

**POLYCYCLIC AROMATIC COMPOUNDS  
IN WOOD SOOT EXTRACTS FROM HENAN, CHINA**

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## ABSTRACT

Polycyclic aromatic compounds (PAC) are organic compounds composed of two or more fused benzene rings. These compounds are ubiquitous in the environment and some are found to be mutagenic and carcinogenic. High rates of esophageal cancer in the Henan Province of China had led to the suspicion that PAC from domestic coal and wood combustion are the main cause. Extraction of PAC from wood soot was done with a Soxhlet apparatus using dichloromethane as the solvent and concentration of the solution using a Kuderna Danish apparatus. Analysis of the different PAC was performed by high performance liquid chromatography (HPLC) with diode-array ultraviolet-visible absorbance detection and by gas chromatography-mass spectrometry (GC/MS). HPLC retention time and UV absorbance spectral matches between sample components and reference standards present unequivocal identification of the PAC. Results showed that 84 compounds composed of oxygenated PAC, alkylated PAH, cyclopenta-fused PAH, and benzologues of pyrene, fluoranthene, and perylene were identified. There were a total of 35 compounds (3 oxygenated PAC, 5 methylated PAH and ethynyl-substituted PAH, 3 cyclopenta-fused PAH, and 24 benzologues of pyrene, fluoranthene, and perylene) that have never been reported before as products of wood combustion. Aromatic compounds detected in the GC/MS were 17 oxygenated, 14 methylated and ethynyl-substituted, and 8 nitrogen-substituted. Yields showed that 5- and 6-ring PAH dominate the wood soot extract. These groups represent the most carcinogenic and mutagenic PAH, specifically the C<sub>24</sub>H<sub>14</sub> group, and comprise 66% of the total amount of PAH contained in the soot. The PAH with the highest yield are benzo[*a*]pyrene, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene. The high yield and the large number of PAC present in the soot suggest that the PAC may be contributing factors in the high rate of esophageal cancer in Henan, China.

## CHAPTER 1. INTRODUCTION

### 1.1 Wood as a Fuel

Wood has long been used for a variety of purposes. It is used in the pulp and paper industry, construction and furniture industry, methanol production, and utilized as fuel for domestic heating and cooking. In rural areas where there is access to cheap fuel, wood provides the necessary energy in homes. It has been found that wood can provide about two-thirds the energy content of coal. The heating value of wood, ranging from 8780 to 9500 Btu/lb, depends on the composition (Tillman).

Wood is composed of three basic polymers: cellulose ( $C_6H_{10}O_5$ ) which is about 43%; lignin ( $C_9H_{10}O_3(OCH_3)_{0.9-1.7}$ ) which is about 22 - 29%; hemicelluloses such as xylan ( $C_5H_8O_4$ ) which is about 28 - 35%; and some extractives and minerals or ash (Tillman, Cheremisnoff). It is highly oxygenated and contains no sulfur so the problem of  $SO_2$  emission is eliminated. The proximate analysis of hard pine-wood shows: 82.2 wt% volatiles, 53.5 wt % elemental carbon, sulfur below 0.1 wt % and nitrogen 0.1 wt % (Kozinski). The typical ultimate analysis of a hardwood is 52 wt% C, 6.3 wt% H, 40.5 wt% O, 0.1 wt% N, and 1.0 wt % ash (Tillman). Softwoods contain 23 - 33% lignin while hardwoods have 16 - 25% lignin. Some examples of softwoods are pine, fir, larch and cedar. Hardwood examples are birch, elm, gum, and oak.

### 1.2 Wood Combustion

The process of wood combustion involves three steps: 1) water evaporation in which heat is required to evaporate the moisture in wood; 2) distillation and combustion of volatile organic matter with oxygen thereby producing heat; and 3) combustion of the fixed carbon at high temperature (Cheremisnoff). In the second step, the holocellulose (cellulose and hemicellulose) promotes the release of volatiles and lignin which primarily promotes char (Tillman).

One of the major problems with wood combustion is the occurrence of incomplete combustion. During incomplete combustion, gaseous pollutants such as CO, NO<sub>x</sub>, SO<sub>x</sub> and solid particulate matter are emitted (Zimmerman). More so, toxic polycyclic aromatic compounds (PAC) are released. It is detected in both the gaseous phase (smoke, particulate emission), the solid phase (soot, fly ash, tars, creosote), and in the condensable liquids.

A study has shown that during biomass (refers to wood, bagasse, agricultural residue, scrap wood, and the like) combustion in reductive atmosphere, PAC are released. The lower molecular weight polycyclic aromatic hydrocarbons (PAH), between 2 to 4 rings, composed 80-89% of the emissions. High levels of naphthalene, acenaphthylene, phenanthrene, fluoranthene, and pyrene are detected while heavy PAH such as benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, and dibenz[*a,h*]anthracene are released in low concentration (as cited by Conde, 2005a).

In pyrolysis, the smoke produced can be condensed. This produces a liquid that can be separated into two phases. One is an aqueous phase consisting of alcohols, ketones, and other low molecular weight volatile compounds. The other is an oily phase that contains moisture, wood creosote, and polymeric pitch (as cited by Pimenta). Studies show that creosote contains up to 85% of PAH (as cited by Ikarishi).

The amount and composition of PAC and particulate matter released during wood combustion is affected by several factors: type of appliance, burn rate, wood type, configuration, temperature, and moisture content of wood. Studies have shown that small residential wood stoves have higher emissions as compared to large-scale combustors.

Nielsen has observed that combustion in small wood stoves produced high levels of PAH emissions. It was estimated that about 10 - 30 mg of higher PAH are emitted during burning of 1 kg of virgin wood producing approximately 8 m<sup>3</sup> of flue gas per kg of fuel. “Lower quality” fuels

such as scrap wood and waste briquettes may even increase the emission levels ten times or more. In another study by Ramdahl (as cited by Freeman), total concentration of the 16 priority PAH was  $3000 \mu\text{g}/\text{m}^3$  and concentrations of  $60 \mu\text{g}/\text{m}^3$  for benzo[*a*]pyrene, a known carcinogen, have been measured in flue emissions from small residential stoves compared with ambient PAH concentrations which are usually of the order of a few nanograms/ $\text{m}^3$ . The Environmental Protection Agency (EPA) has identified 16 priority PAH as 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-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene, which are possibly carcinogenic (Jenkins 1996b).

The high emission in small wood stoves can be attributed to the fact that incomplete combustion often occurs. In batch-type combustion, wherein the fuel is added at a time, there is not enough mixing of air and combustible gas leading to incomplete combustion (as cited by Oraveinan). Sometimes, the combustion temperature is not high enough thereby promoting the formation of lower molecular weight PAH. However, comparing a wood stove with a fireplace, the high emissions in the wood stove can be attributed to the high temperature and long smoldering conditions. High temperature, greater than  $600^\circ\text{C}$ , favors the emission and formation of high molecular weight PAH (McDonald and Conde 2005a). On the other hand, large-scale combustion with a burning rate of hundreds kg/hr is better controlled, more complete, and results in lower formation of PAH than small-scale combustion such as domestic cook stoves (Oanh 1999).

Soot is a major carrier of PAC. A large variety of heavy PAH is adsorbed on the surface of soot particles. The term soot is referred to a carbonaceous solid produced during combustion when conditions are such as to allow gas-phase condensation reactions of the fuel and its

decomposition products to compete with further decomposition and oxidation. Presence of soot also represents fuel or energy loss. It is regarded as an environmental hazard as the size of the soot particle enables it to penetrate deep into the respiratory tract (as cited by Kozinski). As cited by Jonker, the undesirable effects of soot are as follows: a) strong sorption for PAH with high levels of toxicity, b) large production worldwide, c) strong optical absorption of solar radiation, thereby influencing our climate, acts as a scavenger of volatile pollutants, and as catalyst for various reactions while transported through the atmosphere, d) inert which makes the material a long-term sink of carbon but also an excellent sedimentary tracer of fires and fossil fuel use over geological time, and e) can be inhaled because of its size.

### **1.3 Polycyclic Aromatic Compounds**

As mentioned in the previous section, PAC are toxic substances released from combustion. PAC are organic compounds composed of two or more fused benzene rings. It can contain oxygen. On the otherhand, PAH refer to PAC that are composed of only carbon and hydrogen. PAH are classified as hydrophobic and relatively insoluble in water. They have high affinity for organic matter, therefore being easily adsorbed in solid particles such as soot, soil, sediment, food, and other materials (as cited by Liu).

Polycyclic aromatic hydrocarbons can exist in various isomeric forms. As the molecular weight of the polycyclic aromatic hydrocarbons increase, the larger the number of possible isomers are formed. Not all of the possible isomers have been studied and reported. The carcinogenicity and mutagenicity of each of the polycyclic aromatic hydrocarbons also vary from each isomer to the other. PAH may be classified based on the number of aromatic rings. The table on the following page (Table 1.1) shows the possible number of theoretical *cata*-condensed isomers as the aromatic rings is increased (as cited by Harvey). The isomers increase as the number of rings increases. Although only a small fraction of the isomers have been reported in

literature. This implies the difficulty of identifying possible PAH in a sample especially those of high molecular weight.

Table 1.1. Theoretical number of *cata*-condensed PAH isomers

Formula	No. of Rings	Theoretical Isomers
C <sub>10</sub> H <sub>8</sub> -C <sub>22</sub> H <sub>14</sub>	2-5	20
C <sub>26</sub> H <sub>16</sub>	6	37
C <sub>30</sub> H <sub>18</sub>	7	123
C <sub>34</sub> H <sub>20</sub>	8	>411
C <sub>38</sub> H <sub>22</sub>	9	>1,489
C <sub>42</sub> H <sub>24</sub>	10	>5,572
C <sub>46</sub> H <sub>26</sub> -C <sub>58</sub> H <sub>34</sub>	11-14	>1,600,000

PAC from solid fuel combustion can be formed from pyrolysis and pyrosynthesis. The former implies cracking of the organic compounds into smaller fragments in the absence of air at high temperatures, while the latter refers to the recombination of the unstable fragments into more stable PAC (Roth, Wornat 2001b, Kozinski). It has been observed that high rates of pyrolysis/pyrosynthesis resulted in faster rates of formation of PAC and an increase in their total concentrations (Kozinski).

PAC are ubiquitous compounds in the environment. Emission from combustion may be through two independent ways: a) gas or vapor phase (smoke) consisting of semi-volatile and volatile compounds directly from a combustion facility, and/or b) emitted with the solid or particulate phase (fly ash, soot) and then evaporated or dissipated into the environment as well (as cited by Liu, Khalili). Aside from anthropogenic sources, PAC are also produced from environmental occurrences such as volcanic eruption, forest fires, and the like (Harvey). So far, a number of studies have been focused on the anthropogenic sources of PAC. As product of incomplete combustion, they are commonly found in coal tars and petroleum residues (Harvey 2002, Schmidt, Grimmer 1983b, Wornat 1998,1999b, 2000, 2001b, Ledesma, Schubert, Wise 1988b, Marvin), wood emission and biomass combustion (Ramdahl 1982a, 1982b, 1983,

Kamens 1985, 1989, Pakdel, Fine 2001, 2002, 2004a, 2004b, Hays 2002, 2003, Pimenta, Tan, Gullett, Hedberg, Shauer, Khalili, Gachanja, Jenkins 1996a, Howsam 2000, Lee 2005, Handa, McDonald), contaminated soil (Pace, Čáslavský), and air, water and urban aerosols (Čáslavský, Allen), and carbon black (Simonsick, Peaden) just to name a few.

A lot of interest has been drawn in the study of PAC because of its mutagenic and carcinogenic effects (May). Dibenz[*a,h*]anthracene was the first chemically pure substance reported to induce cancer (as cited by Shou). For a number of years, benzo[*a*]pyrene has been found to be the most carcinogenic of all the PAH. In recent years, special focus is given to the higher molecular weight PAH of greater than 300. The higher molecular weight PAH with 5 or 6 rings causes the most severe carcinogenic effect (as cited by Conde, 2005a). According to Schmidt (1987), molecular weight of greater than 300 accounts for about 50% of the total carcinogenicity upon topical application to the skin of mice while benzo[*a*]pyrene caused only 10-11% of the tumor incidences.

Nevertheless, there are some problems associated with the study of the higher molecular weight PAH. Wise (1988a, 1993) and Allen have mentioned that PAH with molecular weight of 302 has received little attention because of a) low concentration in samples and not abundant in air and ranges from 0.01 - 1.0  $\mu\text{g/g}$ , b) large number of possible isomers and only some of the 65 isomers have been synthesized, c) limited availability of reference standards, and d) many of them co-elute from gas and liquid chromatography columns. Additionally, Peaden cited that low vapor pressure of higher molecular weight PAH makes it difficult to chromatograph and lower resolution obtainable from columns.

#### **1.4 Wood vs. Coal**

In many industrialized nations, coal is used for domestic heating and cooking. Coal combustion, just like wood combustion, poses a major environmental problem. The combustion

products of coal also release undesirable levels of toxic PAC. The PAC products in coal combustion are quite different compared to wood combustion. Coal contains amounts of sulfur and nitrogen which when burned produce levels of SO<sub>x</sub> and NO<sub>x</sub>. Aside from these, some of the PAC products of coal contain sulfur and nitrogen which are absent in products of wood combustion.

Indoor smoky coal emissions give the highest indoor concentrations of fine particles (< 10 µm) associated with high extractable organic mass, followed by wood emissions and smokeless coal emissions (Chuang 1992b). In a study by Oanh 1999, wood combustion produced the highest particulate matter emission (51 mg/kg) and highest amount of PAC in particulate matter, while coal briquette burning produced the lowest particulate matter (7 mg/kg) and lowest PAC in particulate matter phase. Comparing the PAC emissions from coal and wood, results show that wood and peat emitted higher amounts of PAC by energy unit than the bituminous coal (Mastral).

It was found that the ratio of benzo[*a*]pyrene in particulate matter was also highest for wood fuel which is 10.5 mg/g and 0.18 mg/g for coal briquettes. The emission factor of benzo[*a*]pyrene can exceed that from coal on an energy equivalent basis with a factor of 100 (as cited by Oanh, 1999). Also, residential wood combustion alone, was estimated to account for greater than 30% of anthropogenic PAC emission in eastern North America (as cited by Oanh 1999).

One study in wood combustion showed that the concentration of the 16 priority PAH, were 2.01 µg/m<sup>3</sup> measured over the cooking period of 45 - 60 min. The particulate emission factors ranged from 2.0 - 3.2 mg/kg of fuel burned (as cited by Venkataraman). Also, another study on wood waste combustion generated fly ash and soot with levels of benzo[*a*]pyrene in the range 51.7 - 329.1 mg/kg (Kakareka).

Wood combustion is indeed a major source of atmospheric pollutants. As many carcinogenic and mutagenic PAH are emitted, there is an increased risk that people exposed to these compounds are endangering their health.

### 1.5 Wood and Coal Usage in China

In developing countries like China, the use of solid fuels such as wood, biomass, and coal is prevalent specifically in rural areas. It was reported by Zhang and Smith (2005) that in 2003, about 80% of the energy consumed by rural households was in the form of solid biomass. Table 1.2 shows the use of biomass (includes wood) as fuel in cooking in four provinces in China in 2005 (Jin). It can be seen that 3 out of 4 provinces use biomass as the main cooking fuel. But only 2 of the 4 provinces have flues and only 1 that has it higher than the eave of the house. This somehow implies that most of the emissions are probably inhaled by the homeowners.

Table 1.2. Energy Technology in the Study Households (Number reported as % households)

<b>Main Cooking Fuel</b>	<b>Gansu</b>	<b>Guizhou</b>	<b>Inner Mongolia</b>	<b>Shaanxi</b>
Coal	1.6	81.4	8.0	48.2
Biomass (wood and crop residue)	98.4	17.9	91.7	51.8
Liquefied Petroleum Gas (LPG)	0	0.1	0.3	0
Biogas	0	0.6	0	0
<b>Commonly Used Cooking Stoves</b>				
Biomass stove	98.8	40.8	95.2	66.1
Coal Stove	2.7	75.5	44.0	57.1
Fire Pan	15.4	0.2	7.9	0.1
Open Fire	8.0	0.3	0.6	0.1
Other	0.1	0.6	1.1	0.1
<b>Ventilation Characteristics of Wood Stoves</b>				
With flue	96.7	30.3	97.1	11.6
Flue going out of the house	94.4	18.4	94.4	6.7
Flue higher than eave	22.8	8.6	82.6	6.1

### 1.6 Health Effects

The use of solid fuels for domestic heating and cooking has adverse effects on the health of an individual. According to Smith and Ezzati (as cited by Jin), more than 500,000 annual

deaths in 2000 in developing countries of the Western Pacific region, where 85% lives in China, has been caused by indoor air pollution. There are several factors that caused this: climate and geography, housing, fuels and stoves, cultural such as income, food type and food preparation.

In rural places of China, wood, coal, and other biomass are used for domestic cooking in unvented stoves (Zhang). The fumes that result from burning these types of fuel are typical products of wood and coal combustion, including soot particles. Since soot is suspended in the air and also forms deposits on the bottom of pots used for cooking (and possibly other surfaces), it is likely that inhabitants of the household were able to consume soot particles to some degree. According to Yasuhara, PAC are adsorbed on airborne particulate matter of a specific size, one that aids their penetration of the human respiratory system. Also, PAC are formed during incomplete combustion of hydrocarbon fuels and are precursors of soot (Yu). PAC growth is related to soot (Weilmunster) and at low temperature more soot is formed (as cited by Zimmermann).

In recent years there have been reports on the alarming rates of esophageal cancer in the Henan Province of China (as cited by Roth). Henan is the most populated province in China comprising around 97 million people (China Statistical Yearbook 2005). Its economy is dependent on agricultural products such as wheat, cotton, rice and maize. Henan is relatively a poor province.

Studies reveal that the ingestion of soot from unvented wood- and coal-burning stoves (as cited by Oanh 1999, Wornat 2001b), which contain PAC, could be a factor in this increased incidence of cancer. It has been found that the high lung cancer mortality in rural areas of China is related to the use of smoky coal for domestic heating or cooking (as cited by Oanh, 1999).

Specifically in the Linxian county of Henan, China, esophagectomies showed three striking findings: arteriosclerosis, myxoid degeneration of nerves, and anthracotic lymph nodes.

The latter was histologically similar to those seen in association with smoking or coal exposure (as cited by Roth). Based on the study, Linxian women have a higher rate of lymph node anthracosis than men. This mostly indicates that the cause is environmental pollution since smoking is done by men. Moreover, Linxian county is completely rural with no source of industrial pollution and no vehicle exhaust. Therefore the most likely source of environmental pollution has been the use of coal in homes for heating and cooking. In addition, high levels of benzo[*a*]pyrene has been found in their staple foods (as cited by Roth).

Not only coal combustion is accounted for this indoor pollution, but wood and biomass combustion should also be accounted. As seen in Table 1.2, biomass is the main cooking fuel than coal except for Guizhou. It has been shown that the use of biofuel such as wood, plants, and biomass results in high emission of PAC. This is attributed to the high volatile content which leads to a higher possibility of incomplete burning. In developing countries, 90% of the total fuel consumption is biofuel and 90% uses wood for cooking (as cited by Oanh 1999).

Perhaps one of the contributing factors of indoor pollution in domestic homes is poor kitchen ventilation specifically lack of properly designed exhaust. The situation is worsened by the use of low efficiency woodstoves and the type of fuel used (as cited by Oanh, 1999). In rural houses of developing countries, the PAH level was found to be in the range 100 - 10,000 ng/m<sup>3</sup> compared to just 20 ng/m<sup>3</sup> in traffic areas and 20 - 100 ng/m<sup>3</sup> in cigarette smoking areas (as cited by Oanh, 1999).

Other diseases related to prolonged exposure to indoor pollution targets the lungs which include rhinitis, faucitis, tonsillitis, pneumonia, and bronchitis. There have been studies that the best evidence for increased risk of chronic obstructive pulmonary diseases (COPD) in adult women comes from years of cooking on unvented stoves. It is also the cause for increased risk of acute lower respiratory infections in children under 5 yrs living in households

with use of biomass fuels, particularly when the cultural practice involves high exposure to infants (Zhang).

The adverse health effects are not only restricted in China, but it has affected people worldwide. The northeastern region of Iran, also, has a high rate of esophageal squamous cell carcinoma (ESCC). It has been suspected that PAC from unknown sources may be the main contributor causing the cancer (Kamangar). In Kenya, carcinoma of the nasopharynx has been reported to occur more commonly among populations where cooking is done in small, poorly, ventilated kitchens (as cited by Gachanja). Also, higher incidence of *cor pulmonale* leading to cardiac disease, of chronic obstructive lung disease and of bronchitis, in biofuel users in India, has been documented (as cited by Venkataraman). A documented list of health effects in wood combustion appears in Appendix A.

## **1.7 Goal**

At present, a lot of people are still dependent on wood for domestic heat and cooking. The incidence of lung related disease and early deaths are still alarming. A thorough identification and quantification of the PAC found in wood soot is necessary. The main objective of this study is to identify and quantify the polycyclic aromatic hydrocarbons in wood soot extracts from domestic-burning stoves in Henan Province of China with the use of high performance liquid chromatography with ultraviolet/visible light detection (HPLC/UV-vis) and gas chromatography- mass spectrometry (GC/MS). Carcinogenic and mutagenic PAC will also be listed.

## CHAPTER 2. PAC IN SOOT FORMATION

The mechanisms shown in this chapter represent the basic process in the formation and growth of different groups of PAC. The first one shows how oxygenated PAC are formed followed by the alkylated and cyclopenta-fused compounds. Lastly, the mechanisms show the growth of the large PAH.

Richter has reviewed the formation and growth of soot. He mentioned that the growth from small molecules like benzene to a larger PAH involves some addition of C<sub>2</sub>, C<sub>3</sub>, and other small PAH units to form PAH radicals and other reactions such as addition and recombination.

### 2.1 Oxygenated Compounds

The presence of oxygen in the environment promotes the formation of oxygenated PAC. It has been suggested that the formation of oxygenated PAC follows three mechanisms: a) oxidation and dehydration, b) oxidation and CO elimination, and c) radical addition, dehydration and oxidation (as cited by Sandrowitz).

The formation of naphthalene-1,8- dicarboxylic anhydride from acenaphthylene and 4-oxa-benzo[*cd*] pyrene-3,5-dione from cyclopenta[*cd*]pyrene follows mechanism (a) as proposed by Swallow (Sandrowitz). The OH radicals attack the ring structure forming an intermediate PAC then loses H<sub>2</sub>O to form the oxygenated PAC.

Mechanism (b) was suggested for the formation of 4H-cyclopenta[*def*] phenanthren-4-one from pyrene and cyclopenta[*def*]chrysene-4-one from benzo[*a*]pyrene (as cited by Sandrowitz). Finally, mechanism (c) has been suggested for the formation of benzanthrone from naphthalene radical and lignin radical. This mechanism has also been suggested for the formation of 6H-benzo[*cd*]pyren-6-one.

These PAC are thought to have been formed during the combustion process while the other oxygenated PAC identified were believed to have been formed post combustion

(Sandrowitz). This is the case for anthraquinone, phenalenone, and 9-fluorenone wherein oxidation (d) is the only process as there is not enough heat to break the C-C bonds. The methylene carbon in fluorene, for example, undergoes oxidation to produce a carbonyl group (Ledesma).

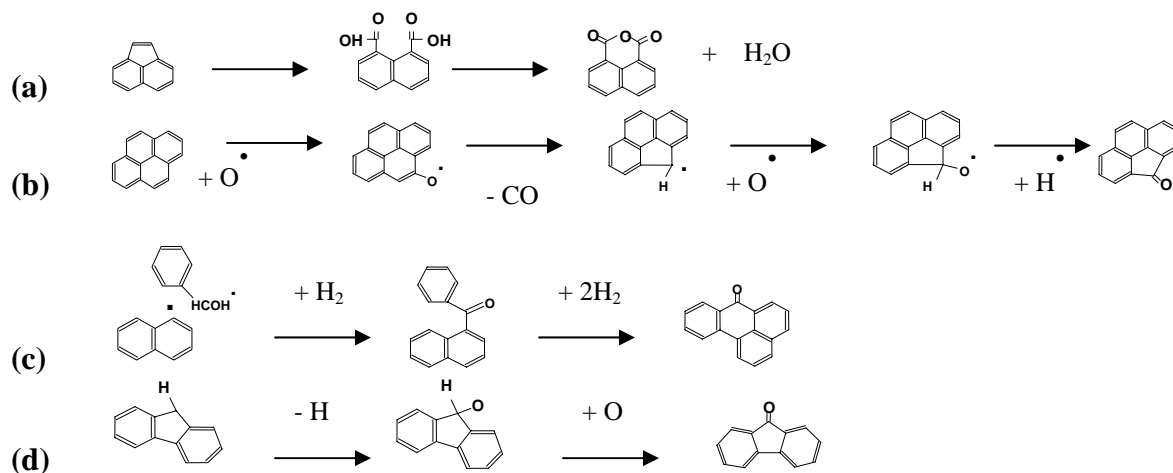


Figure 2.1 Proposed Mechanism for Oxygenated PAC

Another theory on the occurrence of oxygenated PAC, normally in the form of polycyclic aromatic ketones (PAK), is the oxidation of the highly reactive methylene PAH (as cited by Ramdahl 1983).

## 2.2 Methylated, Ethynyl-substituted and Cyclopenta-fused Compounds

It is suggested that the formation of cyclopenta-fused PAH is the addition of  $C_2H_2$  to aryl radicals (as cited by Marsh 2000b). This mechanism also yields ethynyl-substituted PAH. Mechanism (a) presents formation of 1-ethynyl-naphthalene from  $C_2H_2$  addition adjacent to a valley followed by H loss from the vinyl radical. The same mechanism is drawn for 1-ethynyl-naphthalene from a pyrene radical.

Acenaphthylene is formed using mechanism (b) with  $C_2H_2$  addition adjacent to a valley followed by cyclization and H loss. The same mechanism is followed by acephenanthrylene from phenanthrene, cyclopenta[*cd*]pyrene from pyrene, and cyclopenta[*bc*]coronene from

coronene. Acephenanthrylene could undergo this mechanism for the second time to form cyclopent[hi]acephenanthrylene. Mechanism (c) shows the  $C_2H_2$  addition without an adjacent valley leading to formation of 2-ethynynaphthalene. Finally, mechanism (d) shows the formation of corannulene from  $C_2$  addition to fluoranthene (Lafleur 1996a).

