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Sampling and Analysis of Polycyclic Aromatic Hydrocarbons and N-Alkanes in Ambient Air

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) and n-alkanes have received an increased attention over the past decades mainly due to their toxicological effects and chemistry in the atmosphere. They distribute in atmosphere between vapour and particle phases, which influence their atmospheric transport and rate of removal by wet and dry deposition. In this study, the main objective was to adapt, modify and test an analytical method to determine the presence and concentrations for the total amounts of gas and particle phase n-alkanes and PAHs in ambient air. In order to test the extraction efficiency, uncoated quartz fiber filters and those coated with XAD-4 resin were spiked with known amounts of n-alkane and PAH standard solution and were subjected to an ultrasonic extraction procedure that was previously developed for analysis of methyl nitrophenols in atmospheric samples. For both filter types, the extraction efficiency for PAHs and n-alkanes were found to be somewhat low especially for those with high vapour pressures. When some spiked filters were subjected to Soxhlet extraction, the recoveries improved for most PAHs whereas for n-alkanes, the recoveries were similar to those from ultrasonic extraction. However, for both the extraction methods, it was found that the XAD-4 coating did not influence the extraction of the target compounds.

A high volume air sampler was used to sample both gas and particle phase PAHs and n-alkanes on XAD coated filters. From atmospheric samples collected at York University, all 16 PAHs and C_{13} to C_{25} n-alkanes that were under investigation have been detected and quantified. Large sample masses of these compounds were obtained which would allow future isotopic composition measurements for these compounds. All samples were analysed using gas chromatography-mass spectrometry (GC-MS). In case of PAHs, the most abundant compounds in ambient samples were naphthalene, phenanthrene and fluorene, which was consistent with various studies in literature. For n-alkanes, the carbon preference index (CPI) was calculated and was close to 1 for all atmospheric samples, which indicated their anthropogenic contribution to the atmosphere.

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1. INTRODUCTION

Semi-volatile organic compounds (SVOCs) tend to distribute in the atmosphere between the vapour and particulate phases in a ratio that depends on temperature and their physical properties, particularly the subcooled liquid vapour pressure. According to Junge (1977), SVOCs are compounds with vapour pressures that fall within the range of 10^{-2} to 10^{-6} Pa and may exist in part in the gas phase, and in part, adsorbed or absorbed in particles. A compound with vapour pressure higher than 10^{-2} Pa will exist in the gas phase and that with vapour pressure less than 10^{-6} Pa will exist in the particle phase (Junge, 1977). The vapor-to-particle distribution of SVOCs in the atmosphere is an important factor which governs their atmospheric transport and removal rate by wet and dry deposition and their eventual uptake by vegetation (Bidleman et al., 1986; Leal-Granadillo et al., 2000). The partitioning of SVOCs between gas and particle phases may also influence their photochemical and non-photochemical transformations since many of these reactions occur exclusively or predominantly under homogeneous (gas phase) or heterogeneous (substrate adsorbed to aerosol) conditions (Bidleman et al*.* 1986).

In this study, the two classes of SVOCs under investigation are n-alkanes and polycyclic aromatic hydrocarbons (PAHs). n-Alkanes are an important class of organic compounds in ambient aerosols and their homologue distribution may indicate different pollution sources (Stephanou, 1992; Li et al., 2010). The source of n-alkanes in aerosol samples is indicated by carbon preference index (CPI), which gives the relative abundance of compounds containing odd and even number of carbon atoms (Stephanou, 1992). N-alkanes are emitted by both biogenic and anthropogenic sources. Anthropogenic sources include fossil fuel combustion, petroleum residues and biomass burning while biogenic emissions include particles shed from epicuticular plant waxes and from direct suspension of pollen, microorganisms and insects (Leal-Granadillo et al., 2000; Li et al*., 2010*). Furthermore, n-alkanes have negative health impact and those with more than 16 carbon number can cause skin cancer (Bi et al., 2003). Studies suggest that many n-alkanes can exist in the gas phase as well as in the particle phase at ambient temperature. It was reported by Kadowaki (1994) that the elevated concentrations of particulate n-alkanes in winter are attributable to the change of the gas to particle partitioning that depends on the ambient temperature. The distributions of n-alkanes as a function of ambient temperature is shown in Figure 1.1, which shows that n-alkanes lower than C_{20} exist in the gas phase and those higher than C_{29} exist in the particle phase, in the range of -10^{o}C to 40^{o}C. Under normal circumstances, their gas-to-particle distributions are not affected by temperature. However, the gas to particle distributions of n-alkanes from C_{21} upto C_{28} depends on ambient temperature (Kadowaki, 1994).

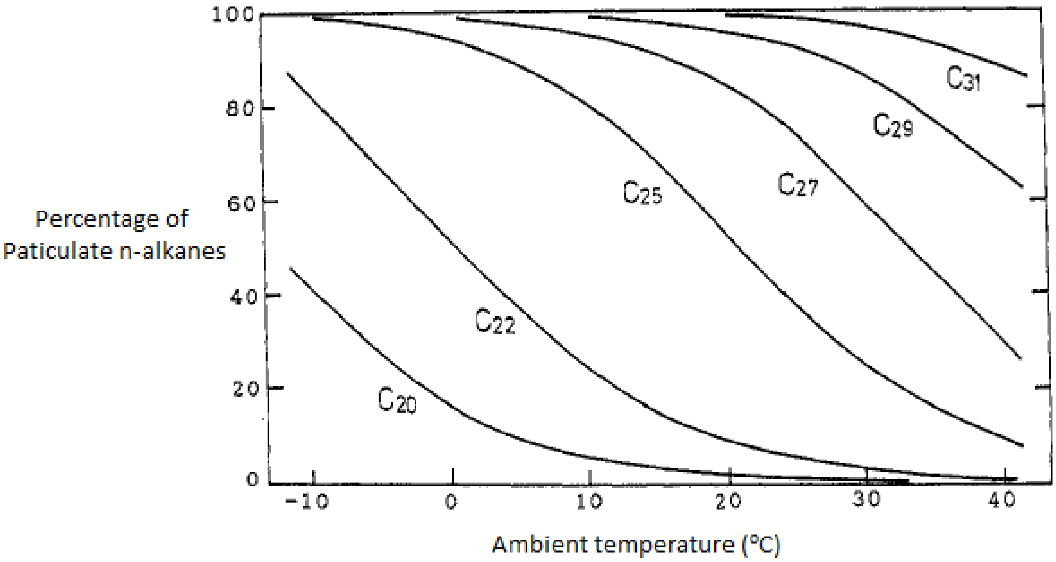


Figure 1.1: Vapour to particle partitioning of n-alkanes as a function of ambient temperature predicted by the Junge model (Kadowaki, 1994)

PAHs, on the other hand, are of environmental concern due to their carcinogenic, toxic and mutagenic properties in conjunction with their continual and widespread atmospheric emissions (Leal-Granadillo et al., 2000; Liu et al. 2007). PAHs are also shown to have anti-estrogenic activities (Tran et al., 1996; Clemons et al., 1998). Some sources of atmospheric PAHs include incomplete combustion of fossil fuels and other organic matter and forest fires (Cincinelli et al., 2000; Leal-Granadillo et al., 2000; Liu et al. 2007). Although there are hundreds of individual PAHs present in the environment, only 16 PAHs have been classified by the U.S. Environmental Protection Agency (USEPA) as priority pollutants

(U.S. Environment Protection Agency, 1998; Demircioglu et al., 2011). The 16 PAHs are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene. PAHs have unique chemical and physical characteristics and thus a good understanding of their characteristics, particularly their reactivity and vapor pressure is essential. The vapor pressure for 14 PAHs at 25°C is reported by Junge et al. (1977) whereby PAHs in urban aerosols with vapour pressures between 10^{-2} and 10^{-6} Pa are expected to exist in both gas and particulate phase (Figure 1.2).

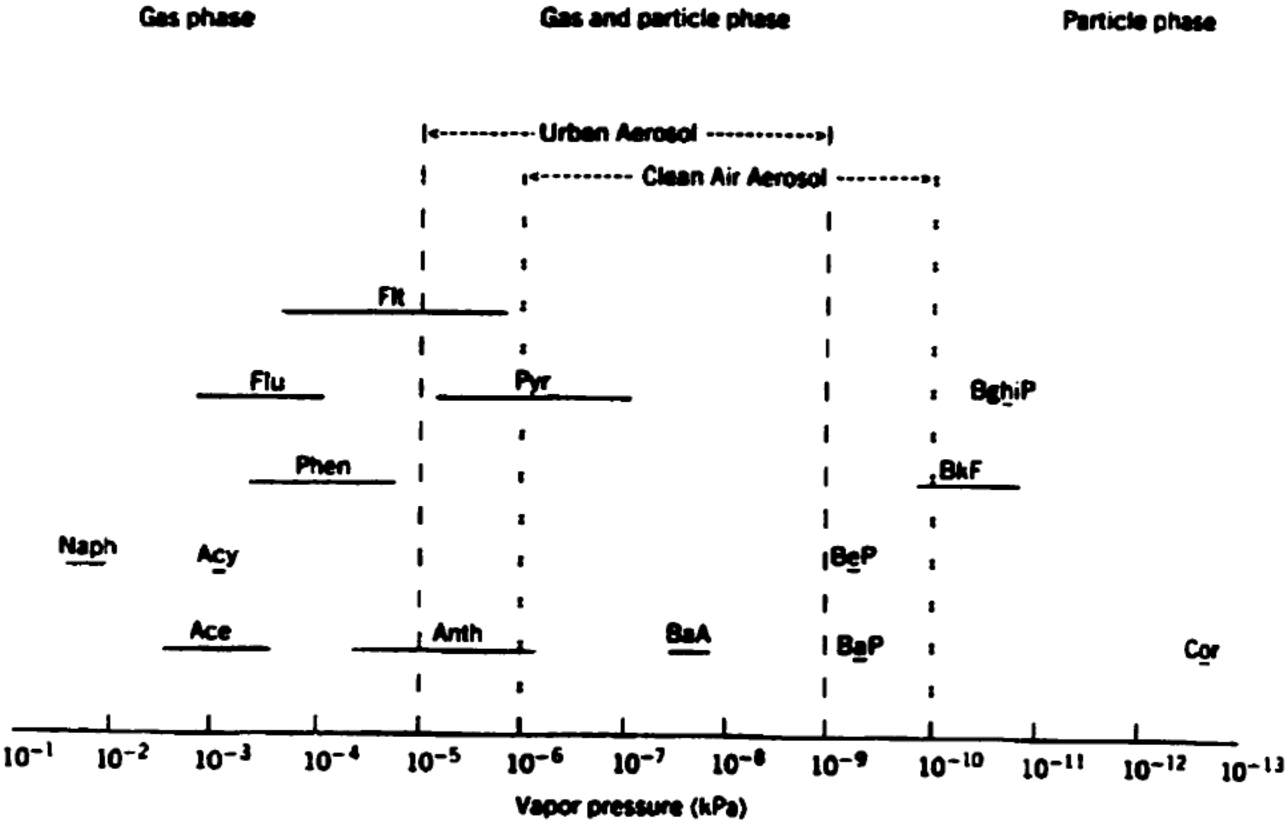


Figure 2.2: **The range of Vapor Pressures for various PAHs, along with the predicted vapour-particle distribution for urban and clean air aerosol as reported by Junge. Abbreviations: Ace (acenaphthene); Acy (acenaphthylene); Anth(anthrax); BaA (benz[a]anthracene); BaP (benzo[a]pyrene; BeP (benzo[e]pyrene; BghiP (benzo[g,h,i]perylene; BkF (benzo[k]fluoranthene; Cor (coronene); Flt (fluoranthene) Flu (Fluorene); Naph (naphthalene); Phen (phenanthrene); Pyr (pyrene)** (Adapted from Junge, 1977, sited in Irei, 2002)

In addition to having harmful health effects, atmospheric aerosols play a significant role in the global radiative forcing of the climate system (Simoneit, 1999; Kavouras et al., 1999). Aerosols influence the radiative balance of the Earth through absorption and scattering of solar radiation back to space and by increasing the amount of solar radiation that clouds reflect. However, the highly variable aerosol concentrations in the atmosphere make it difficult to estimate aerosol radiative forcing (Simoneit, 1999; Kavouras et al., 1999). Furthermore, the lack of understanding of production mechanisms of secondary aerosols and their unknown concentrations in the atmosphere make this estimation more complex. Thus, a better understanding of aerosols is important in making scientific predictions of radiative forcing effect on the climate.

