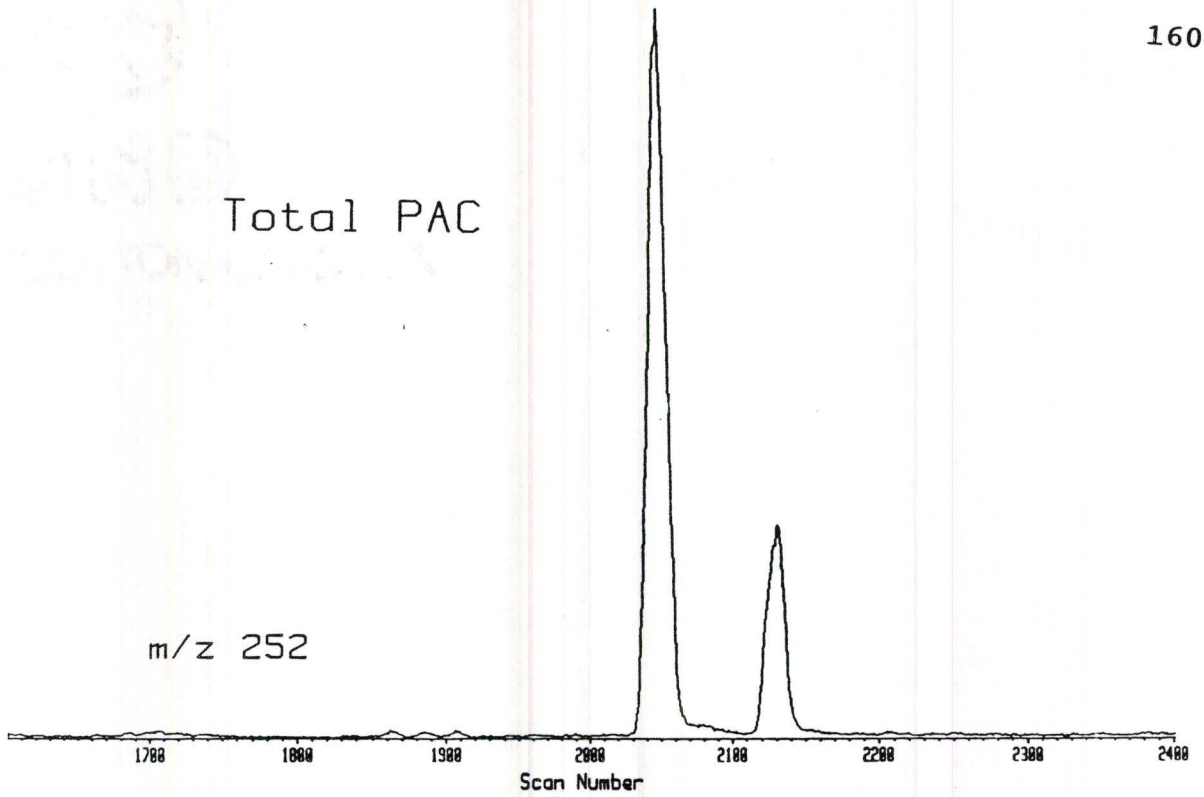


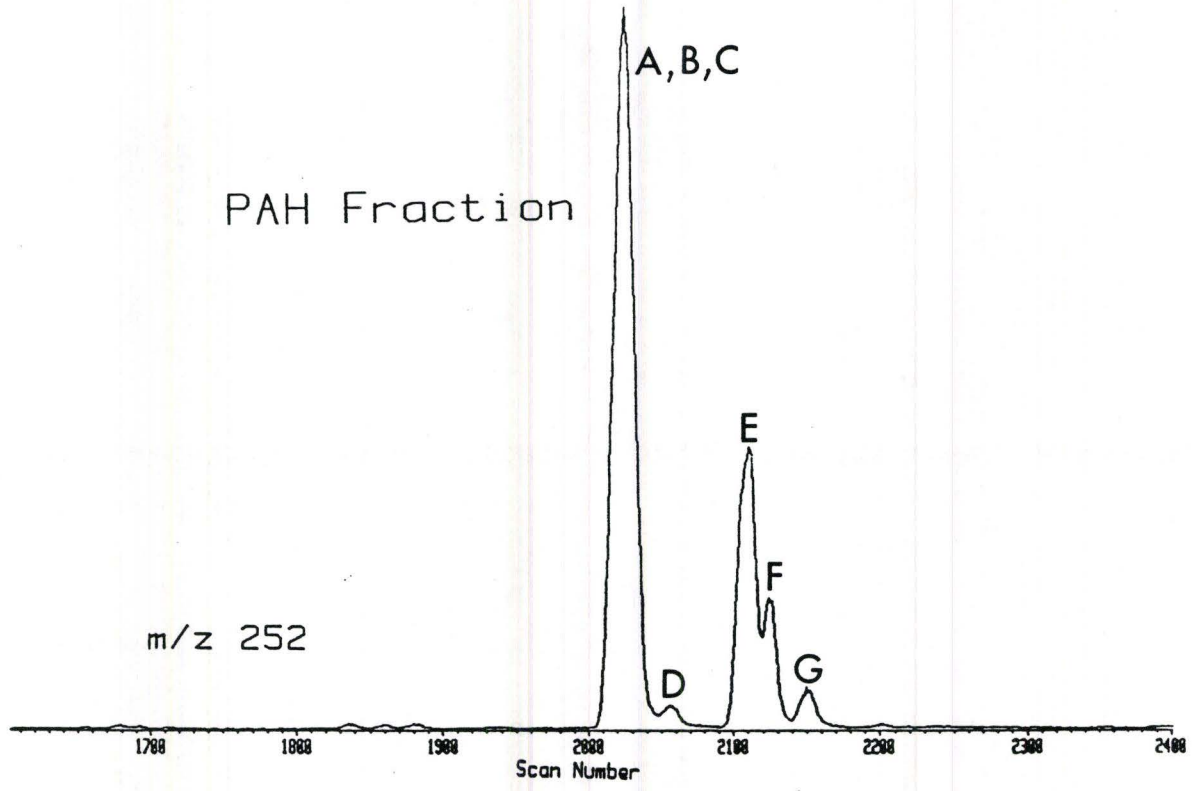
Figure 4-10: The 179-PANH in the NBS urban dust could not be detected without fractionation. In the m/z 179 mass chromatogram for the total PAC fraction, only the M+1 ions for the 178-PAH could be detected since they were present in much higher abundance than the 179-PANH.

matrix effects. This problem was unique to two cases: for PAH with the molecular weights 252 and 202. This resolution problem seemed to be unique to the NBS urban dust sample. No other samples that were examined in this study, exhibited this resolution problem. Figure 4-11 compares the mass 252 chromatograms before and after fractionation. This problem merits further investigation since one does not want to encounter it in routine analyses.

In summary, analysis of a complex sample by GC-MS may require fractionation, or at least knowledge of the regions where co-elution could mask components. For the NBS urban dust sample, the third order chromatography method did not provide sufficient resolution to aid in the detection of these components. Awareness of these problems areas was very useful for future analyses. However, extensive fractionation of the sample was time-consuming and could introduce contamination. Therefore, it was necessary to decide whether fractionation would be practical. The PAC fraction of the dust was very complicated. It contained many more PAH derivatives than other particulate samples that were examined in this study. Fractionation was necessary for this sample. In general, it may not be required. To determine whether the total PAC could be adequately analyzed by GC-MS, a method to quickly profile the sample was required. Normal-phase HPLC was shown to

Figure 4-11: Comparison of the m/z 252 mass chromatograms of the NBS urban dust obtained for the total PAC fraction and the PAH fraction. As illustrated, the resolution of the components has been enhanced by fractionation. The peak identities are: A=benzo[j]fluoranthene, B=benzo[b]fluoranthene, C=benzo[k]fluoranthene, D=unidentified 252-PAH, E=benzo[e]pyrene, F=benzo[a]pyrene, G=perylene.


Total PAC
m/z 252
1700
1800
1900
2000
2100
2200
2300
2400
Scan Number


A,B,C
PAH Fraction
E
F
G
D
m/z 252
1700
1800
1900
2000
2100
2200
2300
2400
Scan Number

effectively separate the PAH from the PAH derivatives. Therefore, the use of normal-phase HPLC-MS as a preliminary screening technique could provide information about the nature of the sample. The mass chromatograms of the PAC where co-elution was shown to be a problem in GC-MS analyses could be examined to determine whether fractionation would provide worthwhile information.

IV.5 GC Retention Indices

Retention data has been used extensively to aid in the identification of a variety of different compounds classes (113 and the references cited therein). Retention indices (RI) have proven to be far more reproducible and more suitable for inter-laboratory comparisons than retention times (114). Lee and coworkers developed a method of RI calculation using a first order linear interpolation fit of PAH, based on the fact that the reproducibility of retention data increases with the similarity of the samples to the standards (113). However, even RI are somewhat sensitive to experimental conditions. The GC conditions used in this study affected the results. A first order linear interpolation fit was not appropriate where a nonlinear temperature program was used. In this study, a modified calculation system based on an interpolation of a cubic spline fit was used. This method involved plotting

the retention time of the standards versus their assigned retention index and fitting a curve to the experimental data. Since more points were needed, fluorene, pyrene, and benzo[a]pyrene were added as secondary standards to improve the fit. These compounds were used because they were present in most environmental samples and can be detected easily by GC-MS. The index values used for these standards were the ones calculated by Lee and coworkers (113). The standard marker compounds and their corresponding RI are fluorene (268.2), phenanthrene (300.0), pyrene (351.2), chrysene (400.0), benzo[a]pyrene (453.4), and picene (500.0). These RI values and their corresponding scan numbers were entered into the program "Curve Fitter-PC", a program that is available through Interactive Microware, Inc., to calculate the fitted curve. One hundred points were calculated to define each curve. These points were entered into a template, designed in LOTUS 1-2-3, and were then used in the formula listed in Appendix 3 to calculate the retention indices of the sample components. Figure 4-12 shows the cubic spline fit curves that were obtained for each of the three different GC columns. It was obvious from examination of the curves that an increase in the polarity of the stationary phase increased the retention of these components. There was also a significant increase in retention of the higher molecular weight components on the

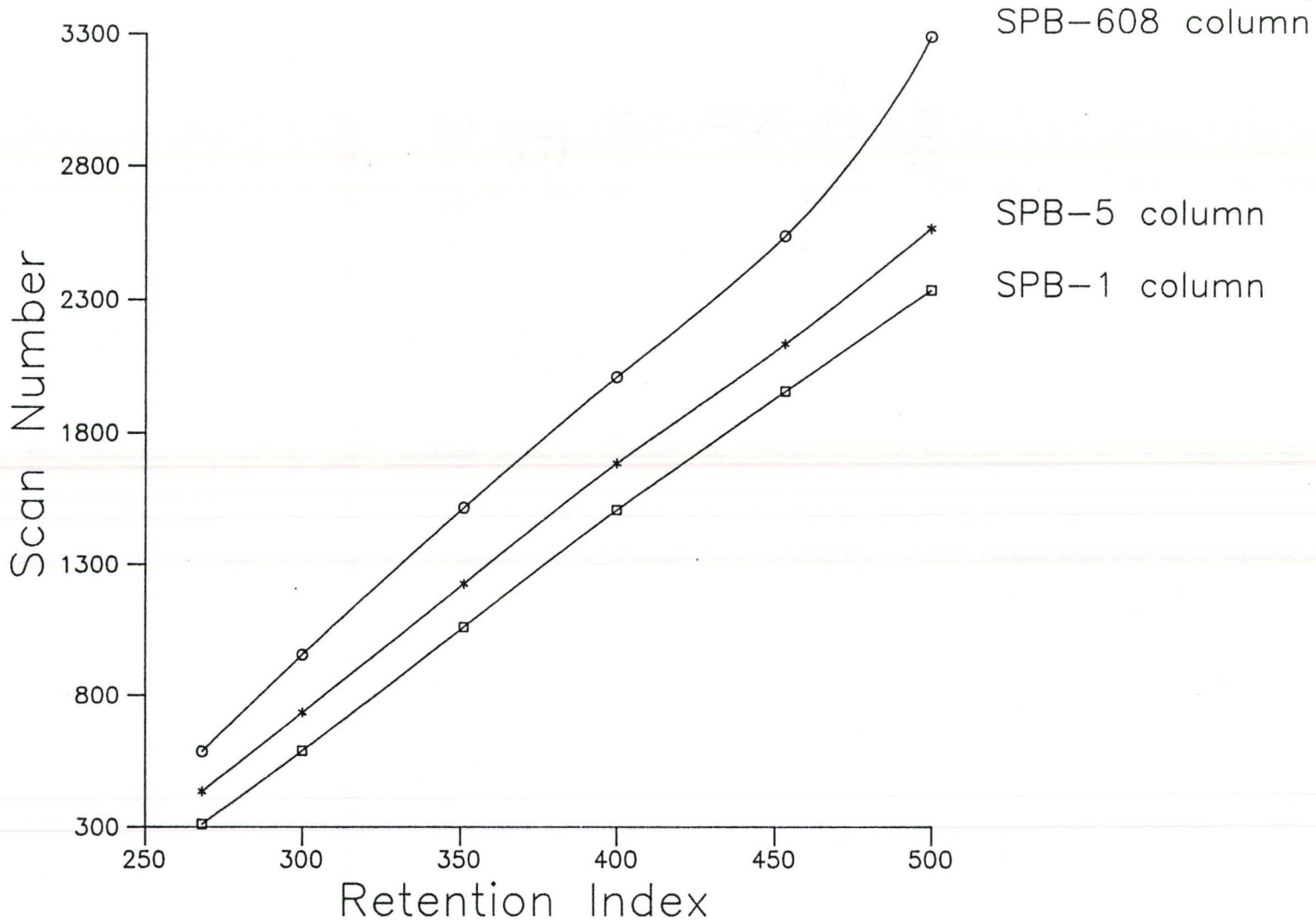


Figure 4-12: The calibration curves (for each GC column) used in the calculation of the retention indices for the components in the NBS urban dust sample.

SPB-608 column. Unlike the linear interpolation, the cubic spline interpolation provides a better fit to both linear and nonlinear data sets (119) and has been proven to be very useful when applied to this method of PAC RI calculation (Appendix 3). By using this method, the retention indices were very easy to calculate and quite comparable to the literature values (for the SPB-5 column) included in Table 4-2.

IV.6 Retention Increments

In addition to utilizing the retention index information obtained for each column, the retention increment was also used to provide supplementary information on the nature of the components. The use of retention increments has been popular for a number of years (114, 116, 117 and the references cited therein). However, its application to PAC analyses is still not common. Korhonen has published a number of articles on the effects of increasing chlorine substitution on retention in aromatic systems (144, 145, 146, 147, and the references cited therein). The retention increments are determined under isothermal and temperature programming operation on a non-polar and a polar column (144, 145, 146, 147). The incremental effect of chlorine substitution on elution temperature was determined. However, the differences in

retention of the compounds on the two columns were not compared. Korhonen has also examined retention increments due to nitro substitution of PAH (118). Only one non-polar column was used, and the increments were determined under various operating conditions.

Instead of varying the temperature, the difference in retention of a component could be determined on two different stationary phases. With the general increase in popularity of dual column methods (112, 110), this information should be readily available, and could be useful in confirmation of the identity of a compound.

The difference in retention of the PAC on the three columns was due to the difference in the polarity of the stationary phases and as illustrated in Figure 4-1, the interactions of the PAH and PAH derivatives were slightly different on each column. An attempt was made to correlate the difference in retention indices determined on two different columns with the compound type. The retention increments (ΔRI) of the components were determined for SPB-1 versus SPB-5, and SPB-5 versus SPB-608 stationary phases. The data did appear to follow some general trends, and the results are presented in Table 4-3. The alkylated PAH should be retained longer on the less polar stationary phase (relative to the PAH) and therefore their ΔRI should be positive. Conversely, the ΔRI for the PAH derivatives

Table 4-3: Observed trends in the ΔRI values for selected compound classes in the NBS urban dust sample.

Compound Type[1]	ΔRI[2] (1-5)	ΔRI[3] (5-608)
C_x-PAH[4]	+0.3 -- +1.0	+0.9 -- +3.3
H2-PAH	+0.3 -- +1.7	+1.0 -- +2.4
PASH	-0.1 -- -0.4	-3.1 -- -0.6
C_x-PASH[4]	+0.1 -- +2.8	+1.0 -- +12.3
PAK	-2.2 -- +1.5	-3.9 -- +5.5
PAQ	-3.2 -- -0.7	-2.8 -- -0.7
C_x-PAQ[4]	-1.4 -- +0.3	-5.0 -- +2.7
PAHK	+0.2 -- +0.8	+0.8 -- +3.6
C_x-PAHK[4]	+0.2 -- +0.8	+0.8 -- +3.6

RI: Retention index

[1] Acronyms for compound types are explained in Figure 1-2.

[2] RI(SPB-1) - RI(SPB-5)

[3] RI(SPB-5) - RI(SPB-608)

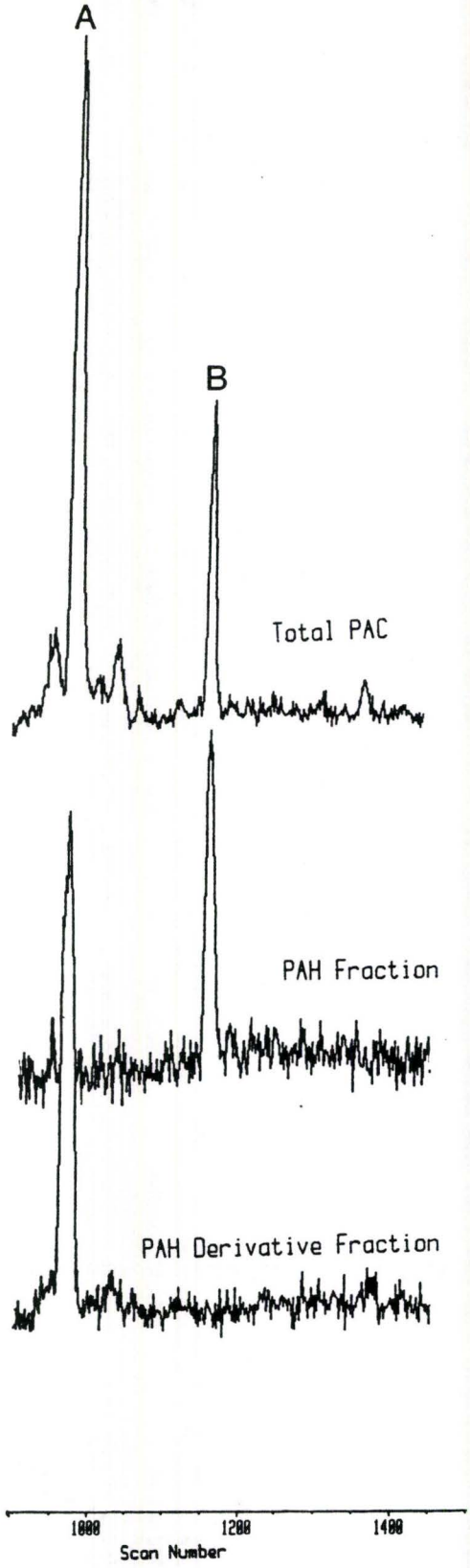
[4] C_x represents compounds that have alkyl substituents.