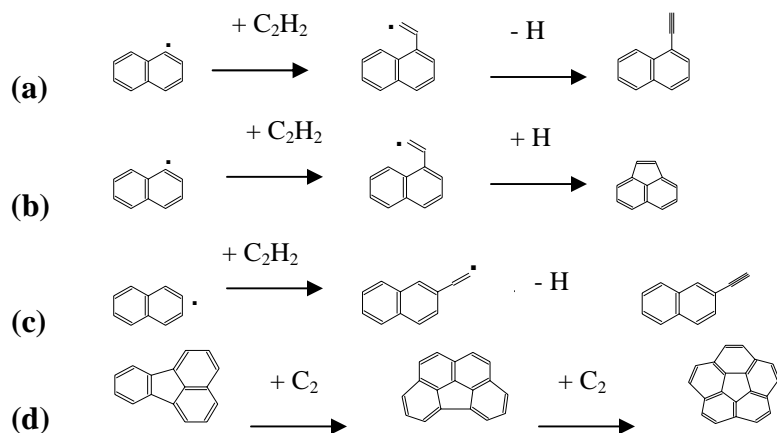


Figure 2.2. Formation Mechanism for Ethynyl-substituted and Cyclopenta-fused PAH.

Methylnaphthalenes, methylpyrenes and methylcoronenes are formed by the addition of  $CH_2$  in the base PAH. Whereas, 2,2'-binaphthalene may have been formed by the addition of two 2-methylnaphthalenes with a loss of  $C_2H_6$ .

### 2.3 High Molecular Weight PAH

The following mechanisms show annelation processes of smaller PAH to larger PAH. Mechanism (a) shows the addition of a  $C_1$  which is most likely a methyl group that cyclizes. This mechanism yields PAH such as methylene-benzo[*a*]pyrene which is not found in the wood soot extract sample. Mechanism (b) is the addition of a  $C_2$  fragment (acetylene, ethylene, two methyl groups or ethyl side chain) that yields a larger PAH or a cyclopenta-fused PAH as mentioned above. Mechanism (c) is the addition of a  $C_4H_2$  fragment (or butyl side chain). The  $C_{24}H_{14}$  group may be formed by two consecutive steps of this mechanism from either pyrene or fluoranthene. Mechanism (d) is the addition of a  $C_6H_2$  fragment (or a phenyl group) (Schmidt).

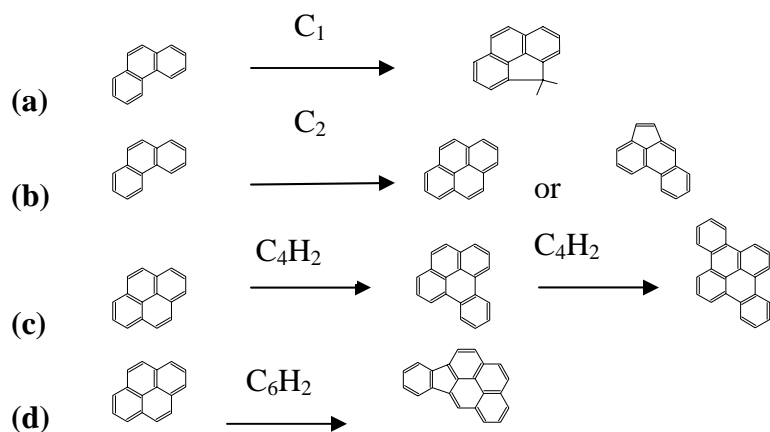


Figure 2.3. Annelation from Smaller PAH to Larger PAH

Fetzer (1996) presented a zigzag route for the formation of large PAH from smaller PAH which follow the addition of a  $C_2$  or  $C_4$ . The formation of naphtho[8,1,2-*abc*]coronene from dibenzo[*e,ghi*]perylene is also presented in Figure 2.5. It has formed isomeric intermediate PAH: benzo[*a*]coronene (a), benzo[*pqr*]naphtho[8,1,2-*bcd*] perylene (b), phenanthro[5,4,3,2-*efghi*]perylene (c). These 3 isomers have all been found in the wood soot extract sample.

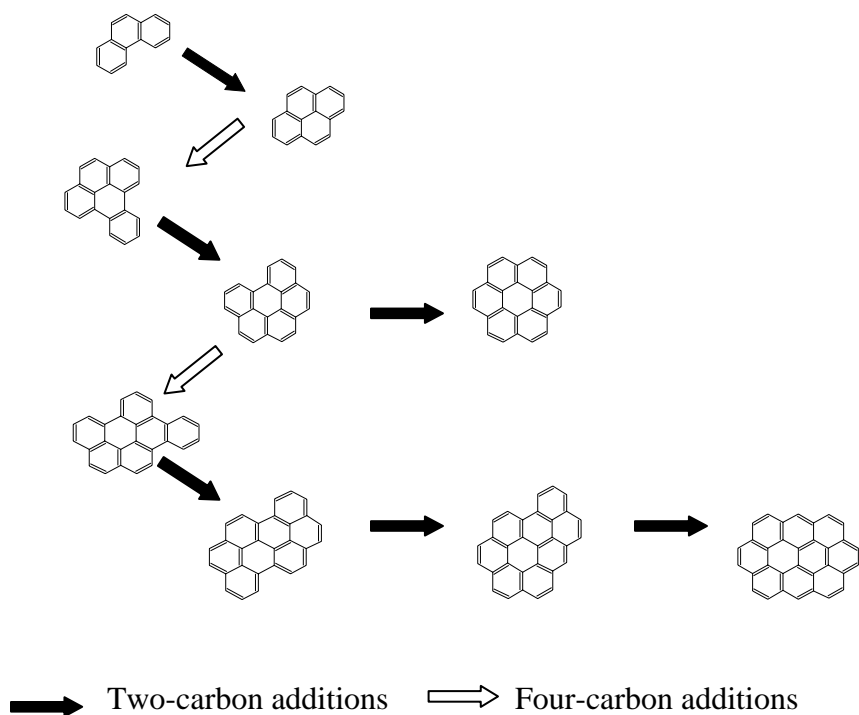


Figure 2.4. Naphthalene zigzag build-up route to large condensed PAH

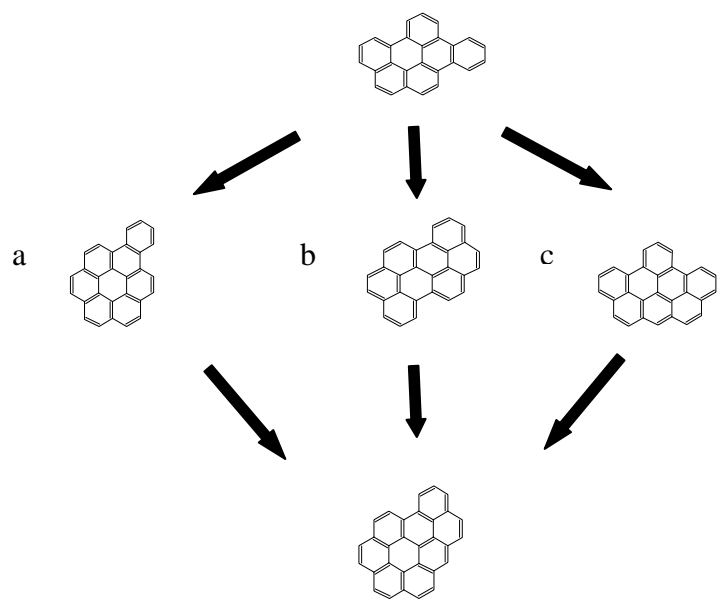


Figure 2.5. Formation of naphtho[8,1,2-*abc*]coronene

## CHAPTER 3. METHODOLOGY

There are a number of different methods or techniques to extract the PAC from solid samples like soot. Even the choice of the extracting solvent is critical in order to extract all the PAC contained in a sample. The analytical instrument is also important to separate the PAC compounds and be able to quantify each.

Extraction yield depends on the method and on the type of solvent used (Hollender). The International Conference Air Quality in Europe: Challenges for the 2000s has pointed out that the use of different sampling system and the analytical method results to about 40% discrepancy (as cited by Mastral).

This chapter presents the different extraction and analytical techniques used as well as the various solvents used for extraction. It is followed by the technique used in this research.

### 3.1 Extraction Techniques

The choice of an extraction method of PAC in soot or sediment is critical. The various extraction methods used are ultrasonic (Nielsen, Oanh 1999, Sandrowitz, Wornat 2001b, as cited by Bartle), Soxhlet (Kozinski, Chuang 1992a, Khalfi, Ramdahl 1983, Pace, Simonsick, Peaden, Jinno, Kamens 1985, 1989, Jenkins 1996a, Gachanja, Howsam 2000, 2001, Tan, Khalili, Hedberg, Conde 2005a, Wornat 1998, Bartle), Soxtec (Stutaro), thermal (Liu), accelerated solvent extraction (ASE) (Čáslavský) and supercritical fluid extraction (SFE) (Lang). Jonker has mentioned that for soot and sediment samples, it is best to avoid less rigorous techniques such as sonication or ultrasonic extraction. Of all the other extraction techniques available, Soxhlet extraction is the most frequently used since it is simple and inexpensive to use. It also gives the same recoveries as the other methods. Extraction time using the Soxhlet varies. According to Liu, 1 - 10 g of sample extracted with dichloromethane for 6 hours is appropriate to use which would give an average of PAC concentration of 0.6 ppm.

After Soxhlet extraction, it is necessary to concentrate the solution. Concentration provides a greater retention of the PAC in the solvent. Study has shown that solute is most easily lost in diluted solution than in concentrated solution because the thicker film provides better retention (as cited by Cheng). Moreover, it was observed that concentrating the solution to 3 ml resulted to 93% recoveries of the 16 priority PAH. Higher recoveries of PAH were observed if the final volume is greater than 3 ml (Cheng). Concentration can also be done with the use of a Kuderna-Danish evaporator after Soxhlet (Chuang 1992a). Other evaporation techniques involve free evaporation (N<sub>2</sub> blowdown) and rotary evaporation. The N<sub>2</sub> blowdown can be used after concentrating the solution in a Kuderna-Danish apparatus. It is specifically used for concentrating small volumes. However, this is recommended to be used for solutes of very low vapor pressure (Cheng).

### **3.2 Extraction Solvents**

It is necessary to use the best solvent to extract all the PAH in the sample. The choice of best solvent depends on the nature of sample. Studies have shown that different types of solvent are used to extract PAC. The commonly used solvents are: dichloromethane, toluene, hexane, cyclohexane, benzene, methanol, hexane/acetone, DCM/methanol, DCM/hexane, benzene/methanol, benzene/2-propanol (Jonker).

A study by Ikarishi on four different types of extracting solvent (dichloromethane, methanol, hexane, and saline) for PAC in creosote-treated wood was compared. Results showed that dichloromethane yields the highest concentration of PAC. Another study by Rey-Salgueiro on the extraction of PAC in ashes showed that dichloromethane resulted in PAC recoveries of higher than 80% (81 - 97%). The other solvents compared in decreasing order of recovery were: dichloromethane > ethyl acetate > ethyl acetate/hexane (3:7) > benzene > acetone/hexane (1:2) > hexane. Additionally, another solvation order presents THF > chlorobenzene > methylene

chloride > benzene > toluene > xylene >> isooctane (Pace). Methanol has also been found to extract more inorganic and organic material other than PAC (as cited by Bartle).

Solvents that were used for various samples are: dichloromethane for wood waste (Khalifi), coal fly ash (Liu), charcoal (Gachanja), wood (Zou), beech wood (Branca), coal and wood (Lee 2005), coal (Sandrowitz, Wornat 1998, 2000, 2001a, 2001b, Ledesma), indoor air particles (Chuang 1992a), wood bark (Stutaro), sediment (Brenner), soil (Čáslavský, Howsam 2001), wood and cereal straw (Ramdahl 1982a, 1983, Jenkins 1996a, 1996b), corn strover (Jenkins 1996a), leaves (Howsam 2000), creosote oil (Ikarishi), diesel exhaust particulate (Jinno), airborne soot particles (Kamens 1989), tree bark (Stutaro), particulate matter (Oanh 1999), dichloromethane/methanol for coal tar (Marvin), chlorobenzene for soil sample (Pace), methylene chloride for carbon black (Simonsick, Peaden), methylene chloride in n-pentane for crude coke oven tar (Wise 1988), toluene for wood emission particles (Gachanja) and pine needles (Lang), acetone/hexane for wood emission particle (Khalili), benzene/methanol for soil and sediments (as cited by Bartle), and cyclohexane for oils and fats (as cited by Bartle).

As each solvent provides advantages and disadvantages on the type of sample being extracted, no universal best solvent for soot can be defined (Jonker).

### **3.3 Analytical Techniques**

Since most of the PAH present in environmental samples, such as soot, are isomeric, it is necessary to use an analytical procedure that would give high separation and detection to be able to characterize each individual isomer. The different analytical techniques commonly used are gas chromatography (GC), gas chromatography-mass spectrometry (GS-MS) (Kozinski, Ramdahl 1982a, 1983, Lee 2005, Kamens 1985, 1989, Branca, Zou, Nielsen, Hays 2002, 2003, Howsam 2000, Stutaro, Lang, Fine 2001, 2002, 2004a, 2004b, Tan, Khalili, Pimenta, Ikarishi, Conde 2005a, Kakareka, Schauer, Pakdel, Hedberg, Jenkins 1996a, 1996b, Gullett, Simonsick),

liquid chromatography-mass spectrometry (LC-MS), liquid chromatography-fluorescence detection (LC-FD), high performance liquid chromatography with fluorescence detection (HPLC-FD) (Gachanja, Freeman, Oanh 1999, Pace, Peaden), high performance liquid chromatography- ultraviolet/visible light detection (HPLC-UV/vis) (Wornat, 1998, 1999a, 1999b, 2000, 2001a, 2001b, Khalfi, Oanh 2002, Sandrowitz, Marsh 2000c, 2000d, 2005, Ledesma), supercritical fluid chromatography, spectrometry of nuclear magnetic resonance (NMR), and use of laser mass such as laser detection-resonance enhanced multiphoton ionization-time-of-flight mass spectrometry (LD-REMPI-TOFMS) (Hauler, Čáslavský) and Fourier transform laser microprobe mass spectrometry (FT-LMMS) (Zimmermann, McDonald).

Of all the analytical techniques presented above, HPLC presents a reliable separation and detection method suitable for isomeric PAH. Studies have confirmed the advantages of HPLC. According to Yasuhara, HPLC using a reverse-phase column has been known to show high resolution for analysis of PAC. HPLC has been used in the study of high molecular weight PAH followed by ancillary measurements by UV/vis, fluorescence, or mass spectrometry (Pace). Also, since the UV spectrum depends so strongly on the electronic structure of the molecule, the location of substituent groups is detected (Marsh 2000c).

Compared with GC, HPLC provides better detection of isomeric PAH (Bartle). GC is unreliable in measuring individual isomers because of co-elution (Wise 1993). GC is only partially successful in separating numerous isomers and mass spectrometry provides little differentiation among the various isomers (Sauvain, Wise 1988).

The advantages of using the HPLC over GC includes: a) usage for low volatility PAH especially the large PAH, b) differentiates large number of isomers possible for the same molecular formulae, c) offers “full spectra” since isomeric PAH differ in their spectra (Fetzer, 1985) and the ultraviolet absorption and fluorescence spectroscopy provides sensitivity in the

detection of PAH (Bartle), d) provides selectivity since better interactions of the solute with both the stationary and mobile phases (Bartle), and e) provides useful fractionation technique for isolation of PAH (Bartle).

However, according to Bemgård, ordinary HPLC has poor separation efficiency compared with GC. Fetzer pointed out that photodiode array UV and fluorescence detectors or mass spectrometry must be used if complete structural assignments are to be made. The full-spectrum UV/vis absorbance or fluorescence detectors, such as those utilizing a photodiode array, are ideal for PAH detection since the spectrum of each PAH isomer has enough characteristic maxima and minima to form a unique pattern, allowing identification and differentiation from the other possible isomers according to Clar (Fetzer 1985). Moreover, liquid chromatography when coupled to a computerized photodiode array detector, can both separate these molecules and differentiate the isomeric types because each isomeric PAH has a unique characteristic UV/vis absorbance spectrum (Jinno).

Reversed-phase liquid chromatography also presents an advantage over the normal phase liquid chromatography since the latter separates PAH on the number of aromatic carbon atoms whereas the former on chemically bonded  $C_{18}$  phases provides excellent selectivity for the separation of isomeric PAH and alkyl-substituted PAH (May, Bartle). Reversed-phase liquid chromatography provides greater resolution of isomers than gas chromatography (Wise, 1988).

Based on the type of column used, the  $C_{18}$  bonded-phase packing is preferred because it achieves better separation of isomeric PAH than octadecyl bonded silicas (as cited by Pace).

### **3.4 Materials and Equipment**

Wood soot samples were taken from the bottom of woks used in cooking from different homes in Henan Province, China. These samples were placed in sealed bottles wrapped in aluminum foils. These were sent to us by the National Cancer Institute. The twelve samples were

labeled Yang 1, Yang 2, Yang 3, Yang 6, Yang 8, Yang 9, Yang 10, Sun 1, Sun 3, Sun 4, Sun 6, and Sun 8.

The wood soot samples were analyzed using the gas chromatograph-mass spectrometry (GC/MS) and high-performance liquid chromatograph with UV/visible light detection (HPLC-UV/vis).

The GC/MS model is Agilent 6890 Series GC with Agilent 5973N MSD. It is equipped with both the mass spectrometry detector (MSD) with HP-5MS column (30 m length; 0.25 mm I.D.; 0.25  $\mu\text{m}$  film; temperature of 60  $^{\circ}\text{C}$  to 325  $^{\circ}\text{C}$ ) and flame ionization detector (FID) with HP-5 column (30 m length; 0.32 mm I.D.; 0.25  $\mu\text{m}$  film; temperature of 60  $^{\circ}\text{C}$  to 325  $^{\circ}\text{C}$ ). The carrier gases are helium, air, and hydrogen.

The HPLC-UV/vis model is Hewlett-Packard Model 1050 Series chromatograph with Diode-Array UV detector. It is equipped with a reversed-phase Pinnacle II PAH column containing alkyl-bonded silica with high carbon load (5  $\mu\text{m}$  particle size; 250 x 4.6 mm; 110  $\text{\AA}$  pore size).

### **3.5 Extraction**

Wood soot samples were weighed at approximately 1 g. This was placed in a 3 mm Pyrex glass thimble and inserted in a Soxhlet apparatus. Extraction of PAC was done for 6 hours using 250 ml dichloromethane as the extracting solvent until the solvent becomes clear. The condenser was passed with ice cold water to ensure that all the PAC in the DCM will not evaporate since the solvent has a boiling temperature of 40  $^{\circ}\text{C}$ . The PAC/DCM solution was then concentrated in a Kuderna-Danish apparatus until 3 - 5 ml of mixture was left.

### **3.6 Analysis**

The concentrated sample of PAC in DCM was then prepared for analysis in the HPLC-UV/vis and the GC/MS.

Approximately 0.2 - 0.6 ml of the sample was added to 0.1 ml of dimethyl sulfoxide (DMSO) in a vial. The solution was evaporated by nitrogen to remove the DCM. The resulting sample (25  $\mu$ l) was then injected manually on the HPLC. The mobile phases used were 60:40 water/acetonitrile, acetonitrile, and DCM, programmed on different time intervals (ramped over 40 min to 100% ACN, then ramped over an additional 40 min to DCM). The flowrate was kept at 1.3 ml/min with temperature at 25 °C. The diode array detector measures the UV absorbance over broad band of 190 - 520 nm. The resulting chromatogram presents the different PAC that were then identified by matching the retention time and UV absorbance spectra with reference standards using the Chemstation program.

Reference standards are commercially available as well as specially synthesized. Standards specially synthesized by chemists are: 1-ethynynaphthalene and 2-ethynynaphthalene from Scott and Necula (Marsh 2000d), 4-oxa-benzo[*cd*]pyrene-3,5-dione, acephenanthrylene and cyclopent[*hi*]acephenanthrylene (Lafleur 1993), corannulene (as cited by Sandrowitz), cyclopenta[*cd*]pyrene (as cited by Sandrowitz, Wornat 2001a), dibenzo[*a,j*]coronene and indeno[1,2,3-*cd*]fluoranthene (Clar 1964b), naphtho[2,1-*a*]pyrene (Lafleur, Schmidt 2001), naphtho[1,2-*b*]fluoranthene (Schmidt 2001), naphtho[1,2-*a*]pyrene (Seidel 2005, Poster), cyclopenta[*bc*]coronene (as cited by Wornat 2001a), dibenzo[*cd,lm*]perylene (Fetzer 1984, 1988), benzo[*a*]coronene and benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene (Fetzer 1986, 1995, Lafleur 1996b, as cited by Wornat 2001a), naphtho[8,1,2-*abc*]coronene and ovalene (Fetzer 1984, Fetzer 1985b, Clar 1964b), phenanthro[5,4,3,2-*efghi*]perylene (Fetzer 1994a, Clar 1964b), dibenzo[*e,ghi*]perylene (Clar 1964b), dibenzo[*b,ghi*]perylene (Zander), and some of the UV absorbance spectra were found from literature: benzo[*a*]fluoranthene and phenanthro[2,3-*a*]pyrene (Clar, 1964a and as cited by Wornat 2001a).

For the GC/MS analysis, 20  $\mu$ l of the concentrated sample of PAC in DCM was injected in the MSD and FID ports. The injection temperature was at 40 °C. The MSD detects the unknown PAC with reference standard by matching the retention time and the mass spectra. The FID provides quantification of the unknown PAC. The GC was used to determine the lower molecular weight PAC and aromatics.

Reference standards at three different concentrations (16 priority PAH, anthraquinone, 9-fluorenone, dibenzofuran, coronene, and perylene) were injected in both the HPLC-UV/vis and the GC/MS. These provided the response factors needed for the calculation of the concentration and yield of each PAC. Since not all the identified PAC are commercially available, the response factors of the commercially available PAC were used depending on the structure closest to it.

## CHAPTER 4. RESULTS AND DISCUSSION

Results and discussion of the analysis from the HPLC-UV/vis and GC/MS are presented in this chapter. The HPLC chromatogram is shown with the different PAC identified. As some of these PAC have not been previously reported as products of wood combustion, the unequivocal identification, by matching the UV absorbance spectra of the reference standard with the sample, is presented. The PAC are discussed in separate groups (oxygenated, methylated, ethynyl-substituted and cyclopenta-fused, 2- to 6-ring PAH,  $C_{24}H_{14}$ , and high molecular weight PAH) for the HPLC results. The GC/MS results are discussed afterwards. The quantification of the PAH, which includes the GC/MS results, is presented together with the mutagenic and carcinogenic activity. The chapter concludes with the comparison between PAC from soot extracts of coal-burning stoves and wood-burning stoves in Henan, China.

### 4.1 HPLC Chromatogram

Figures 4.1 and 4.2 present the HPLC-UV/vis chromatogram of the wood soot extract of Yang 3 as this sample has the most PAC identified than the rest. The HPLC chromatograms of the other wood soot extract samples are presented in Appendix A. The chromatograms show a hump at ~ 45 minutes indicating a change in the mobile phase from ACN to DCM.

A total of 84 polycyclic aromatic compounds have been identified in all the twelve wood soot extracts. Since the samples are environmental and not products of controlled laboratory reactors, the 84 PAC are not always present in each of all the twelve wood soot extracts. The PAC identified can be grouped into: oxygenated, cyclopenta-fused, alkylated aromatics which include the methylated and ethynyl-substituted, 2- to 10-ring PAH with benzologues of anthracene, fluoranthene, pyrene, perylene, and coronene.

The following is the list of the identified PAC in their respective elution order: acenaphthenequinone, naphthalene-1,8- dicarboxylic anhydride, phenalenone, 2-naphthaldehyde,

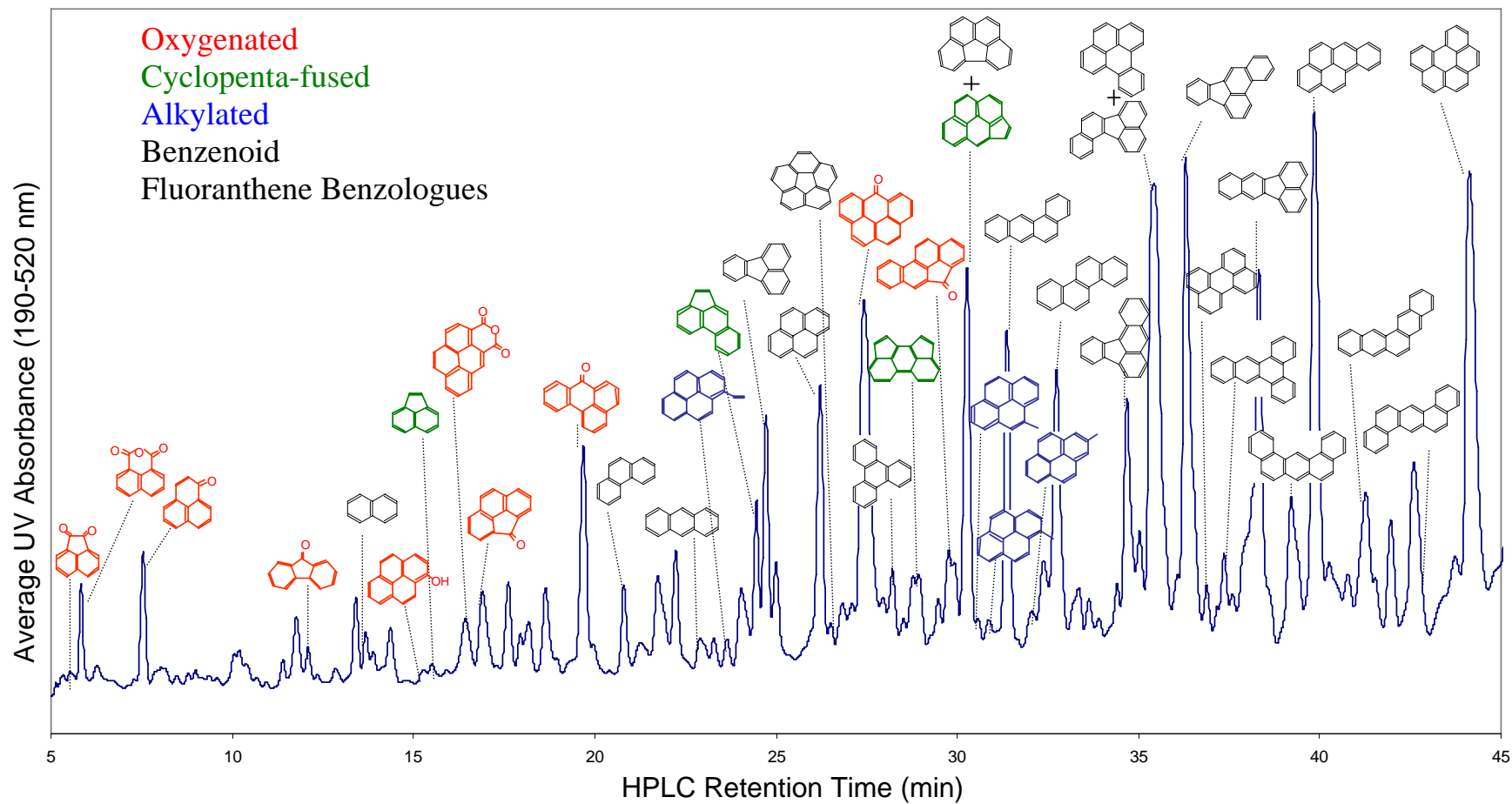


Figure 4.1 HPLC Chromatogram of Yang 3 from 5- 45 minutes.