Due to their importance in atmospheric chemistry, this research project focuses on concentrations and distribution analysis of SVOCs in ambient air, which in turn, contributes towards an understanding of the role of SVOCs in atmospheric processes. Thus, the objective of this research project is to adapt and modify an analytical method to determine the presence, concentrations and possibly the distributions of SVOCs, in particular, n-alkanes and PAHs in the ambient air. The target compounds are n-alkanes from C_{13} to C_{25} and the 16 USEPA Priority PAHs, which provides the advantage of covering a wide range of vapour pressures. The method used in this study is adapted and modified from the method originally developed by Dr. Sophie Moukhtar et al. (2010) and optimised by Rosaline Busca (2010) and Marina Saccon (2013) which involves GC-MS analysis of nitrophenols in the atmosphere. In this study, ambient n-alkane and PAH monitoring involved high volume air sampling onto quartz fiber filters coated with XAD-4^{TM} resin to collect gas and particulate matter (PM). All sampling were conducted on the roof of the Petrie Science and Engineering building at York University. The sampling process was followed by chemical analysis of the samples which included sample preparation, extraction of the filters with acetonitrile using ultrasonic agitation or Soxhlet extraction and reduction of the extract volume to approximately 100 µL. Finally, instrumental analysis was conducted using GC-MS which allowed identification and quantification of n-alkanes and PAHs in ambient air.

Previous studies on hydrocarbons in atmospheric particulate matter have focused on the particulate phase only, providing information on the heavier organic compounds and neglecting the lighter ones, prevalent in the vapour phase (Leal-Granadillo et al., 2000). The present study focuses on both the particulate and vapour phases since the lighter compounds are more abundant in the urban atmosphere and may react with other pollutants to form more toxic derivatives (Leal-Granadillo et al., 2000). The results of the study will help to provide more detailed insights into the most important sources as well as loss processes of n-alkanes and PAHs in ambient air.

2. THEORY AND BACKGROUND

This chapter gives a brief review of the techniques that were previously used to sample PAHs and n-alkanes in the atmosphere, and the concentrations obtained. The sampling technique chosen for this project is also described.

2.1. Ambient Measurements of PAHs and n-alkanes

There is a great amount of data concerning the atmospheric concentrations of PAHs and they vary considerably depending on location. These studies, mainly driven by toxicological effects of these compounds, have reported measurements of gas and particle phase in different locations by several techniques. Table 2.1 lists the ambient concentrations of PAHs in other cities reported in the literature.

The most widespread collection system of PAHs consists of glass or quartz fiber filter to collect the particle bound fraction, followed by one or more gas traps such as polyurethane foam (PUF), organic resins, (Tenax, XAD, Chromsorb) or PUF-resin combinations (Possanzini et al., 2004). Odabasi and coworkers in 1999 reported the ambient concentrations of PAHs at an urban site in Chicago, where they used a modified high volume air sampler and collected particles on glass fiber filters. The gas phase compounds were collected in a modified cartridge containing XAD-2 resin placed between layers of PUF plugs (Odabasi et al., 1999). In 2002, Park and coworkers employed a high volume PUF sampler for sampling atmospheric PAHs at an urban site in Seoul, Korea. Particle phase and gas phase were collected using quartz fiber filters and PUF respectively (Park et al., 2002). However, Possanzini and coworkers adopted a different approach to determine ambient PAH concentrations in downtown Rome in 2004, where they used a XAD-4 coated glass annular denuder-quartz fiber filter system and by doing so, they were able to separate gas and particle phase PAHs (Possanzini et al., 2004). While most of these studies focused on polluted areas, Cotham and Bidleman (1995) reported the ambient PAH concentrations obtained at a rural site in Green Bay, USA.

Table 2.1: Ambient PAH concentrations at various locations

Compound	**Seoul, Korea[a] (ng m^{-3})**		**Chicago, USA[b] (ng m^{-3})**	**Green Bay, USA[c] (ng m^{-3})**	**Rome, Italy[d] (ng m^{-3})**		**London, UK[e] (ng m^{-3})**
	Gas	Particle	Gas + Particle	Gas + Particle	Gas	Particle	Gas + Particle
Naphthalene	11.09	0.14	NA	NA	687	12	NA
Acenaphthylene	7.26	0.12	NA	NA	39	4.6	NA
Acenaphthene	3.14	0.21	76.9	NA	57	2.2	2.1
Fluorene	6.20	0.26	74.8	3.3	18	0.9	13.4
Phenanthrene	15.03	1.46	200.3	6.7	71	7.2	76.1
Anthracene	2.52	0.18	14.1	0.06	5.6	0.5	5.0
Fluoranthene	5.83	2.27	44.1	1.4	18	3.5	7.4
Pyrene	10.31	2.25	24.6	0.6	7.6	9.2	6.8
benz(a)anthracene	0.80	1.82	2.1	0.14	0.4	1.4	0.8
Chrysene	0.84	2.78	3.6	0.35	0.5	3.9	1.5
benzo(b)fluoranthene	NA	4.89	2.3	0.47	0.7	6.8	1.1
Benzo(k)fluoranthene	NA	4.89	1.9	0.47	0.7	6.8	1.0
Benzo(a)pyrene	NA	2.55	1.6	0.12	0.3	2.4	0.6
Indeno(1,2,3-c,d)pyrene	NA	3.59	1.2	0.12	ND	1.6	NA
Dibenz(a,h)anthracene	NA	0.55	NA	NA	NA	NA	NA
Benzo(g,h,i)perylene	NA	3.21	1.1	0.18	0.5	2.4	4.4

a. Park et al., 2002 (Annual average, 1998-99) b. Odabasi et al. 1999 (Summer-Fall, 1995) c. Cotham and Bidleman, 1995 (Winter, 1988) d. Possanzini et al. 2003 (Annual average, 2002-03) e. Halsall et al. 1994 (Annual average, 1992); NA: not analysed; ND: not detected.

In addition to PAHs, there exists a huge amount of information regarding ambient concentrations and source identification of various n-alkanes. Cincinelli and coworkers reported the concentrations of various n-alkanes in an industrial area (Prato, Italy) where air was drawn through a quartz fiber filter to collect particles and then through two PUF plugs to collect vapour phase compounds (Cincinelli et al., 2007). Bi and coworkers also used a similar approach to report the ambient n-alkane measurements in urban air of Guangzhou, China. This sampling technique appears to be the most widespread method for atmospheric n-alkane measurements. In addition, Hauser and Pattison (1972) also reported the ambient particulate phase concentrations of n-alkanes in urban atmosphere of Los Angeles, USA. Typical atmospheric concentrations of n-alkanes in various locations are given in Table 2.2. In general, atmospheric concentrations of n-alkanes are much higher than those of PAHs. This is because, in addition to anthropogenic sources, n-alkanes emitted in the atmosphere have strong biogenic sources, which include particle shed from epicuticular waxes of vascular plants and direct suspension of pollen, microorganisms and insects (Bi et al., 2003). PAHs, on the other hand, are mainly produced from man-made activities such as fossil fuel combustion.

Table 2.2: **Ambient n-alkane concentrations at various locations**

Compound	**Guangzhou, China[a] (ng m^{-3})**	**Athens, Greece[b] (ng m^{-3})**		**Prato, Italy[c] (ng m^{-3})**		**Oviedo, Spain[d] (ng m^{-3})**		**Los Angeles, USA[e] (ng m^{-3})**
	Gas + Particle	Gas	Particle	Gas	Particle	Gas	Particle	Particle
C$_{13}$	3.26	NA	NA	NA	NA	NA	NA	NA
C$_{14}$	3.03	0.83	0.10	NA	NA	NA	NA	NA
C$_{15}$	2.53	1.83	0.15	~3	ND	ND	ND	NA
C$_{16}$	3.31	3.89	0.09	~8	ND	~2	ND	NA
C$_{17}$	2.91	4.00	0.10	~15	ND	~8	ND	0.1
C$_{18}$	4.07	5.07	0.19	~22	~0.5	~23	ND	0.8
C$_{19}$	5.67	5.20	0.31	~30	~0.5	~16	ND	4
C$_{20}$	7.98	3.92	0.52	~33	~1	~9	~0.5	8
C$_{21}$	13.16	5.05	0.76	~31	~1	~4	~1	11
C$_{22}$	16.73	3.86	0.76	~25	~3	~3.5	~2	18
C$_{23}$	15.78	3.97	1.41	~19	~4	~1	~2.5	28
C$_{24}$	11.03	2.70	1.50	~13	~8	~0.5	~4	34
C$_{25}$	10.69	2.17	2.71	~8	~14	~0.5	~6	43

a. Bi et al., 2003 (Summer, 2001) b. Mandalakis et al., 2002 (Summer, 2000) c. Cincinelli et al., 2007 (Annual average, 2002). Approximate concentration in the gas and particle phases are given here, which were obtained from the graph provided in the original article. d. Leal-Granadillo et al., 2000 (Winter, 2000). Approximate concentration in the gas and particle phases are given here, which were obtained from the graph provided in the original article. e. Hauser and Pattison, 1972 (Winter, 1970). NA = not analysed ND = not detected

Sampling ambient air using a high volume air sampler on to a quartz fiber filter, while allowing components in the gas phase to pass through is a common method used to collect PM from ambient air (Finlayson-Pitts, 2000). As a result, this technique was employed in this research to sample particle phase PAHs and n-alkanes. From Table 2.1, it is clearly evident that most PAHs are not present in high quantities in the urban atmosphere. Therefore, it is advantageous to sample a large volume of air in order to obtain high enough sample masses and concentrate the PAHs to levels above the analytical limit of detection. High sample masses were also desired to evaluate sampling methods suitable for future isotope ratio measurements for these compounds. This is one of the reasons why the use of annular diffusion denuders was avoided. Although the annular diffusion denuders would also allow the separation of the gas and the particle phase PAHs and n-alkanes, the denuder coating limits the success of this method since presently available coatings can only be used at slow sample flow rates (Environment Australia, 1999).

This research project employed the use of XAD-4 resin as the coating for quartz fiber filters to collect both gas and particle phase PAHs and n-alkanes. One of the reasons that aided in the choice of XAD-4^{TM} coated filters was that the filter sampling technique and the ultrasonic extraction procedure for nitrophenols had already been developed and tested in Dr. Rudolph's group by Dr. Moukhtar. Thus, it was decided to use the same for n-alkane and PAH analysis.

XAD-4 is a suitable adsorbent for coating the filters since it strongly retains the compound of interest. Generally, a suitable adsorbent must meet the following criteria: (1) it should not sample the more abundant air components like the permanent gases, water vapour or carbon dioxide, (2) it must not chemically react with the analyte during or after sampling and finally, (3) it must have a high operative capacity, which refers to the ability to trap and hold organic molecules and is related to the surface area of the adsorbent and how strongly the organic compounds are adsorbed. The adsorbent, XAD-4 used in this project is a polystyrene divinylbenzene copolymer resin, which is porous, hydrophobic, non-polar and insoluble in water and most organic solvents. Although XAD-2 appears to be the more common adsorbent to sample particle and vapour phase PAHs and n-alkanes, XAD-4 was preferred because it has more than twice the surface area of XAD-2 (780 m^2 g^{-1} compared to 300 m^2 g^{-1}, Kennedy, 1973). In general, it is often desirable to use an adsorbent with high surface area (having a suitable polarity) for efficient trapping of compounds from ambient air.

3. METHODOLOGY

The detailed description of the experimental method used in this research is given below and includes the sampling and storage process of quartz and XAD-4^{TM} coated quartz filters, the extraction procedures, the instrumental description and finally the description of the tests conducted to show the validation of the method, as well as the calculations involved.

3.1. Sampling Procedure

Prior to sampling, all 8" x 10" quartz fiber filters (Pallflex Fiber Filters – 2500QAT) were baked at 850°C for a period of 24 hours in a large muffle furnace (Fisher Scientific Model 550-58) to remove organic contaminants. Sampling was done using a high volume TE-6001 PM-10 mass flow controlled air sampling system. The samplers were equipped with an adapter containing 40 impactor jets that collects particles larger than PM-2.5 on an oil wetted surface. The adapter allowed PM with an aerodynamic diameter of 2.5 µm or less to be transmitted through the impactor and collected on a clean, XAD-4 coated 8" x 10" quartz fiber filter, at a sample flow rate of 1.13 m^3 min^{-1}. Calibration of the high-volume sampler was done by measuring the difference in column height of a water manometer from the orifice of a TE-5028A calibrator, at varying flow rates. The manometer readings were converted to actual flow rates they represent by using the manometer reading, ambient temperature and pressure of the day during calibration and the certified values from the calibration kit. The flow recorder readings were corrected to the ambient temperature and pressure of the day during calibration. The sampling was conducted for approximately 24 hours, corresponding to a total sampled air volume of $1627 m^3$. All sampling were conducted on the roof of Petrie Science and Engineering building at York University. After sampling, the filters were stored individually in glass mason jars in a freezer until further analysis.

3.2. Extraction Procedure

Prior to extraction, all glassware used were first thoroughly cleaned and rinsed with distilled water, acetone (Chromasolv® Plus, ≥ 99.9% purity) and acetonitrile (Chromasolv® Plus, ≥ 99.9% purity). Two extraction procedures were utilized in this research project, with some filters being subjected to ultrasonic extraction while others were extracted with Soxhlet extraction.

3.2.1. Ultrasonic Extraction

The ultrasonic extraction procedure used in this research was adapted and modified from the original method developed by Moukhtar et al. (2011). A simplified schematic is shown in Figure 3.1.