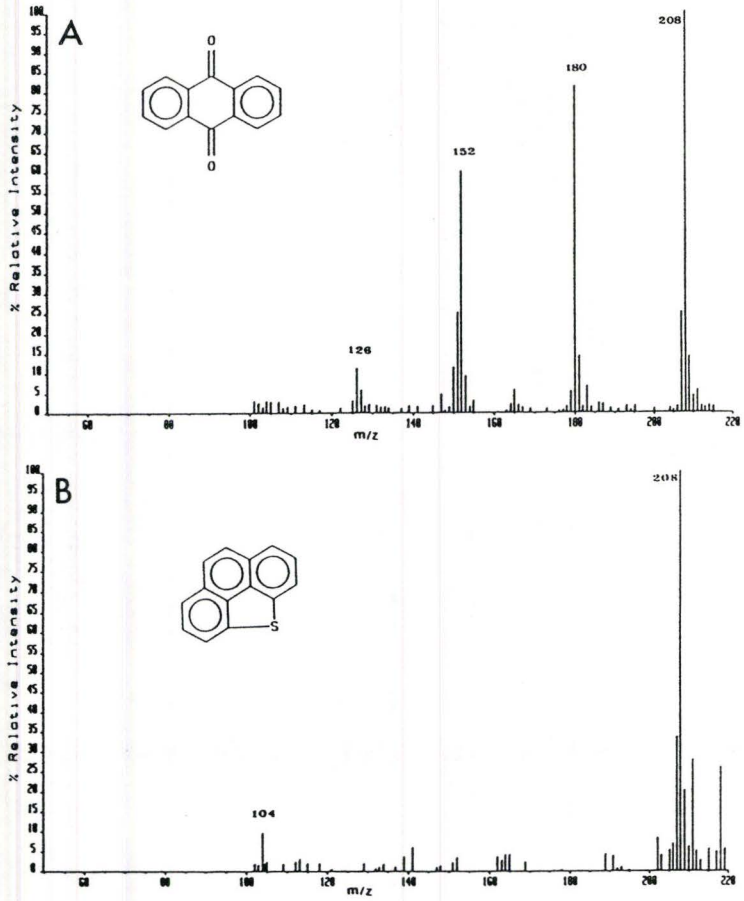
should be negative, since they were more polar and hence would not be retained as long. However, this supposition only appeared to hold for the polycyclic aromatic quinones. The ΔRI values for other PAH derivatives were not necessarily negative. Some of the ΔRI values calculated for compounds that eluted in the PAH region from the normal-phase HPLC column, were negative. Initial investigation of the data seemed to indicate that these negative values could be correlated with the sulfur heterocycles that elute in this region (Table 4-3). A number of components were tentatively identified as sulfur heterocycles. For example, in Table 4-2, two sulfur heterocycles with negative ΔRI values were confirmed by a number of techniques. The oxygen heterocycles also eluted in this region. No conclusions could be made on the ΔRI values for these compounds but, it appeared that these compounds would also have a negative ΔRI. Examination of the results in Table 4-3, indicated that only a few of the compound classes could be actually correlated with a definite trend in the ΔRI values. The interaction between the PAC and the stationary phase was obviously quite complicated, and in most cases could not be generalized to adequately correlate ΔRI data with compound class.

IV.7 Application of the Peak Detection Method

The power of the combination of the third order chromatography method and the peak detection routine for sample analysis and data interpretation was illustrated by examination of the m/z 208 mass chromatogram (Figure 4-13). Two of the peaks were identified as molecular ions. Tentative assignments were made after examination of the key fragment ions and the mass spectra. After fractionation of the sample, one of the compounds was detected in the PAH derivative fraction. This compound was probably a quinone of a 178-PAH, due to the characteristic fragmentation pattern in the mass spectrum with its distinctive successive losses of two [CO] fragments. The mass spectrum is shown in Figure 4-13. The other component eluted in the PAH region. The mass spectrum suggested a sulfur containing-compound by the presence of its characteristic isotopic clusters (Figure 4-13). The use of retention indices was important to be able to identify the particular isomers of these compounds (Table 4-2). The ΔRI value for the peak eluting in the PAH region was negative, indicating a sulfur heterocycle. For the other peak, the ΔRI was also negative, characteristic of a quinone. The identities of these species were confirmed as anthraquinone and phenanthro[4,5-bcd]thiophene. The

Figure 4-13: Identification of the species in the m/z 208 mass chromatogram of the NBS urban dust sample. Peak identities: A=anthraquinone, B=phenanthro[4,5-bcd]thiophene.


A
B
Total PAC
PAH Fraction
PAH Derivative Fraction
1000
1200
1400
Scan Number


A
O
O
208
180
152
126
% Relative Intensity
m/z
B
S
208
104
% Relative Intensity
m/z

tabulated results are listed in Table 4-2. The retention indices for these compounds were quite comparable to the literature values.

IV.8 Choice of GC Columns

The NBS dust sample was analyzed using three different GC capillary columns. One aim of this study was to evaluate the three columns to determine the best one for PAC analyses and a complementary one that would be useful for the third order chromatography method. These columns should have significantly different separation selectivities. The SPB-5 stationary phase consists of 5% phenyl-methyl silicone. This stationary phase has been used extensively for PAC analyses for a number of years (1, 2, 3, 148 and the references cited therein). This type of column has proven to be capable of separating the components efficiently. Also, the column bleed is quite low. High column bleed is a problem in GC-MS since trace sample components can be missed due to the high background levels. The ion source becomes contaminated more quickly and sensitivity is lost.

The choice of the complementary column was between the SPB-1 and the SPB-608 column. The SPB-1 column could not separate the PAC as efficiently as the SPB-5. However, this column's stationary phase was also used extensively for

PAC analysis and was significantly different from the SPB-5 column. In addition, a large amount of retention data is available in the literature that can be used to identify the components (1, 2, 3, 148 and the references cited therein).

The SPB-608 column showed great potential for PAC analyses. It was capable of separating more components than the SPB-5, even after fractionation of the PAC into a PAH and PAH derivative fraction. Unfortunately, there were a number of problems associated with it, that eventually proved that the SPB-608 column would not be viable for this type of analysis. The upper temperature limit of the column was rather low for PAC analyses (290^{o}C), and as a result, the bleed was very high. However, the most severe problem associated with using this column, was the significant increase in retention time of the components. For compounds with a molecular weight above 278, the peaks were retained too long and were too broad for accurate scan number measurement. Some of the higher molecular weight compounds were retained much longer than the total analysis time and in subsequent analyses appeared as "ghost peaks". These problems are illustrated in Figure 4-1 for the standard PAC mixture, the difference in the retention of picene on the SPB-5 column to the SPB-608 column was nearly twenty-five minutes and the higher molecular weight compounds were not detected. Examination of the retention curves for the three

columns also illustrated this problem (Figure 4-12). The curves for the SPB-1 and SPB-5 columns were nearly parallel, while the curve for the SPB-608 column was very non-linear. Due to problems associated with the SPB-608 column, the complementary column used in later analyses, was chosen to be SPB-1.

IV.9 Conclusions

The application of a third order chromatography technique and the semi-automated peak detection routine to the analysis of the NBS urban dust sample resulted in substantial improvements in the detection of the sample components. This study also showed that a sample as complicated as the NBS dust must be fractionated. The data from the GC-MS analyses of the NBS urban dust has been tabulated in Appendix 2. All of this information was used to build a database that could be applied to future analyses of similar samples. Fractionation of the sample and subsequent analysis, provided information on the regions where co-elution of the PAH and PAH derivatives could create serious problems in reliable peak assignment. Knowledge of these regions was important in the detection of potential sources of error in the data analysis.

CHAPTER V: The Hamilton Airborne Particulate Sample

The methods developed for the isolation and determination of PAC in environmental samples were applied to a typical urban airborne particulate sample collected in Hamilton. It was important that these methods were applicable to the small sample size of typical environmental samples. Therefore it was important that these methods could be satisfactorily applied to the total PAC fraction without the necessity of further fractionation.

Two Hi-Vol filter samples, supplied by the Ontario Ministry of the Environment, were combined and fractionated using the alumina/LH-20 clean-up scheme. The PAC fraction was isolated and subsequently analyzed, using GC-FID, GC-HRMS and the third order chromatography method with the semi-automated peak detection routine.

V.1 Comparison of the NBS dust and the Hamilton Sample

As noted in the preceding chapter, there were a number of errors in the identification of components in the NBS dust sample, due to its complexity. However, the Hamilton airborne particulate sample was much simpler and

contained only a fraction of the PAH derivatives observed in the NBS sample. This point was illustrated by comparison with their total ion current chromatograms obtained from the normal-phase HPLC-MS analyses (Figures 3-9 and 3-8). The individual mass chromatograms were also compared with the results from the NBS dust sample. As illustrated in Figures 3-11 and 3-12, the mass chromatograms for the Hamilton particulate sample were much simpler. Most of the problems that were observed in the analysis of the NBS dust sample were not present in this sample. Therefore, further fractionation was not necessary.

V.2 GC-FID Analyses

The GC-FID chromatogram using the SPB-5 column, for the total PAC in the Hamilton airborne particulate sample is presented in Figure 5-1. It should be noted that this chromatogram was strikingly similar to the chromatogram obtained for the PAH fraction of the NBS dust (Figure 4-5). This similarity was added proof that the airborne particulate sample was much simpler. The GC-FID chromatogram of the Hamilton airborne particulate sample using the SPB-1 column is presented in Figure 5-2.

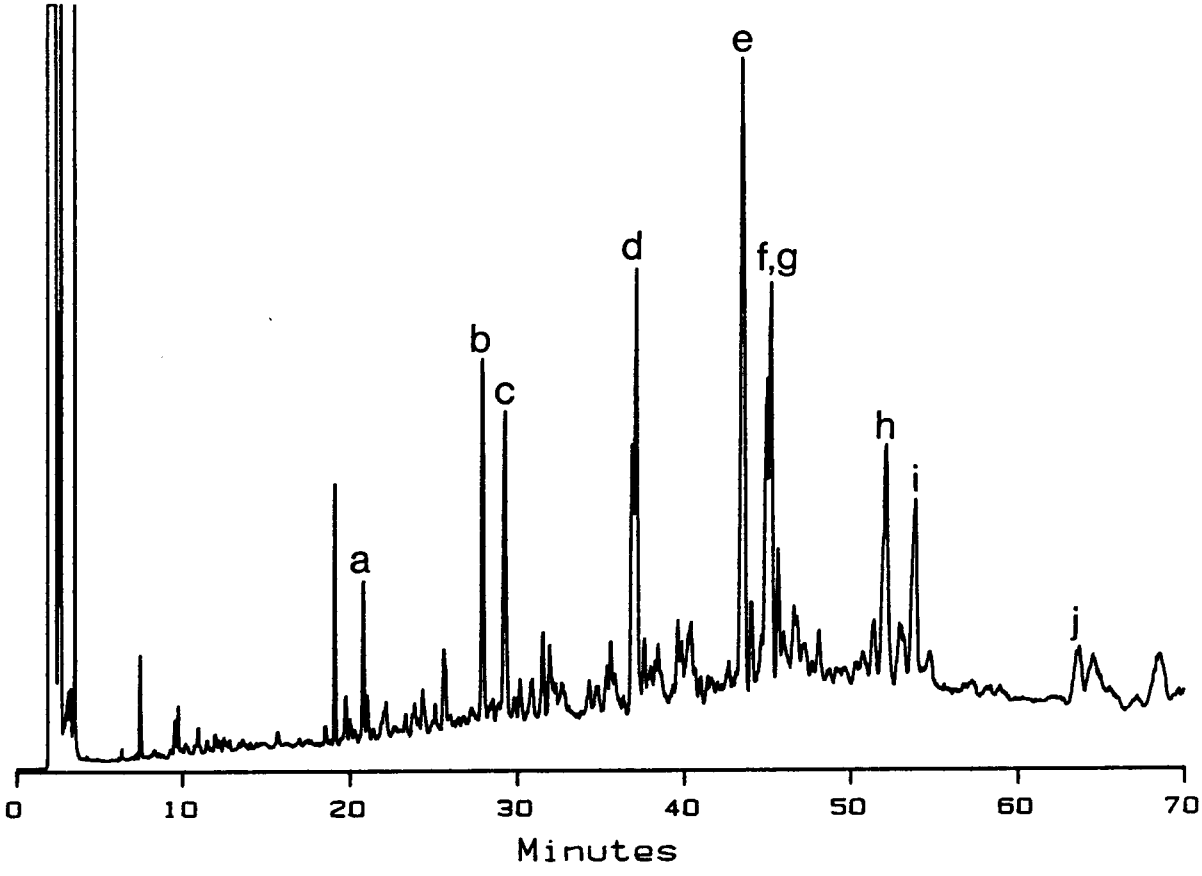


Figure 5-1: The GC-FID chromatogram of the Hamilton airborne particulate sample using the SPB-5 column. The peak identities are: a=phenanthrene; b= fluoranthene; c=pyrene; d=chrysene/triphenylene; e=benzofluoranthenes; f= benzo[e]pyrene; g=benzo[a]pyrene; h=C3-216-PASH; i=C3-216-PASH; j=302-PAH.

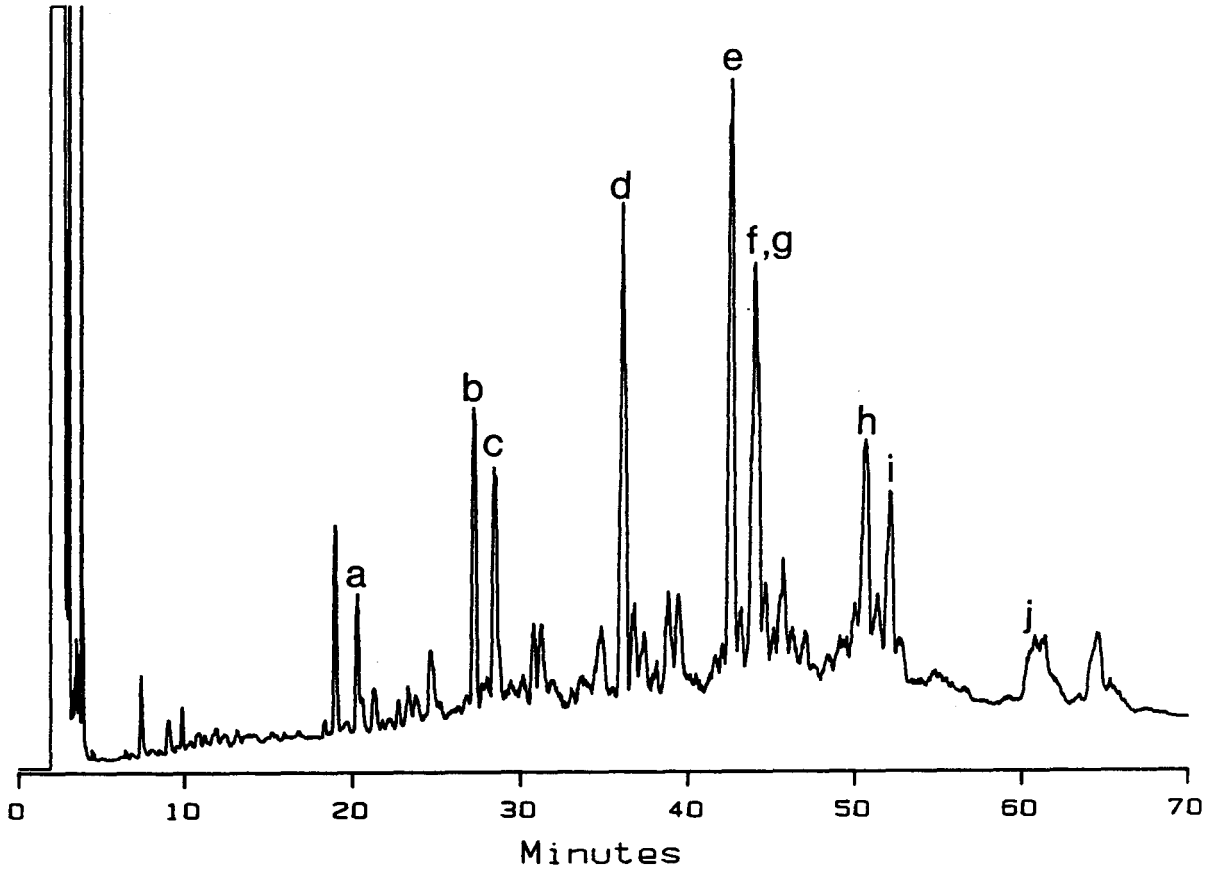


Figure 5-2: The GC-FID chromatogram of the Hamilton airborne particulate sample using the SPB-1 column. The identified species are: a=phenanthrene; b=fluoranthene; c=pyrene; d=chrysene/triphenylene; e=benzofluoranthenes; f=benzo[e]pyrene; g=benzo[a]pyrene; h=C3-216-PASH; i=C3-216-PASH; j=302-PAH.

V.3 Application of the Third Order Chromatography Method

The third order chromatography method was done using the SPB-1 and the SPB-5 columns. All of the results have been tabulated and are presented in Appendix 4. Table 5-1 lists some of the sample components that have been positively identified. The database generated from the characterization of the PAC in the NBS urban dust (SRM 1649) was employed to aid in the identification of the individual components. In total, over 350 PAC were detected in this sample.

Peak detection was much easier with this sample. The compounds that could not be detected in the NBS dust without fractionation, could be detected here. For example, the odd-massed molecular ions were easily identified in this sample (Appendix 4). The retention indices and increments were calculated in the manner previously described. The calibration curves for the retention index results are presented in Figure 5-3. They were virtually identical to those obtained from the NBS dust analyses (Figure 4-12).

A GC-HRMS analysis was also done using the SPB-5 column to aid in the identification of some of the components by providing exact mass measurements. This information is also presented in Appendix 4.

Table 5-1: Compounds identified in the Hamilton airborne airborne particulate sample.

Observed Mass (Error (mmu))	Retention Indices SPB-1	SPB-5	ΔRI[1] (1-5)	Identity
166	268.2	268.2	0.0	Fluorene
167.073(-5)	308.4	308.5	-0.1	Carbazole
168	---	---	--	Dibenzofuran[2]
178.078(-2)	300.0	300.0	0.0	Phenanthrene
178	302.2	301.5	0.8	Anthracene
180	292.6	293.0	-0.4	Fluorenone
184.034(-4)	295.2	295.4	-0.2	Naphtho[1,2-b]thiophene
190	321.5	321.6	-0.1	4H-Cyclopenta[def]phenanthrene
202.078(-1)	343.9	343.4	0.5	Fluoranthene
202.078(3)	351.2	351.2	0.0	Pyrene
208.052(.2)	329.2	329.9	-0.7	Anthraquinone
208.034(4)	347.7	348.5	-0.8	Phenanthro[4,5-bcd]thiophene
216.094(2)	368.5	367.8	0.6	Benzo[a]fluorene
226.078(-3)	390.7	390.1	0.6	Benzo[ghi]fluoranthene
228	400.0	399.0	1.0	Benz[a]anthracene
228.094(-8)	400.0	400.0	0.0	Chrysene/Triphenylene
229.089(-4)	392.3	391.8	0.6	Benzo[c]acridine
252.094(-.4)	443.1	441.9	1.2	Benzofluoranthene
252.094(2)	453.4	452.2	1.2	Benzo[e]pyrene
252.094(2)	453.4	453.4	0.0	Benzo[a]pyrene
252.094(.6)	456.9	456.2	0.7	Perylene
278.109(-.8)	500.0	500.0	0.0	Picene

RI: retention index

[1] RI(SPB-1) - RI(SPB-5)

[2] No retention data available, compounds eluted before first standard.

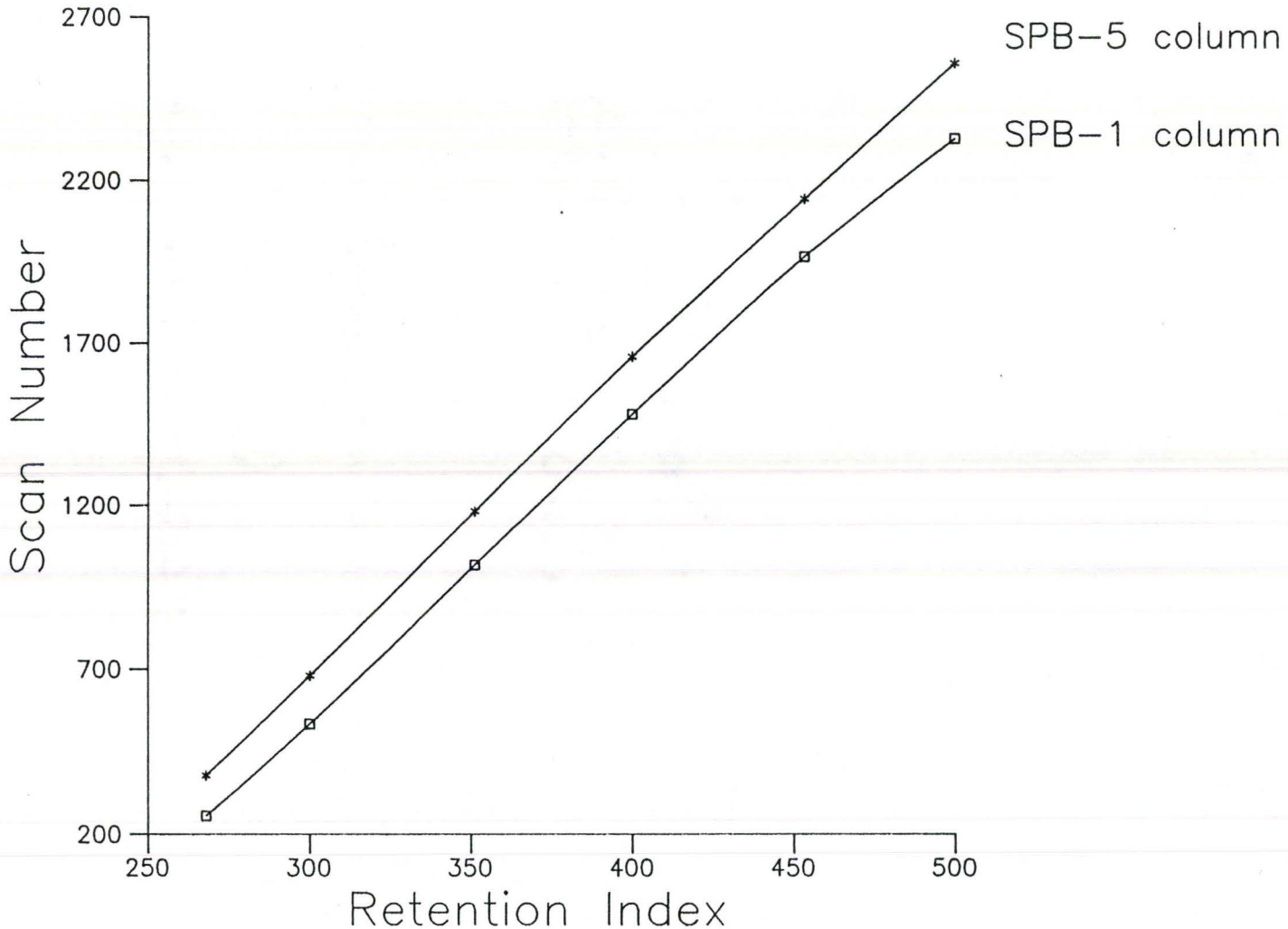


Figure 5-3: The calibration curves (for each GC column) used in the calculation of the retention indices for the components in the Hamilton airborne particulate sample.