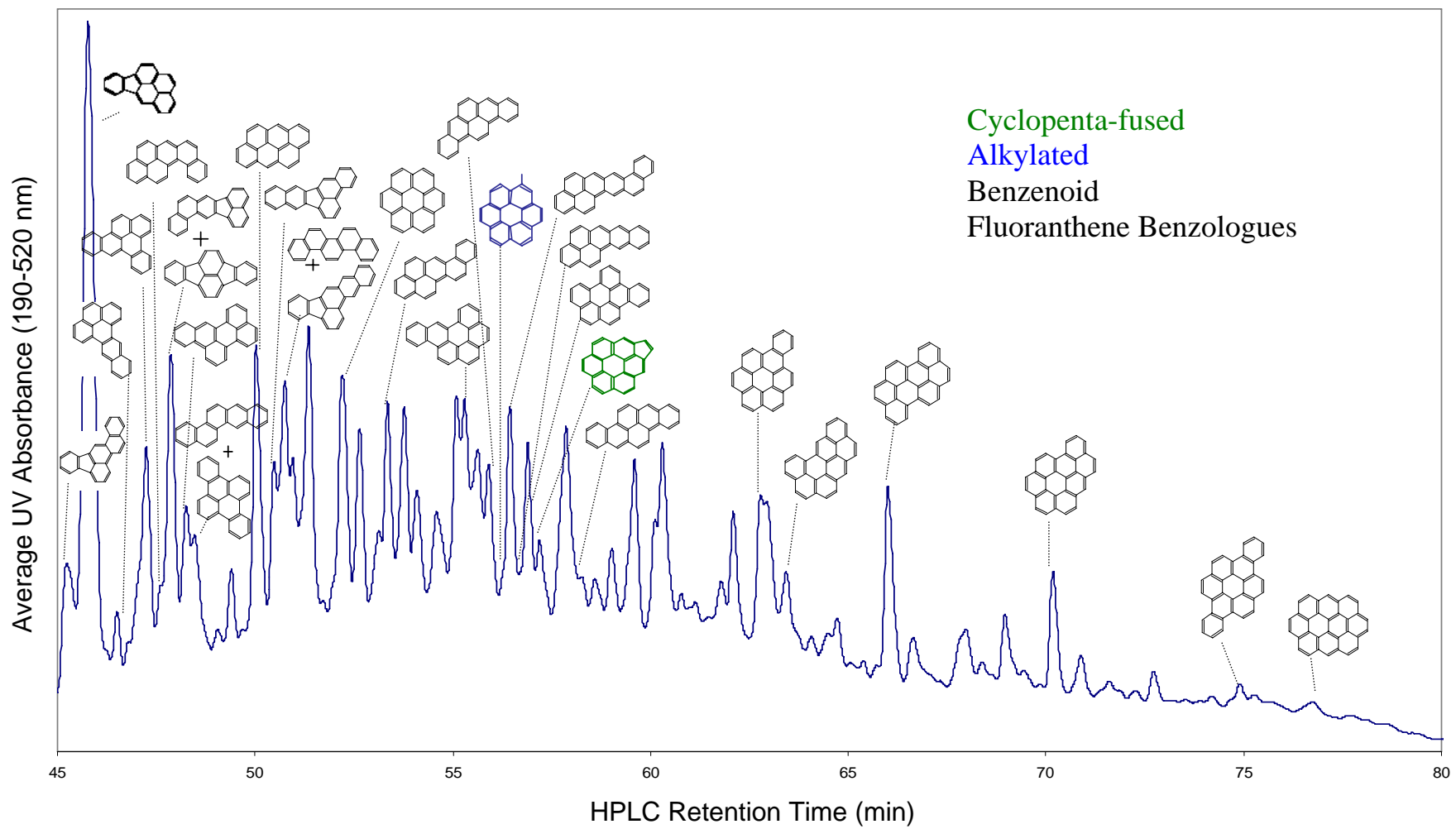


Figure 4.2 HPLC Chromatogram of Yang 3 from 45- 80 minutes.

1-naphthaldehyde, 9-fluorenone, anthraquinone, naphthalene, 1-hydroxypyrene, 1-ethylnaphthalene, acenaphthylene, 2-ethylnaphthalene, 4-oxa-benzo[*cd*]pyrene-3,5-dione, 4H-cyclopenta[*def*]phenanthren-4-one, 1-methylnaphthalene, 2-methylnaphthalene, dibenzofuran, benzanthrone, phenanthrene, anthracene, 1-ethynylpyrene, acephenanthrylene, fluoranthene, pyrene, corannulene, benzo[*c*]phenanthrene, 6H-benzo[*cd*]pyren-6-one, triphenylene, cyclopent[*hi*]acephenanthrylene, benzo[*a*]fluorene, cyclopenta[*def*]chrysene-4-one, benzo[*ghi*]fluoranthene co-elutes with cyclopenta[*cd*]pyrene, 4-methylpyrene, 1-methylpyrene, benz[*a*]anthracene, 2-methylpyrene, chrysene, 2,2'-binaphthalene, benzo[*a*]fluoranthene, benzo[*j*]fluoranthene co-elutes with benzo[*e*]pyrene, benzo[*b*]fluoranthene, perylene, dibenz[*a,c*]anthracene, benzo[*c*]chrysene, benzo[*k*]fluoranthene, dibenz[*a,j*]anthracene, benzo[*a*]pyrene, pentaphene, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene, naphtho[1,2-*b*]fluoranthene, indeno[1,2,3-*cd*]pyrene, naphtho[2,3-*e*]pyrene, dibenzo[*a,e*]pyrene, naphtho[1,2-*a*]pyrene, indeno[1,2,3-*cd*]fluoranthene co-elutes with naphtho[1,2-*k*]fluoranthene, benzo[*b*]perylene, dibenzo[*e,l*]pyrene co-elutes with benzo[*b*]chrysene, anthanthrene, naphtho[2,3-*b*]fluoranthene, dibenzo[*b,k*]fluoranthene co-elutes with picene, coronene, naphtho[2,1-*a*]pyrene, dibenzo[*b,ghi*]perylene, dibenzo[*a,i*]pyrene, methyl coronene, phenanthro[2,3-*a*]pyrene, naphtho[2,3-*a*]pyrene, dibenzo[*e,ghi*]perylene, cyclopenta[*b,c*]coronene, dibenzo[*a,h*]pyrene, benzo[*a*]coronene, phenanthro[5,4,3,2-*efghi*]perylene, benzo[*ghi*]naphtho[8,1,2-*bcd*]perylene, dibenzo[*cd,lm*]perylene, benzo[*pqr*]naphtho[8,1,2-*bcd*] perylene, naphtho[8,1,2-*abc*]coronene, dibenzo[*a,j*]coronene, and ovalene.

## 4.2 Oxygenated Compounds

Oxygenated polycyclic aromatic compounds are usual products of wood combustion. Most of them are polycyclic aromatic ketones (PAK). According to Kamens (1989), a significant

portion of the extractable organic matter from wood soot particles is composed of semi-polar and polar oxygenated compounds. There is special interest in this group of PAC since it is speculated that they pose some health risks. U.S. EPA has reported that oxygenated and hydroxylated PAC have been linked to endocrine disruption effects (Gullet).

Oxygenated compounds elute earlier than the other groups of PAH in the Pinnacle II column. With the use of the HPLC-UV/vis, 14 oxygenated PAC were identified in all the samples and for Yang 3, 10 oxygenated PAC were identified. Of these 14, 11 were previously reported as products of wood combustion. The table below lists several studies pertaining to the identification of the oxygenated PAC as products of wood combustion in the particle phase and/or gas phase.

Table 4.1. Oxygenated PAC as Products of Wood Combustion.

PAH Compound	Reference
2-Naphthaldehyde	wood emission particles (Ramdahl 1982a)
1-Naphthaldehyde	wood emission particles (Ramdahl 1982a)
Dibenzofuran	particles in duff <sup>1</sup> burning (Tan), wood pyrolysis liquid of <i>Eucalyptus grandis</i> (Pimenta), wood tar (Pakdel), eucalyptus emission (Ré-Poppi)
Naphthalene-1,8-dicarboxylic anhydride	Wood emission particles (Hays 2002, Kamens 1989)
Phenalenone	wood emission particles (Ramdahl 1983, Fine 2001, 2002, 2004a, 2004b, Schauer), wood smoke particle (Kamens 1985), wood tar (Pakdel), wood emission gas phase (Schauer), eucalyptus emission (Ré-Poppi)
9-Fluorenone	wood emission particles (Ramdahl 1982a, 1983, Hedberg, Schauer, Fine 2001, 2002, 2004a, 2004b, Hays 2002), wood emission gas phase (Schauer, Hays 2002), wood gasification (Pakdel), wood smoke particle (Kamens 1985, 1989), particles in duff burning (Tan)
Anthraquinone	wood smoke particle (Kamens 1985, 1989), wood combustion (Ramdahl 1982a), wood emission particles (Fine 2001, 2002, 2004a, 2004b)
4H-cyclopenta[def]phenanthren-4-one	wood combustion (Ramdahl 1982a), wood emission particles (Ramdahl 1983), wood smoke particle (Kamens 1989)
Benzanthrone	wood smoke particle (Kamens 1985, 1989), wood emission particles (Fine 2001, 2002, 2004a, 2004b, Schauer), wood tar (Pakdel), wood combustion (Ramdahl 1982a), wood emission gas phase (Schauer)
6H-benzo[cd]pyren-6-one	wood combustion (Ramdahl 1982a, 1983)

(Table continued)

Cyclopenta[def]chrysene-4-one	tentative structural assignment for MW 254 in wood emission particles (Ramdahl 1983)
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<sup>1</sup>Duff is the thick layer fermentation and humus matter consisting of needles, leaves, twigs, branches and barks in various stages of decay in natural forest floor (Tan)

The oxygenated PAC found in the wood soot sample that has never been reported before in any wood combustion products are acenaphthenequinone, 4-oxa-benzo[*cd*]pyren-3,5-dione, and 1-hydroxypyrene. Figures 4.3 to 4.5 present the UV absorbance spectra of the newly identified oxygenated PAC in the wood soot extracts.

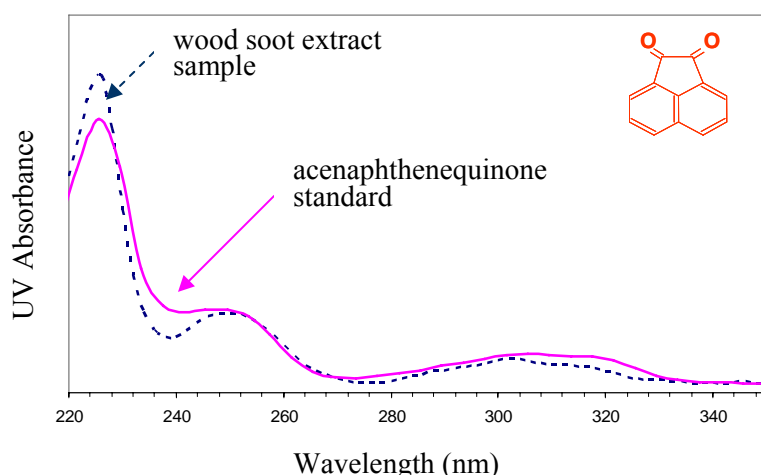


FIGURE 4.3. UV absorbance spectra of the reference standard of acenaphthenequinone and of the wood soot extract sample having the same HPLC retention time.

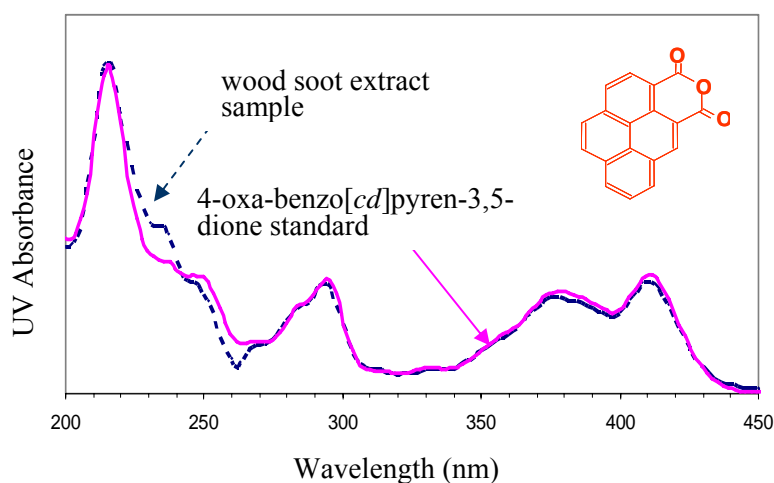


FIGURE 4.4. UV absorbance spectra of the reference standard of 4-oxa-benzo[*cd*]pyren-3,5-dione and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in an extra peak at 230-240 nm.

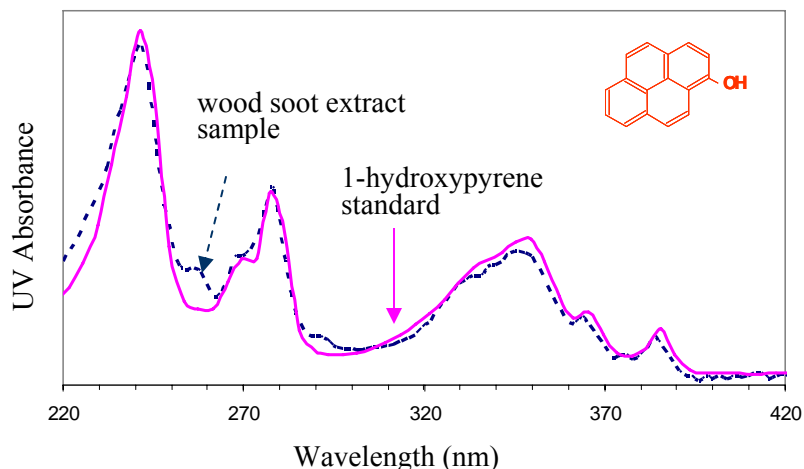


FIGURE 4.5. UV absorbance spectra of the reference standard of 1-hydroxypyrene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in an extra peak at 250-260 nm.

Fine (2004a) has found several oxygenated PAC in the gas phase such as xanthone, methylnaphthol, methoxynaphthol, 1,4-naphthenedione, and naphthols. These light aromatics were not found in all the wood soot samples. Because of their high volatility, it is possible that they have stayed in the gaseous form and did not condense in the soot. However, the GC/MS analysis shows trace amounts of xanthone and 1,4-naphthalendione.

Some of the peaks exhibit co-elution with an unidentified compound. The co-elution compound produces extra peak (or the absence of peak) or an augmentation of the peak height (Marsh 2005). This will be further illustrated in the section on  $C_{24}H_{14}$  PAH.

#### 4.3 Methylated, Ethynyl-substituted and Cyclopenta-fused PAH

According to Chuang (as cited by Oanh 2002) the presence of 3- to 4-ring alkylated PAH may be linked to the high incidence of lung cancer in Xuan Wei homes in China.

In the wood soot extract, there were 15 PAH identified in this group. In previous studies, some of these PAH have already been identified as products of wood combustion. In particular, 1-methylnaphthalene and 2-methylnaphthalene have been found in the gas phase of foliar fuels

(Hays 2002), tree bark (Stutaro), wood stove emissions (Alfheim), smoke emission from pine wood (McDonald, Conde 2005a), oak, pine, and eucalyptus gas phase emission (Schauer). Separately, 2-methylnaphthalene have been found in wood tar (Pakdel), agricultural woods and forest woods emissions (Jenkins 1996), eucalyptus emission (Ré-Poppi), and leaves of oak, ash, and hazel (Howsam 2000).

In some of the wood soot extract samples, the level of 1-methylnaphthalene is too high. This can be seen from the HPLC/UV-vis chromatograms of Sun 1, Sun 3, Sun 4, and Sun 8 (Appendix A). This can be due to a 1-methylnaphthalene standard that was calibrated in the HPLC/UV-vis by a researcher in our group using the said compound as a fuel. As a result, the standard may have interfered with the chromatogram of the wood soot extracts. All measures were taken to clean the column and the injector port but, still, a considerable amount of the standard was probably left and was later on detected in the HPLC/UV-vis. However, we are certain that other than the 1-methylnaphthalene, the identification and yield of the other PAC were not affected.

Moreover, Hedberg has found 1-methylpyrene, 2-methylpyrene, and 4-methylpyrene and methylchrysenes in birch wood emission. In the same way, Ramdahl (1982b), Alfheim, and Ré-Poppi have detected 1-methylpyrene, 2-methylpyrene, and 4-methylpyrene, methylphenanthrenes and methylantracenes in birch and spruce wood emission, wood stove emission, and eucalyptus emission respectively. Fine (2001, 20002, 2204a, 2004b) has found methylphenanthrenes and methylantracenes as combustion products of woods grown in the different parts of the United States. It is surprising that these were not found in the wood soot extract samples since some methylated compounds such as methylnaphthalenes, and methylpyrenes were identified. Some of these methylated compounds may have been too volatile to condense or they may have undergone dealkylation (as cited by Sandrowitz). As discussed in

the next section, chrysene, anthracene, and phenanthrene are not resistant to high temperature unlike naphthalene and pyrene. This could also be true for their methylated counterparts.

Cyclopenta-fused refers to PAH that contain 5-carbon rings at the periphery. There were studies that cyclopenta[*cd*]pyrene is at least as biologically active as benzo[*a*]pyrene (as cited by Marsh, 2000b). Also, according to Wornat, it was observed that an increase in combustion temperature causes an increase in soot yield and cyclopenta-fused group (Marsh, 2000b).

It is interesting to find ethynyl and cyclopenta-fused PAH in the wood soot extract since they play an important role in soot formation (Marsh 2000d). Ethynyl-PAH appears to be precursors to cyclopenta-fused PAH (as cited by Wornat 2000). The cyclopenta-fused PAHs are intermediate species in the growth of PAH because the five-membered rings may introduce curvature in otherwise planar *peri*-condensed PAH, eventually leading to C<sub>60</sub> and other fullerene molecules (as cited by Marsh 2000d).

There are 5 cyclopenta-fused PAH identified in the wood soot extract. Acenaphthylene, one of the 16 priority PAH set by EPA, is often found as a product of wood combustion. The other commonly found as a product of wood combustion is cyclopenta[*cd*]pyrene. It was reportedly been found in the particle phase of foliar fuel (Hays 2002), emission in hardwoods (Lee), oak, pine, and eucalyptus emission particle (Schauer), wood emission (Khalili, Tan, Alfheim) and birch wood emission (Hedberg).

Another PAH commonly found in wood combustion products is retene. Retene, 1-methyl-7-isopropylphenanthrene (MW 234, b.p. 390 °C), is formed from abietic acid and primaric acid found in pine wood resin (as cited by Benner). It is often reported as a product of wood combustion found in the emission particles particularly in softwoods like pinewood (Benner, Gullett), oak and eucalyptus (Schauer) since softwoods are highly resinous (Cheremisnoff). Due to this, retene has been used a trace compound for softwoods. However,

Hedberg questions the validity of retene as a trace compound since it has also been identified in some hardwoods. Fine (2001, 2002, 2004a, 2004b) has reported retene in hardwoods but in smaller amount (0.008 - 0.018 mg/g) compared to softwood (1.987 - 3.893 mg/g). The same result has been found by McDonald but retene in softwood is 4 times as those in hardwood. Lee also cited retene in hardwood emission. In the wood soot extract, not a single trace of retene was found in all the samples. It is possible that the wood used all came from hardwood. This is somewhat a relief since it has been found that retene is chronically toxic to developing stages of rainbow trout (as cited by Houvinen).

On the other hand, several studies show that hardwood emission rate is higher compared to softwood. McDonald reported that the highest volatile organic compounds emission rates of 21.8 g/kg of fuel are observed from burning hardwoods in wood stove and the lowest emission rates (5.8 g/kg) are from softwoods burned in fireplace. Also, comparing the composite emission rates from fireplace, hardwood is 5.7 g/kg while softwood is 5.1 g/kg. Although emission rate is not directly proportional to PAH emission rate, particulate emission also poses some health risk. Moreover, it is reported that the production of more complex PAH are expected to be enriched in the wood stove emission. Since hardwood emissions are the highest in wood stove then complex PAH formation is expected to be formed.

Figures 4.6 to 4.11 present the UV absorbance spectra of the 5 newly identified methylated and ethynyl-substituted PAH (1-ethynyl-naphthalene, 2-ethynyl-naphthalene, 1-ethynyl-pyrene, 2,2'-binaphthalene, and methyl coronene) and 3 newly identified cyclopenta-fused PAH (acephenanthrylene, cyclopent[hi]acephenanthrylene, and cyclopenta[b,c]coronene) in the wood soot extract as products of wood combustion. 2,2'-binaphthalene has been mentioned as a possible substance of eucalyptus combustion by Ré-Poppi using GC-MS. In this regard, it is still considered a newly identified compound as a product of wood combustion.

Methyl coronene and cyclopenta[*b,c*]coronene are discussed in the section on high molecular weight PAH.

It is surprising to find 1-ethylnaphthalene, 2-ethylnaphthalene and acenaphthylene, although not necessarily together in the wood soot sample. From the yield data in Appendix B, it can be seen that 1-ethylnaphthalene and 2-ethylnaphthalene does not appear together but acenaphthylene appears in both. Based from previous study of Marsh 2000b, it was observed that 1-ethylnaphthalene has never been found with 2-ethylnaphthalene and acenaphthylene. It was suggested that path (b) and (c) of Figure 2.2 is active and path (a) is inactive. It was illustrated that the only ethynyl-PAH observed was formed from C<sub>2</sub>H<sub>2</sub> addition that does not promote cyclization to a cyclopenta-fused ring. Otherwise, if the cyclopenta-fused product is present, the ethynyl-PAH is not. But in this case, the spectral match suggests strong evidence of the presence of 1-ethylnaphthalene together with the 2-ethylnaphthalene and acenaphthylene.

From a recent study on catechol pyrolysis in our group, Robles incorporated oxygen and a small amount of calcium carbonate. He found that it promoted the formation of 1-ethylnaphthalene with the presence of acenaphthylene. He, therefore, speculated that the calcium carbonate acted as a catalyst to increase the potential energy level of path (a) in Figure 2.2, thereby, enabling the formation of 1-ethylnaphthalene. If this is true, then the presence of 1-ethylnaphthalene in the wood soot extract is justified. Wood ash contains an appreciable amount of calcium carbonate and the quantity in hardwoods is three times higher than in softwoods (Utzinger). It is possible that a small amount of wood ash was accidentally included in the wood soot during sampling. This could also somehow add to the speculation that the wood used was hardwood.

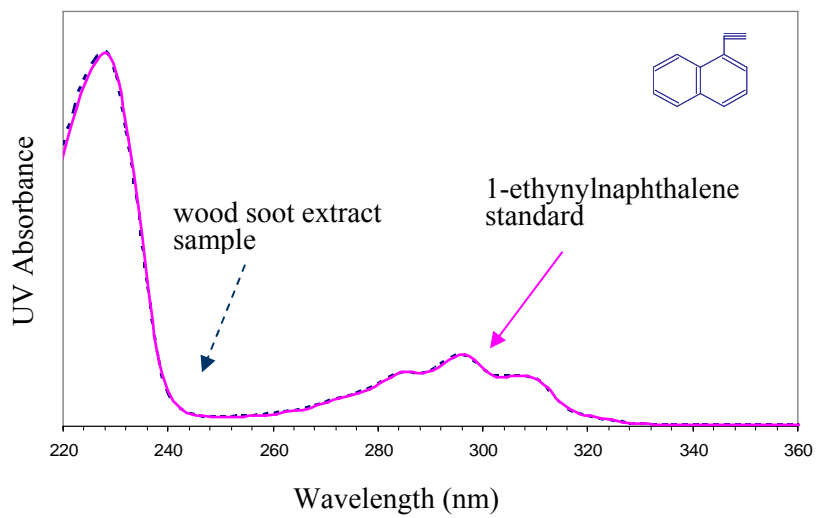


FIGURE 4.6. UV absorbance spectra of the reference standard of 1-ethylnaphthalene and of the wood soot extract sample having the same HPLC retention time.

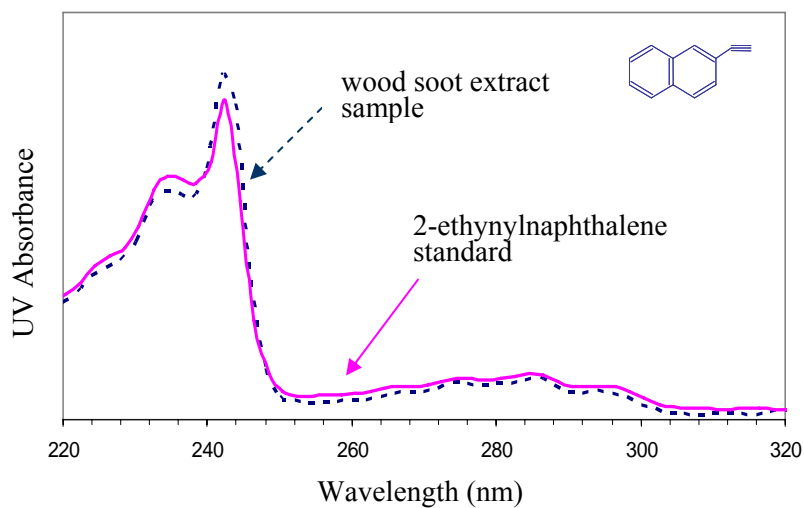


FIGURE 4.7. UV Absorbance spectra of the reference standard of 2-ethylnaphthalene and of the wood soot extract sample having the same HPLC retention time.