An 8" x 10" filter (quartz or XAD-4™ coated) was cut into 8 pieces and placed in 120 mL amber jar. One of the pieces was spiked with 1 µg of each of the 16 PAHs and 4 µg of each of C_{13}-C_{25} n-alkanes. This was done in order to check for the recoveries of the compounds of interest (see section 4.4.2 below). No atmospheric filters were extracted using this ultrasonic extraction procedure. Once spiked, the filter pieces in the jar were then submerged in 15 to 20 mL acetonitrile (Pestanal® grade, for pesticide residue analysis) and stirred with a glass stirring rod. The jar was placed in a Bransonic Ultrasonic Cleaner (Model 3310R-DTH) and sonicated for 15 minutes. The solution was then transferred with a pipette into a syringe equipped with a 0.2 µm PTFE syringe filter (Chromatographic Specialties, Inc.) to remove particles larger than 0.2 µm. The filtered solution was then collected into a round-bottomed flask. The extraction and the filtration steps were conducted three additional times and the filtered extracts were combined. The volume of combined extracts in the round-bottomed flask was reduced to approximately 1 mL using a rotary evaporator at 44°C. It was then transferred to a 4 mL conical vial (PIERCE) using a pipette. The round-bottomed flask was rinsed three additional times by adding 3 to 5 mL of acetonitrile to the flask, evaporating it each time to 1 mL and adding it to the same conical vial. This combined solution was further evaporated in the conical vial and the volume was reduced to approximately 100 µL by passing a flow of ultra-high pure (UHP) nitrogen over the solution. Finally, half the solution was saved in a glass vial and stored in a freezer for a second analysis if needed. The remaining solution was obtained in another glass vial to be analyzed by GC-MS.

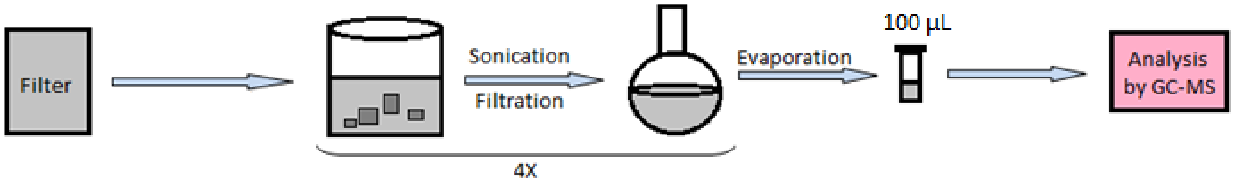


Figure 3.1: Schematic of the ultrasonic extraction procedure carried out for spiked filter analysis

3.2.2. Soxhlet Extraction

An 8" x 10" filter (quartz or XAD-4™ coated), cut into 8 pieces, was placed in a glass thimble (Figure 3.2b) and extracted by Soxhlet extraction with 150 mL of acetonitrile (pestanal® grade, for pesticide residue analysis) for approximately 20 hours. The extraction temperature was 82°C, which is the boiling point of the solvent. A simplified schematic is shown in Figure 3.2a. Prior to extraction, one of the 8 pieces of the filter was spiked with 1 µg of each of the 16 PAHs and 4 µg of each of C_{13} to C_{25} n-alkanes. This was done to check for the recoveries of the target compounds using this extraction method (see section 3.4.2. below). Once the extraction was complete, the extract was filtered using a syringe equipped with a 0.2 µm PTFE syringe filter. The filtered solution was then collected into a second round-bottomed flask. The original flask was rinsed with acetonitrile two more times and the filtered extracts were combined. The volume of the combined extracts was then reduced to 1 mL in a rotary evaporator at 44°C and transferred to a 4 mL conical vial. The round-bottomed flask was rinsed three additional times by adding 3 to 5 mL of acetonitrile to the flask, evaporating it each time to 1 mL and adding it to the same conical vial. This combined solution was further evaporated in the conical vial and the volume was reduced to approximately 100 µL by passing a flow of UHP nitrogen over the solution.

Prior to GC-MS analysis, 10 µL of $\simeq$ 100 ng µL^{-1} hexamethylbenzene solution was added to the 100 µL solution as a volumetric standard (VS). It was stirred for approximately 5 minutes with a magnetic stirring bar and then half the solution was saved in a glass vial and stored in a freezer for a second analysis if needed. The remaining solution was transferred to another glass vial to be analysed by GC-MS.

All 8" x 10" atmospheric filters were spiked with 1 µg of PAH internal standard mix, comprised of acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} and 4.28 µg of alkane internal standard, nonadecane-d_{40} ($C_{19}D_{40}$) and were then extracted using Soxhlet extraction as described.

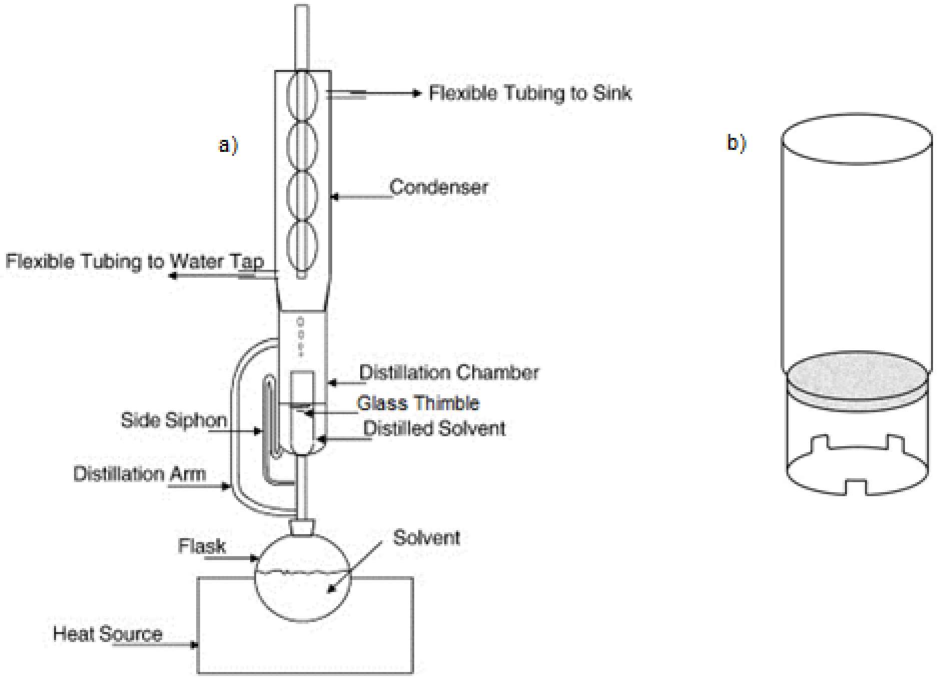


Figure 3.2: Schematic of a) Soxhlet extraction apparatus b) Glass thimble used for spiked and atmospheric filter analysis

3.3. Gas Chromatographic-Mass Spectrometric Analysis

For determining concentrations of the 16 PAHs and C_{13} to C_{25} n-alkanes target compounds, a HP 5890 Series II gas chromatograph, equipped with HP 5972 Series mass selective detector (MSD, Hewlett Packard) was used. 1 µL, splitless injections were made using a HP 6890 auto sampler. UHP Helium (5.0 grade, 99.999%, Linde) was used as the carrier gas at a flow rate of 2 mL min^{-1}. A schematic of major components of GC-MS instrumental setup is shown in Figure 3.3.

The gas chromatographic portion of the experiment was based on a 142 minute temperature program (Figure 3.4). The column used was a DB-5MS (Agilent Technologies Inc. – 5% diphenol and 95% dimethyl polysiloxane,) 60 m length x 0.25 mm inner diameter x 1 µm film thickness capillary column. The approximate retention times of the compounds of interest are shown in Table 3.1.

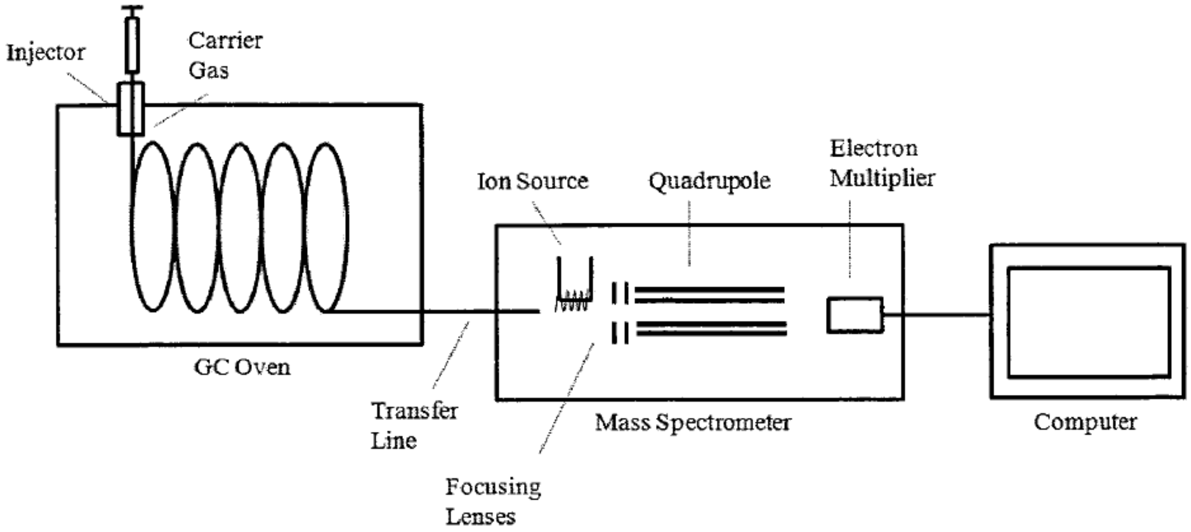


Figure 3.3: Schematic of major components of the GC-MS instrumental set up

An injection of the acetonitrile solvent was performed once between injections of different samples in order to purge the column and injector of contaminants. These injections were programmed with the same temperature program as shown in Figure 3.4.

The mass selective detector used for detection was calibrated with perfluorotributylamine (PFTBA) and maximum sensitivity tunings were made frequently to ensure highest instrumental sensitivity. The acquisition mode was total ion current (TIC) scan mode which detects all ions at all retention times. Each sample was run twice using the TIC method.

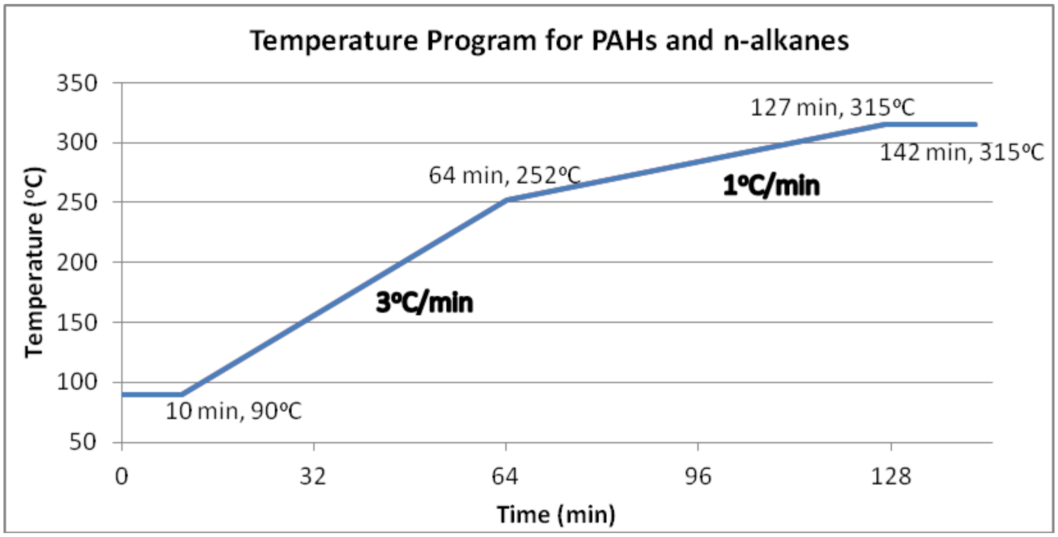


Figure 3.4: The GC temperature program

Table 3.1: Approximate retention times of eluted compounds of interest obtained from DB5-MS column used in their analysis

Target Compound	Retention Time (min)	Target Compound	Retention Time (min)
PAH		**n-Alkane**	
Naphthalene	30.53	C_{13}	35.33
Acenaphthylene	43.80	C_{14}	40.10
Acenaphthene	45.23	C_{15}	44.54
Fluorene	49.52	C_{16}	48.69
Phenanthrene	57.46	C_{17}	52.62
Anthracene	57.90	C_{18}	56.33
Fluoranthene	67.49	C_{19}	59.85
Pyrene	69.75	C_{20}	63.20
Benz[a]anthracene	84.33	C_{21}	66.54
Chrysene	84.82	C_{22}	70.21
Benzo[b]fluoranthene	101.03	C_{23}	74.28
Benzo[k]fluoranthene	101.50	C_{24}	78.74
Benzo[a]pyrene	106.28	C_{25}	83.60
Indeno[1,2,3-c,d]pyrene	123.80		

Dibenz[a,h]anthracene	124.27		
Benzo[g,h,i]perylene	127.66		
PAH Internal Standard		**n-alkane Internal Standard**	
Acenaphthene-d_{10}	44.96	$C_{19}D_{40}$	58.75
Phenanthrene-d_{10}	57.36		
Chrysene-d_{12}	84.70		

Target compounds in spiked filters and in atmospheric filters were identified using the GC retention times, the mass spectrum fragment patterns and the relative abundances of the ions. The retention times in the spiked and atmospheric filters were compared to those in standard solutions. An example of determining phenanthrene in an atmospheric filter is shown in Figure 3.5.