V.4 Conclusions

The difficulties encountered in the analysis of the total PAC in the NBS dust were not present in this sample. The combination of the third order chromatography method and the semi-automated peak detection routine was easily applied to the total PAC fraction from a typical airborne particulate sample.

CHAPTER VI: CONCLUSIONS AND FUTURE WORK

VI.1 Conclusions

Two clean-up methods have been investigated for the isolation of PAC in airborne particulate samples. The alumina/LH-20 method has been shown to be superior to the silica/LH-20 method in separating PAC from potential interferences, such as phenolic compounds.

Using the results obtained in this study, the value of the denuder bundle in reduction of artifact formation could not be determined with certainty. Laboratory tests have shown that during the exposure of filters to ozone-spiked air, the denuder does reduce the formation of PAH derivatives. However, no effect was observed during the laboratory exposure of the samples to nitric acid-spiked air. More experiments are required to justify that these results are not anomalies. No differences have been detected between the standard and denuder Hi-Vol samplers under ambient sampling conditions during the field study experiments. The likely explanation of this data is that artifact reactions on filters from Hi-Vol samplers were not

significant under the particular sampling conditions.

The use of normal-phase HPLC has been shown to be an excellent method for routine profiling of samples. The distribution of PAC between the PAH and PAH derivative fractions was determined easily using normal-phase HPLC-MS. Using mass chromatograms as a means of detection, the selectivity of detection was greatly enhanced. This profiling method was used to compare the PAC in samples, qualitatively and/or quantitatively.

The application of the third order chromatography technique and the semi-automated peak detection routine to the analysis of the NBS urban dust sample has resulted in substantial improvements in the detection of sample components. Over 500 different PAC were detected in the NBS urban dust sample. Fractionation of the sample, and subsequent analysis, provided information when co-elution of the PAH and PAH derivatives created serious problems in reliable peak assignment. Key fragment ions and retention indices obtained from the three different GC columns were all incorporated into a database that could be used in future analyses of PAC.

The analysis of a typical airborne particulate sample using the third order chromatography method and the semi-automated peak detection routine was shown to be easily

applied to the PAC fraction without the need for further separation. In total, over 350 PAC were identified in this sample.

VI.2 Future Work

Further experimentation is necessary to determine whether the denuder does reduce artifact formation during Hi-Vol sampling. Laboratory experiments should be performed under strict control, using a combination of gases to try to emulate field conditions. Many more field samples should be examined to try to determine the extent, if any, of artifact formation.

The method of retention index calculation needs to be refined to include more of the later eluting compounds. A compound such as benzo[rst]pentaphene could be used as an index marker. In addition, the application of a retention index calculation system using a cubic spline fit curve for reversed-phase HPLC data is currently being investigated.

More work is required to determine the identities of the many PAH derivatives that are present in the NBS dust sample. These are the types of compounds that would be expected to appear during sampling over an extended period of time, and this information may prove to be useful when applied to the denuder experiments.

The greatest disadvantage of the semi-automated peak detection routine is the amount of operator time required in data interpretation. Programs need to be developed so that data analysis can be completely handled by the computer.

Instead of using only GC, third order chromatography could also be performed by combining different chromatographic methods such as GC, reversed-phase HPLC, or supercritical fluid chromatography with mass spectrometry. Since the selectivity of these techniques is so different, confirmation of a component is more likely. In addition, by simply combining different columns, temperatures (or temperature gradients) and mobile phases, retention data can be obtained that would be useful in the identification of the components.

The use of reverse-phase HPLC-MS/DAD is currently being investigated (95). The structural information obtained from the ultraviolet/visible spectra would provide valuable information that could be used to identify the PAC isomers.

CHAPTER VII: EXPERIMENTAL

VII.1 Materials

Dichloromethane (DCM), acetonitrile, and methanol were HPLC-grade and acetone was distilled-in-glass quality purchased from Caledon Laboratories Ltd. (Georgetown, Ontario). Hexane was distilled-in-glass quality from BDH Chemicals Canada (Toronto, Ontario). Benzene and chloroform were reagent grade (Caledon Laboratories Ltd.) and were re-distilled prior to use. The PAC standards were purchased from Aldrich Chemical Co. (Milwaukee, WI). A Milli-Q water purification system (Millipore Corp., Bedford, MA), equipped with two carbon filters, one ion exchange filter and a 0.22 μm filter, was used to further purify distilled water.

VII.2 Samples

The National Bureau of Standards urban dust standard reference material (SRM 1649) was used for the development and evaluation of analytical techniques.

The field study samples were supplied by Concord Scientific Corporation. The sampling was performed on the

roof of the Hamilton Beach Rescue Unit Association in Hamilton, Ontario. Four high volume (Hi-Vol) particulate samplers, supplied by the Ontario Ministry of the Environment, were used to collect the samples. Two of them were modified to accept a denuder housing. The sampling conditions are listed in Table 7-1.

The filter samples used for the dynamic laboratory study were collected on the roof of the Concord Scientific Corporation building by standard Hi-Vol samplers. This location was within 100 meters of the Highway 401 and 500 meters from the intersection of Highway 401 and the Allen Expressway in Downsview, Ontario. These filter samples were then cut in half and exposed to airstreams containing either ozone or nitric acid, when one half of each filter was protected by a denuder and the other half was not protected. This experiment was designed to mimic field conditions and is described in detail elsewhere (50). Flow rates were adjusted to compensate for the smaller surface area. Conditions used for the collection and exposure of the filters are listed in Tables 7-2 and 7-3 respectively.

The two Hamilton urban airborne particulate samples, provided by the Ontario Ministry of the Environment, were collected over 24 hours for a total volume of 1631 m^3 each, on Gelman glass fibre filters using Hi-Vol samplers at the North Park monitoring station.

Table 7-1: A summary of the sampling conditions for the field study samples that were supplied by Concord Scientific Corporation.

A: Samples that were analyzed by GC-FID after separation into PAH and PAH derivative fractions.

	S2-2 Denuder	S2-4 Standard
Sample Volume	1843 m^3	1631 m^3
Particulate Weight	251.3 mg	308.8 mg

Conditions during sampling

Mean Ozone Concentration: 49 ppb

Mean Nitrogen Dioxide Concentration: 39 ppb

Mean Temperature: 20.9°C

Mean Level of Nitric Acid: 3.73/2.66 fg/m^3

B: The total PAC extract of these samples were analyzed by normal-phase HPLC-UVD and HPLC-MS.

	S5-1 Denuder	S5-3 Standard
Sample Volume	1631 m^3	1631 m^3
Particulate Weight	169.7 mg	146.7 mg

Conditions during sampling:

Ozone Concentration: 42 ppb

Nitrogen Dioxide Concentration: 55 ppb

Temperature: 14.1°C

Mean level of Nitric Acid: 2.76/5.37 fg/m^3

Table 7-2: A summary of the sampling conditions during the collection of filters used in dynamic exposure experiment.

Sampling Date (1985)	Volume of Air Sampled (m^3)	Filter Designation for Exposure	Test
July 29	1631	F9	O_3
29	1631	F10	O_3
August 1	3262	F11	O_3
1	3262	F12	O_3
7	1631	F13	O_3
7	1631	F14	O_3
14	1631	F15	O_3
14	1631	F16	O_3
October 1	1631	F17	HNO_3
2	1631	F18	HNO_3
3	1631	F19	HNO_3
4	1631	F20	HNO_3

Table 7-3: A summary of conditions used for the dynamic exposure of preloaded Hi-Vol filters.

Filter	Concentration[1] (ppb)	Time (min)	Volume (m^3)
Ozone Exposure Conditions			
F9S	200	1440	21.6
F10S	200	1440	21.6
F11S	190	1565	23.48
F12S	200	1440	21.6
F13S	200	1440	21.6
F15S	200	1650	24.75
F16S	190	1500	22.5
Ozone Denuder Exposure Conditions			
F9D	30->80[2]	1440	21.6
F10D	15->35[2]	1440	21.6
F11D	25->65[2]	1565	23.48
F12D	35->75[2]	1440	21.6
F13D	20->65[2]	1440	21.6
F15D	10->50[2]	1650	24.75
F16D	25->45[2]	1500	22.5
Nitric Acid Exposure Conditions			
F17S	70	1380	20.7
F18S	60.5	1440	21.6
F19S	80	1440	21.6
F20S	43	1800	27.0
Nitric Acid Denuder Exposure Conditions			
F17D	1.2	1380	20.7
F18D	7.5	1440	21.6
F19D	1	1440	21.6
F20D	1.2	1800	27.0

[1] The concentration of the gas was measured after passing through the filter.

[2] Concentration at start of run.

VII.3 Denuder Hi-Vol Sampler

High volume (Hi-Vol) particulate samplers were modified by Concord Scientific Corporation (Downsview, Ontario) to accommodate the denuder bundle. The alteration consisted of an extension housing (29 x 36 cm aluminum tray) to support the denuder tube bundle above the Hi-Vol filter. The denuder tube bundle consisted of 1250 convoluted Kraft paper tubes (Precision Paper Tube, Mississauga) that were each 61 cm long, 9.5 mm O.D., 7.9 mm I.D. and secured together in a 28 cm x 34 cm matrix bundle (Figure 1-4).

VII.4 Filter Handling

Gelman Type AE glass fibre filters were heated in a muffle furnace at 400^{o}C for two hours, and then were wrapped in aluminum foil and stored in zip lock bags. After collection, the filter samples were again wrapped in aluminum foil and placed in zip lock bags, and if not extracted immediately, they were stored in the freezer.

VII.5 Extraction

The samples supplied by Concord Scientific were provided as DCM extracts after Soxhlet extraction. The NBS urban dust sample and the Hamilton airborne particulate sample were also extracted using Soxhlet extraction. Pre-extracted glass wool was placed in the bottom of the Soxhlet to prevent losses of the particulate. For extraction of the NBS urban dust sample, a portion was transferred to a glass Soxhlet thimble with a glass frit. Glass wool was also placed in the bottom of the thimble to prevent the dust from plugging the glass frit. The sample was extracted (24 hours) with 500 mL of DCM (protected from light with aluminum foil) with a 15-18 minute cycle time. The sample was then extracted similarly with 500 mL of methanol. The Hamilton filter samples were rolled up to fit in the Soxhlet and extracted using the same procedure.

VII.6 Sample Clean-up Procedures

The Soxhlet extracts were concentrated to 5-20 mL using a Buchi/Brinkmann Rotavapor rotary evaporator (Brinkmann Instruments, Rexdale, Ontario). The extract was filtered using a 10 mL teflon Luer-lock Hamilton syringe (Chromatographic Specialities Ltd., Brockville, Ontario) connected to a 13 mm Swinny stainless steel filtering unit

with a 0.5 μm teflon (FH) filter (Millipore Corp., Bedford, MA).

The DCM extracts supplied by Concord Scientific were concentrated to 250 μL under a gentle stream of nitrogen and stored in teflon-capped vials in the freezer prior to clean-up.

The extracts obtained from the NBS dust sample were made up to 25 mL in volumetric flasks and 10 mL aliquots from each extract were used in the clean-up stage. The 10 mL aliquot from the methanol extract was taken to dryness. DCM (3 x 2 mL) was added to the residue, and it was gently swirled in an ultrasonic bath for 30 seconds. The DCM insoluble material was allowed to settle and the DCM was removed with a syringe. The DCM soluble portion of the methanol extract was combined with the 10 mL aliquot from the DCM extract and used immediately.

The Hamilton filter extracts were concentrated to 2 mL under a gentle stream of nitrogen prior to clean-up and stored in teflon-capped vials in the freezer.

VII.6.1 Silica/LH-20 Clean-up Method

For the silica/LH-20 clean-up method (Figure 1-5), the extract was concentrated to 1 mL of DCM and quantitatively passed through a silica solid phase extraction (SPE) cartridge (Sep-pak, Waters Associates Inc.,

Milford, MA) that had been previously washed with 5 mL of DCM. In total, 10 mL of DCM was passed through the cartridge and collected for further fractionation. Methanol (10 mL) was then used to elute a second fraction. Both fractions were taken to dryness under a gentle stream of dry nitrogen and weighed. The DCM fraction was redissolved in 250 μL of DCM and injected onto a 31 cm x 2.5 cm I.D. Sephadex LH-20 column (Pharmacia Fine Chemicals, Dorval, Quebec) that was connected to a Beckman 153 fixed wavelength (254 nm) UV detector (Beckman Canada, Toronto, Ontario) equipped with a 5 mm pathlength cell. The flow rate was maintained at 5 mL/min using a Beckman single-headed reciprocating pump. The system was previously conditioned in the mobile phase hexane/methanol/DCM (1:4:3). The eluate passed through the detector, and was collected into 250 mL graduated cylinders. The cut-points were determined using PAC standards: naphthalene, pyrene, and coronene. The first fraction, 0-96 mL, contained the aliphatic material and the aromatic fraction was contained in the 96-300 mL range. Both fractions were concentrated to 5 mL using a rotary evaporator and then evaporated to dryness under nitrogen and stored in the freezer in vials with teflon-lined caps. Filter blanks or solvent blanks were taken through the clean-up scheme concurrently with the samples to ensure the integrity of the procedure.

VII.6.2 Alumina/LH-20 Clean-up Method

The sample was fractionated by the alumina/LH-20 clean-up method, using essentially the procedure described by Later and coworkers (86, 87, 139). The activated alumina (Fisher Scientific Neutral Alumina A-950 (Brockman Activity I)) was dried overnight at 160°C and allowed to cool for fifteen minutes in a desiccator prior to use. The procedure requires quantitatively transferring the extract into a 50 mL round-bottomed flask and slowly adding 3 grams of alumina while stirring the mixture with a spatula. The sample was stirred while the solvent was slowly evaporated under a gentle stream of nitrogen until the alumina appears slightly damp. The flask was then placed on the rotary evaporator and the remaining solvent was removed with gentle warming. The sample-coated alumina was then placed into a column (1.5 cm I.D., 30 cm long with a glass frit bottom) already packed with 6 grams of fresh alumina.

Six fractions were obtained by passing solvents of increasing polarity through the column (Figure 1-6). The aliphatic compounds were eluted in the first fraction (A1) with 30 mL of hexane. The A2 and A3 fractions (combined to give A23) were collected by elution with 50 mL benzene followed by 70 mL chloroform (1% ethanol). The components of increasing polarity were eluted by passing 50 mL MeOH (A4), 50 mL MeOH/H_2O (A5), and 50 mL H_2O (A6) respectively

through the column. The fractions were concentrated by rotary vacuum evaporation and taken to dryness using a stream of dry nitrogen gas and weighed. The aromatics in the A23 fraction were then isolated using the Sephadex LH-20 column in the manner described in the previous section. Solvent blanks were taken through the clean-up scheme in parallel with the samples to ensure the integrity of the procedure.

VII.6.3 Normal-Phase HPLC Fractionation

After isolating the PAC fraction, further fractionation was done for some samples, using semi-preparative normal-phase HPLC (amino-cyano bonded phase) (see section VII.8 for details) with a hexane/DCM mobile phase at a flow rate of 4.2 mL/min. The aromatic fraction, collected from the Sephadex LH-20 step, was dissolved in 20 μL of DCM and washed into a 100 μL loop with 60 μL of hexane. In total, three fractions were obtained. The first fraction, collected from 0 to 10.6 minutes contained any residual aliphatic material that was not removed by the Sephadex LH-20 step. The next fraction (10.6 to 24.4 min) contained the PAH. The PAH derivatives were contained in the last fraction (24.4 to 56.0 minutes). The cut-points were established by a normal-phase HPLC-MS analysis of the sample. The mass spectral data were

examined to determine the regions where the PAH and PAH derivatives elute. The peak positions in the UV absorbance chromatograms were then correlated with these results.

VII.7 Gas Chromatography

A Varian 3700 gas chromatograph (Georgetown, Ontario) equipped with an on-column injector (J + W Scientific, Orangevale, CA) and a flame ionization detector were used for the GC-FID analyses. High purity helium (Canadian Liquid Air, Montreal, Que.), after being passed through a gas purifier containing self-indicating drying agent and molecular sieves (Alltech Associates, Deerfield, IL), an oxygen trap and an indicating oxygen trap (Chromatographic Specialties, Brockville, Ontario), was used as the carrier gas at a linear velocity of 35 cm/s (determined at room temperature). Hydrogen (regular grade) and air (breathing quality) with flow rates of 30 and 300 mL/min respectively, were used for the flame ionization detector. The dry nitrogen makeup gas (passed through a gas purifier containing self-indicating drying agent and molecular sieves) has a flow rate of 30 mL/min.

The GC operating conditions were the same for the GC-FID and GC-MS analyses. The J + W injectors allowed the initial 15 cm of the column to be pulled out of the oven for injection of the sample at room temperature; following

injection, the column was reinserted into the oven. The oven temperature was programmed from 60° to 130°C at 20°C/min, then 130°C to 300°C at 4°C/min and held for 40 minutes.

For the early profiling work, the field study samples were analyzed using a DB-5 column (30 m x 0.25 mm I.D., 0.25 μm phase thickness) (J + W Scientific, Orangevale, CA). Three fused-silica capillary columns (30 m x 0.25 mm I.D., 0.25 μm phase thickness) were used for the evaluation of the third order chromatography method and the stationary phases were SPB-1, SPB-5, and SPB-608 (Supelco, Inc., Bellefonte, Pennsylvania).

A 64K Apple II+ microcomputer equipped with an Interactive Microware (State College, PA) "Adalab" interface card and "Ada-amp" amplifier with multiplexing and programmable attenuation was used for chromatography data acquisition. A HP7470A digital plotter was used for plotting the data. All software for data acquisition, plotting and data analysis was written by M.A. Quilliam and R. Mann.

VII.8 Liquid Chromatography

HPLC analyses were performed on a Hewlett-Packard HP1090 liquid chromatograph equipped with a Rheodyne 7012 fixed loop (20 or 100 μL) injection valve (Cotati, CA), a

built-in HP1040A diode-array detector, a ternary DR5 pumping system, and a HP79994A analytical workstation for data aquisition (Hewlett-Packard, West Germany). An HP7470A digital plotter was used to plot the data.

Profile analyses were performed on an analytical normal-phase column (25 cm x 4.6 mm I.D.) with 10μm PAC packing (amino-cyano bonded phase) (Whatman Inc., Clifton, NJ). The hexane/DCM mobile phase was programmed linearly from 100% hexane (held for 5 minutes) to 99% hexane (after 10 minutes), to 95% hexane (after 15 minutes) and reaching 100% DCM after 40 minutes at a flow rate of 1 mL/min.