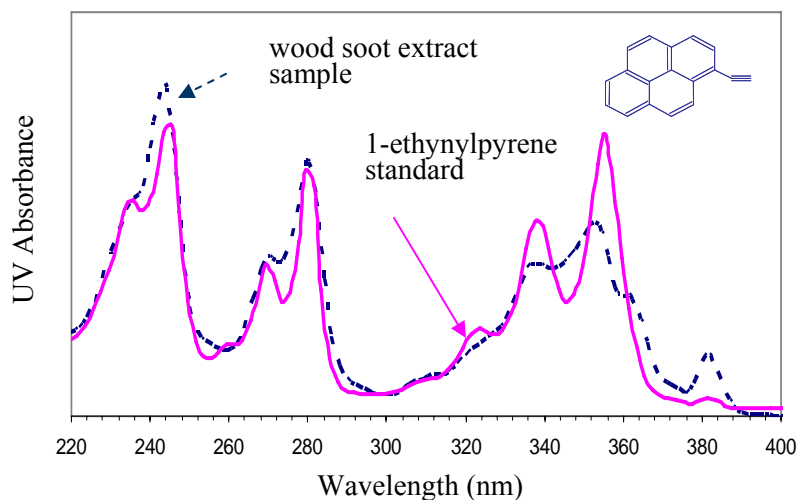


FIGURE 4.8. UV absorbance spectra of the reference standard of 1-ethynylpyrene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in smaller peaks at 320-360 nm and an augmented peaks at 235-245 nm and 375-390 nm.

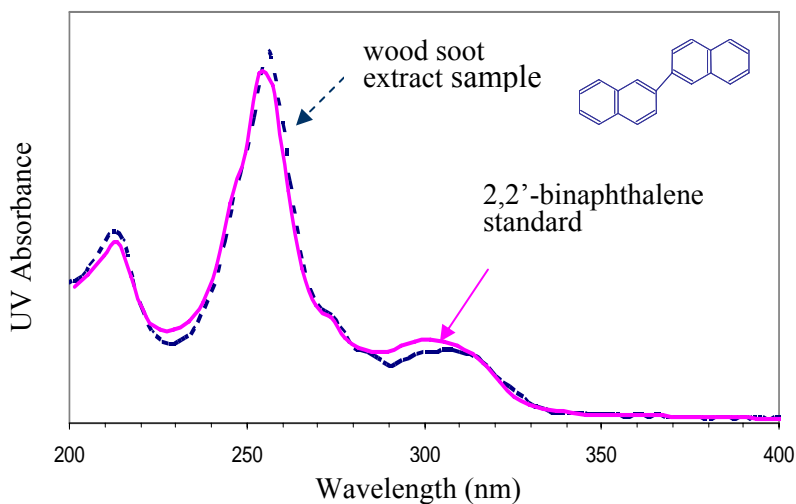


FIGURE 4.9. UV absorbance spectra of the reference standard of 2,2'-binaphthalene and of the wood soot extract sample having the same HPLC retention time.

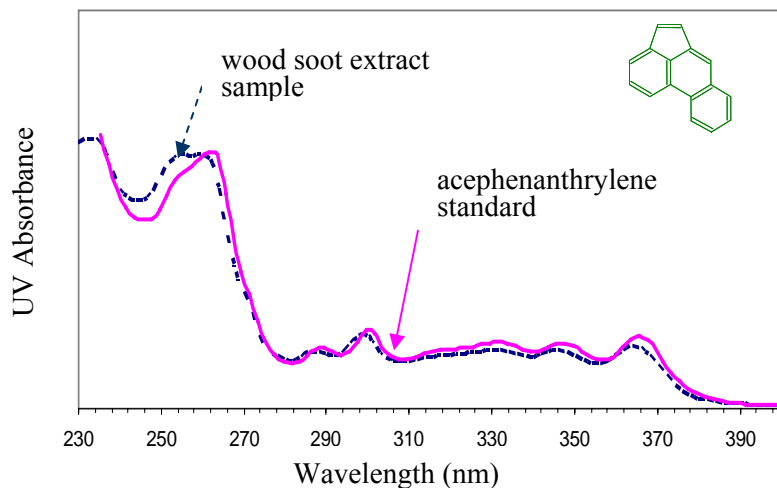


FIGURE 4.10. UV absorbance spectra of the reference standard of acephenanthrylene and of the wood soot extract sample having the same HPLC retention time.

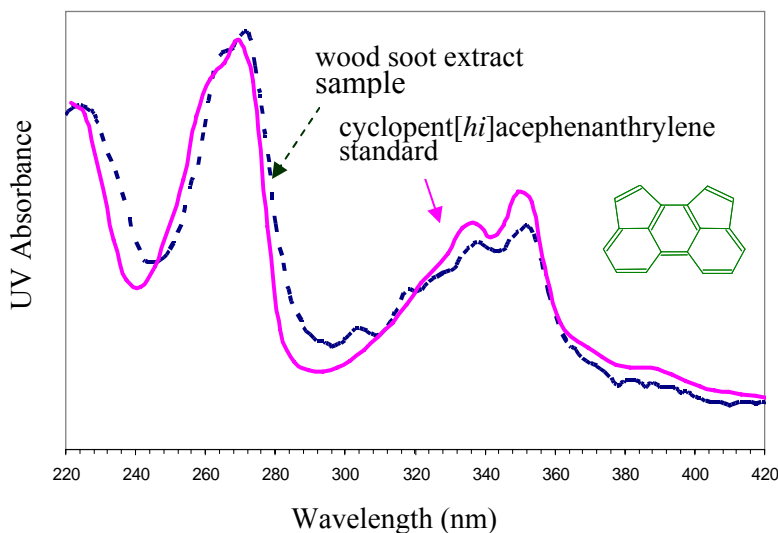


FIGURE 4.11. UV absorbance spectra of the reference standard of cyclopent[hi]acephenanthrylene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in an extra peak at 300-310 nm.

#### 4.4 2 to 6-ring PAH

The table below lists previous studies that reported the presence of 2- to 6-ring PAH as products of wood combustion. The 6-ring PAH with molecular weight of 302 are grouped separately. Except for acenaphthene and fluorene, the 14 other priority PAH (naphthalene,

acenaphthylene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene) are often found as products of wood combustion, and hence omitted in the table.

Table 4.2. 2- to 6-ring PAH as Products of Wood Combustion

PAH Compound	Reference
Benzo[ <i>a</i> ]fluorene	birch wood emission (Hedberg), birch and spruce (Ramdahl 1982b), wood stove emission (Alfheim), eucalyptus emission (Ré-Poppi)
Benzo[ <i>c</i> ]phenanthrene	birch wood emission (Hedberg), hardwood emission (Lee 2005), eucalyptus emission (Ré-Poppi)
Triphenylene	pine and oak particle emission (Gullett), wood particle emission and in gas phase for <i>eucalyptus</i> (Schauer), particles in duff burning (Tan), wood pyrolysis liquid of <i>Eucalyptus grandis</i> (Pimenta), oak and fir particle emission (Hays 2003), beech veneer (Handa), birch and spruce (Ramdahl 1982b), wood stove emission (Alfheim), eucalyptus emission (Ré-Poppi)
Benzo[ <i>ghi</i> ]fluoranthene	wood emission (Freeman), wood stove emission (Alfheim), eucalyptus emission (Ré-Poppi)
Benzo[ <i>j</i> ]fluoranthene	particles in duff burning (Tan), wood emission particles (Fine 2001, 2002, 2004a, 2004b), hardwood emission (Lee 2005), wood emission particle (Schauer), pine and oak emission (Gullett), oak and fir particle emission (Hays 2003), wood stove emission (Alfheim)
Benzo[ <i>a</i> ]fluoranthene	oak and fir particle emission (Hays 2003), eucalyptus emission (Ré-Poppi)
Benzo[ <i>e</i> ]pyrene	birch wood emission (Hedberg, Jenkins 1996a, Freeman), wood emission particles (Fine 2001, 2002, 2004a, 2004b, Hays, Gachanja), hardwood emission (Lee 2005), wood emission particle (Schauer, Khalili), particle and gaseous emission from softwood and hardwood (McDonald), pine and oak emission (Gullett), leaves of oak, ash, hazel (Howsam 2000), particles in duff burning (Tan), oak and fir particle emission (Hays 2003), beech veneer (Handa), birch and spruce (Ramdahl 1982b), wood stove emission (Alfheim), eucalyptus emission (Ré-Poppi)
Perylene	birch wood emission (Hedberg, Jenkins 1996a), wood pyrolysis liquid of <i>Eucalyptus grandis</i> (Pimenta), particles in duff burning (Tan), wood emission particles (Fine 2001, 2002, 2004a, 2004b, Gachanja), wood emission particle (Schauer), leaves of oak, ash, hazel (Howsam 2000), oak and fir particle emission (Hays 2003), beech veneer (Handa), birch and spruce (Ramdahl 1982b), wood stove emission (Alfheim), eucalyptus emission (Ré-Poppi)
Dibenz[ <i>a,c</i> ]anthracene	particles in duff burning (Tan), hardwood emission (Lee 2005), oak and fir particle emission (Hays 2003), beech veneer (Handa)
Pentaphene	pine and oak emission (Gullett), oak and fir particle emission (Hays 2003)

(Table continued)

Dibenz[ <i>a,j</i> ]anthracene	oak and fir particle emission (Hays 2003), eucalyptus emission (Ré-Poppi)
Benzo[ <i>b</i> ]chrysene	pine and oak emission (Gullett), oak and fir particle emission (Hays 2003), eucalyptus emission (Ré-Poppi)
Picene	pine and oak emission (Gullett), oak and fir particle emission (Hays 2003), beech veneer (Handa)
Indeno[1,2,3- <i>cd</i> ]fluoranthene	birch wood emission (Hedberg), wood emission particles (Fine 2001, 2002, 2004a, 2004b), wood emission particle (Schauer)
Anthanthrene	wood emission particle (Schauer), particles in duff burning (Tan), wood emission particles (Fine 2001, 2002, 2004a, 2004b), hardwood emission (Lee 2005), oak and fir particle emission (Hays 2003), eucalyptus emission (Ré-Poppi)

As mentioned, acenaphthene and fluorene were not found in the wood soot extract since they are too volatile and are usually found in the gaseous phase (McDonald, Oanh 1999, Kakareka, Lee 2005). Still, trace amounts of fluorene were found using the GC/MS. Schauer found acenaphthene and fluorene in the gas phase emission of pine (Conde 2005a), oak, and eucalyptus. Alfheim also detected them in wood stove emission. On the other hand, Pimenta found fluorene in wood pyrolysis liquid of *Eucalyptus grandis*. Khalili found it both in the gaseous phase and the particulate matter phase. Separately, fluorene was reported in the gas phase of tree bark (Stutaro) and pine (Hays 2002) and acenaphthene in wood tar (Pakdel). Small amount of fluorene was also found in the particulate emission (Jenkins 1996a, Zou).

It can be seen that the majority of the polycyclic aromatic hydrocarbons have rings greater than 4. This indicates that the combustion temperature was very high. This was the same observation by Liu that as temperature increases, the production of light polycyclic aromatic hydrocarbons is less likely than that of other PAH with higher molecular weight. This is expected since the light polycyclic aromatic hydrocarbons, 2 to 3 rings, are volatile and therefore they tend to stay in the gas phase (Howsam 2000). Predominant polycyclic aromatic hydrocarbons in the gas phase (wood smoke) emission samples were acenaphthylene, naphthalene, anthracene, phenanthrene, benzo[*a*]pyrene, and benzo[*e*]pyrene (Khalili). However

there are some light polycyclic aromatic hydrocarbons that are resistant to high temperature. The wood soot on the bottom of the woks may have been exposed to high temperature ( $> 600\text{ }^{\circ}\text{C}$ ) for a long time. Some of the polycyclic aromatic hydrocarbons may have been adsorbed in the soot and these were the ones that are resistant to temperature change.

In a study by Khalfi, fluorene, phenanthrene, benzo[*a,h*]anthracene, and chrysene emissions significantly decreased from 954 - 1077  $^{\circ}\text{C}$ . But indeno[1,2,3-*cd*]pyrene, naphthalene, acenaphthylene, fluoranthene, pyrene, and benzo[*a*]pyrene were resistant to an increase in temperature. This has been confirmed by Levendis in the combustion of tires where fluoranthene, benzo[*a*]pyrene, pyrene, acenaphthylene did not change with an increase in temperature.

In wood combustion products, polycyclic aromatic hydrocarbons with rings greater than 4 are not often reported. Hauler studied wood combustion soot using LD-REMPI-TOFMS and has assigned benzofluoranthenes, perylene, benzo[*a*]pyrene for MW 252 and dibenzoanthracenes for MW 278. Consequently, Zimmermann using FT-LMMS has assigned corannulene for MW 250, benzofluoranthenes, perylene, benzo[*a*]pyrene, benzo[*b*]pyrene for MW 252, and dibenzanthracenes for MW 278. Previously, dibenz[*a,j*]anthracene have been found in coal tar (Wise 1988b), and brown coal (Grimmer 1983b). Also benzo[*b*]chrysene has been identified in carbon black (Simonsick) and brown coal (Grimmer 1983b).

As these molecular weight assignments do not indicate strong evidence of the presence of a particular isomeric polycyclic aromatic hydrocarbons, the unequivocal identification of the PAH in the wood soot extract, with the use of UV absorbance spectral match, is presented. Figures 4.12 to 4.13 present the UV absorbance spectra of 2 newly identified polycyclic aromatic hydrocarbons as products of wood combustion (corannulene and benzo[*c*]chrysene).

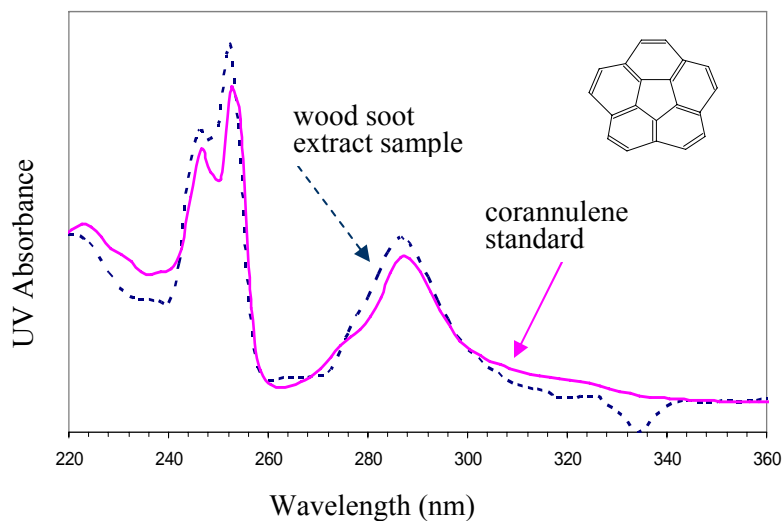


FIGURE 4.12. UV absorbance spectra of the reference standard of corannulene and of the wood soot extract sample having the same HPLC retention time.

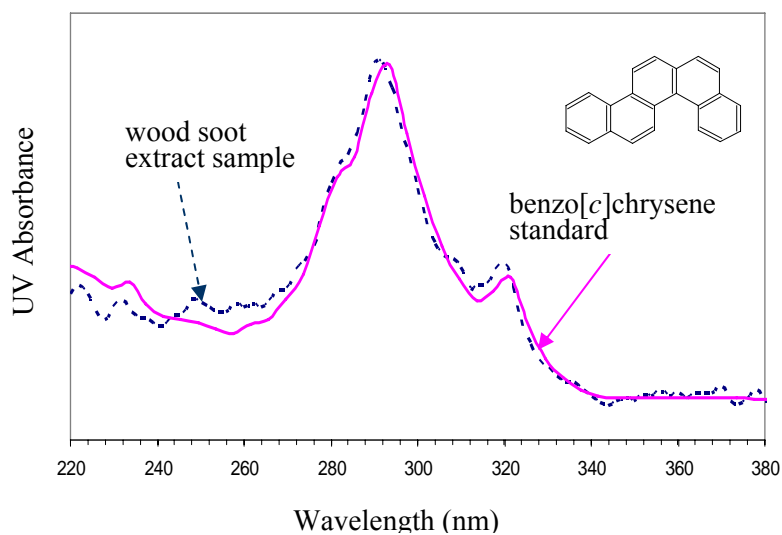


FIGURE 4.13. UV absorbance spectra of the reference standard of benzo[c]chrysene and of the wood soot extract sample having the same HPLC retention time.

#### 4.5 C<sub>24</sub>H<sub>14</sub> Compounds

This group of compounds with molecular weight 302 has been of special interest because of its known mutagenic and carcinogenic behavior. In fact, Durant 1999, reported that dibenzo[*a,l*]pyrene is one of the most genotoxic PAH ever tested. It is 50-fold more mutagenic to human MCL-5 cells than benzo[*a*]pyrene (as cited by Durant 1999). Also, dibenzo[*a,e*]pyrene,

dibenz[*a,h*]pyrene, and dibenzo[*a,i*]pyrene were tested to be genotoxic but less potent than dibenzo[*a,l*]pyrene (as cited by Durant 1999). A study by Durant also revealed that PAH with molecular weight 302 contributed 30% of the total mutagenicity of the PAH in air particulate. The most active mutagens reported were naphtho[2,1-*a*]pyrene, dibenzo[*b,k*]fluoranthene, dibenzo[*a,i*]pyrene, dibenzo[*a,e*]pyrene, naphtho[2,3-*a*]pyrene, and naphtho[2,3-*e*]pyrene (Schubert).

Although there are more than 85 possible isomers of this group, only a few are available as reference standards. According to Wise, 1993, there is a difficulty in the measurement of individual PAH in environmental samples due to: a) they are generally present at levels of 5-20 times lower than PAH of similar molecular weight that are routinely measured; b) contain large number of possible isomers which makes it hard to identify; c) many are not sufficiently resolved on conventional GC and LC; and d) unavailability of reference standards.

Previous studies have identified C<sub>24</sub>H<sub>14</sub> PAH as products of coal (Wornat 2001b, Lee 2005, Schmidt, Chuang 1992a, 1992b, Grimmer 1983b), catechol (Wornat 2001a), diesel combustion (Sauvain), constituents of coal tar (Ledesma, Schubert, Wise 1988b, Marvin), carbon black (Simonsick, Peaden), contaminated soil (Pace, Čáslavský), and air, water and urban aerosols (Čáslavský, Allen). However, only a few C<sub>24</sub>H<sub>14</sub> isomers have been reported as products of wood combustion. Lee (2005) has reported dibenzo[*a,e*]pyrene and dibenzo[*a,i*]pyrene as combustion products of seasoned hardwood (mainly beech) based from a GC-MSD analysis. Handa also reported dibenzo[*a,i*]pyrene as product of beech veneer pyrolysis using HPLC. Zimmermann and Hauler also have previously reported benzo[*b*]perylene and dibenzo[*b,k*]fluoranthene from mass spectrometry data (FT-LMMS) using wood as combustion material. Naphtho[2,3-*a*]pyrene was observed from soot taken on a chimney where firewood was burned and analyzed with the use of GC/MS and HPLC/FLS (Yasuhara). Although Lee 2005,

Zimmermann, and Hauler have reported the presence of some of the C<sub>24</sub>H<sub>14</sub> PAH isomers, their method of analysis do not specifically pinpoint the isomers mentioned. The FT-LMMS cannot distinguish isomeric PAH. Based only on the molecular weight, other isomers could have also been reported. Therefore, it is still considered that dibenzo[*a,e*]pyrene, benzo[*b*]perylene, and dibenzo[*b,k*]fluoranthene are newly identified C<sub>24</sub>H<sub>14</sub> PAH from wood soot extracts.

The following figures present the unequivocal identification of the eleven newly identified C<sub>24</sub>H<sub>14</sub> PAH from wood soot extracts as products of wood combustion. Naphtho[2,3-*a*]pyrene and dibenzo[*a,i*]pyrene are no longer presented since they were previously identified. Figures 4.14 to 4.24 show the UV absorbance spectra of the reference standards with the UV absorbance spectra of the components in the wood soot extracts.

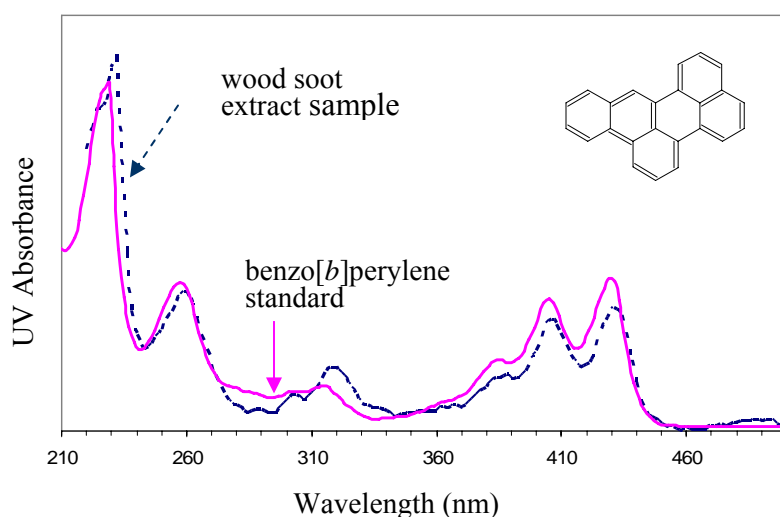


FIGURE 4.14. UV absorbance spectra of the reference standard of benzo[*b*]perylene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in an augmented peak at 310-330 nm.

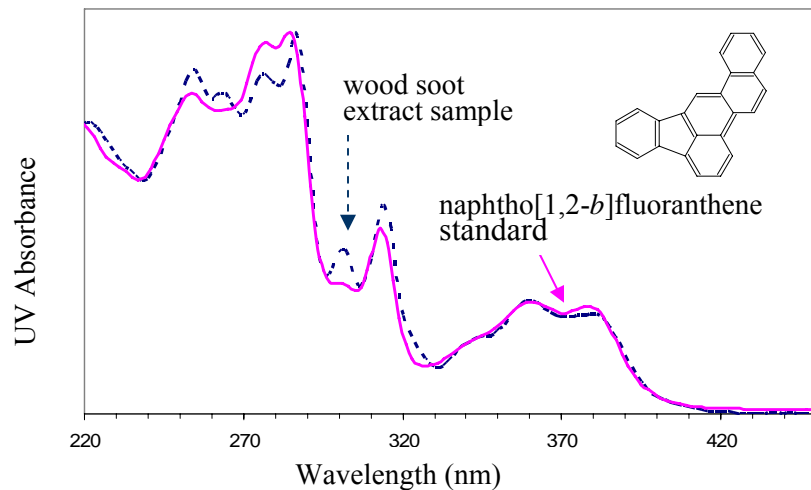


FIGURE 4.15. UV absorbance spectra of the reference standard of naphtho[1,2-*b*]fluoranthene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in an extra peak at 260-270 nm.

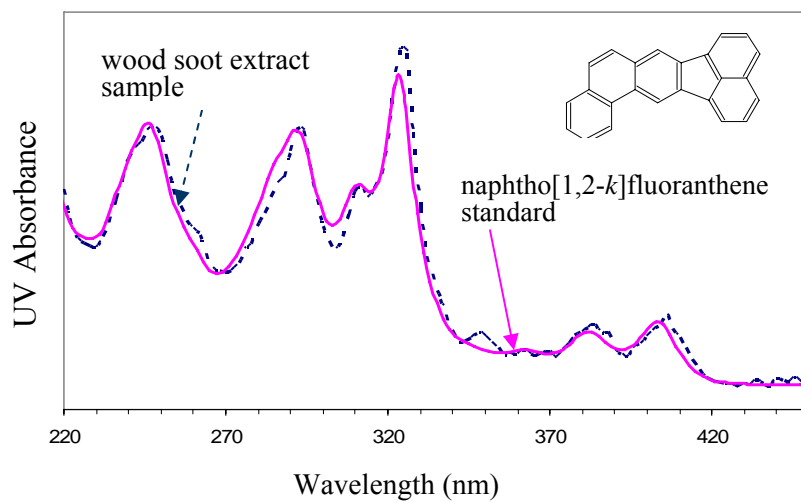


FIGURE 4.16. UV absorbance spectra of the reference standard of naphtho[1,2-*k*]fluoranthene and of the wood soot extract sample having the same HPLC retention time.

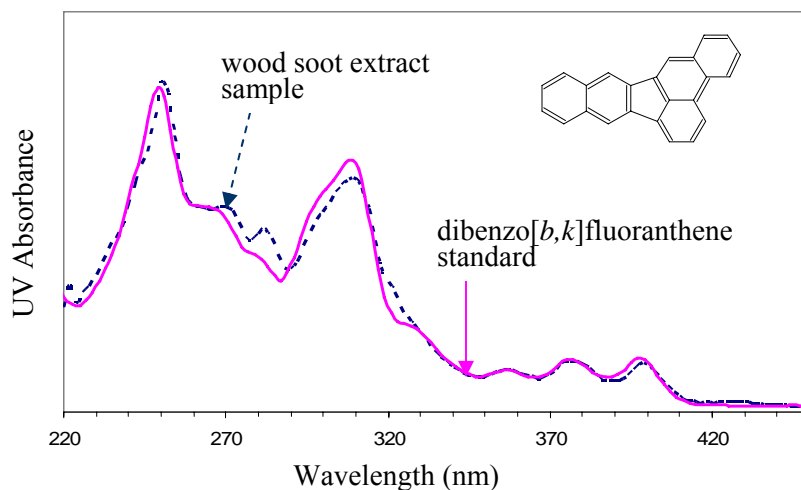


FIGURE 4.17. UV absorbance spectra of the reference standard of dibenzo[*b,k*]fluoranthene and of the wood soot extract sample having the same HPLC retention time.

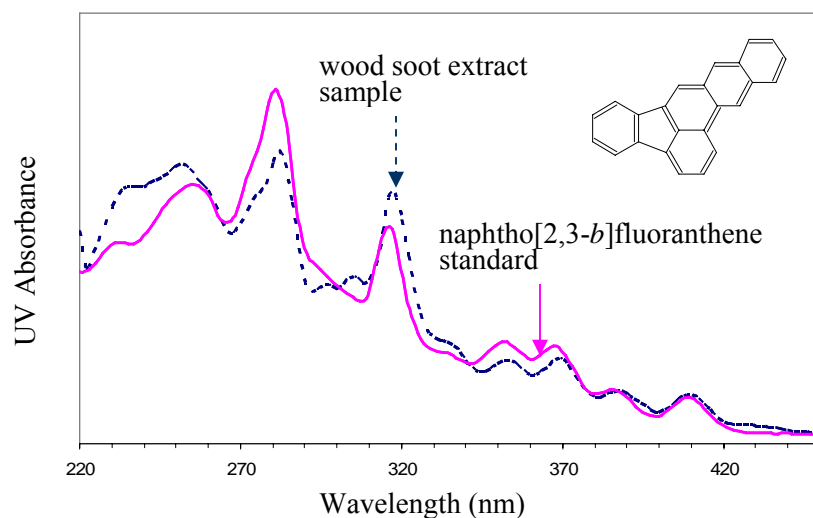


FIGURE 4.18. UV absorbance spectra of the reference standard of naphtho[2,3-*b*]fluoranthene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with picene resulting in an extra peak at 290-310 nm.