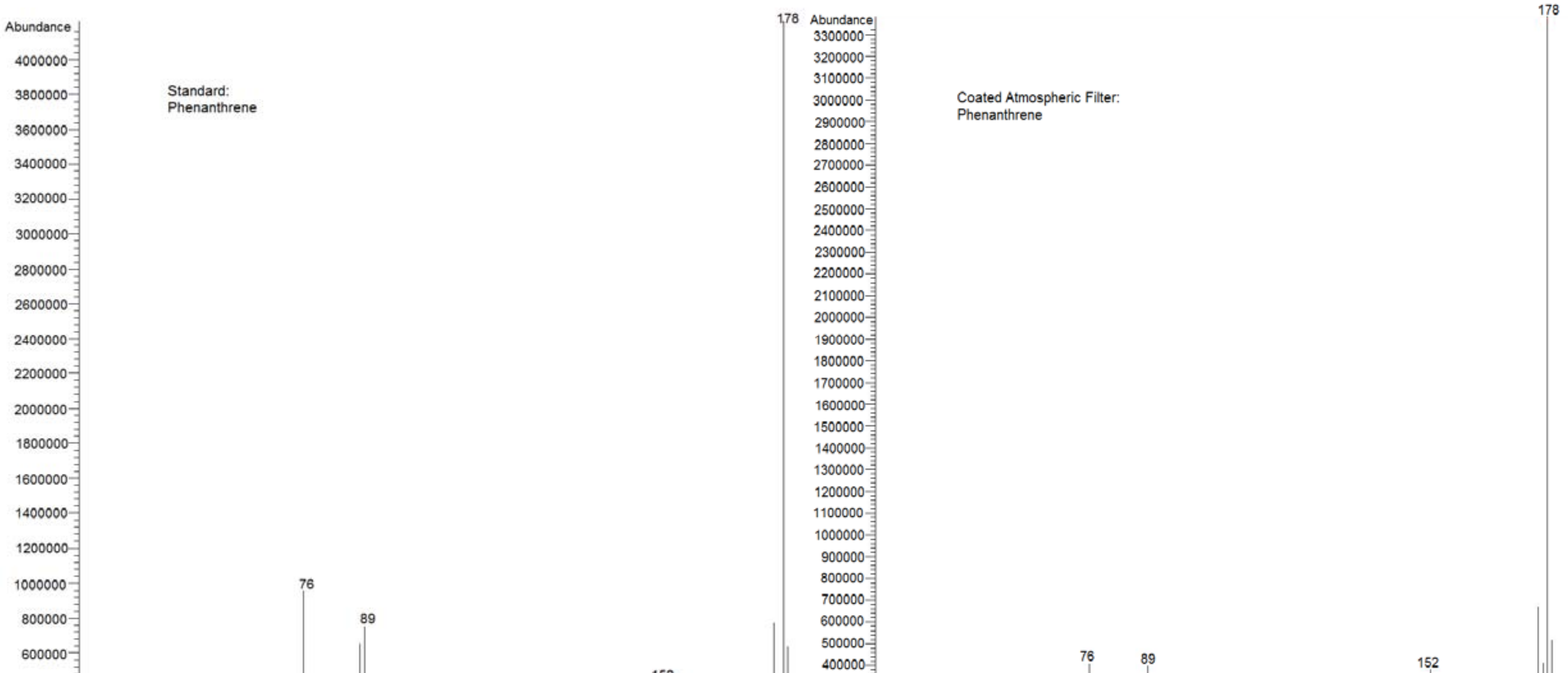


Figure 3.5: Determination of phenanthrene based on the comparison of mass spectra of a standard and an atmospheric filter. The GC retention time was 57.46

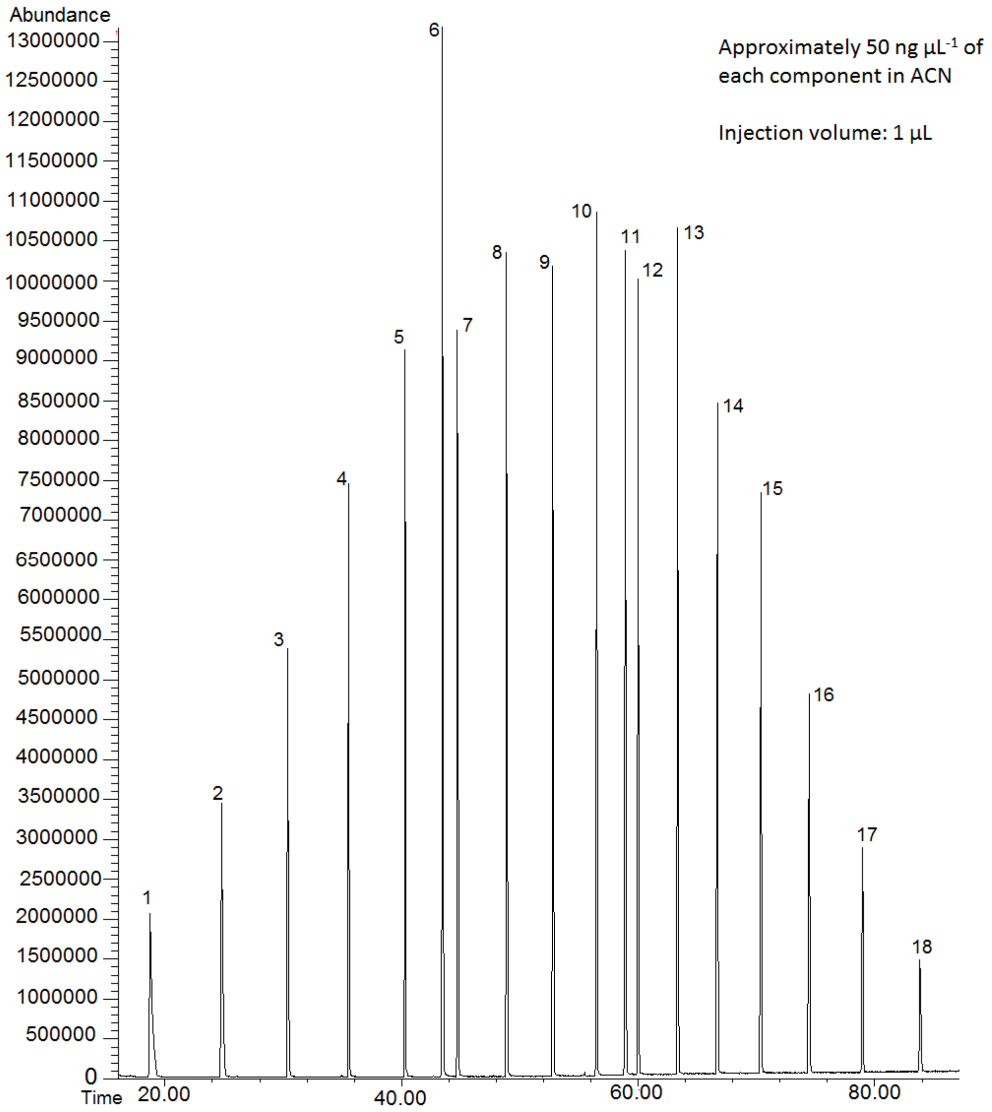
Regular calibrations were made using standard solutions, which were run twice for each calibration to check for reproducibility. For evaluation of the chromatograms obtained in the scanning mode, chromatographic traces for the most abundant mass fragment ions for each compound of interest were extracted and manually integrated. The mass to charge ratios of fragment ions that were selected are shown in Table 3.2. The sums of these peak areas, in abundance units, were plotted against the concentrations of the compounds to obtain calibration curves. Peak areas for target substances in spiked and atmospheric filters were determined in the same manner.

Table 3.2: m/z of fragment ions for each compound of interest that were selected and extracted

Target Compound	m/z	Target Compound	m/z
PAHs		**n-Alkanes**	
Naphthalene	129, 128	C_{13}	85, 71
Acenaphthylene	152, 151	C_{14}	85, 71
Acenaphthene	154, 153	C_{15}	85, 71
Fluorene	166, 165	C_{16}	85, 71
Phenanthrene	178, 176	C_{17}	85, 71
Anthracene	178, 176	C_{18}	85, 71
Fluoranthene	202, 200	C_{19}	85, 71
Pyrene	202, 200	C_{20}	85, 71
Benz[a]anthracene	228, 226	C_{21}	85, 71
Chrysene	228, 226	C_{22}	85, 71
Benzo[b]fluoranthene	252, 250	C_{23}	85, 71
Benzo[k]fluoranthene	252, 250	C_{24}	85, 71
Benzo[a]pyrene	252, 250	C_{25}	85, 71
Indeno[1,2,3-c,d]pyrene	277, 276		
Dibenz[a,h]anthracene	279, 278		
Benzo[g,h,i]perylene	277, 276		

PAH Internal Standard		**n-alkane Internal Standard**	
Acenaphthene-d_{10}	164, 160	$C_{19}D_{40}$	98, 82
Phenanthrene-d_{10}	188, 94		
Chrysene-d_{12}	240, 236		

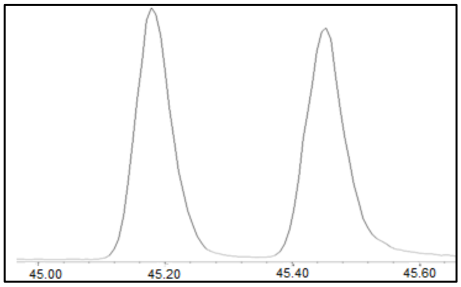
Examples of chromatograms obtained using TIC mode for a standard solution containing all the target n-alkanes and for a standard solution containing all the target PAHs are shown in Figure 3.6. The overlapping peaks (peak 11 and 12) for PAH standard solution were resolved using different mass fragments for each of the compounds, as shown in Figure 3.7. An example of calibration curve for docosane ($C_{22}H_{46}$) using the selected mass fragment ions is shown in Figure 3.8. A linear response was obtained for each compound of interest. Calibrations were repeated after a series of spiked filter and ambient measurements and after performing any maintenance operations on the GC or MSD. In order to quantify target compounds in ambient samples, their masses were determined using calibration slopes and the sum of the peak areas for the same m/z ratios used in the calibration (refer to section 3.4.3 for calculation to determine their atmospheric concentrations).

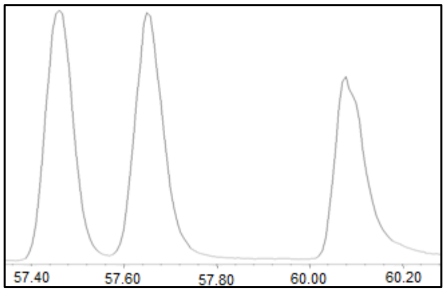


Approximately 50 ng μL^{-1} of each component in ACN

Injection volume: 1 µL

Figure 3.6: Chromatogram in TIC mode of a standard mixture of n-alkanes under investigation. (1) C_{10} (2) C_{11}, (3) C_{12}, (4) C_{13}, (5) C_{14}, (6) hexamethylbenzene (VS), (7) C_{15}, (8) C_{16}, (9) C_{17}, (10) C_{18}, (11) $C_{19}D_{40}$ (IS), (12) C_{19}, (13) C_{20}, (14) C_{21}, (15) C_{22}, (16) C_{23}, (17) C_{24}, (18) C_{25}