The semi-preparative normal-phase column used for fractionation was a 25 cm x 9.4 mm Magnum-9 column with 10μm PAC packing (Whatman Inc., Clifton, NJ). The fractionation of the samples obtained from Concord Scientific Corporation were performed using the Magnum-9 PAC column with a one step gradient elution. The mobile phase (0.5% isopropanol/hexane) was held for 15 minutes and then programmed through a linear gradient to 30% isopropanol/hexane over 15 minutes and held for 30 minutes at a flow rate of 4.2 mL/min. All other analyses that employed normal-phase HPLC utilized the improved gradient elution with the hexane/DCM mobile phase. Guard cartridges, 15 x 3.2mm, with an amino bonded phase were used for all of the normal-phase HPLC columns (Brownlee Labs Inc., Santa

Clara, CA).

For the reversed-phase HPLC analyses, a Vydac 201TP (C18 bonded phase) 10 μm, 25 cm x 4.6 mm I.D. column was used. A C18 bonded phase guard cartridge, 15 x 3.2mm, was used to protect the column (Brownlee Labs Inc., Santa Clara, CA). A linear gradient from 60% acetonitrile/water to 100% acetonitrile over 30 minutes, at a flow rate of 1 mL/min was used.

VII.9 Mass Spectrometry

VII.9.1 GC-MS Analyses

The GC-MS analyses were performed on a ZAB-E mass spectrometer (VG Analytical, Altrinchan, U.K.) equipped with a Hewlett-Packard 5890A gas chromatograph with an on-column injector (J+W Scientific, Orangevale, CA). The ionization mode was electron-impact (70 eV nominal energy). Data was collected using the VG-11/250 data system. The oven temperature was programmed from 60° to 130°C at 20°C/min and from 130°C to 300°C at 4°C/min and held at 300°C for 40 minutes. The transfer line from the GC to the MS was maintained at 280°C. The source temperature was maintained at 200°C, and the instrument resolution was adjusted to approximately 1000 (10% valley definition). The mass spectrometer was configured to scan from 320 to 100 u at

1.35 sec/decade with an interscan delay of 0.3 sec. This gave an approximate scan to scan cycle time of 1 sec.

For the GC-HRMS analyses, the GC and mass spectrometer conditions were essentially the same with a few important changes. The mass spectrometer was setup to scan from 350 to 130 u at 3.5 sec/decade with an interscan delay of 0.5 sec. The instrument resolution was adjusted to approximately 5000. Perfluorokerosene was used as the reference compound and was continuously bled into the ion source at low level.

VII.9.2 HPLC-MS Analyses

A VG Micromass 7070F mass spectrometer (VG Analytical, Altrinchan, U.K.) equipped with a VG moving-belt LC-MS interface and the HP1090 liquid chromatograph was used for the normal-phase HPLC-MS analyses. The source temperature was maintained at 250°C and the instrument resolution was adjusted to approximately 1000. A 20 μL sample loop was used for injections. The separations were performed using the analytical normal-phase HPLC column with the hexane/DCM mobile phase gradient described in the earlier section. The column was connected with the shortest possible length of stainless steel tubing (0.13 mm I.D.) to a VG spray deposition probe that was used to partially evaporate the mobile phase and deposit the effluent onto the

moving polymide belt. The belt interface was operated with a belt speed of 1.2 cm/sec. A belt washer (using methanol at 1 mL/min) in combination with the sample evaporator heater (actual temperature not measured) was used to prevent the occurence of "ghost" peaks in the chromatogram. To compensate for the changing mobile phase composition, the spray deposition unit temperature was adjusted throughout the run so that the effluent was maintained as a fine spray. Data was collected using the VG-11/250 data system. The mass spectrometer was operated in the electron ionization mode (70 eV nominal energy), scanning from 500 to 90 u at a rate of 2 sec/decade with a 1 sec interscan delay.

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CHAPTER IX: APPENDICES

APPENDIX 1: A listing of all the programs written to process data using the VG-11/250 data system on the mass spectrometer.

Appendix 1 (continued)

Program Name : NUMGEN Program
Function: Number Generator

This program generates a listing of numbers that can be used in plotting the mass chromatograms. In this example, the mass chromatogram for m/z 128, and all the mass chromatograms from m/z 142 to m/z 304 are desired. A list file named MZLIST is created containing the m/z values to be plotted.

Program Listing:

```
.%31=142
.'MZLIST, 1,,2'=128
.%40=2
.LABEL LOOP
.'MZLIST, %40'=%31
.%40=%40+1
.%31=%31+1
.BLE LOOP,%31,304
.=FINISHED
```

Appendix 1 (continued)

Program Name: CHRPLT
Program Function: Automated Plotting of Selected Mass Chromatograms

This program will call up GC-MS files (or LC-MS files) from the list file GCFILE (LCFILE) and create the mass chromatograms using the m/z values listed in MZLIST. The mass chromatograms will then be plotted in PLO CHR according to parameters specified in the macros PC1U and PC5U. The difference between these two macros is that PC1U updates the parameters so that the mass chromatograms are plotted with a magnification factor of 1, while PC5 plots with a factor of 5.

Program Listing:

```
@PC1U (or @PC5U)
.REPEAT FILE=GCFILES
.REPEAT MZ=MZLIST
CHR "FILE"
'DEL
.%48="MZ"
C %48
'X
.WAIT CHR
PLO CHR "FILE"
.WAIT PLO
.NEXT MZ
.NEXT FILE
```

Macros:

```
PC1U:  PLO CHR (BXP 4;TRB 1;SRB 1000;OFF 0;CPL 0;DPS 0;CNT
IHP;NS 1;NT A;DTZ Y;TR B;CMR -;SPM 1;CNP N;CPT PP1;CAT 0)/U

PC5U:  PLO CHR (BXP 4;TRB 1;SRB 1000;OFF 0;CPL 0;DPS 0;CNT
IHP;NS 1;NT A;DTZ Y;TR B;CMR 5,1,4000 BK;SPM 1;CNP N;CPT
PP1;CAT 0)/U
```

Appendix 1 (continued)

Program Name: PLOTSP
Function: To Plot Selected Mass Spectra

This program will print mass spectra for those scan numbers contained in the list file SCNLST. The mass spectra are plotted in two boxes. The first box plots from mass 40-180. The second box plots from mass 180-320.

Program Listing:

```
.REPEAT FILE=GCFILES
SPE "FILE"
.REPEAT SCN=SCNLST
.%33="SCN"
S%33
BX2

.RETURN
D40,180

.RETURN
D180,320
@H
BX1
D40,320
.NEXT SCN
.NEXT FILE
'X
```

**NOTE: This program was written in conjunction with J. Visentini (McMaster University).

Appendix 1 (continued)

Program Name: HRPLT Program
Function: Listing of High-Resolution Mass Spectral Values

This program will give a listing of the high resolution values for selected scan numbers located in the list file HRDLST. The GC-MS files are located in GCFILES. The parameters in the LIS SPE program can be updated using the macro LS prior to running the program.

Program Listing:

```
@LS
.REPEAT FILE=GCFILES
.REPEAT HR=HRDLST
.%45=HR
LIS SPE "FILE"#%45/L
.WAIT LIS
.PAUSE M,2
.NEXT HR
.NEXT FILE
```

Macro:

```
LS: LIS SPE (HM 305;LM 160;INT 0.000;LIM 350; MMH 0.500; MML
0.500; DPM 4; DPI 1; SPS YES; RFP NO; NGP YES; PGS YES; LPF
1; PSM NO; SMS 0.000 MBI NO; PBI NO; PTC NO; TAM NO; ABI
YES; PKN NO; NSP YES; CNT NO; PST NO; PFT NO; PSF NO;)/U
```

Appendix 2: The PAC tentatively identified in the PAC fraction of the NBS urban dust sample (SRM 1649). The sample was examined as the total PAC fraction using the three GC capillary columns, and subsequently re-examined using the SPB-5 column after separation into a PAH and PAH derivative fraction. The components were subsequently assigned according to the fraction in which they were detected.

Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
1	240	DERIV	146	118	---	---	---	---	---	116-PAQ[5]
2	438	DERIV	"149"[6]		---	268.7	270.3	---	-1.6	PHTHALATE
3	990	PAH	"149"		328.5	326.8	317.1	1.7	9.7	PHTHALATE
4	1147	PAH	"149"		350.8	343.1	341.4	7.7	1.7	PHTHALATE
5	1526	DERIV	"149"		384.1	382.6	376.7	1.5	5.8	PHTHALATE
6	1673	PAH	"149"		404.2	398.8	351.1	5.5	47.6	PHTHALATE
7	1752	DERIV	"149"		413.3	407.9	385.1	5.4	22.8	PHTHALATE
8	1762	?[7]	"149"		415.3	409.1	383.7	6.2	25.4	PHTHALATE
9	1983	DERIV	"149"		441.0	435.7	408.5	5.3	27.2	PHTHALATE
10	2110	?	"149"		467.7	450.9	421.5	16.8	29.4	PHTHALATE
11	2199	DERIV	"149"		492.2	461.0	431.6	31.2	29.4	PHTHALATE
12	146	PAH	154		---	---	---	---	---	C1-140-PAH,152-H2-PAH[5]
13	293	PAH	154	153,152	---	---	---	---	---	C1-140-PAH,152-H2-PAH[5]
14	180	PAH	156	141	---	---	---	---	---	C2-128-PAH,C1-140-PAF[5]
15	202	PAH	156		---	---	---	---	---	C2-128-PAH,C1-140-PAF[5]
16	228	PAH	156	141	---	---	---	---	---	C2-128-PAH,C1-140-PAF[5]
17	251	PAH	156		---	---	---	---	---	C2-128-PAH,C1-140-PAF[5]
18	370	DERIV	162	152,143	---	---	269.7	---	---	116-PASXK[5]
19	237	DERIV	163		---	---	---	---	---	118-NPAH[5]
20	433	PAH	166	165	268.2	268.2	268.2	0.0	0.0	FLUORENE
21	ND[8]	DERIV	167.073(-2)		---	---	---	---	---	CARBAZOLE
22	287	PAH	168		---	---	---	---	---	C2-140-PAH,166-H2-PAH[5]
23	300	PAH	168		---	---	---	---	---	C2-140-PAH,166-H2-PAH[5]
24	336	PAH	168	139	---	---	---	---	---	DIBENZOFURAN[5]
25	454	PAH	168		271.3	270.4	270.9	0.9	-0.5	C2-140-PAH,166-H2-PAH
26	ND	DERIV	169	168,167	---	---	---	---	---	C2-140-PANH
27	320	PAH	170	155	---	---	---	---	---	C3-128-PAH[5]
28	353	PAH	170	155	---	---	---	---	---	C3-128-PAH[5]

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
29	378	PAH	170	155	---	---	---	---	---	C3-128-PAH[5]
30	401	PAH	170	155	---	---	---	---	---	C3-128-PAH[5]
31	437	PAH	170	155	269.7	268.6	---	1.1	---	C3-128-PAH
32	479	PAH	170	165	272.4	273.1	276.0	-0.7	-2.9	C3-128-PAH
33	733	PAH	178	176,152	300.0	300.0	300.0	0.0	0.0	PHENANTHRENE
34	749	PAH	178		301.7	301.7	---	0.0	---	ANTHRACENE[9]
35	ND[8]	DERIV	179.073(-2)	178	---	---	---	---	---	178-PANH
36	ND	DERIV	179.073(+.3)		---	---	---	---	---	178-PANH
37	ND	DERIV	179		---	---	---	---	---	178-PANH
38	425	DERIV	180	152,151,150	---	---	273.2	---	---	166-PAK
39	610	PAH	180	165	287.6	287.0	282.8	0.6	4.2	C1-166-PAH,C2-152-PAH
40	617	PAH	180	165	288.6	287.7	284.4	0.9	3.3	C1-166-PAH,C2-152-PAH
41	634	PAH	180	165	290.4	289.5	287.0	0.8	2.6	C1-166-PAH,C2-152-PAH
42	672	DERIV	180.057(-.7)	152,151,150	292.5	293.6	295.4	-1.0	-1.8	FLUORENONE
43	732	DERIV	180		299.8	299.9	300.1	-0.1	-0.2	166-PAK
44	944	DERIV	180	152	321.6	322.0	---	-0.4	---	166-PAK[9]
45	436	PAH	182		269.7	268.5	---	1.2	---	C1-166-PAF,C3-140-PAH[9]
46	451	PAH	182		271.4	270.1	---	1.4	---	C1-166-PAF,C3-140-PAH[9]
47	488	PAH	182	181	274.7	274.0	271.3	0.7	2.7	C1-166-PAF,C3-140-PAH
48	496	PAH	182	181	273.9	274.9	278.0	-1.0	-3.1	C1-166-PAF,C3-140-PAH
49	507	PAH	182	181	277.2	276.1	---	1.1	---	C1-166-PAF,C3-140-PAH[9]
50	525	PAH	182	181	278.6	278.0	276.0	0.6	2.0	C1-166-PAF,C3-140-PAH
51	ND	DERIV	183		332.1	---	307.8	---	---	C3-140-PANH
52	560	PAH	184		276.9	281.7	270.6	-4.8	11.1	166-PASH,C4-128-PAH
53	585	PAH	184	169	279.1	284.3	273.7	-5.2	10.6	C4-128-PAH
54	618	PAH	184		280.4	287.8	277.4	-7.4	10.5	166-PASH,C4-128-PAH
55	634	PAH	184		284.0	289.5	280.8	-5.5	8.7	166-PASH,C4-128-PAH
56	658	PAH	184	169	286.8	292.1	285.7	-5.3	6.4	C4-128-PAH

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Cmpd no.		Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
57		692	PAH	184	152	295.3	295.7	296.3	-0.4	-0.7	NAPHTHO[1,2-b]THIOPHENE
58		692	?[7]	184		295.3	295.7	297.2	-0.4	-1.5	166-PASH,C4-128-PAH
59		705	PAH	184		297.9	297.0	302.1	0.8	-5.1	166-PASH,C4-128-PAH
60		731	PAH	184		303.9	299.8	306.1	4.1	-6.3	166-PASH,C4-128-PAH
61		723	DERIV	188	160	291.7	298.9	300.8	-7.2	-1.8	C3-116-PAQ,C3-116-PAXK
62		914	PAH	190	189,188,187	319.1	318.9	315.0	0.2	3.9	190-PAH
63		939	PAH	190	189,188,187	321.8	321.5	320.2	0.3	1.4	4H-CYCLOPENTA[def]PHENANTHRENE
64		904	PAH	192	191,165	319.2	317.9	313.8	1.4	4.1	C1-178-PAH,190-H2-PAH
65		912	PAH	192	191,165	319.2	318.7	315.0	0.5	3.7	C1-178-PAH,190-H2-PAH
66		948	PAH	192	191,165,152	322.8	322.5	319.1	0.3	3.4	C1-178-PAH,190-H2-PAH
67	CT[10]		PAH	194	179	---	---	---	---	---	C2-166-PAH
68	CT		DERIV	194	165	---	---	---	---	---	178-PAHK,C1-166-PAK
69	CT		DERIV	194	165	---	---	---	---	---	178-PAHK,C1-166-PAK
70	CT		PAH	194	179	---	---	---	---	---	C2-166-PAH
71		800	DERIV	194	165	307.0	307.0	305.0	-0.0	2.0	178-PAHK,C1-166-PAK
72	*	834	?	194	165	?	?	?	?	?	?[11]
73	*	853	?	194	195	?	?	?	?	?	?
74	*	853	?	194		?	?	?	?	?	?
75	*	856	?	194	165	?	?	?	?	?	?
76	*	872	?	194	165	?	?	?	?	?	?
77		896	DERIV	194	165	316.9	317.1	343.3	-0.2	-26.2	178-PAHK,C1-166-PAK
78		584	PAH	196		286.6	284.2	276.7	2.3	7.5	C4-140-PAH
79		605	PAH	196		288.5	286.5	278.7	2.0	7.8	C4-140-PAH
80		620	PAH	196	195	290.2	288.1	281.7	2.2	6.4	C4-140-PAH
81		658	PAH	196	181	294.0	292.1	285.4	1.9	6.7	C4-140-PAH
82		668	PAH	196	181,152,151	294.9	293.1	286.0	1.8	7.1	C4-140-PAH
83		687	PAH	196	195	297.2	295.2	287.8	2.0	7.3	C4-140-PAH
84		858	DERIV	196	168	312.5	313.1	314.0	-0.6	-0.9	166-PAQ,166-PAXK

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
85	991	DERIV	196	168	332.3	326.9	330.5	5.4	-3.6	166-PAQ,166-PAXK
86	843	PAH	198	197,165,152	312.3	311.5	308.7	0.8	2.9	C1-166-PASH,C4-140-PAF
87	873	PAH	198	197,165,152	315.3	314.7	311.6	0.7	3.0	C1-166-PASH,C4-140-PAF
88	910	PAH	198	197,165,152	318.7	318.5	317.0	0.2	1.5	C1-166-PASH,C4-140-PAF
89	910	?[7]	198		319.6	318.5	317.0	1.1	1.5	C1-166-PASH,C4-140-PAF
90	1015	PAH	198	165,152	331.8	329.4	330.9	2.4	-1.5	C1-166-PASH,C4-140-PAF
91	ND[8]	PAH	202		---	---	---	---	---	202-PAH
92	1151	PAH	202	201,200,198	344.0	343.5	341.5	0.5	2.0	FLUORANTHENE
93	1226	PAH	202	201,200,198	351.2	351.2	351.2	0.0	0.0	PYRENE
94	ND	DERIV	203.073(-2)		---	---	---	---	---	202-PANH
95	ND	DERIV	203.073(-2)		---	---	---	---	---	202-PANH
96	ND	DERIV	203.073(-2)		---	---	---	---	---	202-PANH
97	847	PAH	204		312.3	311.9	310.7	0.3	1.2	C1-190-PAH,202-H2-PAH
98	1016	PAH	204	203,202,151	330.2	329.5	325.8	0.7	3.7	C1-190-PAH,202-H2-PAH
99	1116	PAH	204		339.4	339.8	335.1	-0.5	4.8	C1-190-PAH,202-H2-PAH
100	1116	?	204		339.4	339.8	341.4	-0.5	-1.5	C1-190-PAH,190-PAK
101	1133	DERIV	204.057(-4)	176,175	340.8	341.6	342.7	-0.8	-1.1	190-PAK
102	1149	PAH	204	176,175	343.3	343.3	342.7	0.1	0.6	C1-190-PAH,202-H2-PAH
103	1225	PAH	204	176,175	350.6	351.1	351.1	-0.5	-0.0	C1-190-PAH,202-H2-PAH
104	1230	PAH	204		351.8	351.6	349.8	0.2	1.8	C1-190-PAH,202-H2-PAH
105	1041	PAH	206	191,190,189	333.7	332.1	325.5	1.6	6.6	C2-178-PAH,202-H4-PAH
106	1066	PAH	206	191,190,189	336.5	334.7	327.2	1.8	7.5	C2-178-PAH,202-H4-PAH
107	1083	PAH	206	205,190,189	338.1	336.4	328.7	1.7	7.7	C2-178-PAH,202-H4-PAH
108	1083	?	206		338.1	336.4	329.9	1.7	6.5	C2-178-PAH,202-H4-PAH
109	1108	PAH	206	205,191	340.8	339.0	332.5	1.7	6.5	C2-178-PAH,202-H4-PAH
110	1116	PAH	206	204,191,189	341.7	339.8	335.1	1.9	4.8	C2-178-PAH,202-H4-PAH
111	1127	PAH	206	205	341.7	341.0	333.3	0.7	7.6	C2-178-PAH,202-H4-PAH
112	1136	PAH	206	191,189	343.5	341.9	337.0	1.6	4.9	C2-178-PAH,202-H4-PAH