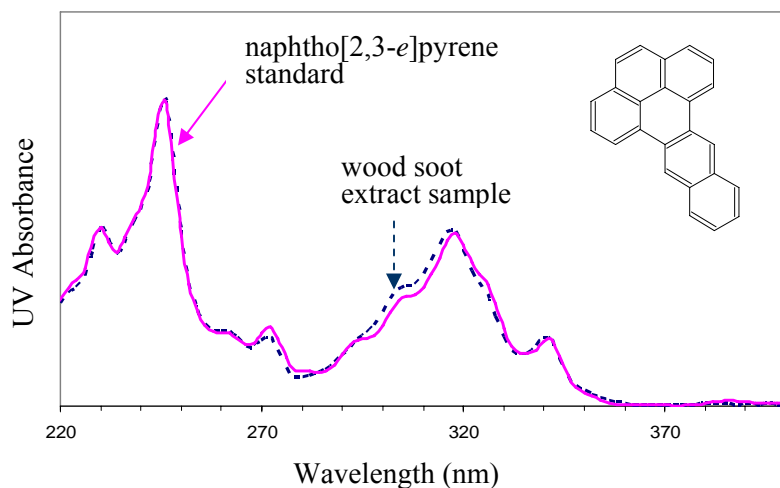


FIGURE 4.19. UV absorbance spectra of the reference standard of naphtho[2,3-*e*]pyrene and of the wood soot extract sample having the same HPLC retention time. (Reference standard from Poster, 2005).

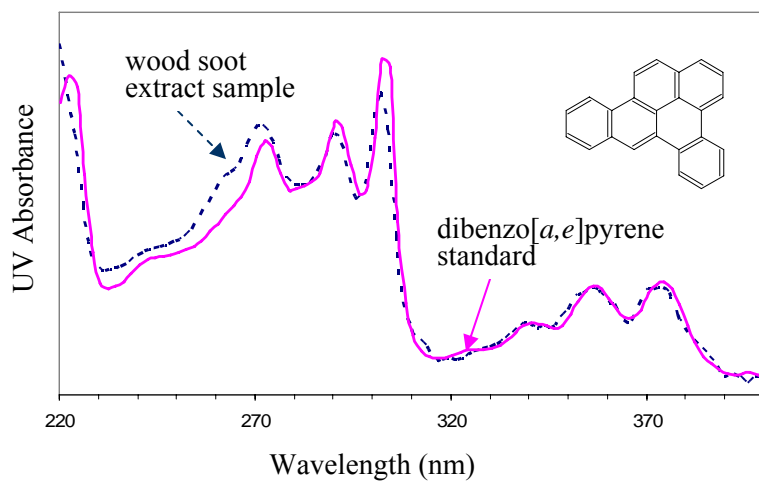


FIGURE 4.20. UV absorbance spectra of the reference standard of dibenzo[*a,e*]pyrene and of the wood soot extract sample having the same HPLC retention time.

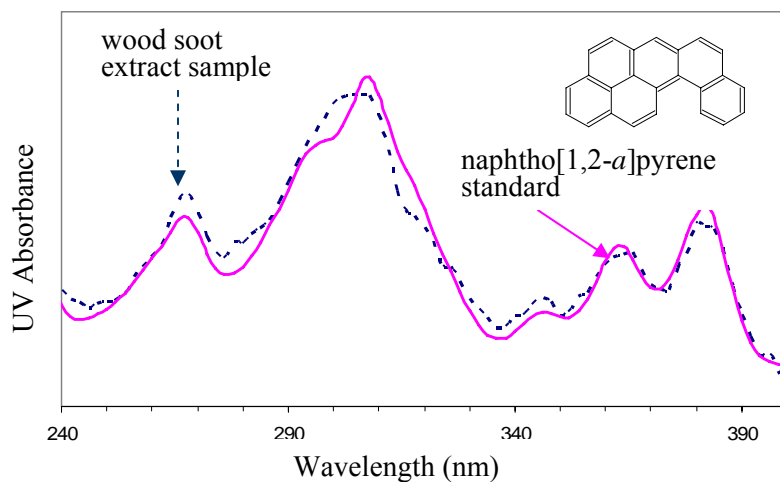


FIGURE 4.21. UV absorbance spectra of the reference standard of naphtho[1,2-*a*]pyrene and of the wood soot extract sample having the same HPLC retention time. (Reference standard from Seidel, 2005).

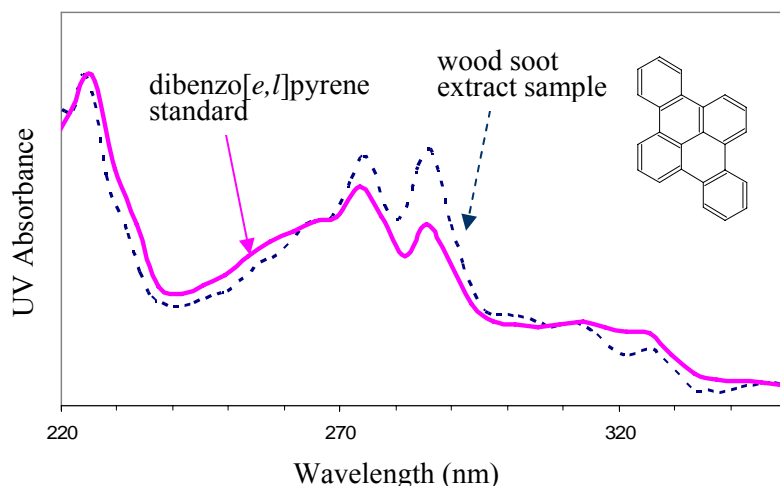


FIGURE 4.22. UV absorbance spectra of the reference standard of dibenzo[*e,l*]pyrene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with benzo[*b*]chrysene component resulting in an augmented peaks at 270-295 nm.

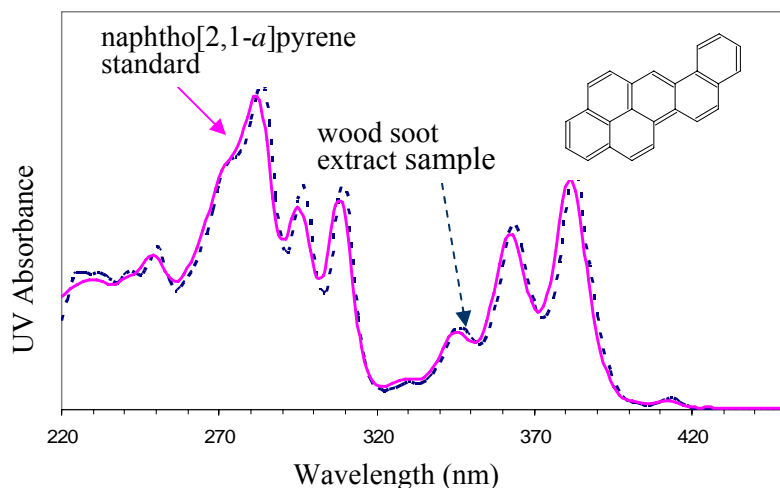


FIGURE 4.23. UV absorbance spectra of the reference standard of naphtho[2,1-*a*]pyrene and of the wood soot extract sample having the same HPLC retention time.

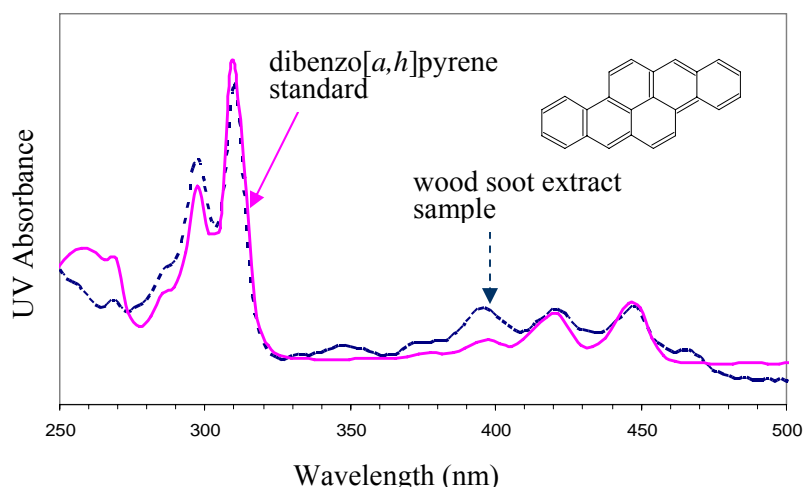


FIGURE 4.24. UV absorbance spectra of the reference standard of dibenzo[*a,h*]pyrene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified component resulting in an extra peak at 325-360 nm.

The UV absorbance spectra of PAH extracts from wood soot often have slight deviations from available reference standards. These deviations are typically the presence (or absence) of a single peak or differences in the relative heights of peaks within a UV absorbance spectrum. This is most likely caused by co-eluting compounds. Another factor is the fact that many of the peaks on the chromatogram are small because concentrations are low.

PAH sometimes co-elute with an unidentified compound. In cases where the co-eluting compound is known, as in dibenzo[*e,l*]pyrene (Figure 4.22), the spectral match can be resolved to show the presence of co-elution (Marsh 2005). Figure 4.25 show that benzo[*b*]chrysene has a major peak at 270 - 295 nm. It can be assumed that the augmented peak at 270 - 295 nm in Figure 4.22 can be attributed to the presence of benzo[*b*]chrysene. Figure 4.26 presents the spectra of dibenzo[*e,l*]pyrene, benzo[*b*]chrysene, and the sum of these two reference compounds. By adding a fraction of benzo[*b*]chrysene to the spectrum of dibenzo[*e,l*]pyrene, the sum of the reference standard now exhibits a spectrum that matches the spectrum of the wood soot sample. Therefore, we can clearly say that the spectrum of the wood soot sample has PAH that are co-eluting. Other peaks in the HPLC/UV-vis chromatogram also show the same trend. It is indicated by a “plus” sign in the chromatograms.

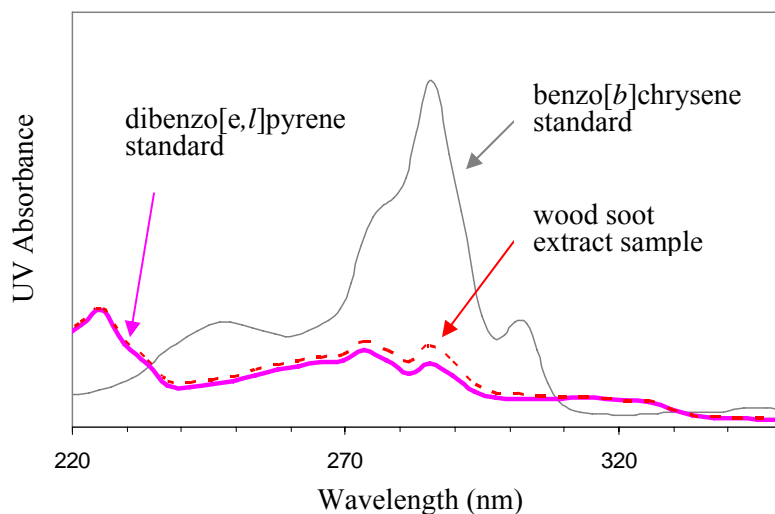


FIGURE 4.25. UV absorbance spectra of the reference standards of dibenzo[*e,l*]pyrene and benzo[*b*]chrysene and of the wood soot extract sample having the same HPLC retention time.

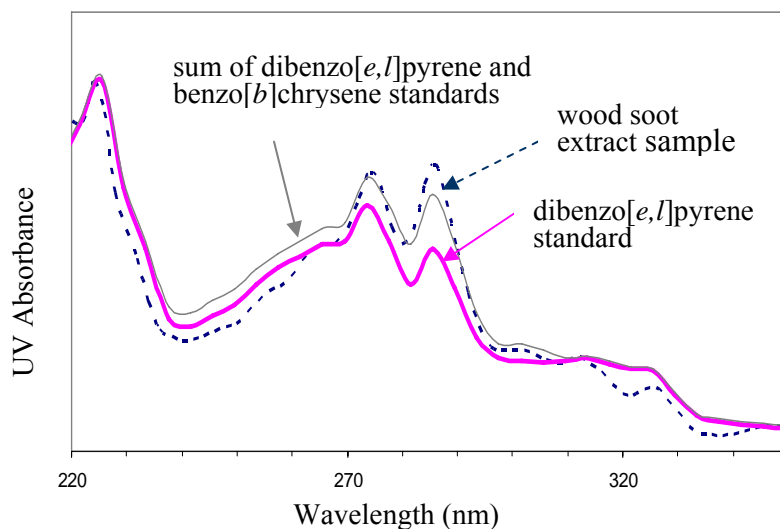


FIGURE 4.26. UV absorbance spectra of the reference standard of dibenzo[*e,l*]pyrene, sum of reference standards dibenzo[*e,l*]pyrene and benzo[*b*]chrysene and of the wood soot extract sample having the same HPLC retention time.

#### 4.6 High Molecular Weight PAH (7 to 10 rings)

PAH with rings greater than 6 are rarely found and reported as products of wood combustion. Except for coronene, the 13 high molecular weight PAH identified in the wood soot extracts has never before been reported as products of wood combustion. Zimmermann and Hauler have assigned tentative PAH based on the mass spectrometry (FT-LMMS) data such as MW 326 (dibenzoperylene), MW 350 (benzo[*a*]coronene), MW 374 (dibenzocoronenes), MW 398 (ovalene), and MW 400 (naphthocoronenes and dibenzocoronenes). They were also able to identify PAH with MW higher than 400.

Previously, some of the high MW polycyclic aromatic hydrocarbons have been identified in soil samples, dibenzo[*a,l*]pyrene and benzo[*a*]coronene, dibenzo[*cd,lm*]perylene (Čáslavský, Pace), carbon black, dibenzo[*cd,lm*]perylene, dibenzo[*b,ghi*]perylene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, ovalene, benzo[*a*]coronene, and phenanthro[5,4,3,2-*efghi*]perylene (Peaden, Simonsick).

It is only with HPLC-UV/vis that the isomers of this group of PAH were unequivocally identified based on the UV absorbance spectra of the sample with the reference standard. Some reference standards are commercially available while others required special synthesis. The following figures present the newly identified PAH of high molecular weight.

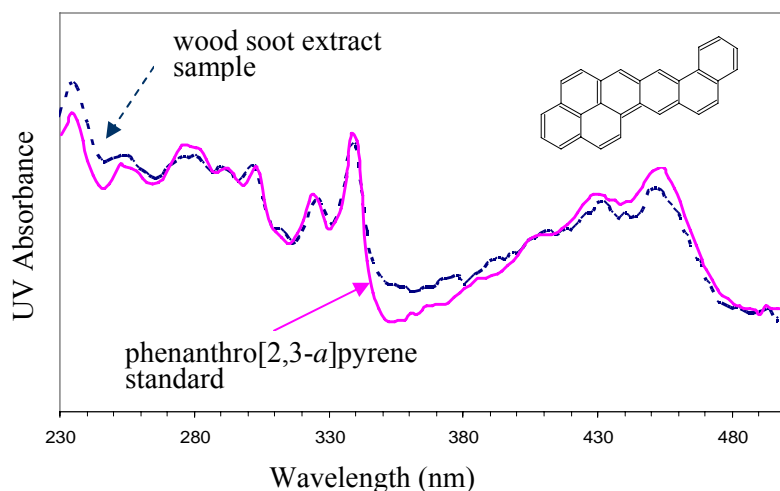


FIGURE 4.27. UV absorbance spectra of the reference standard of phenanthro[2,3-*a*]pyrene and of the wood soot extract sample having the same HPLC retention time.

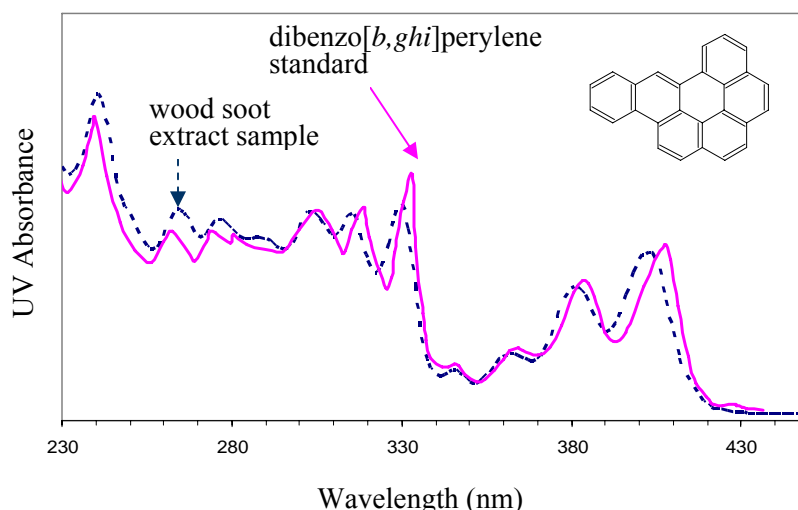


FIGURE 4.28. UV absorbance spectra of the reference standard of dibenzo[*b,ghi*]perylene and of the wood soot extract sample having the same HPLC retention time. The solvent used in the reference standard (ethanol from 230-280 nm; benzene from 280-430 nm) (as cited by Zander) is different from the solvent of the sample (ACN and DCM).

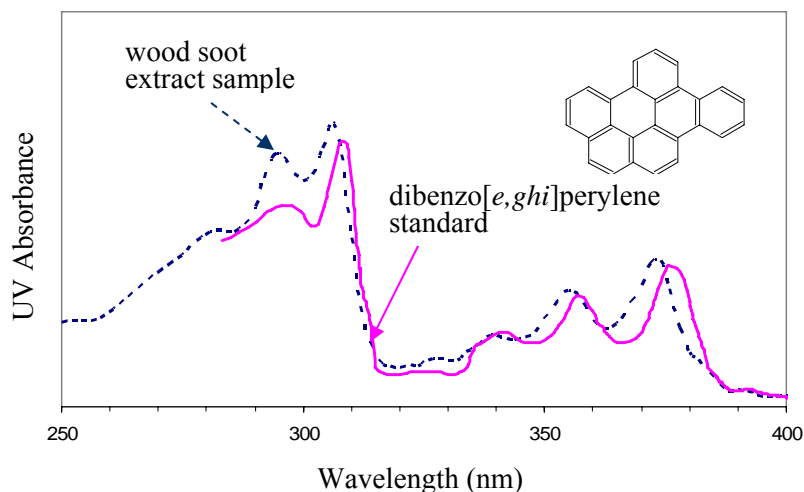


FIGURE 4.29. UV absorbance spectra of the reference standard of dibenzo[*e,ghi*]perylene and of the wood soot extract sample having the same HPLC retention time. The solvent used in the reference standard (benzene) (Clar 1964b) is different from the solvent of the sample (ACN and DCM).

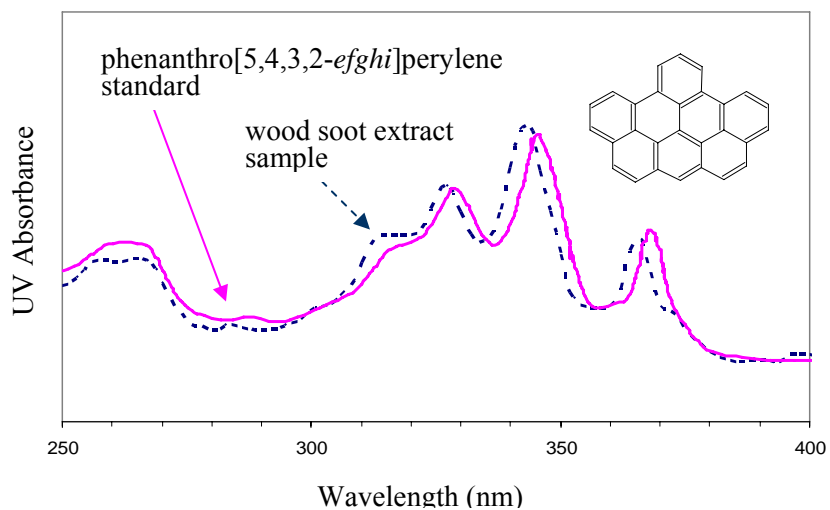


FIGURE 4.30. UV absorbance spectra of the reference standard of phenanthro[5,4,3,2-*efghi*]perylene and of the wood soot extract sample having the same HPLC retention time. The solvent used in the reference standard (benzene) (Fetzer 1994a) is different from the solvent of the sample (ACN and DCM).

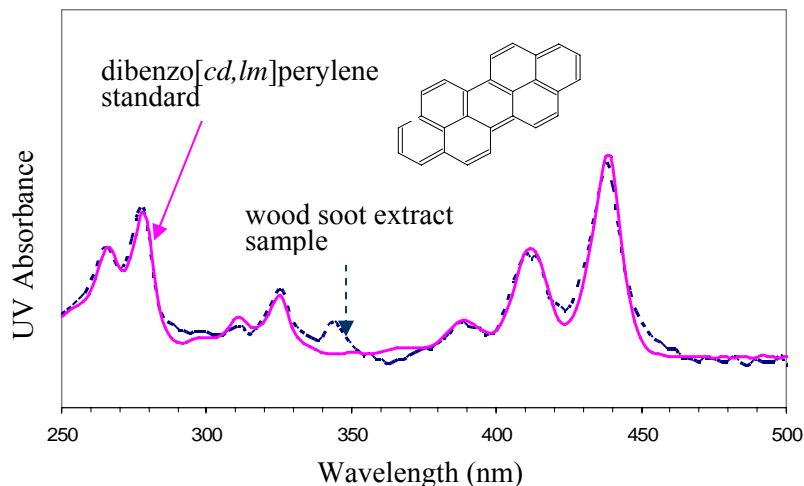


FIGURE 4.31. UV absorbance spectra of the reference standard of dibenzo[*cd,lm*]perylene and of the wood soot extract sample having the same HPLC retention time. It co-elutes with an unidentified compound resulting in an extra peak at 340-360 nm.

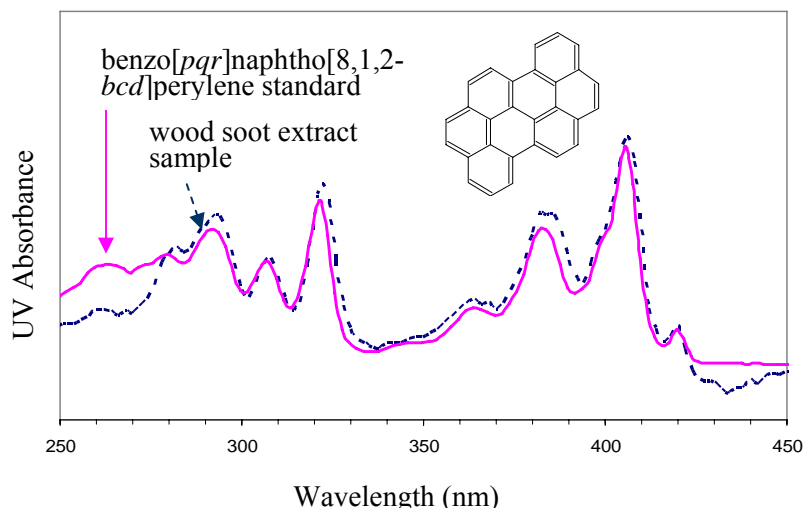


FIGURE 4.32. UV absorbance spectra of the reference standard of benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene and of the wood soot extract sample having the same HPLC retention time.

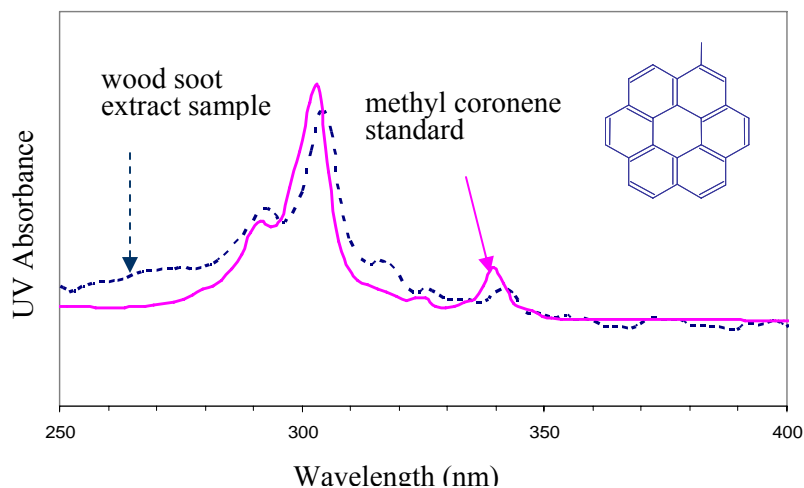


FIGURE 4.33. UV absorbance spectra of the reference standard of methyl coronene and of the wood soot extract sample having the same HPLC retention time. Reference standard used is coronene. The right shift in the spectrum of the wood soot sample indicates the presence of methylated group.

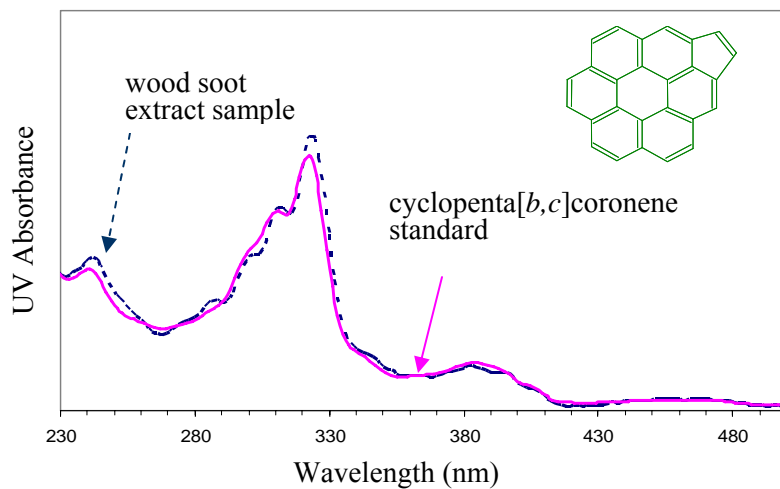


FIGURE 4.34. UV absorbance spectra of the reference standard of cyclopenta[*b,c*]coronene and of the wood soot extract sample having the same HPLC retention time.

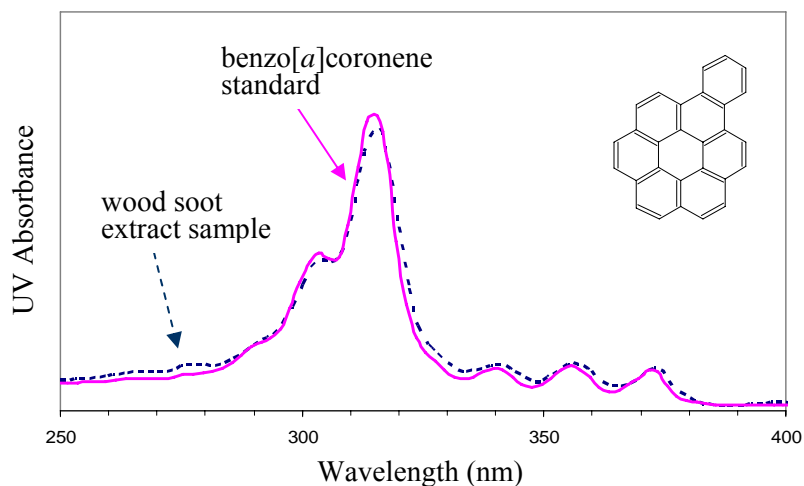


FIGURE 4.35. UV absorbance spectra of the reference standard of benzo[*a*]coronene and of the wood soot extract sample having the same HPLC retention time.