Approximately 10 ng µL^{-1} of each component in ACN

Injection volume: 1 µL

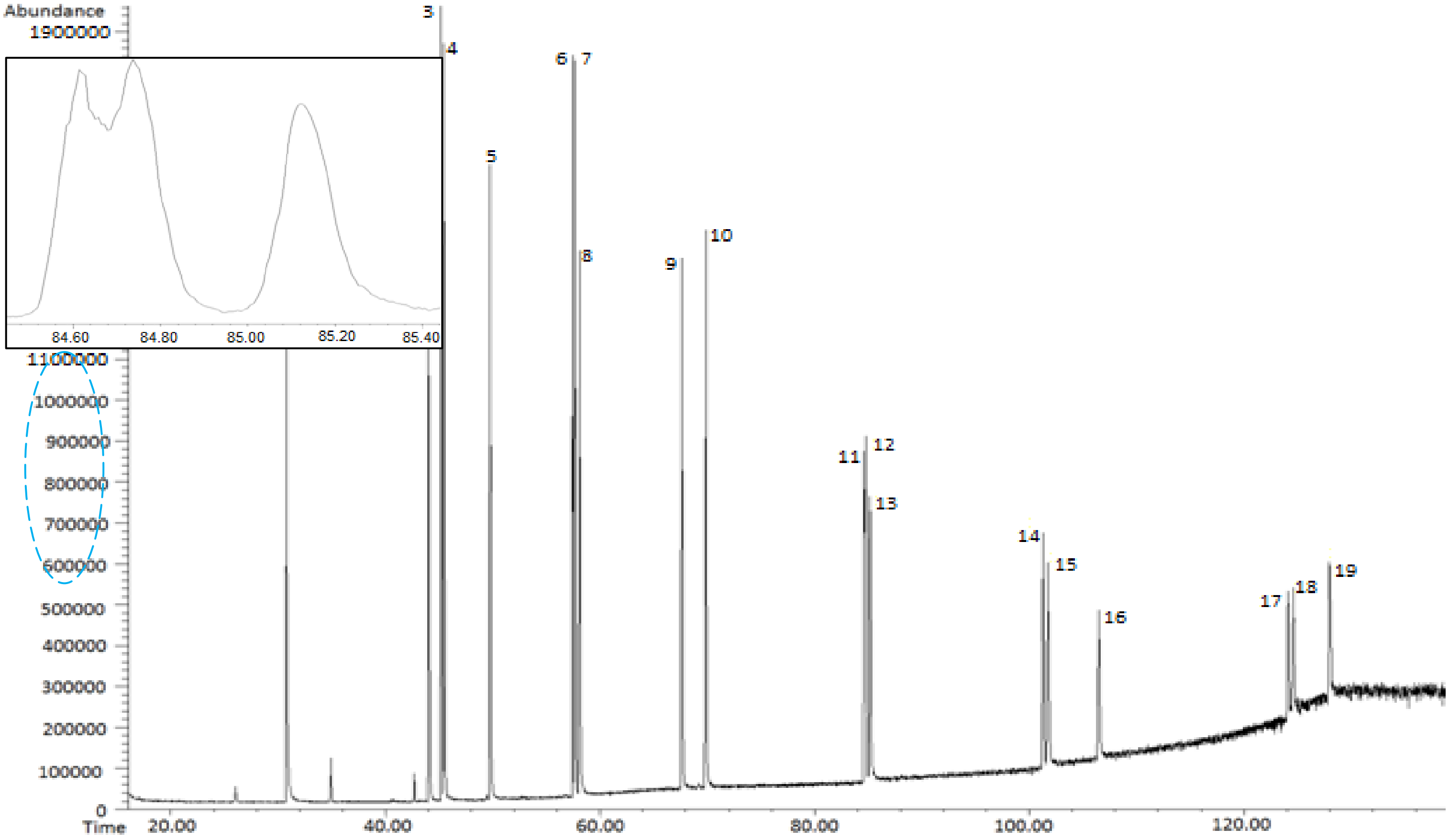


Figure 3.6 (cont.): Chromatogram in TIC mode of a standard mixture of PAHs under investigation. (1) Naphthalene, (2) Acenaphthylene, (3) Acenaphthene-d$_{10}$ (IS), (4) Acenaphthene, (5) Fluorene, (6) Phenanthrene-d$_{10}$ (IS), (7) Phenanthrene, (8) Anthracene, (9) Fluoranthene, (10) Pyrene, (11) Benz[a]anthracene, (12) Chrysene-d$_{12}$ (IS), (13) Chrysene, (14) Benzo[b]fluoranthene, (15) Benzo[k]fluoranthene, (16) Benzo[a]pyrene, (17) Indeno[1,2,3-c,d]anthracene, (18) Dibenzo[a,h]anthracene, (19) Benzo[g,h,i]perylene

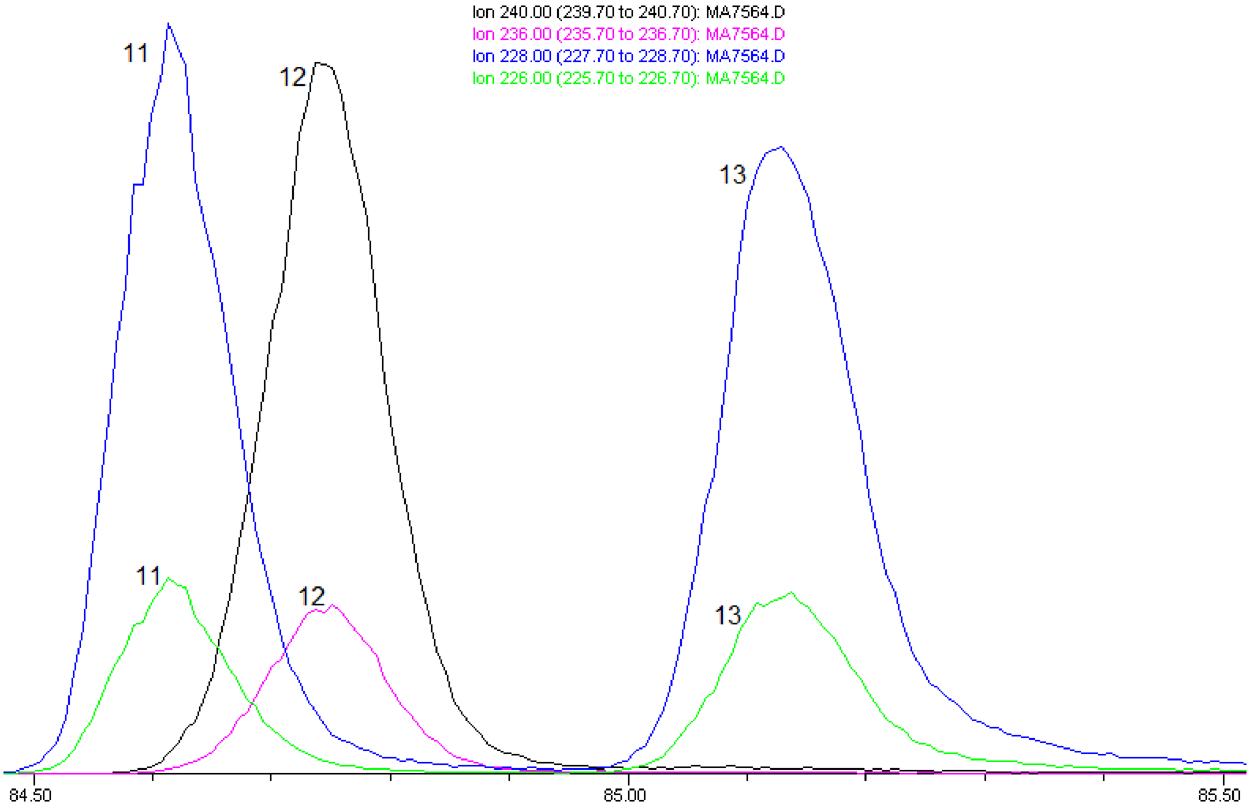


Figure 3.7: Chromatogram showing all mass fragments merged for peaks 11, 12 and 13 for PAH standard solution. (11) benz[a]anthracene, (12) chrysene-d_{12}, (13) chrysene

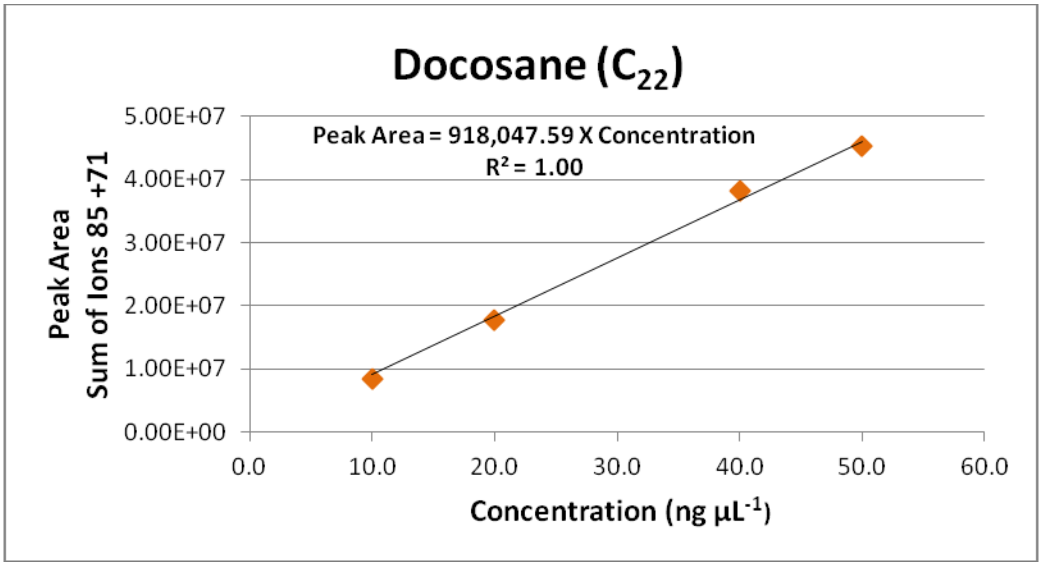


Figure 3.8: An example of calibration curve obtained for docosane ($C_{22}H_{46}$) using specific mass fragment ions

3.4. Description of Conducted Tests

This section covers how the blank values were determined followed by the recovery tests conducted to test the efficiency of extraction with Soxhlet and ultrasonic procedures.

3.4.1. Blank Determining Procedure

One clean Quartz filter and one XAD-4^{TM} coated quartz fiber filter were subjected to ultrasonic extraction procedure described in section 3.2.1. to test for the presence of the target PAHs and n-alkanes. In addition, two quartz filters and two XAD-4^{TM} coated quartz fiber filters were subjected to Soxhlet extraction procedure described in section 3.2.2. In addition, to check for the presence of target compounds in the glass thimble used in Soxhlet extraction, a few extractions were carried out with no filters in the thimble. Prior to extraction, all the blank filters were treated the same way as other spiked and atmospheric filters in terms of their handling. The blank masses were determined using the calibration slopes and the sum of the peak areas for the same mass to charge ratios as used in the calibration. The masses of blank filter values for each compound was used for blank subtraction of all spiked filters and atmospheric samples analysed.

3.4.2. Recovery Tests for the Extraction of Quartz and XAD-4^{TM}coated Filters

In order to calculate recoveries from the spiked filters extracted with ultrasonic extraction, the volume of the completely processed extract was estimated using Eppendorf pipette prior to GC analysis. However, in case of the spiked filters extracted with Soxhlet extraction, the volume of the completely processed extract ($V_{VS,\,f}$) was determined using hexamethylbenzene as a volumetric standard (VS), which was spiked into the final extract prior to GC analysis. The final volume of the processed extract was calculated by:

$$(1) \qquad V_{VS,\,f} = C_{VS,\,i} \times \frac{V_{VS,\,i}}{C_{VS,\,f}}$$

Where,
$V_{VS,\,f}$: Final volume of processed extract (µL)
$C_{VS,\,i}$: Concentration of hexamethylbenzene in spiked solution (ng µL^{-1})
$V_{VS,\,i}$: Volume of hexamethylbenzene spiked in to sample, prior to GC-MS analysis (µL)
$C_{VS,\,f}$: Measured concentration of hexamethylbenzene [Area (AU) / Response (AU µL ng^{-1})]

From the PAHs and n-alkanes initially spiked on the filter, expected masses were calculated as follows:

$$(2) \qquad m_{spiked} = C_{spiked,\,i} \times V_{spiked,\,i}$$

Where,
m_{spiked} : Mass of compound expected (ng)
$C_{spiked,\,i}$: Initial concentration of target compound (ng µL^{-1})
$V_{spiked,\,i}$: Initial volume spiked on the filter (µL)

The actual mass recovered of the PAHs and n-alkanes in the filter extract, after being subjected to the extraction process was calculated by:

$$(3) \qquad m_{target\ compound} = C_{GC} \times V_{VS,f}$$

Where,
$m_{target\ compound}$: Mass of compound recovered (ng)
C_{GC} : Concentration of target compound measured by GC-MS (ng µL^{-1})
$Vvs,_{f}$: Final volume of processed extract estimated or determined using hexamethylbenzene as VS (µL)

The recovery yields of target compounds ($R_{target\ compound}$) or internal standard (R_{IS}) were then calculated by:

$$(4) \qquad R_{target\ compound} = \frac{m_{target\ compound}}{m_{spiked}} \times 100\%$$

3.4.3. Determination of Concentrations from Atmospheric Filters

In order to calculate concentrations of each target compound collected on a XAD coated filter with ambient PM sampled on it, first the final volume of the extract, $V_{Vs,\,f}$, the recovery of the internal standards, R_{IS} , and the mass of each target compound obtained, $m_{target\ compound}$, were calculated as shown in section 3.4.2. Then, the atmospheric concentrations of each compound were calculated by:

$$(5) \qquad C = \frac{m_{target\ compound} - Blank}{R_{IS} \times V_{air}} \times 100\%$$

Where,
C: Atmospheric concentration of a compound (ng m^{-3})
$m_{\text{target compound}}$: Mass of compound recovered (ng)
Blank: Filter blank value (ng)
R_{IS}: Recovery of the internal standard (%)
V_{air}: Total sampled volume of air (m^3)

4. RESULTS AND DISCUSSION

This section presents the results obtained from various tests conducted and results from ambient measurements, all of which are followed by a discussion.