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
113	1161	PAH	206		345.8	344.5	338.9	1.3	5.6	C2-178-PAH,202-H4-PAH
114	1185	PAH	206	191	347.9	347.0	342.0	0.9	4.9	C2-178-PAH,202-H4-PAH
115	1022	DERIV	208.052(-7)	207,180,152	328.7	330.1	332.5	-1.4	-2.4	ANTHRAQUINONE
116	1202	PAH	208		348.4	348.7	349.4	-0.3	-0.7	PHENANTHRO[45-bcd]THIOPHENE
117	790	PAH	210		309.1	306.0	295.5	3.1	10.4	C2-166-PAX,C3-166-PAF
118	815	PAH	210		311.3	308.6	298.6	2.7	10.0	C2-166-PAX,C3-166-PAF
119	837	PAH	210		313.8	310.9	300.1	2.9	10.8	C2-166-PAX,C3-166-PAF
120	847	PAH	210		314.7	311.9	302.2	2.7	9.7	C2-166-PAX,C3-166-PAF
121	857	PAH	210		315.9	313.0	303.3	2.9	9.7	C2-166-PAX,C3-166-PAF
122	CT[10]	DERIV	211		---	---	---	---	---	166-NPAH
123	CT	DERIV	211		---	---	---	---	---	166-NPAH
124	979	PAH	212	211,197	326.9	325.7	321.3	1.2	4.4	C2-166-PASH,C1-166-PASX
125	993	PAH	212	211,197	328.5	327.1	321.3	1.4	5.9	C2-166-PASH,C1-166-PASX
126	1024	PAH	212	211,197	331.8	330.3	324.0	1.5	6.4	C2-166-PASH,C1-166-PASX
127	1051	PAH	212	211,197	335.3	333.1	325.3	2.2	7.9	C2-166-PASH,C1-166-PASX
128	1062	PAH	212	211,197	335.3	334.3	326.9	1.1	7.4	C2-166-PASH,C1-166-PASX
129	1085	?[7]	212		337.8	336.6	330.9	1.1	5.7	C2-166-PASH,C1-166-PASX
130	1085	PAH	212	211,197	337.8	336.6	331.8	1.1	4.9	C2-166-PASH,C1-166-PASX
131	1109	PAH	212	197	340.3	339.1	332.9	1.2	6.2	C2-166-PASH,C1-166-PASX
132	ND[8]	DERIV	214		---	---	---	---	---	C2-140-PASXK
133	1319	PAH	216	215,213	362.3	360.8	355.5	1.5	5.3	216-PAH,C1-202-PAH
134	1357	PAH	216	215,213,189	365.4	364.7	361.4	0.7	3.4	216-PAH,C1-202-PAH
135	1380	PAH	216	215,213,189	368.6	367.1	365.2	1.4	1.9	216-PAH,C1-202-PAH
136	1426	PAH	216	215,213,189	372.9	371.9	369.5	1.0	2.4	BENZO[B]FLUORENE
137	1432	PAH	216	215	374.0	372.6	370.6	1.4	2.0	216-PAH,C1-202-PAH
138	CT	DERIV	217		---	---	---	---	---	216-PANH,202-APAH
139	CT	DERIV	217		---	---	---	---	---	216-PANH,202-APAH
140	CT	DERIV	217		---	---	---	---	---	216-PANH,202-APAH

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Cmpd no.	Scan# [10]	Type [1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI [2] (1-5)	ΔRI [3] (5-608)	Tentative Identity [4]
141	CT	DERIV	217		---	---	---	---	---	216-PANH,202-APAH
142	1173	PAH	218	217,216	347.2	345.7	339.4	1.4	6.3	C2-190-PAH,216-PAF
143	1187	PAH	218		348.6	347.2	340.8	1.5	6.3	C2-190-PAH,216-PAF
144	1200	PAH	218		348.6	348.5	343.2	0.1	5.4	C2-190-PAH,216-PAF
145	1217	PAH	218		351.5	350.3	344.2	1.2	6.1	C2-190-PAH,216-PAF
146	1233	PAH	218	189,163	353.0	351.9	347.2	1.1	4.7	C2-190-PAH,216-PAF
147	1257	PAH	218	189	355.1	354.4	351.1	0.8	3.3	C2-190-PAH,216-PAF
148	1278	PAH	218	189	357.6	356.6	352.4	1.0	4.1	C2-190-PAH,216-PAF
149	1303	PAH	218	189	365.0	359.1	357.0	5.9	2.1	C2-190-PAH,216-PAF
150	1401	PAH	218		369.9	369.3	367.3	0.5	2.0	C2-190-PAH,216-PAF
151	1417	PAH	218		372.4	371.0	367.3	1.4	3.7	C2-190-PAH,216-PAF
152	1212	PAH	220	205	354.3	349.8	340.3	4.5	9.5	C3-178-PAH,C2-190-PAF
153	1234	? [7]	220		354.3	352.0	340.3	2.3	11.7	C3-178-PAH,C2-190-PAF
154	1234	PAH	220	205	354.3	352.0	341.5	2.3	10.5	C3-178-PAH,C2-190-PAF
155	1263	PAH	220	205	357.9	355.0	343.1	2.9	11.9	C3-178-PAH,C2-190-PAF
156	1277	PAH	220	205,190	358.7	356.5	346.2	2.2	10.2	C3-178-PAH,C2-190-PAF
157	1290	PAH	220	205	361.0	357.8	347.8	3.2	10.0	C3-178-PAH,C2-190-PAF
158	1300	PAH	220	205	361.0	358.8	349.9	2.2	8.9	C3-178-PAH,C2-190-PAF
159	1313	PAH	220	205	362.9	360.2	351.5	2.7	8.7	C3-178-PAH,C2-190-PAF
160	1341	PAH	220	205	365.1	363.1	354.9	2.0	8.2	C3-178-PAH,C2-190-PAF
161	1363	PAH	220	205	367.9	365.4	358.3	2.6	7.1	C3-178-PAH,C2-190-PAF
162	1388	PAH	220	205	370.1	368.0	360.6	2.1	7.4	C3-178-PAH,C2-190-PAF
163	1478	DERIV	220.052(-2)		376.7	377.4	380.3	-0.7	-2.9	190-PAQ
164	600	PAH	222	129,128	287.7	285.9	278.8	1.8	7.1	C1-190-PASH,C4-166-PAH
165	1112	DERIV	222		332.0	339.4	337.5	-7.4	1.9	C1-178PAQ,C3-166-PAK
166	1145	PAH	222		341.3	342.8	340.5	-1.5	2.4	C1-190-PASH,C4-166-PAH
167	1161	DERIV	222.068(-6)	194,165	344.3	344.5	343.4	-0.2	1.1	C1-178-PAQ
168	1195	DERIV	222		344.3	348.0	346.3	-3.7	1.7	C1-178PAQ,C3-166-PAK

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
169	1217	DERIV	222	194,165	349.8	350.3	349.4	-0.5	0.9	C2-178-PAHK
170	1248	DERIV	222		354.8	353.5	356.6	1.4	-3.1	C1-178PAQ,C3-166-PAK
171	1332	PAH	222		363.1	362.1	359.5	0.9	2.7	C1-190-PASH,C4-166-PAH
172	1368	PAH	222		366.6	365.9	363.9	0.7	2.0	C1-190-PASH,C4-166-PAH
173	1402	PAH	222		370.0	369.4	367.7	0.5	1.8	C1-190-PASH,C4-166-PAH
174	990	DERIV	223		328.6	326.8	317.3	1.8	9.5	C4-166-PANH
175	1122	PAH	226	211	342.3	340.5	332.9	1.8	7.6	226-PAH,C3-166-PASH
176	1159	PAH	226	225,211	346.8	344.3	334.7	2.5	9.6	226-PAH,C3-166-PASH
177	1188	PAH	226	211,212	349.7	347.3	337.6	2.4	9.7	226-PAH,C3-166-PASH
178	1188	?[7]	226		349.7	347.3	336.6	2.4	10.7	226-PAH,C3-166-PASH
179	1207	PAH	226	225,211,212	351.2	349.2	341.6	2.0	7.7	226-PAH,C3-166-PASH
180	1207	?	226		351.2	349.2	340.3	2.0	9.0	226-PAH,C3-166-PASH
181	1230	PAH	226	225,211,212	353.7	351.6	343.5	2.0	8.1	226-PAH,C3-166-PASH
182	1252	PAH	226	225,211,212	356.1	353.9	345.7	2.2	8.2	226-PAH,C3-166-PASH
183	1281	PAH	226		358.7	356.9	348.1	1.8	8.8	226-PAH,C3-166-PASH
184	1291	PAH	226	225,211,212	360.5	357.9	350.3	2.6	7.6	226-PAH,C3-166-PASH
185	1308	PAH	226	212,211	361.9	359.7	350.6	2.2	9.0	226-PAH,C3-166-PASH
186	1598	PAH	226	227,225,113	391.1	390.4	389.3	0.7	1.0	BENZO[ghi]FLUORANTHENE
187	1580	DERIV	227		389.6	388.4	385.1	1.2	3.3	C3-140-PANH
188	1697	DERIV	227.094(-9)	224,196	402.7	401.5	397.3	1.3	4.2	C3-140-PANH
189	1593	PAH	228	227	390.5	389.8	389.9	0.7	-0.0	228-PAH,C4-140-PASX
190	1671	PAH	228	227,226,225	400.0	398.5	396.5	1.5	2.0	BENZO[a]ANTHRACENE
191	1684	PAH	228	227,202,198	400.0	400.0	400.0	0.0	0.0	CHRYSENE/TRIPHENYLENE
192	1684	PAH	228		400.9	400.0	400.0	0.9	0.0	228-PAH,C4-140-PASX
193	1695	PAH	228	227,226,225	402.6	401.3	400.0	1.4	1.3	228-PAH,C4-140-PASX
194	ND[8]	DERIV	229.089(-6)		---	---	---	---	---	228-PANH
195	ND	DERIV	229.089(-4)		---	---	---	---	---	228-PANH
196	ND	DERIV	229.089(-6)		---	---	---	---	---	228-PANH

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
197	CT[10]	PAH	230	229,215	---	---	---	---	---	C1-216-PAH,C1-214-PAF
198	CT	PAH	230	215	---	---	---	---	---	C1-216-PAH,C1-214-PAF
199	CT	PAH	230		---	---	---	---	---	C1-216-PAH,C1-214-PAF
200	CT	PAH	230	229,215	---	---	---	---	---	C1-216-PAH,C1-214-PAF
201	1264	PAH	230		356.6	355.1	349.1	1.5	6.0	C1-216-PAH,C1-214-PAF
202	1320	PAH	230		362.0	360.9	355.7	1.1	5.2	C1-216-PAH,C1-214-PAF
203	1479	PAH	230		---	377.5	369.6	---	7.9	C1-216-PAH,C1-214-PAF[12]
204	1518	PAH	230		---	381.7	374.6	---	7.1	C1-216-PAH,C1-214-PAF[12]
205	1552	DERIV	230.073(6)	202,201,200	386.0	385.4	384.4	0.6	0.9	216-PAK
206	1596	DERIV	230.073(2)	202,201,200	390.6	390.2	389.8	0.5	0.4	216-PAK
207	1631	DERIV	230.073(7)	202,201,200	394.6	394.0	393.4	0.5	0.6	216-PAK
208	1729	DERIV	230.073(.5)	231,202,201	403.0	405.2	399.7	-2.2	5.5	216-PAK
209	1742	DERIV	230.073(2)	202,201,200	406.7	406.7	410.7	-0.0	-4.0	7-BENZ[de]ANTHRONE
210	1302	PAH	232		363.1	359.0	350.5	4.0	8.5	C3-190-PAH,C1-216-PAF
211	1318	PAH	232		361.0	360.7	351.8	0.3	8.9	C3-190-PAH,C1-216-PAF
212	1338	?[7]	232		365.1	362.8	352.8	2.4	10.0	C3-190-PAH,C1-216-PAF
213	1338	PAH	232		365.1	362.8	353.9	2.4	8.8	C3-190-PAH,C1-216-PAF
214	1357	PAH	232		367.0	364.7	357.1	2.2	7.6	C3-190-PAH,C1-216-PAF
215	1370	PAH	232		368.1	366.1	356.1	2.0	10.0	C3-190-PAH,C1-216-PAF
216	1404	PAH	232	231	371.6	369.6	362.1	2.0	7.5	C3-190-PAH,C1-216-PAF
217	1424	PAH	232		373.9	371.7	364.8	2.2	6.9	C3-190-PAH,C1-216-PAF
218	1450	PAH	232		376.4	374.5	366.8	1.9	7.7	C3-190-PAH,C1-216-PAF
219	1583	PAH	232	189	389.1	388.7	386.9	0.3	1.9	C3-190-PAH,C1-216-PAF
220	1614	PAH	232	189	393.2	392.1	393.5	1.1	-1.4	C3-190-PAH,C1-216-PAF
221	1360	PAH	234	219,204	368.0	365.1	353.8	3.0	11.2	216-PASH,C4-178-PAH
222	1444	PAH	234		376.9	373.8	362.3	3.1	11.5	216-PASH,C4-178-PAH
223	1479	PAH	234		381.1	377.5	365.5	3.6	12.1	216-PASH,C4-178-PAH
224	1582	PAH	234		389.4	388.6	387.1	0.8	1.5	216-PASH,C4-178-PAH

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
225	1611	PAH	234		392.6	391.8	391.8	0.8	-0.0	216-PASH,C4-178-PAH
226	1641	PAH	234		395.9	395.1	394.1	0.8	1.1	216-PASH,C4-178-PAH
227	1695	PAH	234		399.8	401.3	397.0	-1.5	4.3	216-PASH,C4-178-PAH
228	633	PAH	236	221,144	291.7	289.4	281.1	2.3	8.3	C2-190-PASH
229	910	PAH	236	221,144,128	320.2	318.5	306.2	1.7	12.3	C2-190-PASH
230	1161	PAH	236		347.3	344.5	333.1	2.8	11.4	C2-190-PASH
231	1222	PAH	236		353.4	350.8	339.5	2.7	11.2	C2-190-PASH
232	1282	DERIV	236		358.6	357.0	345.7	1.6	11.3	C2-178-PAQ,C3-178-PAHK
233	1350	?[7]	236		363.9	364.0	358.6	-0.1	5.4	C2-178-PAQ,C3-178-PAHK
234	1350	DERIV	236.083(-3)		363.9	364.0	359.6	-0.1	4.4	C2-178-PAQ
235	1350	?	236		363.9	364.0	361.0	-0.1	3.0	C2-178-PAQ,C3-178-PAHK
236	1405	?	236		370.1	369.7	363.9	0.3	5.8	C2-178-PAQ,C3-178-PAHK
237	1405	DERIV	236.083(-7)	221	370.1	369.7	366.1	0.3	3.6	C3-178-PAHK
238	1460	?	236		376.0	375.5	372.8	0.4	2.7	C2-178-PAQ,C3-178-PAHK
239	1460	DERIV	236		376.0	375.5	370.1	0.4	5.4	C2-178-PAQ,C3-178-PAHK
240	1460	?	236		376.0	375.5	377.2	0.4	-1.7	C2-178-PAQ,C3-178-PAHK
241	1525	PAH	236		382.2	382.4	380.4	-0.2	2.1	C2-190-PASH
242	1581	PAH	236		389.2	388.5	387.0	0.7	1.5	C2-190-PASH
243	1643	PAH	236		396.1	395.4	394.1	0.8	1.3	C2-190-PASH
244	1409	DERIV	238		382.5	370.2	377.3	12.4	-7.2	C3-166-PAQ,C3-166-PAXK
245	1459	DERIV	238		382.5	375.4	376.1	7.1	-0.7	C3-166-PAQ,C3-166-PAXK
246	1514	DERIV	238		382.5	381.3	380.9	1.3	0.4	C3-166-PAQ,C3-166-PAXK
247	1528	DERIV	238		382.5	382.8	392.9	-0.2	-10.1	C3-166-PAQ,C3-166-PAXK
248	1562	DERIV	238		382.5	386.4	395.0	-3.9	-8.6	C3-166-PAQ,C3-166-PAXK
249	1584	DERIV	238		385.5	388.8	397.3	-3.3	-8.4	C3-166-PAQ,C3-166-PAXK
250	1697	DERIV	238		402.7	401.5	407.2	1.3	-5.7	C3-166-PAQ,C3-166-PAXK
251	CT[10]	DERIV	239		---	---	---	---	---	238-PANH
252	CT	DERIV	239		---	---	---	---	---	238-PANH

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
253	1240	PAH	240		355.1	352.6	343.0	2.5	9.7	240-PAH,C1-226-PAH
254	1271	PAH	240	225	356.9	355.8	345.0	1.0	10.8	240-PAH,C1-226-PAH
255	1282	PAH	240	225	360.2	357.0	345.9	3.2	11.1	240-PAH,C1-226-PAH
256	1315	PAH	240	225	363.9	360.4	347.8	3.5	12.6	240-PAH,C1-226-PAH
257	1325	PAH	240	225	366.4	361.4	349.9	5.0	11.5	240-PAH,C1-226-PAH
258	1341	PAH	240	225	366.4	363.1	350.6	3.3	12.4	240-PAH,C1-226-PAH
259	1363	PAH	240		368.7	365.4	351.9	3.3	13.5	240-PAH,C1-226-PAH
260	1379	PAH	240	225	370.3	367.0	354.4	3.3	12.6	240-PAH,C1-226-PAH
261	1406	PAH	240	225	372.9	369.9	358.1	3.1	11.8	240-PAH,C1-226-PAH
262	1425	PAH	240	225	374.8	371.8	362.5	2.9	9.3	240-PAH,C1-226-PAH
263	1447	PAH	240	225	376.9	374.2	364.1	2.8	10.0	240-PAH,C1-226-PAH
264	1472	PAH	240	225	379.8	376.8	366.4	3.0	10.4	240-PAH,C1-226-PAH
265	1775	PAH	240	239	412.1	410.6	407.3	1.5	3.3	240-PAH,C1-226-PAH
266	1827	PAH	240		418.4	416.8	413.1	1.6	3.7	240-PAH,C1-226-PAH
267	1868	PAH	240	239,237	427.3	421.8	422.8	5.6	-1.0	240-PAH,C1-226-PAH
268	1612	PAH	242		394.2	391.9	386.4	2.3	5.6	C1-228-PAH,240-PAF
269	1637	PAH	242		396.0	394.7	390.1	1.3	4.6	C1-228-PAH,240-PAF
270	1668	PAH	242		398.6	398.2	398.3	0.5	-0.1	C1-228-PAH,240-PAF
271	1697	PAH	242		403.3	401.5	404.3	1.8	-2.9	C1-228-PAH,240-PAF
272	1754	PAH	242	213	408.8	408.1	407.8	0.6	0.3	C1-228-PAH,240-PAF
273	1776	PAH	242		411.7	410.7	409.9	1.0	0.8	C1-228-PAH,240-PAF
274	1827	PAH	242	241,121	418.3	416.8	413.1	1.4	3.7	C1-228-PAH,240-PAF
275	1839	PAH	242		418.3	418.3	415.6	-0.0	2.7	C1-228-PAH,240-PAF
276	1856	PAH	242		422.0	420.3	418.1	1.6	2.2	C1-228-PAH,240-PAF
277	1874	PAH	242		423.2	422.5	420.5	0.6	2.1	C1-228-PAH,240-PAF
278	439	DERIV	243	155,143	272.5	268.8	---	3.7	---	C2-214-PANH,C1-214-APAH[9]
279	CT[10]	DERIV	244	215	---	---	---	---	---	214-PAQ,228-PAHK
280	CT	DERIV	244		---	---	---	---	---	214-PAQ,228-PAHK

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
281	CT[10]	DERIV	244	215	---	---	---	---	---	214-PAQ,228-PAHK
282	1065	PAH	244	243,166,152	335.1	334.6	331.9	0.5	2.7	C3-202-PAH,C2-216-PAH
283	1403	PAH	244		372.3	369.5	374.6	2.7	-5.0	C3-202-PAH,C2-216-PAH
284	1465	PAH	244		377.8	376.1	377.5	1.8	-1.5	C3-202-PAH,C2-216-PAH
285	1510	PAH	244		382.9	380.8	384.5	2.0	-3.7	C3-202-PAH,C2-216-PAH
286	1536	PAH	244	237,235	382.9	383.6	391.9	-0.8	-8.3	C3-202-PAH,C2-216-PAH
287	1667	PAH	244		398.7	398.1	394.1	0.7	4.0	C3-202-PAH,C2-216-PAH
288	1699	DERIV	244.052(-7)	215	402.6	401.7	398.3	0.9	3.5	214-PAQ
289	1699	?[7]	244		402.6	401.7	395.8	0.9	5.9	228-PAHK,214-PAQ
290	1728	DERIV	244.052(-5)	215	407.1	405.1	402.8	2.1	2.3	214-PAQ
291	1755	DERIV	244.052(-4)	215	409.3	408.2	405.7	1.1	2.5	214-PAQ
292	1792	DERIV	244.052(-.5)	215	413.4	412.6	410.1	0.8	2.5	228-PAHK
293 *	1810	?	244	215	?	?	?	?	?	?[11]
294 *	1810	?	244		?	?	?	?	?	?
295	1886	?	244		424.2	424.0	422.7	0.3	1.3	228-PAHK,214-PAQ
296	1886	DERIV	244.085(-4)	215	424.2	424.0	425.7	0.3	-1.8	228-PAHK
297	1476	PAH	246		380.4	377.2	365.0	3.2	12.2	C4-190-PAH,C2-216-PAF
298	1514	PAH	246		382.4	381.3	368.7	1.2	12.5	C4-190-PAH,C2-216-PAF
299	1549	PAH	246		384.8	385.0	371.2	-0.2	13.9	C4-190-PAH,C2-216-PAF
300	1583	PAH	246		391.2	388.7	374.3	2.5	14.5	C4-190-PAH,C2-216-PAF
301	1608	PAH	246		393.4	391.5	378.7	2.0	12.8	C4-190-PAH,C2-216-PAF
302	1716	DERIV	246.068(.8)		404.7	403.7	404.1	1.0	-0.4	216-PAQ,C1-202-PAQ
303	1743	DERIV	246.068(.2)	218,195,189	408.4	406.8	405.9	1.6	0.9	216-PAQ,C1-202-PAQ
304	1839	DERIV	246.068(-3)	218	417.0	418.3	419.8	-1.3	-1.5	216-PAQ,C1-202-PAQ
305	CT	DERIV	247		---	---	---	---	---	202-NPAH,C4-190-PANH
306	CT	DERIV	247		---	---	---	---	---	202-NPAH,C4-190-PANH
307	1580	DERIV	248		388.0	388.4	389.2	-0.4	-0.8	C2-190-PAQ
308	1713	PAH	248	247	404.9	403.3	399.1	1.6	4.2	C1-216-PASH,C4-190-PAF