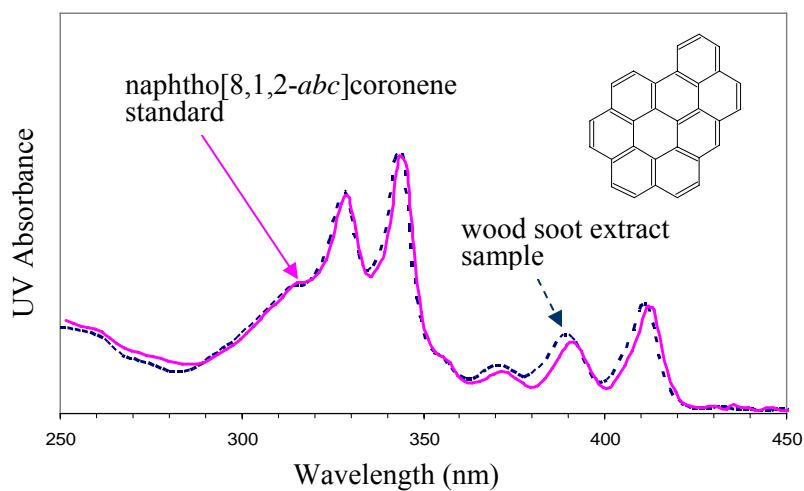


FIGURE 4.36. UV absorbance spectra of the reference standard of naphtho[8,1,2-*abc*]coronene and of the wood soot extract sample having the same HPLC retention time.

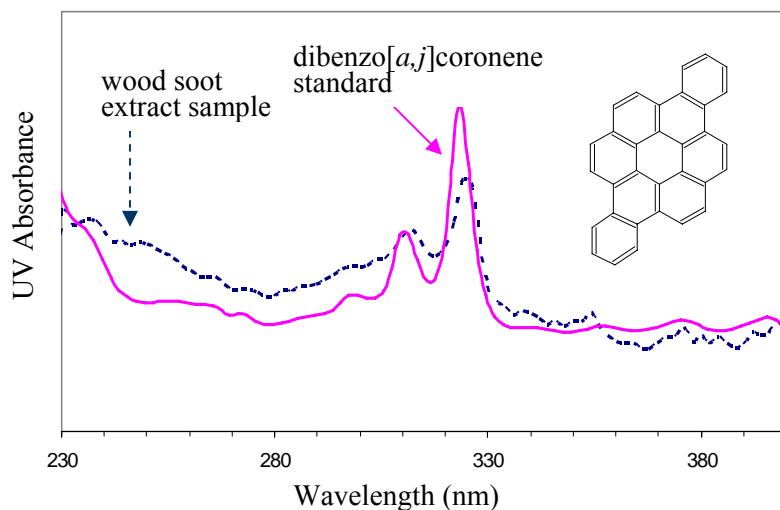


FIGURE 4.37. UV absorbance spectra of the reference standard of dibenzo[*a,j*]coronene and of the wood soot extract sample having the same HPLC retention time. The concentration of the sample is low thereby producing a small peak in the chromatogram. The major peaks at 295-300 nm shows unequivocal match with the reference standard.

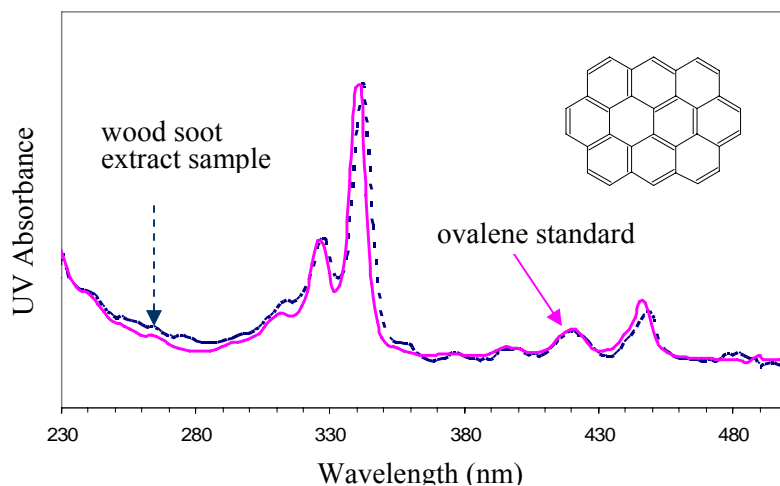


FIGURE 4.38. UV absorbance spectra of the reference standard of ovalene and of the wood soot extract sample having the same HPLC retention time.

As with the other spectral matches, some of the peaks exhibit co-elution with an unidentified compound. Also, the concentration of the sample is low and it results in small peaks in the chromatogram. This can be seen in methyl coronene, dibenzo[*a,j*]coronene, and ovalene.

Spectral matching is presented as the major peaks in the sample matches the peaks in the reference standard.

As some of the reference standards were analyzed using a solvent different from the solvent used for the wood soot extract, a shift in the spectral matches occurred. These are shown in Figures 4.28 to 4.30. Benzene causes the UV absorbance spectra to move several nanometers to the left whereas ethanol would result to the same spectra as DCM. The spectral matching was resolved using the index of refraction between the solvents of the reference compounds (i.e. ethanol and benzene) and the sample (ACN and DCM) (Oña).

For methylated compounds, as in the case of methyl coronene, there is a right shift on the spectrum of the wood soot extract compared to the spectrum of coronene taken as the reference standard. The presence of methylated groups causes bathochromic shifts (B-effect) in the UV absorbance spectra of the compound. According to Jones 1945, the spectrum of the compound is similar in general shape and intensity to the spectrum of the unsubstituted hydrocarbon, that the whole curve is shifted to longer wavelengths. Also, alkyl substitution of the ring does not greatly alter the unique pattern as bathochromic shifts of only a few nanometers are the only change generally observed (as cited by Fetzer 1984).

Figure 4.39 shows a UV absorbance spectrum of a peak after phenanthro[5,4,3,2-*efghi*]perylene. It is suspected to be benzo[*ghi*]naphtho[8,1,2-*bcd*]perylene. Since there is no available reference standard and the UV absorbance spectrum of this compound is unknown; the verification of the compound was inferred from the other isomers of this compound. Based on the bands exhibited, it was deduced that the compound is a perylene benzologue. The mass spectral data verified the molecular weight of the compound. A correlation between the retention time and the length to breadth (L/B) ratio also indicated that this is the compound assumed (McLaine). The verification of this compound is further discussed by McLaine.

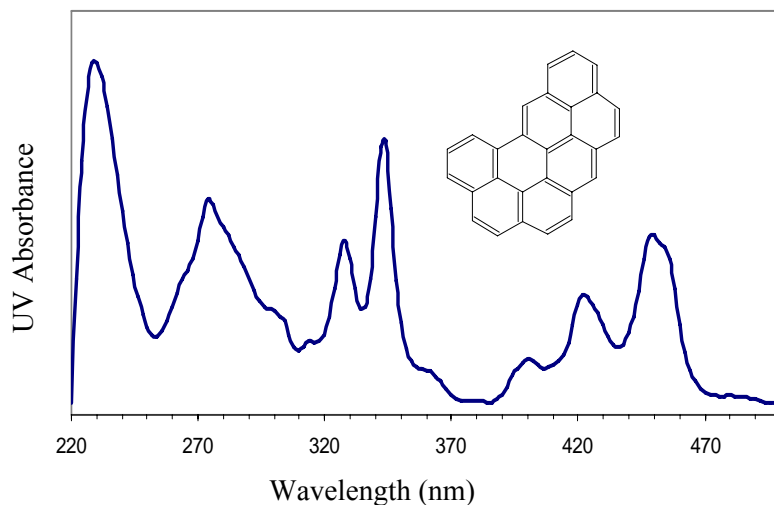


FIGURE 4.39. UV absorbance spectra of benzo[*ghi*]naphtho[8,1,2-*bcd*]perylene.

There are still a lot of unidentified peaks from the chromatogram. Due to a lack of available reference standards, these peaks remain to be unknown.

#### 4.7 GC/MS Results

The GC/MS is generally used to detect the light aromatics since it is more sensitive than HPLC/UV-vis for small-ring PAC. The aromatics detected ranges from 1- to 3-ring compounds of oxygenated, methylated, ethynyl-substituted, and nitrogen-substituted. There were 17 oxygenated, 14 methylated and ethynyl-substituted, and 8 nitrogen-substituted compounds found. The results are presented in Tables 4.11 to 4.13 at the end of the chapter.

#### 4.8 Yield, Mutagenicity and Carcinogenicity

Figure 4.40 presents the majority of the PAH group present in the wood soot extract in the Yang 3 sample. It can be seen that 5- and 6-ring PAH dominate the wood soot extract. These groups represent the most carcinogenic and mutagenic PAH and comprise about 66% of the total amount of PAC contained in the soot. This is followed by the 4-ring PAH containing 15% of the total PAH in the wood soot. The order of abundance of the PAH compounds are as follows:

Table 4.3. Order of Abundance of PAH

Ring Number	Compound	Percentage Abundance
2	C <sub>10</sub> H <sub>8</sub>	1.08
3	C <sub>14</sub> H <sub>10</sub> > C <sub>12</sub> H <sub>8</sub>	1.56
4	C <sub>18</sub> H <sub>12</sub> > C <sub>16</sub> H <sub>10</sub> > C <sub>17</sub> H <sub>12</sub> > C <sub>18</sub> H <sub>10</sub>	15.39
5	C <sub>20</sub> H <sub>12</sub> > C <sub>22</sub> H <sub>14</sub> > C <sub>18</sub> H <sub>10</sub> > C <sub>20</sub> H <sub>10</sub>	34.60
6	C <sub>22</sub> H <sub>12</sub> > C <sub>24</sub> H <sub>14</sub>	30.79
7	C <sub>24</sub> H <sub>12</sub> > C <sub>26</sub> H <sub>14</sub> > C <sub>28</sub> H <sub>16</sub> > C <sub>25</sub> H <sub>14</sub>	9.56
8	C <sub>28</sub> H <sub>14</sub> > C <sub>26</sub> H <sub>12</sub>	5.36
9	C <sub>30</sub> H <sub>14</sub> > C <sub>32</sub> H <sub>16</sub>	1.36
10	C <sub>32</sub> H <sub>14</sub>	0.25

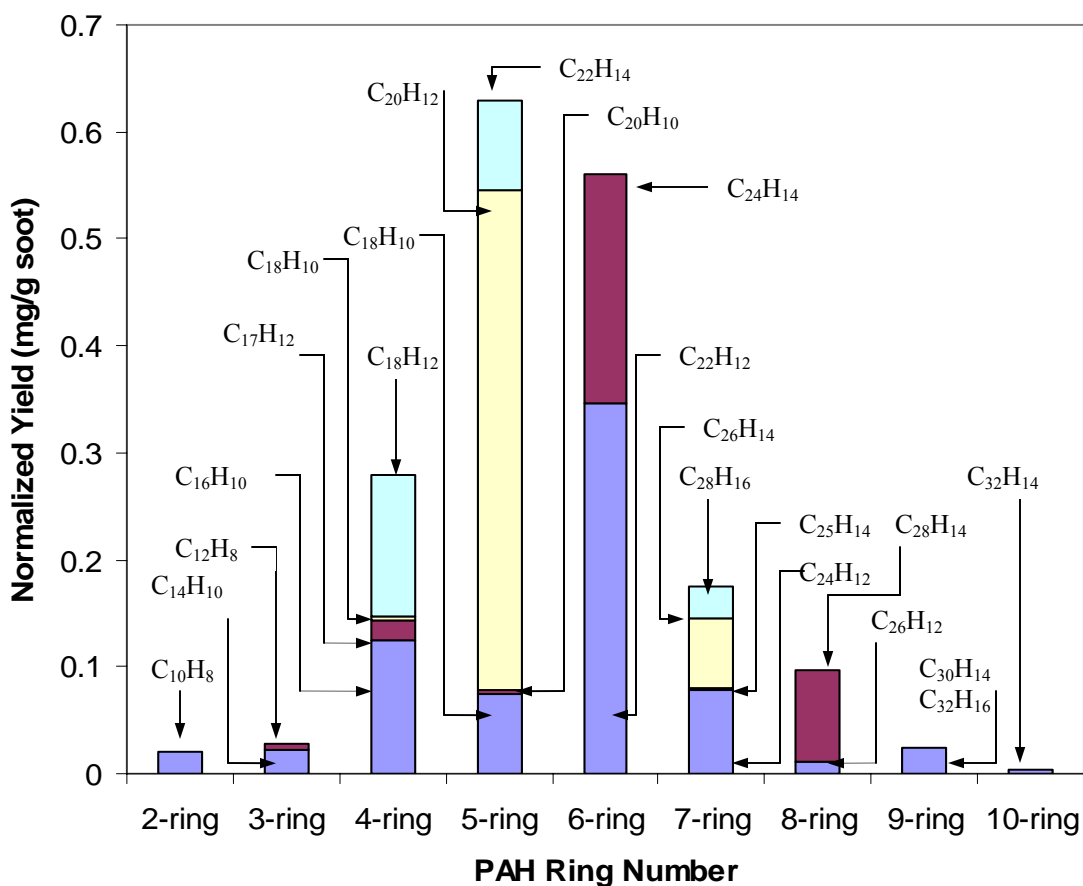


FIGURE 4.40. Yield with respect to PAH ring number

Tables 4.5 to 4.13 (shown at the end of the chapter) present the range of yield, mutagenicity and carcinogenicity of the PAC taken from the twelve wood soot extracts. The itemized yield of each compound in different samples is found in Appendix B.

The yield of the PAC was computed from the response factor of the reference standards and the volume of the sample used. The other identified PAC that do not have the exact reference standard, was estimated based on the closest structural match of the reference standard. The yield values range from  $10^{-4}$  to  $10^{-1}$  mg/g soot.

It can be seen that the concentration or yield of high molecular weight ( $MW > 302$ ) and low molecular weight ( $MW < 252$ ) are low. Hays explained that, generally, PAH with high molecular weight have relatively lower recoveries due to their higher boiling points. It is also possible that they are more tightly adsorbed in the soot particle making extraction difficult. On the other hand, low molecular weight PAH may have been lost during solvent extraction because they are more volatile and more difficult to keep in solution during solution transfer and concentration (Liu).

With regards to the biological aspect of the PAC, the Ames test is most commonly used method to test the mutagenicity of the PAC. The test is used when changes in the PAC structure causes a change in the number of mutations in the *Salmonella* strain (Gelboin).

The carcinogenicity of the PAC is very hard to standardize because of the very large number of variables involved like species, age, strain, sex, hair cycle, mitotic cycle, diet, general toxicity, and site administration (Lee1981). Therefore, Table 4.5 to 4.13 presents some conflicting data on the carcinogenic behavior of the PAC. Overall, it gives an idea on the carcinogenic activity of the different PAC.

As cited by Seidel in 2004, it has been identified that dibenzo[*a,l*]pyrene is the most carcinogenic among all the polycyclic aromatic hydrocarbons. This was analyzed with the use of laser-induced Shpol'ski spectroscopy (Seidel 2004). Naphtho[1,2-*a*]pyrene also showed similar mutagenic activity up to 4 nmol/plate with benzo[*a*]pyrene. Moreover, above 4 nmol/plate, naphtho[1,2-*a*]pyrene was more toxic than benzo[*a*]pyrene (Sharma 2005, Desai).

Naphtho[2,3-*a*]pyrene is a homologue of benzo[*a*]pyrene so it is suspected to be carcinogenic as well (Yasuhara).

It has been found that mutagenic and carcinogenic behavior depends on the structural features of the compound (Sharma 2005). Cyclopenta-fused PAH are thought to be mutagenic. In fact, cyclopenta[*cd*]pyrene was tested to be as biologically active mutagen as benzo[*a*]pyrene (as cited by Marsh 2000b). The localized electronic structure in the cyclopenta ring brings about a metabolic epoxidation of the ring (as cited by Marsh 2000b). The epoxidation results to reaction with nucleic acid and thereby induce cancer in the cell (as cited by Flesher). Also, some alkylated PAH are known to be more carcinogenic than the parent compound (as cited by Chuang 1992b). Studies also show that PAH which contains a fjord region is more carcinogenic than those derived from a bay region (as cited by Sharma 2005). Dibenz[*a*]pyrenes have been shown to more genotoxic than the other PAH (as cited by Durant). Allen and Durant found the following PAH to be carcinogenic, causing skin tumors in mice and mammary cancers in rat: dibenzo[*a,l*]pyrene, dibenzo[*a,h*]pyrene, dibenzo[*a,i*]pyrene, and dibenzo[*a,e*]pyrene. Most of the large PAH (7 to 10 rings) were not tested for mutagenicity. Some researchers believe that the molecular size hinders solubility and molecular transport thereby making them less harmful (as cited by Sandrowitz).

#### **4.9 Coal Soot versus Wood Soot**

The coal soot extracts from Henan, China has been studied using HPLC-UV/vis with a Vydac model 201TP octadecylsilica column. The soot samples were sonicated three times with DCM (Sandrowitz, Wornat 2001b). There were 32 PAC found with 2 newly identified PAC as products of coal combustion. The results from the HPLC/UV-vis in that study are compared with the results from the wood soot extract and the tabulation is shown below.

Table 4.4. PAC Yield in Wood and Coal Soot Extracts

	Wood Soot Extracts	Coal Soot Extracts
OXYGENATED	Yield Range (mg/g soot)	Yield Range (mg/g soot)
2-Naphthaldehyde	0.0008-0.0042	ND
1-Naphthaldehyde	0.0023	ND
Dibenzofuran	0.0016-0.0030	ND
Acenaphthenequinone	0.0001-0.0048	ND
Naphthalene-1,8-dicarboxylic anhydride	0.0007-0.0239	ND
Phenalenone	0.0005-0.0302	ND
9-Fluorenone	0.0015-0.0190	ND
Anthraquinone	0.0005-0.0048	ND
4H-cyclopenta[def]phenanthren-4-one	0.0005-0.0023	<0.00001-0.041
1-Hydroxypyrene	0.0016-0.0024	ND
Benzanthrone	0.0009-0.0394	<0.00001-0.041
4-Oxa-benzo[cd]pyrene-3,5-dione	0.0009-0.0159	<0.00001-0.091
6H-benzo[cd]pyren-6-one	0.0010-0.1658	ND
Cyclopenta[def]chrysene-4-one	0.0001-0.0160	ND
Benzo[b]naphtho[2,1-d]thiophene	ND	<0.00001-0.226

METHYLATED, ETHYNYL-SUBSTITUTED and CYCLOPENTA-FUSED PAH		
	Yield Range (mg/g soot)	Yield Range (mg/g soot)
Acenaphthylene	0.0004-0.0131	ND
Acephenanthrylene	0.0001-0.0261	<0.00001-0.028
Cyclopent[hi]acephenanthrylene	0.0009-0.0112	ND
Cyclopenta[cd]pyrene	0.0002-0.0343	ND
Cyclopenta[b,c]coronene	0.0001-0.0111	ND
1-Methylnaphthalene	0.0013-0.3357	ND
2-Methylnaphthalene	0.0023-0.0071	ND
1-Ethynylnaphthalene	0.0038-0.0108	ND
2-Ethynylnaphthalene	0.0031	ND
1-Ethynylpyrene	0.0003-0.0206	ND
4-Methylpyrene	0.0001-0.0044	ND
1-Methylpyrene	0.0001-0.0060	ND
2-Methylpyrene	0.0002-0.0088	ND
2,2'-Binaphthalene	0.0092	ND
Methyl coronene	0.00005-0.0005	ND

2,3, and 4- RING PAH	Yield Range (mg/g soot)	Yield Range (mg/g soot)
Naphthalene	0.0034-0.0263	ND
Phenanthrene	0.0012-0.0245	0.000052-0.047
Anthracene	0.0002-0.0114	ND
Fluoranthene	0.0005-0.0449	0.000032-0.090
Pyrene	0.0005-0.0533	<0.00001-0.028
Benzo[a]fluorene	0.0002-0.0072	<0.00001-0.161

Benzo[ <i>c</i> ]phenanthrene	0.0002-0.0034	ND
Triphenylene	0.0003-0.0130	<0.00001-0.411
Benz[ <i>a</i> ]anthracene	0.0003-0.0557	<0.00001-0.139
Chrysene	0.0006-0.0640	0.00005-1.014
Benzo[ <i>ghi</i> ]fluoranthene	0.0001-0.0298	ND
Corannulene	0.0009-0.0023	ND

5-RING PAH	Yield Range (mg/g soot)	Yield Range (mg/g soot)
Benzo[ <i>a</i> ]fluoranthene	0.0002-0.0371	ND
Benzo[ <i>j</i> ]fluoranthene	0.0001-0.0518	ND
Benzo[ <i>e</i> ]pyrene	0.0010-0.0779	0.00021-2.125
Benzo[ <i>b</i> ]fluoranthene	0.0008-0.0892	0.00017-3.642
Perylene	0.0002-0.0240	ND
Benzo[ <i>k</i> ]fluoranthene	0.0005-0.0552	<0.00001-0.098
Benzo[ <i>a</i> ]pyrene	0.0007-0.1334	0.0000875-0.628
Dibenz[ <i>a,c</i> ]anthracene	0.0001-0.0114	0.000011-0.119
Benzo[ <i>c</i> ]chrysene	0.00004-0.0035	ND
Dibenz[ <i>a,j</i> ]anthracene	0.0002-0.0246	0.000032-0.598
Pentaphene	0.0001-0.0109	ND
Dibenz[ <i>a,h</i> ]anthracene	0.0002-0.0070	0.000048-0.471
Benzo[ <i>b</i> ]chrysene	0.0002-0.0167	<0.00001-0.072
Picene	0.0002-0.0126	0.00003-0.692

6-RING PAH	Yield Range (mg/g soot)	Yield Range (mg/g soot)
Benzo[ <i>ghi</i> ]perylene	0.0018-0.1322	0.00014-1.164
Indeno[1,2,3- <i>cd</i> ]pyrene	0.0016-0.1506	0.00019-0.542
Indeno[1,2,3- <i>cd</i> ]fluoranthene	0.0001-0.0198	ND
Anthanthrene	0.0003-0.0440	ND
Naphtho[1,2- <i>b</i> ]fluoranthene	0.0003-0.0270	0.000095-0.712
Naphtho[2,3- <i>e</i> ]pyrene	0.0002-0.0078	ND
Dibenzo[ <i>a,e</i> ]pyrene	0.0005-0.0386	0.000021-0.553
Naphtho[1,2- <i>a</i> ]pyrene	0.0003-0.0099	ND
Naphtho[1,2- <i>k</i> ]fluoranthene	0.0003-0.0199	ND
Benzo[ <i>b</i> ]perylene	0.0002-0.0290	ND
Dibenzo[ <i>e,l</i> ]pyrene	0.0001-0.0025	0.00001-1.290
Naphtho[2,3- <i>b</i> ]fluoranthene	0.0003-0.0069	ND
Dibenzo[ <i>b,k</i> ]fluoranthene	0.0003-0.0192	0.000078-0.307
Naphtho[2,1- <i>a</i> ]pyrene	0.0005-0.0292	<0.00001-0.306
Dibenzo[ <i>a,h</i> ]pyrene	0.004	ND
Dibenzo[ <i>a,i</i> ]pyrene	0.0003-0.0184	ND
Naphtho[2,3- <i>a</i> ]pyrene	0.0017	ND

7 to 10-RING PAH	Yield Range (mg/g soot)	Yield Range (mg/g soot)
Coronene	0.0019-0.0788	0.000073-0.500

Dibenzo[ <i>b,ghi</i> ]perylene	0.0001-0.0345	ND
Dibenzo[ <i>e,ghi</i> ]perylene	0.0011-0.0316	ND
Dibenzo[ <i>cd,lm</i> ]perylene	0.0001-0.0024	ND
Benzo[ <i>a</i> ]coronene	0.0006-0.0248	<0.00001-0.152
Phenanthro[5,4,3,2- <i>efghi</i> ]perylene	0.0006-0.0044	ND
Benzo[ <i>ghi</i> ]naphtho[8,1,2- <i>bcd</i> ]perylene	0.0003-0.0170	ND
Benzo[ <i>pqr</i> ]naphtho[8,1,2- <i>bcd</i> ]perylene	0.0003-0.0424	<0.00001-0.100
Phenanthro[2,3- <i>a</i> ]pyrene	0.0003-0.0288	ND
Naphtho[8,1,2- <i>abc</i> ]coronene	0.0008-0.0238	ND
Ovalene	0.0001-0.0046	ND
Dibenzo[ <i>a,j</i> ]coronene	0.0011	ND
Tribenzo[ <i>e,ghi,k</i> ]perylene	ND	<0.00001-0.085

\*ND – denotes not detected

The wood soot extract produced 84 PAC. All the PAC found in the coal soot extract were also found in the wood soot extract except for benzo[*b*]naphtho[2,1-*d*]thiophene and tribenzo[*e,ghi,k*]perylene. The former contains sulfur which is not present in wood. However, traces of benzo[*b*]naphtho[2,1-*d*]thiophene (< 0.1 mg/kg of wood) and dibenzothiophene have been reported on birch wood emission (Hedberg).

It can also be seen that there are more oxygenated PAC in the wood soot extract than the coal soot extract. One possible reason is that wood contains oxygen. Together with the oxygen from air, this would have promoted better formation of oxygenated compounds. Also, wood contains lignin which is responsible in the formation of benzanthrone and 6H-benzo[*cd*]pyren-6-one as shown in Figure 2.1. Moreover, the presence of lignin in wood has been shown to increase formation rate of PAC during combustion (as cited by McDonald). As mentioned in the chapter on PAC formation, most of the PAK were formed from cyclopenta-fused PAH. Since there were more CP-PAH in wood soot than in coal soot, then more oxygenated PAC are present in the wood than in the coal soot.

In the coal soot extract, there is an absence of the methylated and ethynyl-substituted PAH. This has been pointed out by Sandrowitz since ethynyl-substituted have been found in

some products of coal combustion and pyrolysis. Since most of the ethynyl-substituted PAH were naphthalenes, acenaphthylenes, anthracenes and phenanthrenes, the small PAH may have just volatilized and remained in the gas phase.