4.1. Blank Values

Table 4.1 presents the blank values for one quartz filter and one XAD-4^{TM} coated filter extracted using ultrasonic procedure for each compound of interest. A blank subtraction was performed for mass determination of compounds measured in spiked and atmospheric filter extracts. Since only one blank test was conducted for each filter type, more blank tests are necessary in order to check for variability in the blank values. In that case, the average of filter blank measurements needs to be used for blank correction and the uncertainty (standard deviation) of the blank would determine the detection limit for each compound of interest. As observed from Table 4.1, the blank values for two filter types are in low pg m^{-3} range for the PAHs, which are well below the concentration range expected for these compounds in atmospheric samples (refer to Table 2.1 in Section 2.1).

Table 4.1 shows somewhat higher blank values for phenanthrene. For XAD-4^{TM} coated filter, this can be due to possible interference from aromatic impurities present in XAD-4 coating. Phenanthrene is a known impurity in the manufacture of polystyrene-divinylbenzene polymeric resin such as XAD-4 (Lane, 1996). However, if atmospheric concentration of phenanthrene well below

0.1 ng m^{-3} is observed, a more extensive pre-cleaning of the resin beads may be necessary to prepare a more effective adsorbent for future use.

Table 4.1: Blank values for one quartz filter and one XAD-4™ coated filter using ultrasonic extraction procedure. The calculation of blanks as atmospheric concentrations are based on sampled air volume of 1627m^3

Compound	Blank Mass for XAD-4™ coated filter (ng)	High-Volume Blank for XAD-4™ coated filter (ng m^{-3})	Blank Mass for Quartz fiber filter (ng)	High-Volume Blank for quartz filter (ng m^{-3})
PAHs				
Naphthalene	1.1	0.0007	1.3	0.0008
Acenaphthylene	0.4	0.0002	0.2	0.0001
Acenaphthene	1.2	0.0007	1	0.0006
Fluorene	0.3	0.0002	0.6	0.0004
Phenanthrene	5.4	0.003	2.6	0.002
Anthracene	0.7	0.0004	0.2	0.0001
Fluoranthene	0.8	0.0005	0.8	0.0005
Pyrene	0.7	0.0004	1.1	0.0007
Benz[a]anthracene	0.3	0.0002	0.1	0.00006
Chrysene	0.1	0.00006	0.1	0.00006
Benzo[b]fluoranthene	0.4	0.0002	0.1	0.00006
Benzo[k]fluoranthene	0.5	0.0003	0.1	0.00006
Benzo[a]pyrene	1.1	0.0007	0.3	0.0002
Indeno[1,2,3-c,d]pyrene	0.3	0.0002	0.1	0.00006
Dibenz[a,h]anthracene	0.3	0.0002	0.2	0.0001
Benzo[g,h,i]perylene	0.3	0.0002	0.1	0.00006
n-Alkanes				
C_{13}	5.7	0.004	4.4	0.003
C_{14}	31.3	0.02	10.2	0.006
C_{15}	55.1	0.03	20.0	0.01
C_{16}	26.6	0.02	26.1	0.02
C_{17}	37.1	0.02	40.2	0.02
C_{18}	67.3	0.04	40.3	0.02
C_{19}	58.1	0.04	41.1	0.03
C_{20}	45.5	0.03	85.6	0.05
C_{21}	75.2	0.05	84.3	0.05
C_{22}	77.5	0.05	74.8	0.05
C_{23}	83.8	0.05	84.7	0.05
C_{24}	88.2	0.05	86.1	0.05
C_{25}	87.2	0.05	85.9	0.05

In case of the n-alkanes under investigation, Table 4.1 shows that the blank values are in the high pg m^{-3} range for both coated and uncoated filters. However, the concentration range expected for n-alkanes in ambient air is much higher than the blanks observed (refer to Table 2.2 in Section 2.1). In general, atmospheric concentrations of n-alkanes are much higher than those of PAHs.

Two blank quartz filters and two XAD-4^{TM} coated filters were extracted using Soxhlet extraction procedure for each target compound, for which the results are presented in Table 4.2. Typically the detection limit is determined by the variability of the blank values (three times the standard deviation of the blank values). Since only two blanks were analysed for each filter type, the standard deviations (and the detection limits) were not calculated. For both coated and uncoated filters, Test 1 and Test 2 indicate that the blanks are in low pg m^{-3} range for the target PAHs, much below the concentration range expected for these PAHs in atmospheric samples.

Table 4.2: Blank values for two quartz filters and two XAD-4^{TM} coated filters using Soxhlet extraction procedure. The calculation of blanks as atmospheric concentrations are based on sampled air volume of 1627m^3

Compound	Blank Mass for XAD-4^{TM} coated filter (ng)		High-Volume Blank for XAD-4^{TM} coated filter (ng m^{-3})		Blank Mass for Quartz fiber filter (ng)		High-Volume Blank for quartz filter (ng m^{-3})	
PAH	**Test 1**	**Test 2**	**Test 1**	**Test 2**	**Test 1**	**Test 2**	**Test 1**	**Test 2**
Naphthalene	1.1	1.0	0.0007	0.0006	0.9	1.2	0.0006	0.0007
Acenaphthylene	0.2	0.9	0.0001	0.0005	0.7	0.3	0.0004	0.0002
Acenaphthene	1.0	1.3	0.0006	0.0008	0.7	1.2	0.0004	0.0007
Fluorene	0.5	0.9	0.0003	0.0006	1.5	1.4	0.0009	0.0009
Phenanthrene	6.4	7.1	0.004	0.004	1.4	1.9	0.0009	0.001
Anthracene	1.3	1.7	0.0008	0.001	1.5	1.8	0.0009	0.001
Fluoranthene	0.9	0.6	0.0006	0.0004	1.4	0.7	0.0009	0.0004
Pyrene	1.2	0.8	0.0007	0.0005	1.1	0.7	0.0007	0.0004
Benz[a]anthracene	0.2	0.2	0.0001	0.0001	0.1	0.1	0.00006	0.00006
Chrysene	0.1	0.2	0.00006	0.0001	0.1	0.1	0.00006	0.00006
Benzo[b]fluoranthene	0.7	0.3	0.0004	0.0002	0.6	0.6	0.0004	0.0004
Benzo[k]fluoranthene	0.5	0.4	0.0003	0.0002	0.8	0.7	0.0005	0.0004
Benzo[a]pyrene	1.5	0.8	0.0009	0.0005	1.3	0.7	0.0008	0.0004
Indeno[1,2,3-c,d]pyrene	0.3	0.1	0.0002	0.00006	0.5	0.2	0.0003	0.0001
Dibenz[a,h]anthracene	0.2	0.5	0.0001	0.0003	0.8	0.4	0.0005	0.0002
Benzo[g,h,i]perylene	0.4	0.2	0.0002	0.0001	0.2	0.3	0.0001	0.0002
n-Alkanes								
C_{13}	12.5	7.0	0.008	0.004	8.2	1.9	0.005	0.001
C_{14}	39.6	16.0	0.02	0.01	33.8	10.3	0.02	0.006
C_{15}	66.8	17.6	0.04	0.01	64.6	16.9	0.04	0.01
C_{16}	282.1	38.0	0.2	0.02	242.0	33.4	0.1	0.02
C_{17}	316.2	55.7	0.2	0.03	306.7	72.3	0.2	0.04
C_{18}	312.4	48.5	0.2	0.03	307.3	40.4	0.2	0.02
C_{19}	175.5	32.5	0.1	0.02	169.6	22.4	0.1	0.01
C_{20}	124.5	43.7	0.1	0.03	119.4	24.3	0.07	0.01

Table 4.2 (cont.):

C_{21}	112.8	62.3	0.1	0.04	101.3	35.9	0.06	0.02
C_{22}	141.8	80.3	0.1	0.05	133.1	89.0	0.08	0.05
C_{23}	171.5	163.4	0.1	0.1	154.3	211.6	0.09	0.1
C_{24}	282.8	272.4	0.2	0.2	270.8	252.9	0.2	0.2
C_{25}	689.4	684.8	0.4	0.4	668.7	643.7	0.4	0.4

For n-alkanes, the blank values seem to be variable from one test to another. Blank masses from coated and uncoated filter Test 1 are much higher for all n-alkanes when compared to those from Test 2. During the time when Test 1 (for each filter type) were conducted, the Soxhlet apparatus was relatively new and two spiked filter tests were carried out before doing these blank tests. It was suspected that there may be some contamination present in the Soxhlet apparatus itself especially from the glass thimble used, when it was shipped from the supplier. Moreover, the thimble, due to having a larger surface area, possibly retained some n-alkanes from previous spiked tests which were extracted out when quartz blank Test 1 and XAD blank Test 1 were carried out. It is noteworthy to mention that each time the Soxhlet apparatus was used, each part was rinsed three times with distilled water, acetone and acetonitrile. Table 4.3 summarises the tests performed with Soxhlet apparatus in order of their dates.

Table 4.3: Summary of tests conducted with the Soxhlet apparatus in order of their dates

Tests	**Date**
Quartz Recovery Test 1– Quartz filer spiked with 1 µg of PAHs and 4 µg of n-alkanes	January 9 2013
XAD Recovery Test 1 – XAD filer spiked with 1 µg of PAHs and 4 µg of n-alkanes	January 14 2013
Quartz Blank Test 1 – Blank quartz filter analysed	January 15 2013
XAD Blank Test 1- Blank XAD filter analysed	January 22 2013
Soxhlet Blank Test 1 – with no filter	January 24 2013
Soxhlet Blank Test 2 – with no filter*	February 20 2013
Quartz Recovery Test 2 – Quartz filter spiked with 1 µg of PAHs and 4 µg of n-alkanes	February 21 2013
Soxhlet Blank Test 3 – with no filter	February 27 2013
Quartz Blank Test 2 – Blank quartz filter analysed	February 28 2013
XAD Recovery Test 2 – XAD filer spiked with 1 µg of PAHs and 4 µg of n-alkanes	March 20 2013
XAD Blank Test 2 – Blank XAD filter analysed	March 21 2013

*Carried out after four complete Soxhlet extractions

In order to check for contamination present in the Soxhlet apparatus itself (including the glass thimble), blank extractions of the Soxhlet apparatus were carried out with no filter being placed in the thimble. The results of these tests are given in Table 4.4. The blank Soxhlet extraction Test 1 was conducted following two spiked tests and two blank tests (XAD blank Test 1 and quartz blank Test 1) [refer to table 4.2 and 4.3]. It should be noted that the Soxhlet blank values for Test 2 were obtained after performing four complete Soxhlet extractions with no filters. This was done in order to check if there was any reduction in the blank values after four consecutive complete extractions of the Soxhlet. Comparison between Test 1 and Test 2 shows that indeed the blank values decrease significantly after four complete extractions. This indicated that the Soxhlet apparatus was contaminated with n-alkanes, possibly from previous spiked filter extractions. Although four complete blank extractions of the Soxhlet apparatus between each spiked filter tests would be ideal in terms of achieving low blank values for n-alkanes, it is not practical to do so as this is a limited time project. Thus, it was decided that one blank Soxhlet extraction would be carried out between each spiked test. The third Soxhlet blank test (Test 3), which was done following a spiked test (quartz recovery Test 2), shows that the blanks increase slightly for the lighter n-alkanes. However, consistent high blank values observed for the heavy n-alkanes suggested that they seem to be retained more strongly, most likely by the glass thimble due its large surface area. This meant that, although one complete blank extraction of the Soxhlet apparatus between each spiked test may extract out most of the lighter n-alkanes, it may not be sufficient to extract out the heavy n-alkanes from the thimble and more extractions may be necessary. This was one of the potential limitations of using a glass thimble for Soxhlet extraction. Glass thimbles are expensive and therefore, it is not possible to replace them after each extraction. An alternative might be to test and potentially use other types of thimble such as cellulose or paper thimbles. Another alternative, although time consuming, would be to use longer time for blank soxhlet extractions.