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
309	1738	PAH	248	247	407.9	406.2	402.3	1.7	3.9	C1-216-PASH,C4-190-PAF
310	1773	PAH	248	247	411.8	410.4	405.4	1.4	5.0	C1-216-PASH,C4-190-PAF
311	1801	PAH	248	247	414.6	413.7	411.4	0.9	2.3	C1-216-PASH,C4-190-PAF
312	1801	?[7]	248		414.6	413.7	412.6	0.9	1.1	C1-216-PASH,C4-190-PAF
313	1521	DERIV	250		383.9	382.0	375.0	1.8	7.1	C3-178-PAQ,C4-178-PAHK
314	1540	DERIV	250		386.1	384.1	376.4	2.0	7.6	C3-178-PAQ,C4-178-PAHK
315	1583	DERIV	250		390.1	388.7	377.7	1.3	11.0	C3-178-PAQ,C4-178-PAHK
316	1637	DERIV	250		395.7	394.7	382.8	1.0	11.9	C3-178-PAQ,C4-178-PAHK
317	CT[10]	DERIV	252		---	---	---	---	---	C4-166-PAQ
318	CT	DERIV	252		---	---	---	---	---	C4-166-PAQ
319	ND[8]	PAH	252		---	---	---	---	---	252-PAH
320	ND	PAH	252		---	---	---	---	---	252-PAH
321	ND	PAH	252		---	---	445.6	---	---	252-PAH
322	2051	?	252		444.1	443.9	443.0	0.2	1.0	BENZOFLUORANTHENE
323	2051	PAH	252	251,250	444.1	443.9	441.1	0.2	2.8	BENZOFLUORANTHENE
324	2132	PAH	252	251,250	453.4	453.4	453.4	0.0	0.0	BENZO[a]PYRENE
325	CT	DERIV	253		---	---	---	---	---	252-PANH
326	2016	DERIV	253.089(-1)	252,251	439.8	439.7	438.3	0.1	1.4	252-PANH
327	1705	PAH	254		403.1	402.4	402.3	0.7	0.1	BINAPHTHYL,252-H2-PAH
328	1720	PAH	254		405.2	404.1	402.3	1.0	1.8	BINAPHTHYL,252-H2-PAH
329	1739	PAH	254		407.4	406.4	404.5	1.0	1.9	BINAPHTHYL,252-H2-PAH
330	1863	PAH	254		422.1	421.2	418.2	0.9	3.0	BINAPHTHYL,252-H2-PAH
331	1885	PAH	254		424.6	423.8	421.6	0.7	2.3	BINAPHTHYL,252-H2-PAH
332	1906	PAH	254		426.7	426.4	424.2	0.3	2.2	BINAPHTHYL,252-H2-PAH
333	2034	DERIV	254.076(-4)	253,224	443.6	441.9	437.7	1.7	4.1	C3-166-PASXK
334	2054	DERIV	254.076(.2)	253,224	440.8	444.3	445.3	-3.5	-1.0	C3-166-PASXK
335	2054	?	254		440.8	444.3	442.4	-3.5	1.9	C3-166-PASXK,240-PAK
336	2159	DERIV	254.076(.2)	226,225,224	456.1	456.5	459.0	-0.4	-2.5	C3-166-PASXK

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
337	2266	DERIV	254	224	469.1	468.4	467.9	0.7	0.5	C3-166-PASXK,240-PAK
338	CT[10]	PAH	256		---	---	---	---	---	238-PASH,C3-228-PAH
339	CT	DERIV	256		---	---	---	---	---	C1-226-PAHK,226-PAQ
340	CT	DERIV	256		---	---	---	---	---	C1-226-PAHK,226-PAQ
341	CT	PAH	256		---	---	---	---	---	238-PASH,C3-228-PAH
342	CT	DERIV	256		---	---	---	---	---	C1-226-PAHK,226-PAQ
343	CT	PAH	256		---	---	---	---	---	238-PASH,C3-228-PAH
344	1580	DERIV	256		389.3	388.4	386.8	0.9	1.6	C1-226-PAHK,226-PAQ
345	1702	DERIV	256	255,226	402.7	402.1	403.2	0.7	-1.2	C1-226-PAHK,226-PAQ
346	1829	DERIV	256.088(2)	255,226	417.8	417.1	414.1	0.7	3.0	C1-226-PAHK
347	1843	DERIV	256.088(-.5)	226	419.0	418.8	416.8	0.2	1.9	C1-226-PAHK
348	1937	PAH	256	241	431.4	430.2	423.6	1.3	6.6	238-PASH,C3-228-PAH
349	1963	PAH	256	255,241	435.0	433.3	425.5	1.6	7.8	238-PASH,C3-228-PAH
350	1986	PAH	256		437.6	436.1	428.6	1.5	7.5	238-PASH,C3-228-PAH
351	1986	?[7]	256		437.6	436.1	430.3	1.5	5.8	238-PASH,C3-228-PAH
352	2014	PAH	256		441.0	439.5	439.1	1.5	0.4	238-PASH,C3-228-PAH
353	2054	PAH	256		447.4	444.3	442.1	3.1	2.1	238-PASH,C3-228-PAH
354	2075	PAH	256		447.4	446.8	445.0	0.6	1.8	238-PASH,C3-228-PAH
355	CT	DERIV	258		---	---	---	---	---	228-PAQ,C1-228-PAHK
356	CT	PAH	258		---	---	---	---	---	C3-216-PAH,240-PASH
357	CT	DERIV	258		---	---	---	---	---	228-PAQ,C1-228-PAHK
358	CT	DERIV	258		---	---	---	---	---	228-PAQ,C1-228-PAHK
359	CT	PAH	258		---	---	---	---	---	C3-216-PAH,240-PASH
360	CT	DERIV	258		---	---	---	---	---	228-PAQ,C1-228-PAHK
361	CT	DERIV	258		---	---	---	---	---	228-PAQ,C1-228-PAHK
362	CT	DERIV	258		---	---	---	---	---	228-PAQ,C1-228-PAHK
363	CT	PAH	258		---	---	---	---	---	C3-216-PAH,240-PASH
364	ND[8]	PAH	258		---	---	---	---	---	C3-216-PAH,240-PASH

.....continued

Cmpd no.	Scan# [8]	Type [1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI [2] (1-5)	ΔRI [3] (5-608)	Tentative Identity [4]
365	ND	PAH	258		---	---	---	---	---	C3-216-PAH,240-PASH
366	ND	PAH	258		---	---	---	---	---	C3-216-PAH,240-PASH
367 *	1626	? [7]	258		?	?	?	?	?	? [11]
368	1669	PAH	258		401.5	398.3	393.4	3.2	4.9	C3-216-PAH,240-PASH
369	1706	PAH	258		404.5	402.5	396.3	1.9	6.2	C3-216-PAH,240-PASH
370	1753	PAH	258		409.9	408.0	407.6	1.9	0.4	C3-216-PAH,240-PASH
371	1848	DERIV	258	257,230,200	418.7	419.4	421.0	-0.6	-1.6	228-PAQ
372	1901	DERIV	258	257	422.6	425.8	426.5	-3.2	-0.7	228-PAQ
373	1948	DERIV	258	257,230,202	430.0	431.5	433.4	-1.5	-1.9	228-PAQ
374	2096	PAH	258		449.1	449.2	450.1	-0.1	-0.8	C3-216-PAH,240-PASH
375	2096	?	258		449.1	449.2	452.3	-0.1	-3.1	C3-216-PAH,240-PASH
376	ND	DERIV	260		---	---	---	---	---	C1-216-PAQ,C2-202-PAQ
377	1734	PAH	260		406.6	405.8	404.7	0.8	1.1	C3-216-PAF,C2-214-PASH
378	1843	PAH	260		419.1	418.8	415.9	0.3	2.8	C3-216-PAF,C2-214-PASH
379	1868	PAH	260		422.3	421.8	420.7	0.5	1.1	C3-216-PAF,C2-214-PASH
380	1908	DERIV	260		426.9	426.6	434.3	0.2	-7.7	C1-216-PAQ,C2-202-PAQ
381	1822	PAH	262		418.3	416.2	410.7	2.0	5.5	C2-216-PASH,C4-190-PAX
382	1859	PAH	262		422.6	420.7	413.5	1.9	7.1	C2-216-PASH,C4-190-PAX
383	1868	PAH	262		423.6	421.8	415.4	1.8	6.4	C2-216-PASH,C4-190-PAX
384	1891	PAH	262		426.5	424.6	418.4	1.9	6.1	C2-216-PASH,C4-190-PAX
385	1905	PAH	262		427.6	426.3	420.5	1.3	5.8	C2-216-PASH,C4-190-PAX
386	1931	PAH	262		430.1	429.4	423.9	0.7	5.6	C2-216-PASH,C4-190-PAX
387	1953	PAH	262		432.5	432.1	428.7	0.4	3.4	C2-216-PASH,C4-190-PAX
388	1408	DERIV	264		371.2	370.1	364.1	1.1	5.9	C4-178-PAQ
389	1837	DERIV	264		417.2	418.0	420.7	-0.8	-2.6	C4-178-PAQ
390	1985	PAH	264		461.8	436.0	453.6	25.8	-17.6	264-PAH,C4-190-PASH
391	2205	PAH	264		464.7	461.7	459.0	3.0	2.7	264-PAH,C4-190-PASH
392	2251	PAH	264		468.2	466.8	463.8	1.4	3.0	264-PAH,C4-190-PASH

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
393	2305	PAH	264	263	474.1	472.6	471.5	1.4	1.2	264-PAH,C4-190-PASH
394	2033	DERIV	266		437.1	441.8	451.7	-4.6	-9.9	250-PAHK,C1-238-PAK
395	2186	PAH	266	265,264,263	461.8	459.5	453.5	2.2	6.0	266-PAH,C1-252-PAH
396	2197	PAH	266	265	461.8	460.8	455.8	1.0	5.0	266-PAH,C1-252-PAH
397	2224	PAH	266	265,263	465.6	463.8	458.8	1.8	5.0	266-PAH,C1-252-PAH
398	2262	PAH	266	265,263	469.3	468.0	464.2	1.3	3.7	266-PAH,C1-252-PAH
399	2306	PAH	266	265	474.1	472.8	470.4	1.3	2.4	266-PAH,C1-252-PAH
400	CT[10]	DERIV	268		---	---	---	---	---	252-PAHK,238-PAQ
401	CT	DERIV	268		---	---	---	---	---	252-PAHK,238-PAQ
402	CT	DERIV	268		---	---	---	---	---	252-PAHK,238-PAQ
403	CT	DERIV	268.088(-3)		---	---	---	---	---	252-PAHK
404	CT	DERIV	268		---	---	---	---	---	252-PAHK,238-PAQ
405	ND[8]	DERIV	268		---	---	---	---	---	252-PAHK,238-PAQ
406	2038	PAH	268		443.0	442.4	436.4	0.6	6.0	266-PAF,C2-240-PAH
407	2057	PAH	268		445.6	444.6	438.7	0.9	5.9	266-PAF,C2-240-PAH
408	2082	PAH	268		448.2	447.6	442.7	0.7	4.9	266-PAF,C2-240-PAH
409	2101	PAH	268		450.9	449.8	447.6	1.1	2.2	266-PAF,C2-240-PAH
410	2111	PAH	268		450.9	451.0	447.6	-0.0	3.4	266-PAF,C2-240-PAH
411	2132	PAH	268		454.4	453.4	450.8	1.0	2.6	266-PAF,C2-240-PAH
412	2140	PAH	268		454.4	454.3	453.5	0.1	0.8	266-PAF,C2-240-PAH
413	CT	PAH	270		---	---	---	---	---	C3-228-PAH,C1-238-PASH
414	CT	PAH	270		---	---	---	---	---	C3-228-PAH,C1-238-PASH
415	CT	PAH	270		---	---	---	---	---	C3-228-PAH,C1-238-PASH
416	CT	PAH	270		---	---	---	---	---	C3-228-PAH,C1-238-PASH
417	CT	PAH	270		---	---	---	---	---	C3-228-PAH,C1-238-PASH
418	927	DERIV	270		327.4	320.3	---	7.1	---	240-PAQ,C1-226-PAQ
419	1975	DERIV	270		445.4	434.8	421.2	10.7	13.6	240-PAQ,C1-226-PAQ
420	1994	DERIV	270.068(-8)		437.3	437.1	426.6	0.2	10.5	240-PAQ,C1-226-PAQ

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
421	1994	?[7]	270		437.3	437.1	423.9	0.2	13.2	240-PAQ,C3-228-PAH
422	2021	?	270		440.4	440.3	434.9	0.1	5.4	240-PAQ,C3-228-PAH
423	2021	DERIV	270.068(-6)	242,213	440.4	440.3	437.3	0.1	3.1	240-PAQ,C1-226-PAQ
424	2055	DERIV	270	242,213	440.4	444.4	434.9	-4.0	9.5	240-PAQ,C1-226-PAQ
425	2063	DERIV	270.068(-.2)	242,213	444.7	445.3	441.1	-0.6	4.2	240-PAQ,C1-226-PAQ
426	2063	?	270		444.7	445.3	443.0	-0.6	2.4	240-PAQ,C3-228-PAH
427	2090	PAH	270		451.3	448.5	414.9	2.8	33.6	C3-228-PAH,C1-238-PASH
428	2140	PAH	270		455.4	454.3	453.2	1.0	1.1	C3-228-PAH,C1-238-PASH
429	2157	DERIV	270.068(-5)	242,213	456.6	456.3	456.6	0.3	-0.4	240-PAQ,C1-226-PAQ
430	2157	?	270		456.6	456.3	459.4	0.3	-3.1	240-PAQ,C3-228-PAH
431	2336	DERIV	270.068(-.2)	242,213	476.3	476.0	478.8	0.3	-2.8	240-PAQ,C1-226-PAQ
432	CT[10]	PAH	272		---	---	---	---	---	C4-216-PAH,C1-240-PASH
433	CT	PAH	272		---	---	---	---	---	C4-216-PAH,C1-240-PASH
434	1970	DERIV	272		412.4	434.2	411.7	-21.8	22.5	C1-228-PAQ,C3-216-PAK
435	2000	DERIV	272		438.1	437.8	435.1	0.3	2.7	C1-228-PAQ
436	2005	DERIV	272		438.1	438.4	437.2	-0.3	1.2	C1-228-PAQ,C3-216-PAK[9]
437	2040	DERIV	272		445.1	442.6	---	2.5	---	C1-228-PAQ,C3-216-PAK
438	2055	DERIV	272		445.1	444.4	440.9	0.7	3.4	C1-228-PAQ,C3-216-PAK
439	2086	DERIV	272		445.1	448.0	442.3	-3.0	5.7	C1-228-PAQ,C3-216-PAK
440	2106	DERIV	272		449.7	450.4	447.7	-0.7	2.6	C1-228-PAQ,C3-216-PAK
441	2210	PAH	272		449.7	462.2	458.5	-12.5	3.7	C4-216-PAH,C1-240-PASH
442	2261	DERIV	272		466.4	467.9	472.9	-1.4	-5.0	C1-228-PAQ
443	1633	DERIV	274	239	396.0	394.2	389.4	1.8	4.8	C2-216-PAQ,C3-202-PAQ
444	1696	DERIV	274	239	402.9	401.4	397.3	1.5	4.1	C2-216-PAQ,C3-202-PAQ
445	2418	PAH	276	274	486.4	484.7	482.5	1.7	2.2	INDENO[1,2,3-cd]PYRENE
446	2475	PAH	276	274,138	495.4	490.8	489.8	4.7	0.9	276-PAH,C3-216-PASH
447	2508	PAH	276	274,138	495.4	494.2	493.9	1.2	0.3	276-PAH,C3-216-PASH
448	2603	PAH	276	274,272	500.3	---	---	---	---	BENZO[ghi]PERYLENE[9,13]

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LEAF 235 NOT INCLUDED IN PAGE NUMBERING

Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu)) Fragment Ions		Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
449	ND[8]	PAH	278		---	---	---	---	---	278-PAH,C2-250-PAH
450	2019	PAH	278		440.4	440.1	438.3	0.3	1.8	278-PAH,C2-250-PAH
451	2036	PAH	278		442.3	442.1	440.2	0.1	1.9	278-PAH,C2-250-PAH
452	2137	PAH	278		454.8	454.0	451.0	0.8	3.0	278-PAH,C2-250-PAH
453	2150	PAH	278		458.7	455.5	452.4	3.2	3.1	278-PAH,C2-250-PAH
454	2171	PAH	278		458.7	457.9	454.5	0.8	3.3	278-PAH,C2-250-PAH
455	2219	PAH	278		464.7	463.2	456.9	1.5	6.3	278-PAH,C2-250-PAH
456	2251	PAH	278		468.5	466.8	461.9	1.8	4.8	278-PAH,C2-250-PAH
457	2310	PAH	278		474.4	473.2	470.3	1.3	2.9	278-PAH,C2-250-PAH
458	2419	PAH	278		486.0	484.8	485.7	1.2	-0.8	278-PAH,C2-250-PAH
459	2438	PAH	278		492.3	486.9	485.7	5.5	1.2	278-PAH,C2-250-PAH
460	2476	DERIV	278.073(-3)		492.3	490.9	488.3	1.5	2.6	264-PAK
461	2519	PAH	278		496.0	495.4	494.5	0.7	0.9	DIBENZ[a,c]ANTHRACENE
462	2563	PAH	278		500.0	500.0	---	0.0	---	PICENE[9]
463	2595	PAH	278		500.0	---	---	---	---	278-PAH,C2-250-PAH[9,13]
464	CT[10]	DERIV	280	252	---	---	---	---	---	266-PAK,C2-238-PAK
465	CT	DERIV	280.088(-2)		---	---	---	---	---	266-PAK,C2-238-PAK
466	CT	DERIV	280.088(2)	279	---	---	---	---	---	266-PAK,C2-238-PAK
467	CT	PAH	280		---	---	---	---	---	C2-252-PAH,264-PAX
468	CT	PAH	280		---	---	---	---	---	C2-252-PAH,264-PAX
469	CT	PAH	280		---	---	---	---	---	C2-252-PAH,264-PAX
470	CT	DERIV	280.088(5)	279,252	---	---	---	---	---	266-PAK,C2-238-PAK
471	CT	DERIV	280	279	---	---	---	---	---	C2-252-PAH,264-PAX
472	CT	PAH	280		---	---	---	---	---	C2-252-PAH,264-PAX
473	CT	PAH	280		---	---	---	---	---	C2-252-PAH,264-PAX
474	2080	PAH	280		448.2	447.3	441.0	0.9	6.3	C2-252-PAH,264-PAX
475	2116	PAH	280		452.9	451.5	447.0	1.4	4.6	C2-252-PAH,264-PAX
476	2140	PAH	280		455.4	454.3	455.5	1.0	-1.1	C2-252-PAH,264-PAX