With regards to the few cyclopenta-fused PAH identified in the coal soot, it is assumed that the PAH have undergone oxidation. Since the soot is located at the bottom of the woks, it has been exposed to oxygen, light, and heat which promoted the oxidation reaction. This is also confirmed by the identification of oxygenated PAC in the sample (Sandrowitz).














In the wood soot, there were more methylated, ethynyl-substituted, cyclopenta-fused, and PAH with small rings and > 5 rings found than in the coal soot extract. The method of extraction may have been a factor. The use of the Pinnacle II column enabled the identification of these compounds possibly because of better elution with this column. It is also possible that with the sonication method used in the coal soot, not all the PAC were extracted. As mentioned by Jonker, sonication should be avoided for soot and sediment samples. Soxhlet extraction may have been a better method in the extraction of PAC in soot samples. Lastly, the acquisition of new UV absorbance spectra added to the Chemstation library also facilitated the identification of some previously unknown peaks especially the higher molecular weight PAH.

In the coal soot extract, the majority of the component mass is in the 5 to 6 ring groups (Wornat 2001b). This was the same observation for the wood soot extract wherein the majority lies with the formula of  $C_{20}H_{12}$  in the 5-ring and  $C_{24}H_{14}$  in the 6-ring. In the wood soot extract the PAH with the highest yield are benzo[*a*]pyrene, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene while for the coal soot extract, benzo[*e*]pyrene and benzo[*b*]fluoranthene were the highest. It can also be seen that the yield in the coal soot extract are a lot higher than the wood soot extract for the PAH with rings greater than 5. This implies that the amount of PAH adsorbed in the soot were greater in coal than in wood. This is the same observation by Chuang 1992b that

coal emission is higher than wood. However, in the study of Oanh (1999), wood has higher particulate matter and smoke emission than coal. The PAH in particulate matter in wood is 5% of the total 18 PAH while it is only 0.1% and 0.4% in coal. Also, the particulate matter emission rate is 51 mg/kg wood while only 7 mg/kg coal. It was studied that soot from wood stoves contains lighter PAH and that soot formation in a chimney is two to three times more in wood combustion than in coal or oil combustion (DeFre). With regards to the amount of benzo[*a*]pyrene in particulate matter, it is 10.5 mg/g in wood and 0.18 mg/g in coal.

In the thesis of Sandrowitz, it was mentioned that Edwards and Polagye were able to identify 52 PAC from the wood soot extract from Henan, China following the same methodology of the coal soot extract. The PAC identified were also found in the wood soot extract in this study except for biphenyl and 1-phenylnaphthalene. But traces of biphenyl were also found with the use of GC/MS. More so, the identification of corannulene as a product of wood combustion was also reported by Edwards and Polagye. It was noted that corannulene is a proposed intermediate in the formation pathways for fullerenes (Lafleur 1996a).




Table 4.5 OXYGENATED PAH Identified in HPLC/UV-vis

Compound	Structure	Formula	MW	Yield Range (mg/g soot)	Mutagenicity	Carcinogenicity
2-Naphthaldehyde		C <sub>11</sub> H <sub>8</sub> O	156	0.0008-0.0042	Not Mutagenic <sup>h</sup>	Toxic <sup>h</sup>
1-Naphthaldehyde		C <sub>11</sub> H <sub>8</sub> O	156	0.0023	Not Mutagenic <sup>h</sup>	Toxic <sup>h</sup>
Dibenzofuran		C <sub>12</sub> H <sub>8</sub> O	168	0.0016-0.0030	N.D.	0 <sup>l</sup>
Acenaphthenequinone		C <sub>12</sub> H <sub>6</sub> O <sub>2</sub>	182	0.0001-0.0048	N.D.	N.D.
Naphthalene-1,8-dicarboxylic anhydride		C <sub>12</sub> H <sub>6</sub> O <sub>3</sub>	198	0.0007-0.0239	Not Mutagenic <sup>r</sup>	N.D.
Phenalenone		C <sub>13</sub> H <sub>8</sub> O	180	0.0005-0.0302	Mutagenic <sup>f,r,c</sup>	Carcinogenic <sup>c</sup>
9-Flourenone		C <sub>13</sub> H <sub>8</sub> O	180	0.0015-0.0190	Not Mutagenic <sup>c,f,h</sup>	N.D.
Anthraquinone		C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	208	0.0005-0.0048	Not Mutagenic <sup>h,r</sup>	N.D.
4H-cyclopenta[def]phenanthren-4-one		C <sub>15</sub> H <sub>8</sub> O	204	0.0005-0.0023	Not Mutagenic <sup>r</sup>	N.D.
1-Hydroxypyrene		C <sub>16</sub> H <sub>10</sub> O	218	0.0016-0.0024	N.D.	N.D.
Benzanthrone		C <sub>17</sub> H <sub>10</sub> O	230	0.0009-0.0394	Mutagenic <sup>r</sup>	Carcinogenic <sup>c</sup>
4-Oxa-benzo[cd]pyrene-3,5-dione		C <sub>18</sub> H <sub>8</sub> O <sub>3</sub>	272	0.0009-0.0159	Not tested <sup>r</sup>	N.D.
6H-benzo[cd]pyren-6-one		C <sub>19</sub> H <sub>10</sub> O	254	0.0010-0.1658	Mutagenic <sup>r</sup>	N.D.
Cyclopenta[def]chrysene-4-one		C <sub>19</sub> H <sub>10</sub> O	254	0.0001-0.0160	Not tested <sup>r</sup>	N.D.

N.D. – no data

<sup>f</sup> Fluorenone (Ames test), Phenalenone using forward mutation 8-azaguanine assay (as cited by Kamens 1985)<sup>c</sup> as cited by Ramdahl 1983<sup>h</sup> Ames *Salmonella* assay (as cited by Ramdahl 1982)<sup>l</sup> as cited by Lee 1981; 0- noncarcinogenic<sup>r</sup> as cited by Sandrowitz

Table 4.6 METHYLATED, ETHYNYL-SUBSTITUTED and CYCLOPENTA-FUSED PAH Identified in HPLC/UV-vis

Compound	Structure	Formula	MW	Yield Range (mg/g soot)	Mutagenicity	Carcinogenicity
Acenaphthylene		C <sub>12</sub> H <sub>8</sub>	152	0.0004-0.0131	Mutagenic <sup>r</sup>	0 <sup>1</sup>
Acephenanthrylene		C <sub>16</sub> H <sub>10</sub>	202	0.0001-0.0261	Not Mutagenic <sup>r</sup>	N.D.
Cyclopent[hi]acephenanthrylene		C <sub>18</sub> H <sub>10</sub>	226	0.0009-0.0112	Not Mutagenic <sup>r</sup>	N.D.
Cyclopenta[cd]pyrene		C <sub>18</sub> H <sub>10</sub>	226	0.0002-0.0343	Mutagenic <sup>r</sup>	+ <sup>1</sup>
Cyclopenta[bc]coronene		C <sub>26</sub> H <sub>12</sub>	324	0.0001-0.0111	N.D.	N.D.
1-Methylnaphthalene		C <sub>11</sub> H <sub>10</sub>	142	0.0013-0.3357	N.D.	N.D.
2-Methylnaphthalene		C <sub>11</sub> H <sub>10</sub>	142	0.0023-0.0071	N.D.	0 <sup>1</sup>
1-Ethynylnaphthalene		C <sub>12</sub> H <sub>8</sub>	152	0.0038-0.0108	N.D.	N.D.
2-Ethynylnaphthalene		C <sub>12</sub> H <sub>8</sub>	152	0.0031	N.D.	N.D.
4-Methylpyrene		C <sub>17</sub> H <sub>12</sub>	216	0.0001-0.0044	N.D.	N.D.
1-Methylpyrene		C <sub>17</sub> H <sub>12</sub>	216	0.0001-0.0060	N.D.	0 <sup>1</sup>
2-Methylpyrene		C <sub>17</sub> H <sub>12</sub>	216	0.0002-0.0088	N.D.	0 <sup>1</sup>
3-Ethynylpyrene		C <sub>18</sub> H <sub>10</sub>	226	0.0003-0.0206	N.D.	N.D.
2,2'-Binaphthalene		C <sub>20</sub> H <sub>14</sub>	254	0.0092	N.D.	N.D.
Methyl coronene		C <sub>25</sub> H <sub>14</sub>	314	0.00005-0.0005	N.D.	N.D.

N.D. – no data

<sup>1</sup> as cited by Lee 1981, 0- noncarcinogenic, + - up to 33%, weakly carcinogenic<sup>r</sup> as cited by Sandrowitz















Table 4.7 2- to 4-RING PAH Identified in HPLC/UV-vis

Compound	Structure	Formula	MW	Yield Range (mg/g soot)	Mutagenicity	Carcinogenicity
Naphthalene		C <sub>10</sub> H <sub>8</sub>	128	0.0034-0.0263	N.D.	0 <sup>k,l,s</sup>
Phenanthrene		C <sub>14</sub> H <sub>10</sub>	178	0.0012-0.0245	Not Mutagenic <sup>m,n,r</sup>	0 <sup>k,l,n,s</sup>
Anthracene		C <sub>14</sub> H <sub>10</sub>	178	0.0002-0.0114	Not Mutagenic <sup>m,n</sup>	0 <sup>k,l,n,s</sup> , + <sup>s</sup>
Fluoranthene		C <sub>16</sub> H <sub>10</sub>	202	0.0005-0.0449	Mutagenic <sup>m,n</sup> Not Mutagenic <sup>m,n,r</sup>	0 <sup>l,n,s</sup> , Carcinogenic <sup>a</sup>
Pyrene		C <sub>16</sub> H <sub>10</sub>	202	0.0005-0.0533	Not Mutagenic <sup>m,n,r</sup>	0 <sup>l,n,s</sup>
Benzo[ <i>a</i> ]fluorene		C <sub>17</sub> H <sub>12</sub>	216	0.0002-0.0072	Mutagenic <sup>n</sup> Not Mutagenic <sup>r</sup>	0 <sup>r,n</sup>
Benzo[ <i>c</i> ]phenanthrene		C <sub>18</sub> H <sub>12</sub>	228	0.0002-0.0034	Mutagenic <sup>r</sup>	+ <sup>k,l,s</sup>
Triphenylene		C <sub>18</sub> H <sub>12</sub>	228	0.0003-0.0130	Mutagenic <sup>n</sup>	0 <sup>k,l,n,s</sup>
Benz[ <i>a</i> ]anthracene		C <sub>18</sub> H <sub>12</sub>	228	0.0003-0.0557	Mutagenic <sup>d,r</sup> , Both Mut. & Not Mut. <sup>m,n</sup>	+ <sup>k,n,s</sup> , Probably Carcinogenic <sup>e</sup>
Chrysene		C <sub>18</sub> H <sub>12</sub>	228	0.0006-0.0640	Mutagenic <sup>n,r</sup>	+ <sup>k,l,n,s</sup> , Not Carcinogenic <sup>e,n,s</sup>
Benzo[ <i>ghi</i> ]fluoranthene		C <sub>18</sub> H <sub>10</sub>	226	0.0001-0.0298	Not Mutagenic <sup>r</sup>	0 <sup>l,n,s</sup>
Corannulene		C <sub>20</sub> H <sub>10</sub>	250	0.0009-0.0023	N.D.	N.D.

N.D. – no data

<sup>a</sup> as cited by Kozinski<sup>d</sup> as cited by Oros<sup>e</sup> as cited by Ikarishi, Nielsen<sup>k</sup> as cited by Jinno; 0- inactive, + - slight, ++ - moderate, +++ more active, ++++ very active<sup>r</sup> as cited by Lee 1981, 0- noncarcinogenic, + - up to 33%, weakly carcinogenic<sup>m</sup> Grimmer 1983b<sup>n</sup> Grimmer 1983a<sup>r</sup> as cited by Sandrowitz<sup>s</sup> as cited by Flesher

Table 4.8 5-RING PAH Identified in HPLC/UV-vis

Compound	Structure	Formula	MW	Yield Range (mg/g soot)	Mutagenicity	Carcinogenicity
Benzo[ <i>a</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0002-0.0371	N.D.	N.D.
Benzo[ <i>j</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0001-0.0518	Mutagenic <sup>n,r</sup>	++ <sup>l,s</sup> , Both Car. & Not Car. <sup>n</sup>
Benzo[ <i>e</i> ]pyrene		C <sub>20</sub> H <sub>12</sub>	252	0.0010-0.0779	Mutagenic <sup>r</sup> , Both Mut. & Not Mut. <sup>n</sup>	0/+ <sup>l,n</sup> , + <sup>k</sup> , Not Carcinogenic <sup>e,s</sup>
Benzo[ <i>b</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0008-0.0892	Mutagenic <sup>n,r</sup>	++ <sup>l,s</sup> , Both Car. & Not Car. <sup>n</sup> , Possibly Carcinogenic <sup>e</sup>
Perylene		C <sub>20</sub> H <sub>12</sub>	252	0.0002-0.0240	Mutagenic <sup>b,n</sup> , Not Mutagenic <sup>r</sup>	0 <sup>l,n,s</sup>
Benzo[ <i>k</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0005-0.0552	Mutagenic <sup>r</sup> , Not Mutagenic <sup>n</sup>	++ <sup>l,s</sup> , Both Car. & Not Car. <sup>n</sup> , Possibly Carcinogenic <sup>e</sup>
Benzo[ <i>a</i> ]pyrene		C <sub>20</sub> H <sub>12</sub>	252	0.0007-0.1334	Mutagenic <sup>n,r</sup>	++ <sup>l</sup> , ++++ <sup>k,s</sup> , Carcinogenic <sup>a,n</sup> , Probably Carcinogenic <sup>e</sup>
Dibenz[ <i>a,c</i> ]anthracene		C <sub>22</sub> H <sub>14</sub>	278	0.0001-0.0114	Mutagenic <sup>n</sup>	+ <sup>k,l,s</sup> , Not Carcinogenic <sup>n</sup>
Benzo[ <i>c</i> ]chrysene		C <sub>22</sub> H <sub>14</sub>	278	0.00004-0.0035	N.D.	+ <sup>l,s</sup> , 0 <sup>s</sup>
Dibenz[ <i>a,j</i> ]anthracene		C <sub>22</sub> H <sub>14</sub>	278	0.0002-0.0246	Mutagenic <sup>n,r</sup>	+ <sup>k,l</sup> , ++ <sup>s</sup> , Not Carcinogenic <sup>n</sup>
Pentaphene		C <sub>22</sub> H <sub>14</sub>	278	0.0001-0.0109	N.D.	0 <sup>l,s</sup>
Dibenz[ <i>a,h</i> ]anthracene		C <sub>22</sub> H <sub>14</sub>	278	0.0002-0.0070	Mutagenic <sup>r</sup> , Both Mut. & Not Mut. <sup>n</sup>	+ <sup>l,n</sup> , ++ <sup>k,s</sup> , Probably Carcinogenic <sup>e</sup>
Benzo[ <i>b</i> ]chrysene		C <sub>22</sub> H <sub>14</sub>	278	0.0002-0.0167	Not Mutagenic <sup>r</sup>	0 <sup>k,l</sup> , + <sup>s</sup>
Picene		C <sub>22</sub> H <sub>14</sub>	278	0.0002-0.0126	Not Mutagenic <sup>r</sup>	0 <sup>k,l,s</sup> , ++ <sup>s</sup>

N.D. – no data

<sup>a</sup> as cited by Kozinski

<sup>b</sup> Kozinski

<sup>e</sup> as cited by Ikarishi, Nielsen

<sup>k</sup> as cited by Jinno; 0- inactive, + - slight, ++ - moderate, +++ more active, ++++ very active
















<sup>l</sup> as cited by Lee 1981, 0- noncarcinogenic, + - up to 33%, weakly carcinogenic, ++ - above 33%, strongly carcinogenic

<sup>n</sup> Grimmer 1983a



<sup>r</sup> as cited by Sandrowitz

<sup>s</sup> as cited by Flesher

Table 4.9 6-RING PAH Identified in HPLC/UV-vis

Compound	Structure	Formula	MW	Yield Range (mg/g soot)	Mutagenicity	Carcinogenicity
Benzo[ghi]perylene		C <sub>22</sub> H <sub>12</sub>	276	0.0018-0.1322	Mutagenic <sup>n,r</sup>	+ <sup>1</sup> , Not Carcinogenic <sup>e,n,s</sup>
Indeno[1,2,3- <i>cd</i> ]pyrene		C <sub>22</sub> H <sub>12</sub>	276	0.0016-0.1506	Mutagenic <sup>r</sup>	+ <sup>1</sup> ,++ <sup>s</sup> ,BothCar.&Not Car. <sup>n</sup> Possibly Carcinogenic <sup>e</sup>
Indeno[1,2,3- <i>cd</i> ]fluoranthene		C <sub>22</sub> H <sub>12</sub>	276	0.0001-0.0198	N.D.	Carcinogenic <sup>n</sup>
Anthanthrene		C <sub>22</sub> H <sub>12</sub>	276	0.0003-0.0440	Both Mut. & Not Mut. <sup>n</sup>	0 <sup>l,s</sup> , Both Car. & Not Car. <sup>n</sup>
Naphtho[1,2- <i>b</i> ]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0003-0.0270	Not Mutagenic <sup>o</sup>	N.D.
Naphtho[2,3- <i>e</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0002-0.0078	Mutagenic <sup>o</sup>	0 <sup>l</sup> , Not Carcinogenic <sup>g,s</sup>
Dibenzo[ <i>a,e</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0005-0.0386	Mutagenic <sup>o,r</sup> , Not Mutagenic <sup>n</sup>	++ <sup>1,s</sup> , +++ <sup>k</sup> , Carcinogenic <sup>g,j,n</sup>
Naphtho[1,2- <i>a</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0003-0.0099	Mutagenic <sup>p</sup>	N.D.
Naphtho[1,2- <i>k</i> ]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0003-0.0199	Mutagenic <sup>o</sup>	N.D.
Benzo[ <i>b</i> ]perylene		C <sub>24</sub> H <sub>14</sub>	302	0.0002-0.0290	Mutagenic <sup>o</sup>	N.D.
Dibenzo[ <i>e,l</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0001-0.0025	Mutagenic <sup>o</sup>	0 <sup>l,n,s</sup>
Naphtho[2,3- <i>b</i> ]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0003-0.0069	Mutagenic <sup>o</sup>	N.D.
Dibenzo[ <i>b,k</i> ]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0003-0.0192	Mutagenic <sup>o</sup>	0 <sup>l,s</sup>
Naphtho[2,1- <i>a</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0005-0.0292	Mutagenic <sup>o,r</sup>	Carcinogenic <sup>g</sup>
Dibenzo[ <i>a,h</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.004	Mutagenic <sup>o</sup> , Both Mut. & Not Mut. <sup>n</sup>	++ <sup>1</sup> , ++++ <sup>k,s</sup> , Carcinogenic <sup>g,n</sup>

(Table continued)

Dibenzo[ <i>a,i</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.00004-0.0184	Mutagenic <sup>o,n</sup>	++++ <sup>k,s</sup> , Carcinogenic <sup>i,n</sup>
Naphtho[2,3- <i>a</i> ]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0017	Mutagenic <sup>o</sup>	+ <sup>l</sup> , ++ <sup>k</sup> , Carcinogenic <sup>g</sup>

N.D. – no data

<sup>c</sup> as cited by Ikarishi, Nielsen

<sup>g</sup> as cited by Marvin

<sup>j</sup> as cited by Schmidt

<sup>k</sup> as cited by Jinno; 0- inactive, + - slight, ++ - moderate, +++ more active, ++++ very active

<sup>l</sup> as cited by Lee 1981, 0- noncarcinogenic, + - up to 33%, weakly carcinogenic, ++ - above 33%, strongly carcinogenic

<sup>n</sup> Grimmer 1983a




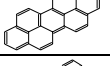




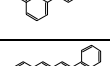



<sup>o</sup> Durant 1999

<sup>p</sup> Desai

<sup>r</sup> as cited by Sandrowitz

<sup>s</sup> as cited by Flesher










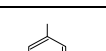
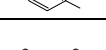
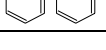
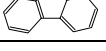
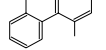
Table 4.10 7- to 10-RING PAH Identified in HPLC/UV-vis

Compound	Structure	Formula	MW	Yield Range (mg/g soot)	Mutagenicity	Carcinogenicity
Coronene		C <sub>24</sub> H <sub>12</sub>	300	0.0019-0.0788	Not Mutagenic <sup>n,r</sup>	0/+ <sup>1</sup> , Carcinogenic <sup>n</sup> , 0 <sup>s</sup>
Dibenzo[ <i>b,ghi</i> ]perylene		C <sub>26</sub> H <sub>14</sub>	326	0.0001-0.0345	N.D.	N.D.
Dibenzo[ <i>e,ghi</i> ]perylene		C <sub>26</sub> H <sub>14</sub>	326	0.0011-0.0316	N.D.	N.D.
Dibenzo[ <i>cd,lm</i> ]perylene		C <sub>26</sub> H <sub>14</sub>	326	0.0001-0.0024	N.D.	+ <sup>1</sup> , Moderate Carcinogenic <sup>i</sup> , 0 <sup>s</sup>
Benzo[ <i>a</i> ]coronene		C <sub>28</sub> H <sub>14</sub>	350	0.0006-0.0248	N.D.	0 <sup>1,s</sup>
Phenanthro[5,4,3,2- <i>efghi</i> ]perylene		C <sub>28</sub> H <sub>14</sub>	350	0.0006-0.0044	N.D.	N.D.
Benzo[ <i>ghi</i> ]naphtho[8,1,2- <i>bcd</i> ]perylene		C <sub>28</sub> H <sub>14</sub>	350	0.0003-0.0170	N.D.	N.D.
Benzo[ <i>pqr</i> ]naphtho[8,1,2- <i>bcd</i> ]perylene		C <sub>28</sub> H <sub>14</sub>	350	0.0003-0.0424	N.D.	N.D.
Phenanthro[2,3- <i>a</i> ]pyrene		C <sub>28</sub> H <sub>16</sub>	352	0.0003-0.0288	N.D.	N.D.
Naphtho[8,1,2- <i>abc</i> ]coronene		C <sub>30</sub> H <sub>14</sub>	374	0.0008-0.0238	N.D.	N.D.
Ovalene		C <sub>32</sub> H <sub>14</sub>	398	0.0001-0.0046	N.D.	N.D.
Dibenzo[ <i>a,j</i> ]coronene		C <sub>32</sub> H <sub>16</sub>	400	0.0011	N.D.	N.D.

N.D. – no data

<sup>i</sup> as cited by Pace<sup>1</sup> as cited by Lee 1981; 0- noncarcinogenic, + - up to 33%, weakly carcinogenic<sup>n</sup> Grimmer 1983a<sup>r</sup> as cited by Sandrowitz<sup>s</sup> as cited by Flesher















Table 4.11 Aromatic Hydrocarbons Identified in the GC/MS

Compound	Structure	Formula	MW	Yield Range(mg/g soot)	Mutagenicity	Carcinogenicity
Benzene		C <sub>6</sub> H <sub>6</sub>	78	0.0064-0.5384	N.D.	N.D.
cyclohexane		C <sub>6</sub> H <sub>12</sub>	84	0.0057-3.7985	N.D.	N.D.
Methylcyclohexane		C <sub>7</sub> H <sub>14</sub>	98	0.0014-0.0538	N.D.	N.D.
Toluene		C <sub>7</sub> H <sub>8</sub>	92	0.0478-1.5718	N.D.	N.D.
Ethylbenzene		C <sub>8</sub> H <sub>10</sub>	106	0.0009-0.0068	N.D.	N.D.
1,2-dimethylbenzene		C <sub>8</sub> H <sub>10</sub>	106	0.0027-0.0110	N.D.	N.D.
Phenylethyne		C <sub>8</sub> H <sub>6</sub>	102	0.0003-0.0129	N.D.	N.D.
Styrene		C <sub>8</sub> H <sub>8</sub>	104	0.0002-0.0090	N.D.	N.D.
1,3-dimethylbenzene		C <sub>8</sub> H <sub>10</sub>	106	0.0092-0.0289	N.D.	N.D.
Biphenyl		C <sub>12</sub> H <sub>10</sub>	154	0.0007-0.0129	N.D.	N.D.
Fluorene		C <sub>13</sub> H <sub>10</sub>	166	0.0034-0.0065	Not Mutagenic <sup>n</sup>	Not Carcinogenic <sup>n,e</sup>
4-methylphenanthrene		C <sub>15</sub> H <sub>12</sub>	192	0.0032-0.0038	N.D.	N.D.
9-methylanthracene		C <sub>15</sub> H <sub>12</sub>	192	0.0010	N.D.	N.D.
2-phenylnaphthalene		C <sub>16</sub> H <sub>12</sub>	204	0.0061-0.0322	N.D.	N.D.




N.D. – no data

<sup>n</sup> Grimmer 1983a<sup>e</sup> as cited by Ikarishi, Nielsen

Table 4.12 Oxygen-containing Aromatics Identified in the GC/MS





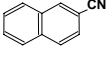



Compound	Structure	Formula	MW	Yield Range(mg/g soot)	Mutagenicity	Carcinogenicity
Furfural		C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96	0.0015-0.0840	N.D.	N.D.
2-methyl-2-cyclopenten-1-one		C <sub>6</sub> H <sub>8</sub> O	96	0.0005-0.0042	N.D.	N.D.
2-cyclohexen-1-one		C <sub>6</sub> H <sub>8</sub> O	96	0.0028-0.0083	N.D.	N.D.
Benzaldehyde		C <sub>7</sub> H <sub>6</sub> O	106	0.0020-0.0082	N.D.	N.D.
Phenol		C <sub>6</sub> H <sub>6</sub> O	94	0.0165-0.1655	N.D.	N.D.
Benzofuran		C <sub>8</sub> H <sub>6</sub> O	118	0.0008-0.0088	N.D.	N.D.
2-hydroxybenzaldehyde		C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122	0.0009-0.0073	N.D.	N.D.
3-methylphenol		C <sub>7</sub> H <sub>8</sub> O	108	0.0037-0.0149	N.D.	N.D.
2-methylbenzaldehyde		C <sub>8</sub> H <sub>8</sub> O	120	0.0010	N.D.	N.D.
3-methylbenzaldehyde		C <sub>8</sub> H <sub>8</sub> O	120	0.0005	N.D.	N.D.
4-methylphenol		C <sub>7</sub> H <sub>8</sub> O	108	0.0079-0.0534	N.D.	N.D.
Benzoic acid		C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122	0.0091-0.0145	N.D.	N.D.
4-hydroxybenzaldehyde		C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122	0.0042-0.0112	N.D.	N.D.
1,4-naphthalenedione		C <sub>10</sub> H <sub>6</sub> O <sub>2</sub>	158	0.0012	N.D.	N.D.