Table 4.4: Blank values for three Soxhlet extractions

Compound	Blank Masses for Soxhlet extraction (ng)		
	Test 1	Test 2*	Test 3
C_{13}	3.5	3.0	2.8
C_{14}	8.1	4.4	4.6
C_{15}	12.6	5.5	6.6
C_{16}	23.2	6.7	7.6
C_{17}	50.7	13.1	17.9
C_{18}	25.2	11.8	13.3
C_{19}	37.7	8.0	16.6
C_{20}	63.0	13.8	32.2
C_{21}	85.3	15.6	62.6
C_{22}	152.8	24.3	142.5
C_{23}	172.8	16.2	182.5
C_{24}	250.1	18.1	262.9
C_{25}	347.4	23.9	677.0

*Carried out after four complete Soxhlet extractions

4.2. Internal Standard Selection and Recoveries

The criteria that must be met when selecting an internal standard (IS) are as follows: (1) it should behave similarly to the target compounds and (2) it must not be found in significant concentrations in the atmosphere. The internal standard mix chosen for analysis of the target PAHs comprised of acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} and the internal standard used for n-alkane analysis was nonadecane-d_{40} ($C_{19}D_{40}$). Deuterated internal standards were chosen due to their negligible concentrations in ambient air and their similar behaviour to the analytes under mass spectrometric conditions. Since they have almost identical chemical and physical properties to the analytes, losses during sample preparation affect the analyte to the same extent as the standard (Zschunke, 2000). In addition, different mass to charge ratios were chosen for the deuterated standard and thus, GC-MS allowed the signals of the fully deuterated internal standards to be distinguished from those due to the analytes even where complete resolution was not achievable.

In section 3.3, Figure 3.6 shows the chromatogram in TIC mode of a standard mixture of PAHs under investigation where it was observed that there was an overlap between benz(a)anthracene and one of the internal standards, chrysene-d_{12}. Since different mass fragments were chosen for each of these compounds, this was not a concern as those mass fragment peaks do not interfere with each other (refer to Figure 3.7 in Section 3.3).

Table 4.5 presents the recoveries of PAHs and n-alkanes obtained from two spiked XAD-4^{TM} coated filters and one quartz filter using the ultrasonic procedure. The recoveries were calculated as shown in section 3.4.2.

Table 4.5: Recoveries of spiked PAHs (1 µg) and n-alkanes (4 µg) for two XAD-4^{TM} coated filters and one quartz filter using ultrasonic procedure

Compound	**XAD-4^{TM} coated Filter Recovery (%)**		**Quartz Filter Recovery (%)**
PAH	**Test 1**	**Test 2**	**Test 1**
Naphthalene	37	27	38
Acenaphthylene	25	19	45
Acenaphthene	23	21	41
Fluorene	39	36	54
Phenanthrene	73	66	76
Anthracene	78	67	85
Fluoranthene	82	75	73
Pyrene	73	69	65
Benz[a]anthracene	97	92	83
Chrysene	89	86	75
Benzo[b]fluoranthene	70	74	61
Benzo[k]fluoranthene	45	46	65
Benzo[a]pyrene	70	65	67
Indeno[1,2,3-c,d]pyrene	70	72	71
Dibenz[a,h]anthracene	85	89	88
Benzo[g,h,i]perylene	65	65	69
n-Alkanes			
C_{13}	4	4	8
C_{14}	15	19	20
C_{15}	37	28	34
C_{16}	45	44	44
C_{17}	68	62	63
C_{18}	63	61	57
C_{19}	85	89	85
C_{20}	77	80	75
C_{21}	78	78	78
C_{22}	72	74	71
C_{23}	63	65	66
C_{24}	45	57	69
C_{25}	28	32	72

Somewhat low recoveries for few compounds (especially the volatile ones) may be explained by the fact that the ultrasonic procedure contains a number of steps with each one creating a potential loss of compounds. However, as seen from Table 4.5, the recoveries found from Test 1 and Test 2 for XAD-4^{TM} coated filters agree well with each other within experimental uncertainty.

In addition to ultrasonic extraction, a different extraction procedure – Soxhlet extraction was carried out for two spiked XAD-4^{TM} coated filters and two quartz filters to determine if there were any improvements in recoveries. It should be noted that one of the coated filters and one of the uncoated filters were also spiked with PAH and n-alkane internal standards to check for their recoveries. The results, given in Table 4.6, indicate that the recoveries improve for most PAHs with the exception of the ones with high volatility, which may be lost during solvent evaporation. It has been reported in literature that, the ultrasonic method, which involves ultrasonic agitation of particulates by means of a solvent, is less efficient than the Soxhlet method for PAH analysis. One reason might be due to the use of ultrasonic bath which may provide less intense extraction energy to disrupt and pulverise the matrix which is needed to increase analyte extractability (Webster, 2006). In addition, one study reported that the ultrasonic method is well suited for samples with higher PAH concentrations such as those obtained from sediments and may not be suitable for airborne particulate samples (Environment Australia, 1999). Thus, the Soxhlet procedure selected was a better choice, particularly for the PAHs. Soxhlet extraction, which is commonly used as a benchmark for total extractable organic residues, allows recovery of analytes from a permeable solid matrix as a solvent is continually evaporated from a flask and condensed in such a manner that it falls into and permeates the matrix, which itself is held in a permeable glass thimble in a siphonable chamber (Webster, 2006).

Table 4.6 shows that, for PAHs, the recoveries obtained from Test 1 and Test 2 for each filter type are similar and thus comparable within experimental uncertainty.

Table 4.6: Recoveries of spiked PAHs (1 µg) and n-alkanes (4 µg) for two XAD-4^{TM} coated filters and two quartz filters using Soxhlet extraction procedure

Compound	XAD-4^{TM} coated Filter Recovery (%)			Quartz Filter Recovery (%)		
PAH	**Test 1**	**Test 2***	**Test 2 Recovery Rel. To IS**	**Test 1**	**Test 2***	**Test 2 Recovery Rel. to IS**
Naphthalene	18	20	0.50	20	14	0.41
Acenaphthylene	32	33	0.83	35	32	0.94
Acenaphthene	48	38	0.95	36	34	1.00
Fluorene	57	51	0.77	44	49	0.75
Phenanthrene	73	69	1.05	65	59	0.91
Anthracene	61	67	1.02	63	69	1.06
Fluoranthene	70	80	0.83	84	85	0.83
Pyrene	97	93	0.97	95	98	0.96
benz(a)anthracene	92	95	0.99	92	97	0.95
Chrysene	94	93	0.97	98	95	0.93
benzo(b)fluoranthene	97	103	1.07	94	96	0.94
Benzo(k)fluoranthene	94	100	1.04	99	98	0.96
Benzo(a)pyrene	94	101	1.05	103	99	0.97
Indeno(1,2,3-c,d)pyrene	97	93	0.97	96	92	0.90
Dibenz(a,h)anthracene	99	102	1.06	98	97	0.95
Benzo(g,h,i)perylene	99	100	1.04	97	94	0.92
Acenaphthene-d_{10} (IS)	-	40	1.00	-	34	1.00
Phenanthrene-d_{10} (IS)	-	66	1.00	-	65	1.00
Chrysene-d_{12} (IS)	-	96	1.00	-	102	1.00
n-Alkanes						
C_{13}	15	10	0.11	13	16	0.18
C_{14}	29	13	0.15	32	19	0.22
C_{15}	43	26	0.30	52	34	0.39
C_{16}	65	33	0.38	71	45	0.51
C_{17}	87	53	0.61	92	61	0.69
C_{18}	101	65	0.75	110	70	0.80
C_{19}	108	84	0.97	114	85	0.97
C_{20}	112	75	0.86	119	74	0.84
C_{21}	114	73	0.84	115	78	0.89
C_{22}	112	79	0.91	108	72	0.82
C_{23}	90	66	0.76	88	61	0.69
C_{24}	76	48	0.55	81	68	0.77
C_{25}	54	26	0.30	89	75	0.85
$C_{19}D_{40}$ (IS)	-	87	1.00	-	88	1.00

*Only Test 2 for each filter type was spiked with internal standards

For n-alkanes, the recoveries obtained from Test 2 for both coated and uncoated filters were compared to the recoveries obtained from the ultrasonic procedure (Table 4.5). It was observed that both extraction methods yield similar recoveries. This suggested that the extraction efficiency for n-alkanes with ultrasonic procedure is similar to that with the Soxhlet method.

In Table 4.6, Test 1 for both filter types indicate somewhat higher recoveries of n-alkanes when compared to Test 2. However, it should be noted that, the recoveries obtained do have some uncertainty since only two tests were conducted for each filter type. One possible reason for higher recoveries obtained in Test 1 might be that the recoveries are biased due to using absolute calibration (and not relative to IS), which is used to determine the actual masses present on the spiked filters and subsequently the recoveries. Therefore, if the GC drifts or changes sensitivity, an incorrect response factor would result in inaccurate masses. In addition, in order to determine the concentration of the volumetric standard, a stable absolute calibration was necessary, which was a bit of a limitation. If the response was not stable, there were higher uncertainties in volume determination. As a result, an overestimation of the volume might have led to an overestimation of the recoveries.

For both ultrasonic and Soxhlet extraction process, it is observed that the recoveries are low for compounds with highest volatility. This may be due to losses during solvent evaporation since both ultrasonic and Soxhlet methods require significant volume reduction to concentrate the sample in the end.

Comparison between the coated and uncoated filters in Table 4.5 and Table 4.6 suggests that the XAD on the coated filters does not influence the extraction of the compounds. However, for the heaviest n-alkanes, the extraction yields appear to be low with the coated filters. This may be due to the high adsorbent nature of XAD-4, which may cause the filters to retain the compounds more strongly than quartz fibers, and so the amount that is extracted may be underestimated. In general, the larger the molecule, the stronger it is adsorbed on to the resin and as a consequence the efficiency of extraction might be low. The heavier PAHs, however, do not seem to follow this trend. The interaction between the rigid PAH molecules and adsorbent might be different compared to the n-alkanes with flexible chains. During the analytical procedure, the extraction time is likely the only time where the resin may have an impact on the recoveries obtained. The ultrasonic procedure used in this research consisted of four extraction steps in total (see section 3.2.1). Rosaline (a graduate student in Dr. Rudolph's group) tested the efficiency of extraction for nitrophenols using the same ultrasonic procedure, which showed that the first four extracts were able to extract majority of the compounds and less than 5% was found in the last two extracts. This, however, was not investigated for the n-alkanes or the PAHs. For the Soxhlet procedure, the extraction time may need to be increased to increase the efficiency of extraction for compounds that are likely to be strongly retained by XAD on the filters.

Table 4.6 presents recoveries of spiked PAHs and n-alkanes relative to the recovery of the internal standards (IS). It should be noted that the recovery for the IS acenaphthene-d_{10} was used for the correction of the compounds: naphthalene, acenaphthylene and acenaphthene and the IS phenanthrene-d_{10} was used for the correction of the compounds: fluorene, phenanthrene and anthracene. For correction of the remaining PAHs, chrysene-d_{12} was used as the IS. The ratios of recoveries relative to the internal standards were close to 1, which confirms that the IS selected were a suitable choice. Naphthalene was the only PAH with recovery ratio significantly lower than 1. The higher vapour pressure of naphthalene makes it inappropriate to use the chosen IS since this underestimates the loss due to evaporation of naphthalene. In future, an alternative can be to use naphthalene-d_8 as the IS to accurately correct for naphthalene.

For n-alkanes, the recovery ratios relative to the IS nonadecane-d_{40} are not constant. N-alkanes lighter than nonadecane-d_{40} have recovery ratios much below 1 which may be due to their higher vapour pressures and thus potential losses. Again, for the heavier n-alkanes, the recovery ratios are much lower than 1, which may be due to potential losses of these compounds as they are possibly retained more strongly by XAD coating or the glass thimble. Consequently the results for these n-alkanes determined by using the IS may be systematically biased towards lower values.

4.3. Ambient Measurements

In addition to the filters subjected to recovery tests and blank tests, two XAD-4™ coated filters were sampled, extracted with Soxhlet extraction procedure and finally analyzed with GC-MS. The concentrations are presented in Table 4.7.

Table 4.7: Concentrations in ng m^{-3} obtained from two XAD filters sampled at York University

Compound	Sampling Time (hours)	X040313A* (ng m^{-3})	X120313A* (ng m^{-3})
PAHs			
Naphthalene	24	23.02	14.62
Acenaphthylene	24	1.75	1.30
Acenaphthene	24	2.36	1.27
Fluorene	24	3.45	4.15
Phenanthrene	24	5.90	7.70
Anthracene	24	0.09	0.09
Fluoranthene	24	0.64	0.96
Pyrene	24	0.39	0.31
Benz[a]anthracene	24	0.03	0.02
Chrysene	24	0.06	0.08
Benzo[b]fluoranthene	24	0.07	0.08
Benzo[k]fluoranthene	24	0.07	0.08
Benzo[a]pyrene	24	0.03	0.04
Indeno[1,2,3-c,d]pyrene	24	0.03	0.03
Dibenz[a,h]anthracene	24	0.04	0.02
Benzo[g,h,i]perylene	24	0.02	0.02
$\sum_{16}$ PAH		38.0	30.8
n-Alkanes			
C_{13}	24	1.85	1.70
C_{14}	24	1.20	1.29
C_{15}	24	1.91	1.54
C_{16}	24	2.70	2.05
C_{17}	24	2.87	2.39
C_{18}	24	4.55	4.81
C_{19}	24	5.47	5.6
C_{20}	24	6.22	6.31
C_{21}	24	7.28	7.23
C_{22}	24	7.15	7.19
C_{23}	24	5.15	5.21
C_{24}	24	4.45	4.48
C_{25}	24	3.29	3.03
$\sum$ n-alkane		54.1	52.8
CPI		1.1	1.0

*Note: Sampled are labelled as follows. X: 8” x 10” XAD coated filter. Numbers: date/month/year of first day of sampling. A: denotes one of the two high-volume samplers used.