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
477 *	2335	?[7]	280		?	?	?	?	?	?[11]
478 *	2388	?	280		?	?	?	?	?	?
479 *	2442	?	280		?	?	?	?	?	?
480 *	2448	?	280		?	?	?	?	?	?
481	2596	DERIV	280.088(2)	252	500.2	---	---	---	---	266-PAK,C2-238-PAK[9,13]
482	2261	DERIV	282		468.9	467.9	468.1	1.0	-0.3	252-PAQ
483	2378	DERIV	282		472.0	480.5	477.6	-8.5	2.9	252-PAQ,C2-240-PAK
484	2555	PAH	282		499.3	499.2	---	0.1	---	264-PASH,C3-240-PAH[9]
485	1904	DERIV	284		424.5	426.2	429.4	-1.7	-3.2	C1-240-PAQ,C3-226-PAHK
486	2054	DERIV	284		444.0	444.3	441.0	-0.3	3.2	C1-240-PAQ,C3-226-PAHK
487	2131	DERIV	284.083(-7)		453.3	453.3	451.1	-0.0	2.2	C1-240-PAQ
488	2384	PAH	284		482.6	481.1	479.0	1.5	2.1	266-PASH,C4-228-PAH
489	2427	PAH	284		487.4	485.7	484.6	1.7	1.1	266-PASH,C4-228-PAH
490	2452	PAH	284		487.4	488.3	487.3	-0.9	1.0	266-PASH,C4-228-PAH
491	2135	DERIV	286		456.8	453.7	451.0	3.1	2.7	C3-228-PAHK,C2-228-PAQ
492	2155	DERIV	286		456.8	456.0	451.0	0.8	5.0	C3-228-PAHK,C2-228-PAQ
493	2328	PAH	286		477.5	475.1	467.2	2.4	8.0	C2-240-PASH
494	2352	PAH	286		480.4	477.7	470.0	2.7	7.7	C2-240-PASH
495	2413	PAH	286		483.5	484.2	472.9	-0.8	11.3	C2-240-PASH
496	2424	PAH	286	187,143	487.0	485.4	484.2	1.7	1.2	C2-240-PASH
497	2425	PAH	288	250,248,144	487.0	485.5	484.2	1.6	1.3	288-PAH
498	2381	PAH	290		482.2	480.8	458.5	1.4	22.3	290-PAH
499	2645	PAH	290		---	---	473.3	---	---	290-PAH[14]
500	2707	PAH	290		---	---	477.9	---	---	290-PAH[14]
501	2751	PAH	290		---	---	480.4	---	---	290-PAH[14]
502	2789	PAH	290		---	---	484.8	---	---	290-PAH[14]
503	2868	PAH	290		---	---	489.2	---	---	290-PAH[14]
504	2474	PAH	292		492.8	490.7	---	2.2	---	C1-278-PAH,290-PAF[9]
505	2503	PAH	292		495.3	493.7	---	1.6	---	C1-278-PAH,290-PAF[9]

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Cmpd no.	Scan#	Type[1]	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	SPB-5	SPB-608	ΔRI[2] (1-5)	ΔRI[3] (5-608)	Tentative Identity[4]
506	ND[8]	PAH	294		---	---	---	---	---	C3-252-PAH,C1-264-PAX
507	ND	DERIV	294		---	---	---	---	---	264-PAQ,278-PAHK
508	ND	PAH	294		---	---	---	---	---	C3-252-PAH,C1-264-PAX
509	ND	DERIV	296		---	---	---	---	---	266-PAQ,C1-252-PAQ
510	2277	DERIV	298		471.1	469.6	---	1.5	---	C2-240-PAQ,C4-226-PAHK[9]
511	2358	DERIV	298		480.0	478.4	---	1.6	---	C2-240-PAQ,C4-226-PAHK[9]
512	2432	DERIV	298		486.4	486.2	---	0.2	---	C2-240-PAQ,C4-226-PAHK[9]
513	2600	PAH	298		500.3	---	---	---	---	C1-266-PASH,C3-240-PAX[14]
514	3135	PAH	300		---	---	---	---	---	300-PAH[14]
515	3179	PAH	300		---	---	---	---	---	300-PAH[14]
516	3341	PAH	300		---	---	---	---	---	300-PAH[14]
517	ND	PAH	302		---	---	---	---	---	302-PAH
518	3130	PAH	302		---	---	---	---	---	302-PAH[14]
519	3163	PAH	302		---	---	---	---	---	302-PAH[14]
520	3163	PAH	302		---	---	---	---	---	302-PAH[14]
521 *	3189	PAH	302		?	?	?	?	?	?[11]
522	3370	PAH	302		---	---	---	---	---	302-PAH[14]
523	2508	PAH	304		494.6	494.2	---	0.3	---	C2-278-PAH[9]
524	2533	PAH	304		497.3	496.9	---	0.4	---	C2-278-PAH[9]
525	2554	PAH	304		500.3	499.1	---	1.3	---	C2-278-PAH[9]
526	2783	PAH	304		501.7	---	---	---	---	C2-278-PAH[9]
527	2885	DERIV	304		---	---	---	---	---	290-PAK[14]
528	1948	PAH	306		432.5	431.5	426.0	1.0	5.6	C2-278-PAH,QUATER-PHENYL
529	2207	PAH	306	302,276,226	464.7	461.9	452.5	2.8	9.4	C2-278-PAH,QUATER-PHENYL
530	2242	PAH	306		473.0	465.8	457.6	7.2	8.2	C2-278-PAH,QUATER-PHENYL
531	2330	PAH	306		477.9	475.3	467.6	2.6	7.7	C2-278-PAH,QUATER-PHENYL
532	1511	DERIV	308	310,239	382.4	380.9	376.1	1.5	4.8	??[15]
533	1696	DERIV	308	310,239	402.7	401.4	397.2	1.4	4.2	??[15]
534	1869	DERIV	314	210,194,77	423.4	421.9	414.7	1.5	7.2	??[15]

.....continued

Appendix 2 (continued)

[1] Type: indicates the fraction (PAH or PAH derivative) where the component was detected.

[2] RI(1-5): RI_{SPB-1} - RI_{SPB-5}

[3] RI(1-608): RI_{SPB-5} - $RI_{SPB-608}$

[4] Tentative Identity: Acronyms are explained in Figure 1-2.

[5] A component that has eluted before the first standard compound and therefore its retention index could not be determined.

[6] "149": The molecular weight for the phthlate ester could not be determined, only the base peak, 149, was detected.

[7] Type ?: A peak that was separated on the SPB-608 column could not be correlated with any peaks in the chromatograms from the other columns.

[8] Type ND: A peak that was not detected in the total PAC fraction. It was only detected after separation into the PAH and PAH derivative fractions.

[9] There were no peaks in the chromatogram from the SPB-608 column that could be correlated with the results from the SPB-5 column.

[10] Type CT: A peak that was resolved after separation of the total PAC in to the PAH and PAH derivative fractions, but could not be correlated with any peaks in the total PAC fraction.

[11] *: A peak that was originally identified as a single component in the total PAC fraction, but was actually an unresolved mixture.

[12] There were no peaks in the chromatogram from the SPB-1 column that could be correlated with the results from the SPB-5 column.

Appendix 2 (continued)

[13] There were no peaks in the chromatogram from the SPB-5 column that could be correlated with the results.

[14] A component that has eluted after the last standard compound and therefore its retention index could not be determined.

[15] ??: Due to lack of information, a tentative identity could not be assigned.

APPENDIX 3: The template and formula used in LOTUS 1-2-3 to calculate the retention indices of the components.

A template was created in LOTUS 1-2-3 that contained a lookup table and the formula listed below. The lookup table was positioned on the spreadsheet such that it would not overlap with any columns created for GC-MS data. The lookup table consisted of four columns. The first and last columns were counters, and were used to determine the position of the appropriate bracketing scans. The middle columns contained scan numbers and their corresponding retention indices. Calculation of these retention indices (RI) was done by fitting the original standard compounds to a cubic spline curve with 100 points, using the program "Curve Fitter PC" (Interactive Microware, Inc.). Fluorene, phenanthrene, pyrene, chrysene, benzo[a]pyrene, and picene were the original standards. These calculated values can be then used to determine the retention indices of the sample components.

This template was then combined with a GC-MS data file that was created in LOTUS 1-2-3. The data file must be designed such that column B contained the scan numbers of the components and column E was empty. The formula used in the calculation of the retention index, was copied into each

cell in column E. The retention indices of all the components identifed by the GC-MS analyses were then determined. The formula is:

```
(B5-@VLOOKUP(B5,L$1001..L$1101,0))
/(@VLOOKUP(@VLOOKUP(B5,L$1001..N$1101,2),K$1001..L$1101,1)
-@VLOOKUP(B5,L$1001..L$1101,0))
*(@VLOOKUP(@VLOOKUP(B5,L$1001..N$1101,2),K$1001..M$1101,2) -
@VLOOKUP(B5,L$1001..M$1101,1))+@VLOOKUP(B5,L$1001..M$1101,1)
```

where the letters in the formula correspond to locations on the spreadsheet.

This formula can be simplified and represented as follows:

$$RI_i = \frac{(S_i - LS)}{(HS - LS)} * (HRI - LRI) + (LRI)$$

where S_i = scan of interest, LS = bracketing low scan, HS = bracketing high scan, HRI = RI for high scan bracket, LRI = RI for low scan bracket, RI_i = retention index.

Appearance of LOTUS spreadsheet:

Columns:	**B**	**E**	**K**	**L**	**M**	**N**
	Scan#	RI	Counter	Scan#	RI	Counter
	S_1	RI_1	1	L1001	M1001	2
	S_2	RI_2	2	L1002	M1002	3
	.	.	.	.	.	.
	.	.	.	.	.	.

Appendix 4: The PAC tentatively identified in the Hamilton airborne particulate matter sample.

Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
1	382	"149"[3]		---	268.7	--	PHTHALATE[4]
2	947	"149"		327.6	327.5	0.2	PHTHALATE
3	1500	"149"		383.8	383.7	0.1	PHTHALATE
4	1754	"149"		412.6	410.5	2.1	PHTHALATE
5	95	154		---	---	--	C1-140-PAH,140-PAK[4]
6	129	156		---	---	--	C1-140-PAF,C2-128-PAH[4]
7	148	156	155,141	---	---	--	C1-140-PAF,C2-128-PAH[4]
8	160	163		---	---	--	118-NPAH[4]
9	183	163		---	---	--	118-NPAH[4]
10	214	163		---	---	--	118-NPAH[4]
11	262	163	155,146	---	---	--	118-NPAH[4]
12	377	166	165	268.2	268.2	0.0	FLUORENE
13	762	167.073(-5)	166	308.4	308.5	-0.1	CARBAZOLE
14	232	168		---	---	--	C2-140-PAH,166-H2-PAH[4]
15	280	168	139	---	---	--	DIBENZOFURAN[4]
16	301	170	155	---	---	--	C3-128-PAH[4]
17	327	170	155	---	---	--	C3-128-PAH[4]
18	350	170	155	---	---	--	C3-128-PAH[4]
19	374	170	155	268.4	---	--	C3-128-PAH[4]
20	385	170	155	269.6	269.0	0.6	C3-128-PAH
21	420	170	155	272.9	272.7	0.1	C3-128-PAH
22	675	170		299.0	299.5	-0.5	C3-128-PAH
23	91	178	163,146,145	---	---	--	??[5]
24	103	178	163,146,145	---	---	--	??[5]
25	159	178	163,145	---	---	--	??[5]
26	680	178.078(-2)	174,152,150	300.0	300.0	0.0	PHENANTHRENE
27	694	178	174,152,150	302.2	301.5	0.8	ANTHRACENE
28	196	179		---	---	--	178-PANH[4]
29	246	179		---	---	--	178-PANH[4]
30	713	179		307.4	303.4	4.0	178-PANH
31	748	179.073(-6)	152,150	307.4	307.0	0.4	178-PANH
32	552	180	179	288.0	286.6	1.4	C1-166-PAH,166-PAK
33	565	180	165	288.0	288.0	0.0	C1-166-PAH,C2-152-PAH
34	584	180		288.0	290.0	-2.0	C1-166-PAH,166-PAK
35	613	180	152,151	292.6	293.0	-0.4	FLUORENONE
36	680	180		300.3	300.0	0.3	C1-166-PAH,166-PAK
37	747	180		306.7	306.9	-0.2	C1-166-PAH,166-PAK
38	929	180	165	320.6	325.6	-5.1	C1-166-PAH,C2-152-PAH
39	882	181	180	306.7	320.8	-14.1	C1-166-PANH
40	380	182		269.1	268.5	0.6	C1-166-PAF,152-PAQ
41	435	182	181	274.7	274.3	0.4	C1-166-PAF,152-PAQ
42	453	182	181	277.3	276.2	1.2	C1-166-PAF,152-PAQ
43	471	182		278.2	278.1	0.1	C1-166-PAF,152-PAQ
44	509	184		286.4	282.1	4.3	166-PASH,C1-140-PAQ
45	636	184.034(-3)		295.2	295.4	-0.2	NAPHTHO[1,2-B]THIOPHENE

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
46	677	184		299.0	299.7	-0.7	166-PASH,C1-140-PAQ
47	719	184		303.7	304.0	-0.3	166-PASH,C1-140-PAQ
48	85	187		---	---	--	C4-116-APAH[4]
49	789	190		308.9	311.3	-2.4	190-PAH
50	890	190	189,188,187	321.5	321.6	-0.1	4H-CYCLOPENTA[def]PHENANTHRENE
51	859	192.094(-9)	190,188,165	319.1	318.5	0.6	C1-178-PAH
52	876	192		322.8	320.2	2.6	C1-178-PAH,190-PAF
53	896	192		322.8	322.2	0.6	C1-178-PAH
54	730	194		308.1	305.2	2.9	C2-166-PAH,178-PAHK
55	748	194		308.1	307.0	1.0	C2-166-PAH,178-PAHK
56	777	194		314.2	310.0	4.2	C2-166-PAH,178-PAHK
57	800	194		---	312.4	--	C2-166-PAH,178-PAHK[6]
58	816	194		---	314.1	--	C2-166-PAH,178-PAHK[6]
59	613	196	195	294.1	293.0	1.1	C4-140-PAH,166-PAQ
60	637	196	195	297.3	295.5	1.7	C4-140-PAH,166-PAQ
61	791	198	197	312.2	311.5	0.7	C1-166-PASH,C2-140-PAQ
62	822	198	197	315.5	314.7	0.8	C1-166-PASH,C2-140-PAQ
63	859	198		318.0	318.5	-0.5	C1-166-PASH,C2-140-PAQ
64	998	198		331.0	332.6	-1.6	C1-166-PASH,C2-140-PAQ
65	1006	198		331.0	333.5	-2.5	C1-166-PASH,C2-140-PAQ
66	834	199	172,155	315.8	315.9	-0.1	C4-128-APAH
67	1104	202.078(-1)		343.9	343.4	0.5	FLUORANTHENE
68	1138	202.078(-2)		347.7	346.8	0.9	202-PAH
69	1181	202.078(3)	203	351.2	351.2	0.0	PYRENE
70	1132	203		347.7	346.2	1.5	202-PANH
71	1164	203		347.7	349.5	-1.8	202-PANH
72	1242	203.073(-3)		357.6	357.4	0.2	202-PANH
73	797	204	203	312.1	312.1	-0.0	C1-190-PAH,190-PAK
74	969	204.094(.6)	203	330.2	329.7	0.5	C1-190-PAH,202-H2-PAH
75	1105	204		342.8	343.5	-0.7	C1-190-PAH,190-PAK
76	1158	204		347.5	348.9	-1.3	C1-190-PAH,190-PAK
77	1188	204.094(6)	189,188	352.3	351.9	0.4	C1-190-PAH,202-H2-PAH
78	1021	206		337.9	335.0	2.9	C2-178-PAH,176-PAQ
79	1037	206		337.9	336.6	1.2	C2-178-PAH,176-PAQ
80	1068	206.109(3)	189	340.9	339.8	1.1	C2-178-PAH
81	1076	206		340.9	340.6	0.3	C2-178-PAH,176-PAQ
82	1090	206		343.7	342.0	1.7	C2-178-PAH,176-PAQ
83	1120	206		347.7	345.0	2.7	C2-178-PAH,176-PAQ
84	1142	206		347.7	347.3	0.5	C2-178-PAH,176-PAQ
85	971	208.052(.2)	181,180,152	329.2	329.9	-0.7	ANTHRAQUINONE
86	1154	208.034(4)		347.7	348.5	-0.8	PHENANTHRO[4,5-bcd]THIOPHENE
87	1407	210		375.7	374.1	1.5	C2-166-PAX,C1-166-PAQ
88	930	212	211	326.2	325.7	0.5	C2-166-PASH,C3-140-PAQ
89	944	212	211	328.6	327.1	1.5	C2-166-PASH,C3-140-PAQ
90	978	212	211	331.2	330.6	0.6	C2-166-PASH,C3-140-PAQ

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
91	1005	212		334.5	333.4	1.2	C2-166-PASH,C3-140-PAQ
92	1034	212		337.7	336.3	1.4	C2-166-PASH,C3-140-PAQ
93	1060	212		340.1	338.9	1.1	C2-166-PASH,C3-140-PAQ
94	628	215.094(-2)	198	293.8	294.6	-0.8	C3-128-NPAH
95	1281	216.094(4)	215,213	362.7	361.3	1.4	216-PAH,C1-202-PAH
96	1317	216.094(-1)	214,213,108	364.9	365.0	-0.0	216-PAH,C1-202-PAH
97	1345	216.094(2)	215,214,188	368.5	367.8	0.6	216-PAH,C1-202-PAH
98	1390	216.094(2)	215,214,189	373.8	372.4	1.4	216-PAH,C1-202-PAH
99	1658	217.089(.9)	218,216,214	402.1	400.2	1.9	216-PANH,C1-202-PANH
100	1725	217		409.7	407.4	2.3	216-PANH,C1-202-PANH
101	1741	217.089(-2)	216,190	409.7	409.1	0.6	216-PANH,C1-202-PANH
102	821	218		307.2	314.6	-7.3	202-PAHK,C2-190-PAH
103	894	218	184,155	315.7	322.0	-6.4	202-PAHK,C2-190-PAH
104	1132	218		348.2	346.2	1.9	202-PAHK,C2-190-PAH
105	1144	218		348.2	347.5	0.7	202-PAHK,C2-190-PAH
106	1190	218.073(.9)		353.1	352.1	1.0	202-PAHK,C1-190-PAK
107	1217	218	189,187	357.7	354.8	2.9	202-PAHK,C2-190-PAH
108	1238	218.073(-1)	189,187	357.7	357.0	0.8	202-PAHK,C1-190-PAK
109	1269	218		360.3	360.1	0.2	202-PAHK,C2-190-PAH
110	1326	218		365.2	365.9	-0.6	202-PAHK,C2-190-PAH
111	1364	218.109(3)		370.4	369.8	0.6	216-H2-PAH,C2-190-PAH
112	1380	218		370.4	371.4	-1.0	202-PAHK,C2-190-PAH
113	637	220	205	296.1	295.5	0.5	C3-178-PAH
114	1173	220		351.2	350.4	0.8	C3-178-PAH,190-PAQ
115	1200	220		354.2	353.1	1.1	C3-178-PAH,190-PAQ
116	1226	220	205	357.9	355.8	2.1	C3-178-PAH
117	1236	220.125(-3)	205	357.9	356.8	1.1	C3-178-PAH
118	1263	220		360.1	359.5	0.6	C3-178-PAH,190-PAQ
119	1303	220		364.1	363.6	0.6	C3-178-PAH,190-PAQ
120	1352	220		368.9	368.5	0.4	C3-178-PAH,190-PAQ
121	1429	220		376.8	376.4	0.4	C3-178-PAH,190-PAQ
122	549	222	165,129	287.0	286.3	0.7	C1-178-PAQ,C1-190-PASH
123	1113	222		345.3	344.3	1.0	C1-178-PAQ,C1-190-PASH
124	1156	222		350.1	348.7	1.4	C1-178-PAQ,C1-190-PASH
125	1173	222	194	350.1	350.4	-0.3	C1-178-PAQ,C1-190-PASH
126	1116	226		341.5	344.6	-3.1	226-PAH,C4-140-PAQ
127	1147	226		346.0	347.8	-1.8	226-PAH,C4-140-PAQ
128	1164	226		349.6	349.5	0.1	226-PAH,C4-140-PAQ
129	1190	226		353.0	352.1	0.8	226-PAH,C4-140-PAQ
130	1214	226		355.7	354.5	1.1	226-PAH,C4-140-PAQ
131	1517	226		384.7	385.4	-0.7	226-PAH,C4-140-PAQ
132	1562	226.078(-3)	225,224	390.7	390.1	0.6	BENZO(ghi)FLUORANTHENE
133	1684	226	225,224	404.1	403.0	1.1	226-PAH,C4-140-PAQ
134	1561	228		390.4	390.0	0.4	228-PAH,214-PAK
135	1647	228	226,225	400.0	399.0	1.0	BENZO[A]ANTHRACENE