For individual samples, the recovery of the IS (specific to the compound) was used as obtained for specific sample in order to correct for potential losses during the extraction process. The recoveries of the IS obtained in case of the two atmospheric filters, as shown in Table 4.8, were similar to those obtained from the spiked filter tests (refer to Table 4.6 in Section 4.2).

Table 4.8: Internal standard recoveries for atmospheric filters X040313A and X120313A

Internal Standard	Recovery (%)	
	X040313A	X120313A
Acenaphthene-d_{10}	37	36
Phenanthrene-d_{10}	62	61
Chrysene-d_{12}	101	94
$C_{19}D_{40}$	83	85

Comparison between Table 4.7 and Table 2.1 (in section 2.1) shows that the ambient concentrations of the volatile PAHs obtained for the two XAD coated filters are consistent with those reported by Cotham and Bidleman (1995), who measured the ambient PAH concentrations at a rural site in Green Bay, USA. In this research project, the two ambient samples were collected on the roof of Petrie Science and Engineering Building at York University, which is located in a mixed industrial-residential area at the northern edge of Toronto about 15 km from the downtown business area and the shore of Lake Ontario. However, the concentrations obtained for the low volatile PAHs are observed to be slightly low compared to those reported by Cotham and Bidleman. Moreover, the ambient PAH concentrations measured in this present study were considerably lower than those reported for different urban sites in other studies. Higher ambient PAH concentrations measured in those urban areas may be attributed to the differences in PAH sources.

As seen from Table 4.7, the major fraction of the vapour and particle phase PAHs was naphthalene. Although naphthalene was identified in the atmospheric filters, it could not be accurately quantified due to not using the right IS at the time of these experiments to correct for its losses due to evaporation. Using Acenaphthene-d_{10} as the IS for naphthalene may underestimate the amounts that were truly captured by the coated filters.

Measured total (gas + particle) PAH concentrations in this study were 38.0 and 30.8 ng m^{-3} for filters X040313A and X120313A, respectively. These values are within the range of previously reported values in other urban and industrial sites around the world (Table 4.9). As seen from Table 4.7, in addition to naphthalene, phenanthrene and fluorene were present in significant levels in ambient samples compared to the other PAHs. For ambient filter X040313A, phenanthrene and fluorene accounted for 16% and 9% of $\sum_{16}$ PAH concentration, respectively, while for filter 120313A, they were 25% and 13%.

Table 4.9: Total PAH concentrations $\sum_{n}$ PAH in ng m^{-3} measured around the world

Location	Number of PAHs included in $\sum$ PAH, n	Industrial (ng m^{-3})	Urban (ng m^{-3})	Sub-urban (ng m^{-3})	Industrial-residential (ng m^{-3})	Rural (ng m^{-3})
Chicago, USA[a]	13		351.8			
Rome, Italy[b]	12		162.4			
London, UK[c]	11		160.6			
Seoul, Korea[d]	13		67.3			
Athens, Greece[e]	10	15.4				
Fuji, Japan[f]	13	46				
Baltimore, USA[g]	13		24			
Green Bay, USA[h]	13					14.4
Izmir, Turkey[i]	14			36		
Toronto, Canada[j]	16				34.4	

a. Odabasi et al., 1999 (Summer-Fall, 1995) b. Possanzini et al., 2003 (Annual average, 2002-03)
c. Halsall et al., 1994 (Annual average, 1992) d. Park et al., 2002 (Annual average, 1998-99)
e. Mandalakis et al., 2002 (Summer, 2000) f. Ohura et al., 2004 (Summer & Winter, 2004) g. Dachs et al., 2000 (Summer & Winter, 1997) h. Cotham and Bidleman, 1995 (Winter 1988) i. Esen et al., 2008 (Annual average, 2004-05) j. This study, 2013 (Early Spring, 2013)

For n-alkanes, Table 4.7 shows that the ambient concentrations obtained using two coated filters were lower compared to those reported in some studies (refer to Table 2.2 in Section 2.1). However, they were found to be similar to those reported by Mandalakis et al. (2002), who measured the ambient n-alkane concentrations at an urban site in Athens, Greece. Figure 4.1 presents the ambient n-alkane concentrations obtained from this study during early spring (for two samples - X040313A and X120313A) and from other urban sites in Guangzhou, China and Athens, Greece during summer.

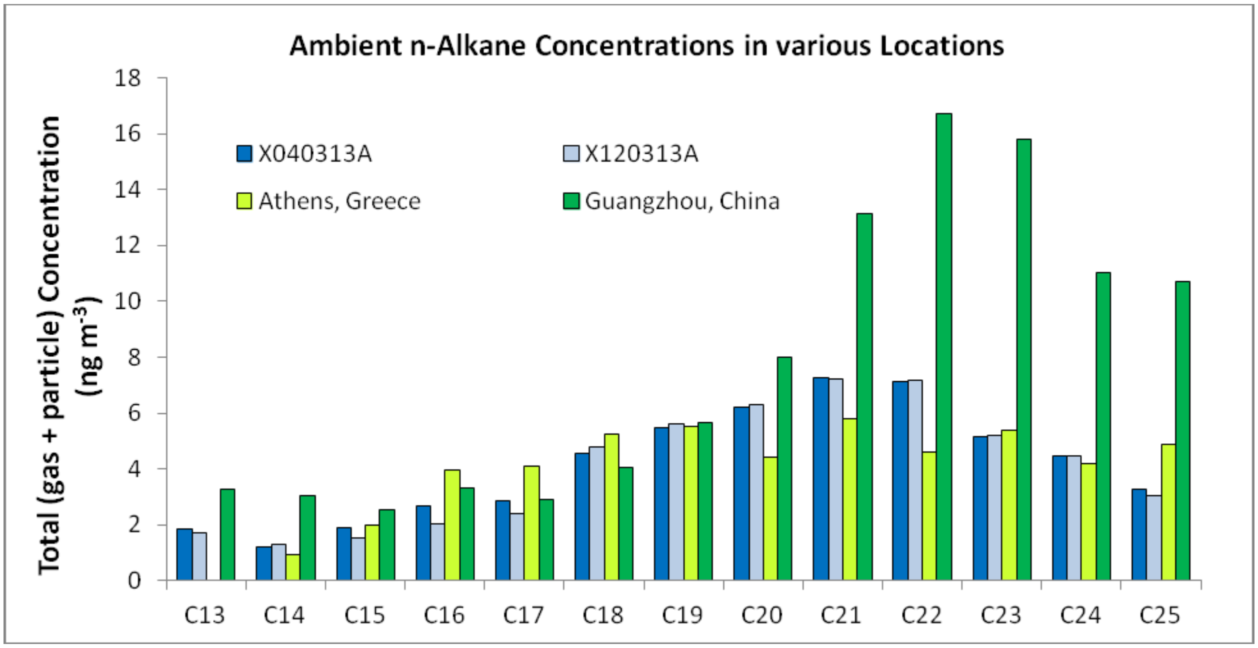


Figure 4.1: Ambient total (gas + particle) n-alkane concentrations obtained from this study and two other locations

The volatile n-alkanes have higher vapour pressures and are susceptible to potential losses. As a result, using $C_{19}D_{40}$ as the IS may result in some uncertainties in the recovery correction for these compounds. For heavy n-alkanes, their recoveries might be biased towards lower values as they are possibly retained more strongly by XAD coating or the glass thimble. Although the presence of uncertainty in recoveries may be a source of error, high atmospheric variability between locations results in different ambient n-alkane concentrations in each location. In addition, it is noteworthy to mention that n-alkane (at least the lighter ones) emissions from vehicles especially passenger cars have been reduced significantly in the last decade due to the use of catalytic convertors and other environmental regulatory steps. Also, there have been serious efforts in the western world to reduce emissions from other industrial activities. Therefore, it may not be surprising that the ambient n-alkane concentrations obtained in this study are lower than those reported in studies that were done many years back.

In order to identify the source of n-alkanes in ambient air, carbon preference index (CPI) was calculated for the two ambient samples. CPI is the concentration ratio of the sum of odd carbon number n-alkanes to the sum of even carbon number n-alkanes across a specified carbon number range (Bray and Evans, 1961). It is recognized that carbon number profiles of n-alkanes derived from epicuticular waxes of terrestrial plants and other biogenic sources show high CPI values >1, with strong odd carbon number predominance while those derived from fossil fuel combustion and other anthropogenic activities are close to 1, with no carbon number predominance. The CPI values calculated for the two ambient samples were near 1, which indicated anthropogenic contribution to ambient air. This was expected as the two ambient measurements were conducted in early spring, when there is little or no plant life present.

It should be noted that, although ambient PAH and n-alkane concentrations for other cities around the world are compared to those obtained in this research project, it is based on a limited number of samples. In addition, no standard or systematic measurement methods have been used in most of the studies. Each study also has unique characteristics in terms of the sampling sites, varying sampling seasons and different methods of sample collection, all of which makes data comparison difficult.

5. CONCLUSION AND FUTURE WORK

Sampling and analysis method for collecting total amount of gas and particle n-alkanes and PAHs has been adapted and modified accordingly. Quartz fiber filters and those coated with XAD-4 resin yielded blank values in low pg m^{-3} range for PAHs and in high pg m^{-3} range for the n-alkanes, which were well below the expected range of concentrations for these target compounds. However, in order to determine the detection limit for each of these compounds, more blank tests need to be conducted in future. For the heavy n-alkanes, higher blanks were obtained with the Soxhlet extraction process, which might be due to stronger retention of these compounds to the glass thimble. As a result, it is important to do more blank tests in future to conclusively determine the origin of these blanks. It is also recommended to find a suitable time saving cleaning procedure for the Soxhlet apparatus (including the glass thimble) in order to effectively reduce contamination from it. A possible option of cleaning the glass thimble might be to bake it at 250°C.

In most cases, XAD-4™ coated filters yielded recoveries of spiked compounds similar to those obtained from uncoated filters, which suggest that the presence of XAD does not influence the ultrasonic or Soxhlet extraction of the target compounds. For both coated and uncoated filters, higher recoveries for PAHs were obtained with Soxhlet extraction method compared to the ultrasonic method, which was consistent with findings in the literature. However, both extraction methods yielded similar recoveries for n-alkanes. Since these findings are based on a limited set of data, it is recommended that more tests are conducted in future in order to be absolutely certain. One recommendation might be to increase the number of sonication and filtration steps as well as sonication times in case of the ultrasonic extraction method to check if the recoveries improve for the target compounds.

The IS mix selected for PAH analysis were suitable choice as the recovery ratios were close to 1 for most compounds. However, high vapour pressures of naphthalene and the light n-alkanes made it inappropriate to use IS acenaphthene-d_{10} and nonadecane-d_{40}, respectively, for recovery correction as they underestimated the losses due to evaporation of these compounds. In future, suitable IS standards have to be chosen for recovery correction of these specific compounds.

All the 16 PAHs that were under investigation were detected in ambient samples, with naphthalene, phenanthrene and fluorene being the most abundant compounds. To our knowledge, there are not many high-volume XAD-4™ coated filter sampling approaches for PAHs and n-alkanes reported in literature. An important implication of high volume sampling is that the sample masses obtained are high enough to be used for future stable carbon isotope ratio measurements for these compounds. In addition, the use of XAD coated filters provided the advantage of incorporating the adsorbent into the particle collecting medium, allowing the total gas and particle concentration to be obtained from only one extracted filter. This greatly reduced time and materials needed for extraction purposes.

For n-alkanes, the calculated CPI values were indicative of anthropogenic contribution. The concentrations of n-alkanes in air were found to be lower compared to those reported in literature for cities such as Prato and Oviedo and were similar to those reported in Athens. However, given these measurements were obtained only in the month of March, the results may not be representative of the annual cycle. In addition, a quantitative comparison with the available data is difficult due to the limited number of data collected as well as different sampling conditions. Thus, more ambient tests need to be conducted throughout the year, which may provide more information on ambient concentrations of the target compounds. It is also noteworthy to mention that, there were no tests conducted to check for sampling efficiency for PAHs and n-alkanes on XAD-4^{TM} coated filters. Thus, this should be a subject of further investigation in future studies.

In summary, the main goal of this project has been achieved, which was to adapt and modify an analytical method to determine the presence and concentrations of total gas and particle phase n-alkanes and PAHs in the atmosphere. Initially, one of the objectives was to determine the atmospheric distributions of n-alkanes and PAHs, but this could not be looked into due to time limitation. As a result, a subject of future studies is to conduct parallel sampling of coated and uncoated filters using two high volume air samplers, which in turn, will allow us to gain more insights into the distribution of these compounds in ambient air.

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