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
136	1656	228.094(-8)	227,226	400.0	400.0	0.0	CHRYSENE/TRIPHENYLENE
137	1682	228	227	403.3	402.8	0.5	228-PAH,214-PAK
138	1578	229.089(-4)	228,227	392.3	391.8	0.6	BENZO[C]ACRIDINE
139	837	230	229	315.3	316.2	-0.9	C1-216-PAH,216-PAK
140	1225	230		355.5	355.7	-0.2	C1-216-PAH,216-PAK
141	1285	230		361.9	361.7	0.2	C1-216-PAH,216-PAK
142	1353	230		364.3	368.6	-4.3	C1-216-PAH,216-PAK
143	1447	230	229	369.3	378.2	-9.0	C1-216-PAH,216-PAK
144	1459	230	229	369.3	379.5	-10.2	C1-216-PAH,216-PAK
145	1485	230.109(-2)	229,216	387.0	382.1	4.9	C1-216-PAH,C2-202-PAH
146	1514	230.109(3)	229,215	387.0	385.1	1.9	C1-216-PAH,C2-202-PAH
147	1551	230		392.0	389.0	3.1	C1-216-PAH,216-PAK
148	1589	230		392.0	392.9	-0.9	C1-216-PAH,C2-202-PAH
149	1649	230.109(3)		400.2	399.3	0.9	C1-216-PAH,C2-202-PAH
150	1703	230.073(-5)	229,202	405.4	405.0	0.4	216-PAK
151	1282	232		362.8	361.4	1.4	C1-202-PAK,C3-190-PAH
152	1305	232		365.1	363.8	1.3	C1-202-PAK,C3-190-PAH
153	1321	232	231	366.4	365.4	1.0	C1-202-PAK,C3-190-PAH
154	1367	232.088(-5)		371.7	370.1	1.6	C2-190-PAK,C1-202-PAK
155	1391	232		374.6	372.5	2.1	C1-202-PAK,C3-190-PAH
156	1414	232		377.8	374.9	2.9	C1-202-PAK,C3-190-PAH
157	1430	232		377.8	376.5	1.3	C1-202-PAK,C3-190-PAH
158	1516	232		386.3	385.3	1.0	C1-202-PAK,C3-190-PAH
159	1327	234		367.5	366.0	1.5	216-PASH,C1-190-PAQ
160	1411	234		376.5	374.5	1.9	216-PASH,C1-190-PAQ
161	1448	234		380.7	378.3	2.4	216-PASH,C1-190-PAQ
162	1548	234.050(-.1)	232,189	389.9	388.7	1.3	216-PASH
163	1580	234	232	396.3	392.0	4.3	216-PASH,C1-190-PAQ
164	1608	234.050(-.1)	232	396.3	394.9	1.3	216-PASH
165	1667	234		401.0	401.2	-0.2	216-PASH,C1-190-PAQ
166	1505	235		384.7	384.2	0.5	??[5]
167	584	236	223,222,128	290.8	290.0	0.9	C2-190-PASH,C2-178-PAQ
168	758	236	221	309.4	308.1	1.3	C2-190-PASH,C2-178-PAQ
169	863	236		319.3	318.9	0.4	C2-190-PASH,C2-178-PAQ
170	1123	236		346.3	345.3	0.9	C2-190-PASH,C2-178-PAQ
171	1185	236		353.0	351.6	1.3	C2-190-PASH,C2-178-PAQ
172	1312	236		364.8	364.5	0.3	C2-190-PASH,C2-178-PAQ
173	1371	236		368.3	370.5	-2.2	C2-190-PASH,C2-178-PAQ
174	984	238		331.6	331.2	0.4	C3-166-PAQ,238-PAH
175	1266	238		360.9	359.8	1.1	C3-166-PAQ,238-PAH
176	1726	240		411.0	407.5	3.5	240-PAH,238-PAF
177	1749	240		411.0	410.0	1.0	240-PAH,238-PAF
178	1803	240	239,238,237	411.0	415.8	-4.9	240-PAH,238-PAF
179	1843	240.094(-2)	239,120	420.9	420.2	0.7	240-PAH

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
181	1582	242		398.2	392.2	6.0	C1-228-PAH,226-PAHK
182	1610	242		398.2	395.1	3.1	C1-228-PAH,226-PAHK
183	1675	242		403.1	402.0	1.1	C1-228-PAH,226-PAHK
184	1698	242		403.1	404.5	-1.4	C1-228-PAH,226-PAHK
185	1725	242.073(-1)	241	408.5	407.4	1.1	240-PAF,226-PAHK
186	1785	242		417.4	413.9	3.6	C1-228-PAH,226-PAHK
187	1803	242.109(.2)	241,226	417.4	415.8	1.6	C1-228-PAH
188	1842	242	226	420.8	420.1	0.7	C1-228-PAH,226-PAHK
189	1749	243.105(.3)	242	403.1	410.0	-6.9	C1-228-PANH
190	1374	244		371.5	370.8	0.7	C2-216-PAH,288-PAHK
191	1432	244		377.3	376.7	0.6	C2-216-PAH,288-PAHK
192	1477	244		382.5	381.3	1.1	C2-216-PAH,288-PAHK
193	1502	244		384.4	383.9	0.5	C2-216-PAH,288-PAHK
194	1621	244		397.1	396.3	0.8	C2-216-PAH,288-PAHK
195	1649	244		403.9	399.3	4.7	C2-216-PAH,288-PAHK
196	1677	244		403.9	402.2	1.7	C2-216-PAH,288-PAHK
197	1697	244		403.9	404.4	-0.5	C2-216-PAH,C3-202-PAH
198	1722	244		410.7	407.1	3.6	C2-216-PAH,288-PAHK
199	1751	244		410.7	410.2	0.5	C2-216-PAH,288-PAHK
200	1801	244		423.0	415.6	7.3	C2-216-PAH,288-PAHK
201	1854	244		423.0	421.4	1.5	C2-216-PAH,288-PAHK
202	1278	246		361.1	361.0	0.1	C4-190-PAH,216-PAQ
203	1278	246		358.8	361.0	-2.2	C4-190-PAH,216-PAQ
204	1447	246		379.7	378.2	1.5	C4-190-PAH,216-PAQ
205	1489	246		384.6	382.5	2.0	C4-190-PAH,216-PAQ
206	1532	246		391.2	387.0	4.2	C4-190-PAH,216-PAQ
207	1555	246		391.2	389.4	1.8	C4-190-PAH,216-PAQ
208	1589	246		394.3	392.9	1.4	C4-190-PAH,216-PAQ
209	1689	248	247	403.6	403.5	0.1	C1-216-PASH,C2-190-PAQ
210	1711	248.066(-1)	247	407.5	405.9	1.7	C1-216-PASH
211	1747	248.066(-1)		412.0	409.8	2.2	C1-216-PASH
212	1776	248		414.0	412.9	1.1	C1-216-PASH,C2-190-PAQ
213	2038	252.094(-.4)		443.1	441.9	1.2	BENZOFLUORANTHENES
214	2065	252.094(-2)		446.3	445.0	1.3	252-PAH
215	2129	252.094(2)		453.4	452.2	1.2	BENZO[e]PYRENE
216	2140	252.094(2)		453.4	453.4	0.0	BENZO[a]PYRENE
217	2165	252.094(.6)		456.9	456.2	0.7	PERYLENE
218	1985	253	251	438.2	436.0	2.2	252-PANH
219	1681	254		403.4	402.7	0.8	C1-240-PAH,240-PAK
220	1697	254		403.4	404.4	-0.9	C1-240-PAH,240-PAK
221	1716	254		403.4	406.4	-3.0	C1-240-PAH,240-PAK
222	1841	254.109(-2)	253	421.4	420.0	1.4	C1-240-PAH
223	1863	254	253,252	425.8	422.4	3.4	C1-240-PAH,240-PAK
224	1885	254.109(-4)	253,252	425.8	424.9	1.0	C1-240-PAH
225	1899	254		427.2	426.4	0.8	C1-240-PAH,240-PAK

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
226	1931	254		431.1	430.0	1.1	C1-240-PAH,240-PAK
227	1982	254		431.1	435.7	-4.6	C1-240-PAH,240-PAK
228	2039	254		443.8	442.0	1.8	C1-240-PAH
229	2065	254		443.8	445.0	-1.2	C1-240-PAH,240-PAK
230	2122	254		452.5	451.4	1.1	C1-240-PAH,240-PAK
231	2143	254.081(0)		452.5	453.7	-1.3	240-PAK
232	2165	254		471.9	456.2	15.7	C1-240-PAH,240-PAK
233	1064	256		335.8	339.3	-3.6	C1-226-PAHK,C2-228-PAH
234	1814	256.088(2)	255	418.6	417.1	1.6	C1-240-PAF,C1-226-PAHK
235	1845	256		422.3	420.5	1.8	C1-226-PAHK,C2-228-PAH
236	1879	256		424.5	424.2	0.3	C1-226-PAHK,C2-228-PAH
237	1915	256	241	429.0	428.2	0.8	C1-226-PAHK,C2-228-PAH
238	1951	256.125(-.2)		433.7	432.2	1.5	C2-228-PAH
239	1965	256		433.7	433.8	-0.1	C1-226-PAHK,C2-228-PAH
240	1997	256		440.3	437.3	2.9	C1-226-PAHK,C2-228-PAH
241	2006	256		440.3	438.3	1.9	C1-226-PAHK,C2-228-PAH
242	2042	256		---	442.4	--	C1-226-PAHK,C2-228-PAH[6]
243	1605	258		395.3	394.6	0.7	C3-216-PAH,240-PASH,228-PAQ
244	1624	258		397.7	396.6	1.1	C3-216-PAH,240-PASH,228-PAQ
245	1650	258		400.0	399.4	0.6	C3-216-PAH,240-PASH,228-PAQ
246	1678	258		403.9	402.3	1.6	C3-216-PAH,240-PASH,228-PAQ
247	1726	258	231,213	409.5	407.5	2.0	C3-216-PAH,240-PASH,228-PAQ
248	1746	258		409.5	409.7	-0.1	C3-216-PAH,240-PASH,228-PAQ
249	1771	258		409.5	412.4	-2.9	C3-216-PAH,240-PASH,228-PAQ
250	1820	258	230,202	419.4	417.7	1.7	228-PAQ
251	1922	258	230	426.3	429.0	-2.6	C3-216-PAH,240-PASH,228-PAQ
252	1998	258		430.6	437.4	-6.9	C3-216-PAH,240-PASH,228-PAQ
253	2043	258.050(-2)		444.0	442.5	1.5	240-PASH
254	2091	258		449.2	447.9	1.3	C3-216-PAH,240-PASH,228-PAQ
255	2107	258.050(-3)		449.2	449.7	-0.5	240-PASH
256	2148	258		455.4	454.3	1.1	C3-216-PAH,240-PASH,228-PAQ
257	1656	260	215	402.5	400.0	2.4	C3-216-PAF,C1-216-PAQ
258	1686	260		405.7	403.2	2.5	C3-216-PAF,C1-216-PAQ
259	1715	260		407.7	406.3	1.4	C3-216-PAF,C1-216-PAQ
260	1738	260		412.1	408.8	3.4	C3-216-PAF,C1-216-PAQ
261	1751	260		412.1	410.2	1.9	C3-216-PAF,C1-216-PAQ
262	1778	260		417.9	413.1	4.8	C3-216-PAF,C1-216-PAQ
263	1837	262		420.9	419.6	1.4	C3-190-PAQ,C2-216-PASH
264	1869	262		425.5	423.1	2.4	C3-190-PAQ,C2-216-PASH
265	1882	262		425.5	424.5	0.9	C3-190-PAQ,C2-216-PASH
266	1905	262		425.5	427.1	-1.6	C3-190-PAQ,C2-216-PASH
267	1920	262		432.3	428.7	3.5	C3-190-PAQ,C2-216-PASH
268	1930	262		432.3	429.9	2.4	C3-190-PAQ,C2-216-PASH
269	2288	262	261	---	470.1	--	C3-190-PAQ,C2-216-PASH[6]
270	2185	264	263,261	---	458.5	--	264-PAH,C4-178-PAQ[6]

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
271	2290	264.094(4)	263	474.9	470.3	4.6	264-PAH
272	2320	264	263	477.9	473.7	4.2	264-PAH,C4-178-PAQ
273	2189	266.109(-.8)	265	464.9	458.9	6.0	266-PAH, C1-252-PAH
274	2223	266.109(1)	265,263,261	464.9	462.7	2.2	266-PAH, C1-252-PAH
275	2250	266.109(-2)	265,263	469.0	465.8	3.2	266-PAH, C1-252-PAH
276	2271	266.1092(-3)		471.9	468.1	3.8	266-PAH, C1-252-PAH
277	2292	266	265	471.9	470.5	1.4	266-PAH, C1-252-PAH
278	1972	268		434.5	434.5	-0.0	252-PAHK,C2-240-PAH
279	2002	268		439.4	437.9	1.5	252-PAHK,C2-240-PAH
280	2046	268	239	442.0	442.8	-0.8	252-PAHK,C2-240-PAH
281	2071	268.089(-6)	239	444.7	445.6	-0.9	252-PAHK, C1-240-PAK
282	2107	268.089(-4)	239	451.4	449.7	1.7	252-PAHK, C1-240-PAK
283	2134	268	239	454.1	452.7	1.4	252-PAHK,C1-240-PAK,266-PAF
284	2168	268		457.5	456.6	0.9	252-PAHK,C1-240-PAK,266-PAF
285	2180	268	239	457.5	457.9	-0.4	252-PAHK,C1-240-PAK,266-PAF
286	2219	268		461.1	462.3	-1.2	252-PAHK,C1-240-PAK,266-PAF
287	2254	268		469.0	466.2	2.8	252-PAHK,C1-240-PAK,266-PAF
288	2273	268		469.0	468.4	0.6	252-PAHK,C1-240-PAK,266-PAF
289	2040	270		438.4	442.2	-3.8	C3-238-PAH,240-PAQ
290	2134	270		454.7	452.7	2.0	C3-238-PAH,240-PAQ
291	2143	270		454.7	453.7	1.0	C3-238-PAH,240-PAQ
292	2167	270		454.7	456.4	-1.7	C3-238-PAH,240-PAQ[6]
293	2205	270		---	460.7	--	C3-238-PAH,240-PAQ[6]
294	2243	270	255	---	465.0	--	C3-238-PAH,240-PAQ[6]
295	2318	270		---	473.4	--	C3-238-PAH,240-PAQ[6]
296	2140	272		---	453.4	--	C1-240-PASH,C1-228-PAQ[6]
297	2162	272		---	455.9	--	C1-240-PASH,C1-228-PAQ[6]
298	2207	272		---	460.9	--	C1-240-PASH,C1-228-PAQ[6]
299	2225	272		---	463.0	--	C1-240-PASH,C1-228-PAQ[6]
300	2254	272		---	466.2	--	C1-240-PASH,C1-228-PAQ[6]
301	2403	276	274	468.4	483.0	-14.6	276-PAH,C3-216-PASH
302	2462	276.097(2)	274,273,272	487.3	489.6	-2.3	C3-216-PASH
303	2503	276.097(.9)	274,273,272	499.0	494.3	4.7	C3-216-PASH
304	2602	276.097(-2)	274,273,138	---	---	--	C3-216-PASH[7]
305	2636	276.097(.9)	274,273,272	---	---	--	C3-216-PASH[7]
306	2136	278		438.4	453.0	-14.6	278-PAH,264-PAK
307	2148	278		438.4	454.3	-16.0	278-PAH,264-PAK
308	2169	278		438.4	456.7	-18.3	278-PAH,264-PAK
309	2213	278		453.6	461.6	-8.0	278-PAH,264-PAK
310	2245	278		453.6	465.2	-11.6	278-PAH,264-PAK
311	2297	278		456.2	471.1	-14.9	278-PAH,264-PAK
312	2378	278		463.4	480.2	-16.8	278-PAH,264-PAK
313	2405	278.109(.2)		474.9	483.2	-8.3	278-PAH
314	2462	278.109(-3)		487.1	489.6	-2.5	278-PAH
315	2513	278.109(-.8)		500.0	495.4	4.6	278-PAH

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Cmpd No.	SPB-5 Scan#	Observed Mass (Error (mmu))	Fragment Ions	Retention Indices SPB-1	Retention Indices SPB-5	ΔRI[1] (1-5)	Tentative Identity[2]
316	2554	278.109(-.8)		500.0	500.0	0.0	PICENE
317	2564	278		500.0	---	--	278-PAH,264-PAK[7]
318	2611	278.109(-2)		---	---	--	278-PAH[7]
319	2367	279		483.7	479.0	4.7	278-PANH
320	2424	279.104(-4)	278	492.0	485.4	6.7	278-PANH
321	2073	280		---	445.9	--	C2-252-PAH,266-PAK[6]
322	2295	280		478.1	470.8	7.2	C2-252-PAH,266-PAK
323	2327	280		483.3	474.4	8.8	C2-252-PAH,266-PAK
324	2372	280.125(-.2)		483.3	479.5	3.8	278-H2-PAH,C2-252-PAH
325	2430	280		491.0	486.0	5.0	278-H2-PAH,C2-252-PAH
326	2512	280		---	495.3	--	C2-252-PAH,266-PAK[6]
327	2609	280		---	---	--	C2-252-PAH,266-PAK[7]
328	2214	282		459.2	461.7	-2.5	264-PASH,C1-252-PAHK
329	2247	282.104(-.9)		469.0	465.4	3.5	266-PAX,C1-252-PAHK
330	2549	282.050(-.9)		---	499.4	--	264-PASH[6]
331	2609	282		---	---	--	264-PASH,C1-252-PAHK[7]
332	2369	284.066(-5)		483.5	479.2	4.3	266-PASH,C2-238-PASH
333	2428	284.066(-2)		490.8	485.8	5.0	266-PASH,C2-238-PASH
334	2470	284		496.5	490.5	6.0	266-PASH,C1-240-PAQ[7]
335	2811	288		---	---	--	288-PAH,C3-216-PAQ[7]
336	2631	290.109(2)		---	---	--	290-PAH,C1-276-PAH[7]
337	2675	290.109(3)		---	---	--	290-PAH,C1-276-PAH[7]
338	2744	290.109(-2)	145	---	---	--	290-PAH,C1-276-PAH[7]
339	2818	290		---	---	--	290-PAH,C1-276-PAH[7]
340	2466	292.088(-2)		496.5	490.1	6.4	276-PAHK,C1-264-PAK
341	2515	292		496.5	495.6	0.9	276-PAHK,C1-278-PAH[7]
342	2613	292		---	---	--	276-PAHK,C1-278-PAH[7]
343	2658	292		---	---	--	C4-190-PASXK[7]
344	2720	292		---	---	--	276-PAHK,C1-278-PAH[7]
345	2781	292		---	---	--	276-PAHK,C1-278-PAH[7]
346	2485	294		459.9	492.2	-32.3	C3-252-PAH,264-PAQ
347	2520	294		468.6	496.2	-27.6	C3-252-PAH,264-PAQ[7]
348	2613	294		475.9	---	--	C3-252-PAH,264-PAQ[7]
349	2284	296		486.5	469.6	16.9	266-PAQ,C1-264-PASH
350	2612	298		---	---	--	C2-240-PAQ,C1-266-PASH[7]
351	3103	300		---	---	--	300-PAH[7]
352	3156	300.094(4)		---	---	--	300-PAH[7]
353	3287	300.094(4)		---	---	--	300-PAH[7]
354	3106	302.109(8)		---	---	--	302-PAH[7]
355	3130	302		---	---	--	302-PAH[7]
356	3219	302		---	---	--	302-PAH[7]
357	3300	302.109(7)		---	---	--	302-PAH[7]
358	2168	306		454.5	456.6	-2.0	C2-278-PAH
359	2210	306		461.8	461.3	0.6	C2-278-PAH

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Appendix 4 (continued)

[1] RI(1-5): RI_{SPB-1} - RI_{SPB-5}

[2] Tentative Identity: Acronyms are explained in Figure 1-2.

[3] "149": The molecular weight for the phthlate ester could not be determined, only the base peak, 149, was detected.

[4] A component that has eluted before the first standard compound and therefore its retention index could not be determined.

[5] ??: Due to lack of information, a tentative identity could not be assigned.

[6] There were no peaks in the chromatogram from the SPB-1 column that could be correlated with the results from the SPB-5 column.

[7] A component that has eluted after the last standard compound and therefore its retention index could not be determined.