(Table continued)

2-naphthalenol		$C_{10}H_8O$	144	0.0010	N.D.	N.D.
1,2-acenaphthylenedione		$C_{12}H_6O_2$	182	0.0074	N.D.	N.D.
Xanthone		$C_{13}H_8O_2$	196	0.0005-0.0078	N.D.	N.D.

N.D. – no data

Table 4.13 Nitrogen-containing Aromatics Identified in the GC/MS

Compound	Structure	Formula	MW	Yield Range(mg/g soot)	Mutagenicity	Carcinogenicity
Pyridine		C <sub>5</sub> H <sub>5</sub> N	79	0.0002-0.0009	N.D.	N.D.
Benzonitrile		C <sub>7</sub> H <sub>5</sub> N	103	0.0052-0.0075	N.D.	N.D.
Quinoline		C <sub>9</sub> H <sub>7</sub> N	129	0.0013	N.D.	+ <sup>1</sup>
Isoquinoline		C <sub>9</sub> H <sub>7</sub> N	129	0.0014	N.D.	0 <sup>1</sup>
2-naphthalene carbonitrile		C <sub>11</sub> H <sub>7</sub> N	153	0.0027	N.D.	N.D.
Phenanthridine		C <sub>13</sub> H <sub>9</sub> N	179	0.0011-0.0037	N.D.	N.D.
Benzo[g]quinoline		C <sub>13</sub> H <sub>9</sub> N	179	0.0007-0.0052	N.D.	0 <sup>1</sup>
9H-fluoren-9-imine		C <sub>13</sub> H <sub>9</sub> N	179	0.0009	N.D.	N.D.

N.D. – no data

<sup>1</sup>Note (as cited by Lee 1981)

0- noncarcinogenic

+ - up to 33%, weakly carcinogenic

++ - above 33%, strongly carcinogenic

## CHAPTER 5. SUMMARY AND CONCLUSION

Wood has long been used for cooking. In rural places of China, wood, coal, and other biomass are used for domestic cooking. These types of solid fuels are known to cause various health problems due to the emissions. In recent years there have been reports on the alarming rates of esophageal cancer in the Henan Province of China (as cited by Roth). Studies reveal that the possible ingestion of soot, from unvented wood-burning and coal-burning stoves containing polycyclic aromatic compounds (PAC) can be a factor (as cited by Oanh 1999, Wornat 2001).

PAC are ubiquitous compounds in the environment. It can be formed from solid fuel combustion through pyrolysis and pyrosynthesis. A lot of interest has been drawn in the study of PAC because of its mutagenic and carcinogenic effects (May). In recent years, special focus is given to the high molecular weight polycyclic aromatic hydrocarbons (PAH) greater than 300. These PAH with 5 or 6 rings cause severe carcinogenic and mutagenic effect (as cited by Conde, 2005a).

In this research, the wood soot samples were taken from the bottom of woks used in cooking from different homes in Henan, China. Polycyclic aromatic compounds in soot were extracted for 6 hours using a Soxhlet apparatus with 250 ml of dichloromethane (DCM) as solvent. The PAC in DCM mixture was concentrated in a Kuderna-Danish apparatus. The concentrated sample is then prepared for analysis using the HPLC-UV/vis equipment Hewlett-Packard Model 1050 Series chromatograph with diode-array UV detector. It is equipped with a reversed-phase Pinnacle II PAH column containing alkyl-bonded silica with high carbon load (5  $\mu\text{m}$  particle size; 250 x 4.6 mm; 110 Å pore size). The column is especially used for polycyclic aromatic hydrocarbons analysis. The mobile phases used were 60:40 water/acetonitrile, acetonitrile, and DCM, respectively programmed on different time intervals. The resulting chromatograph presents the different PAC that are then identified by matching the retention time

and UV absorbance spectra with reference standards that are commercially available and specially synthesized.

The HPLC chromatogram showed 84 PAC composed of oxygenated, methylated, ethynyl-substituted, cyclopenta-fused, and benzologues of pyrene, fluoranthene, perylene, and coronene. UV spectral matches enabled the identification of some new and never been reported PAC as product of wood combustion. In the wood soot extract, there were a total of 35 PAC (3 oxygenated, 5 alkylated, 3 cyclopenta-fused, and 24 benzologues of pyrene, fluoranthene, and perylene) that have never been reported before as products of wood combustion.

Detection of PAH with rings  $< 3$  and aromatics was best done with the use of the GC/MS. According to Sauvain and Wise 1988a, 1988b, GC is only partially successful in separating numerous isomers and mass spectrometry provides little differentiation among the various isomers. For PAC with  $< 3$  rings, the number of possible isomers is less, therefore GC/MS can be used. There were 39 compounds detected composed of 14 aromatic hydrocarbons, 17 oxygen-containing aromatics, and 8 nitrogen-containing aromatics.

PAH quantification showed that 5- and 6-ring PAH dominate the wood soot extract. These groups represent the most carcinogenic and mutagenic PAH and comprise 66% of the total amount of PAH contained in the soot. Out of the 84 PAC identified in the HPLC-UV/vis, approximately 31% is carcinogenic and 42% is mutagenic. With respect to the aromatics detected in the GC/MS, 2.5% are carcinogenic and mutagenic.

Comparing with previous results of coal soot extract from Henan, China, using HPLC-UV/vis and a Vydac model 201TP octadecylsilica column, there were 32 PAC found with 2 newly identified PAC as products of wood combustion namely benzo[*b*]naphtho[2,1-*d*]thiophene and tribenzo[*e,ghi,k*]perylene. Quantification of the coal soot sample yielded the same observation that the majority is composed of 5- and 6-ring PAH. In the wood soot extract the

PAH with the highest yield were benzo[*a*]pyrene, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene while for the coal soot extract, benzo[*e*]pyrene and benzo[*b*]fluoranthene were the highest. Also, yield of the coal soot extract are a lot higher than the wood soot extract for the PAH with rings greater than 5. This implies that the amount of PAH adsorbed in the soot is greater in coal than in wood.

Acquisition of the UV absorbance spectra of several reference compounds made it possible to identify some previously unknown peaks. The use of the Pinnacle column provided better elution of the compounds. The Soxhlet method also provided better extraction of the PAC than the sonication method. Nevertheless, there are still some peaks that are yet to be identified.

## CHAPTER 6. RECOMMENDATIONS

The results of this study provide a broad identification of the PAC in an environmental wood soot sample. Since the samples taken were not from controlled environment, there were some variations in the PAC identified. In this regard, investigation of the PAC in the wood soot extract using controlled conditions is recommended. The formation of the various PAC with respect to the combustion temperature, oxygen amount, burn rate, and wood type should be studied.

As shown in this study, the combustion temperature plays an important role in the formation and emission of the different groups of PAC. The light PAC are known to be released at a lower temperature and the high molecular weight PAH are formed at high combustion temperature.

The amount of oxygen plays an important role on the degree of completeness of combustion. The amount of oxygen can be varied and the PAC formed can be examined. The formation of oxygenated compounds is also an important factor to determine. Also, if different sizes of wood were used, the variation in supply of oxygen might influence the emissions, since it leads to different combustion conditions (Hedberg).

According to Hueglin, the size of emission particles emitted during a wood stove burning cycle was strongly dependent on the state of the combustion process. The particle concentration and mean diameter were highest during the start-up phase and decreased during the intermediate and burn-out phases. It would be interesting to find out the effect of the burn cycle on the formation of soot and PAC.

With regards to the type of wood, softwood and hardwoods can be analyzed. Other type of wood scrap or wood chips can also be investigated. From previous studies, it was shown that hardwood has a higher emission level than softwood in a fireplace (McDonald). Also it was

observed that high levels of PAC are emitted from small wood stoves. “Lower quality” fuel such as wood scrap or wood chips may increase emission levels further ten times or more (Nielsen).

In this case, not only the wood soot should be studied, but also the gas phase, and the condensable liquid. Analysis of each individual group or fractions can also be taken into consideration. Wise1988a has suggested that the PAH mixture can be divided into subfractions based on the number of aromatic rings. Different chromatographic columns can be used to separate each subfraction group.

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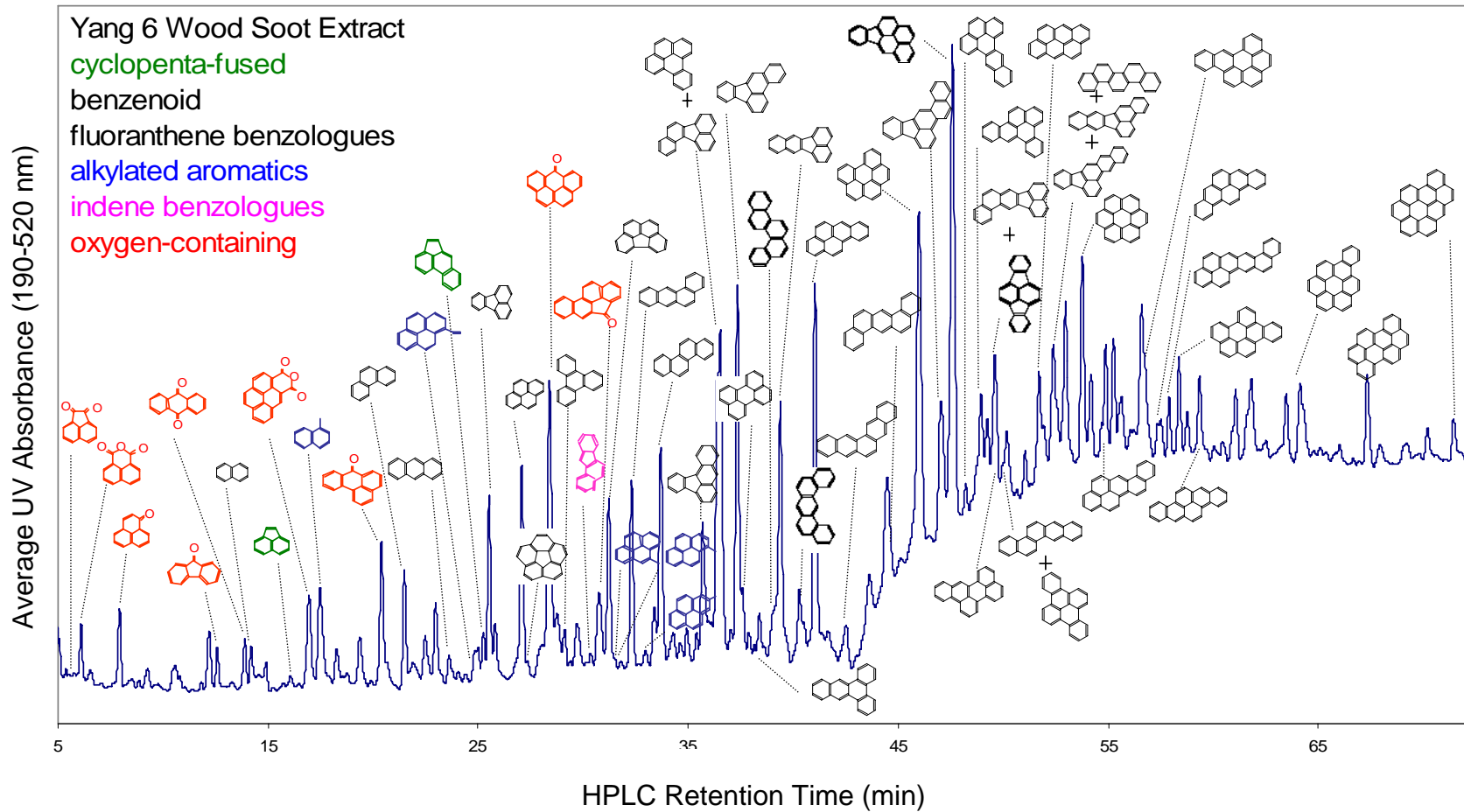
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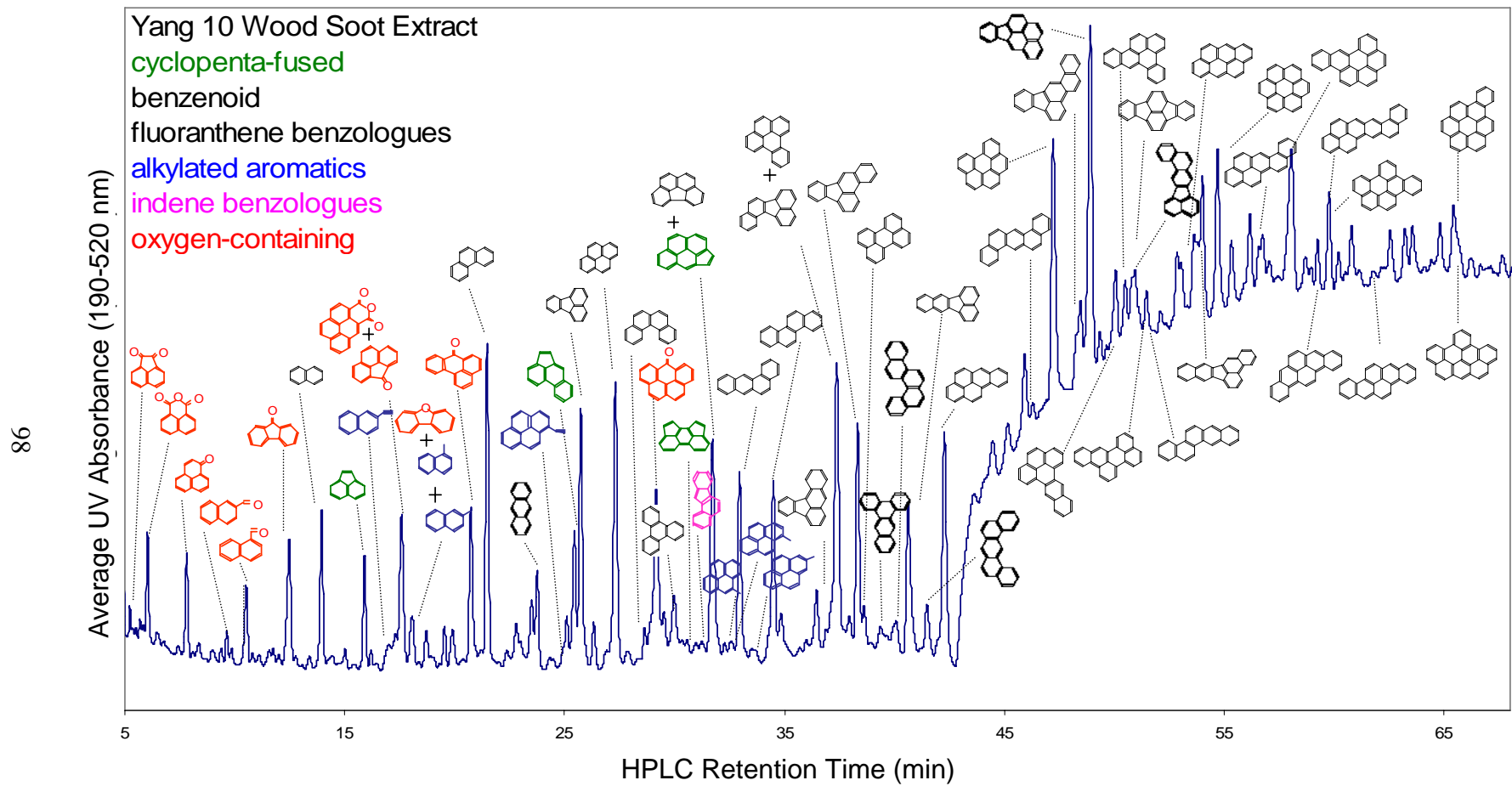
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## APPENDIX A –HPLC CHROMATOGRAMS

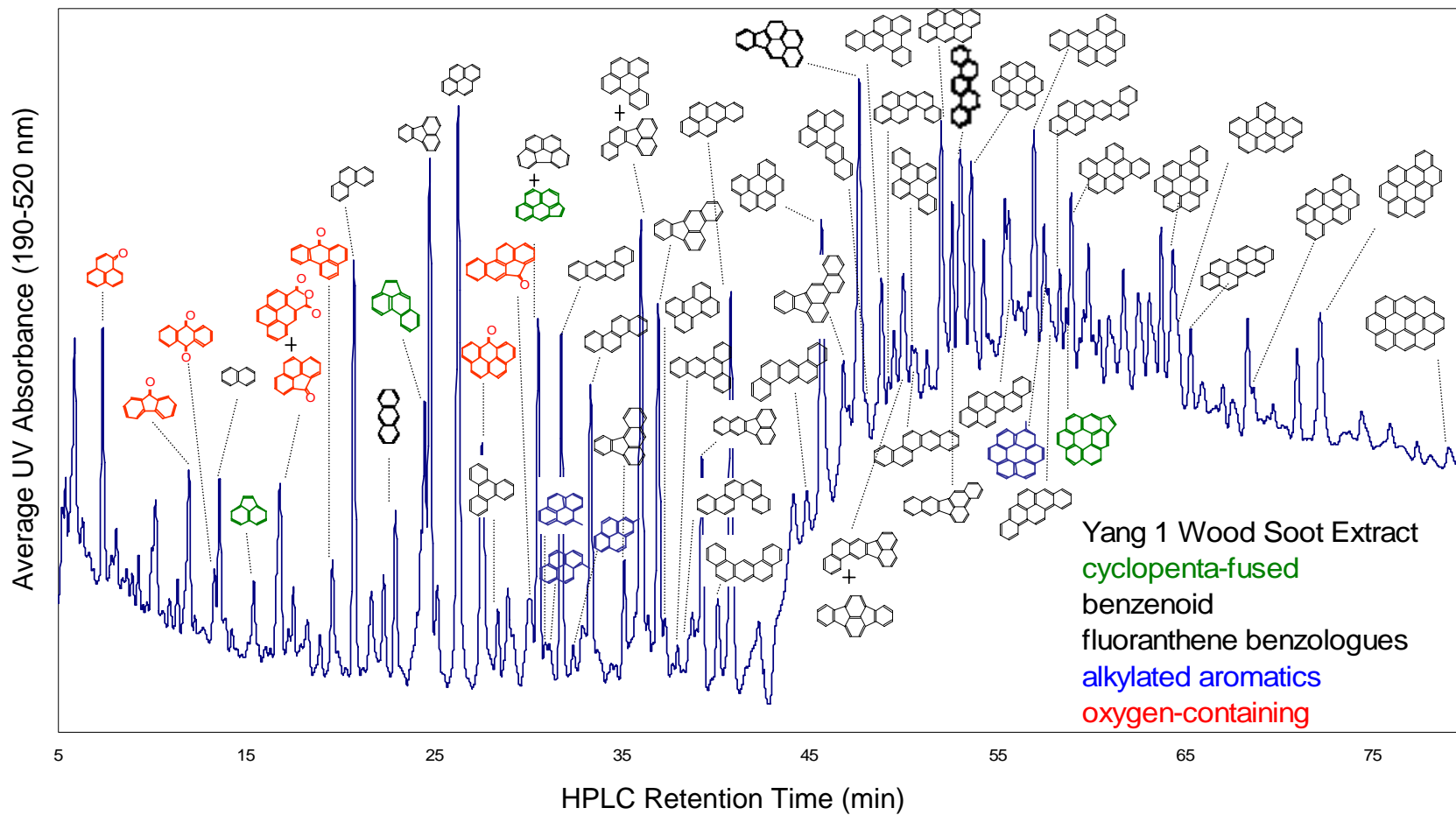
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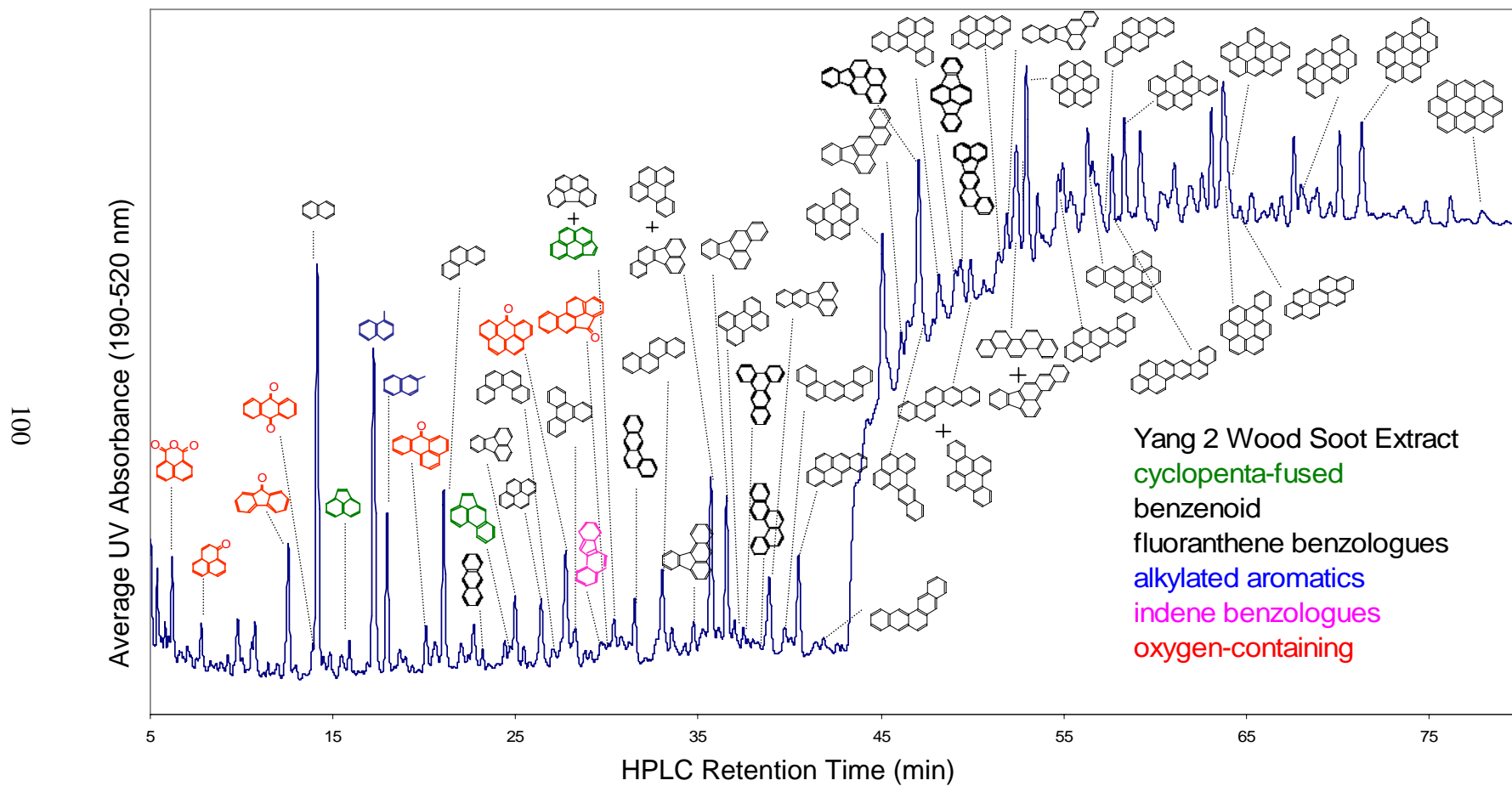
Note: Hump at ~43 min. due to solvent change from ACN to DCM



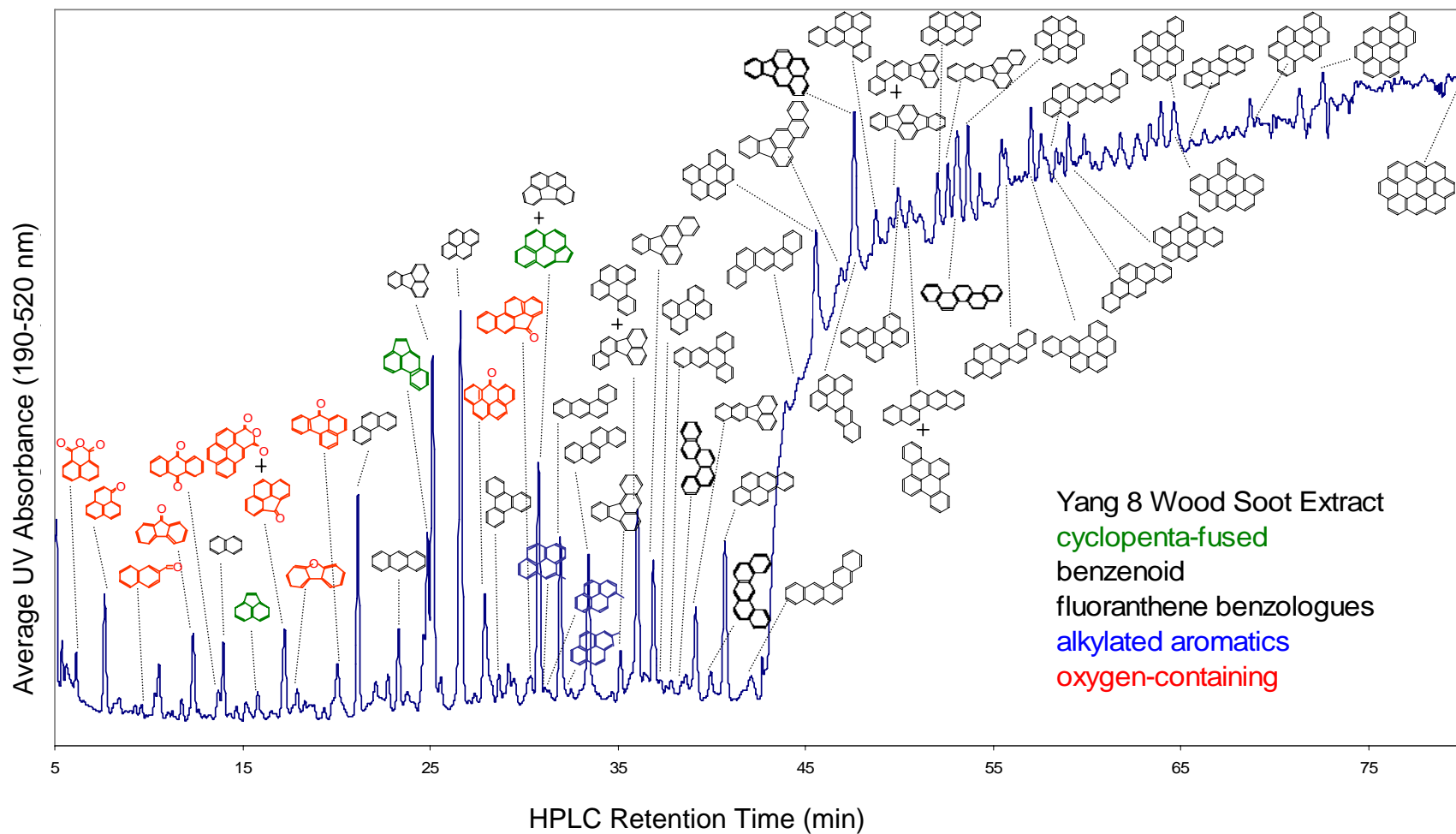
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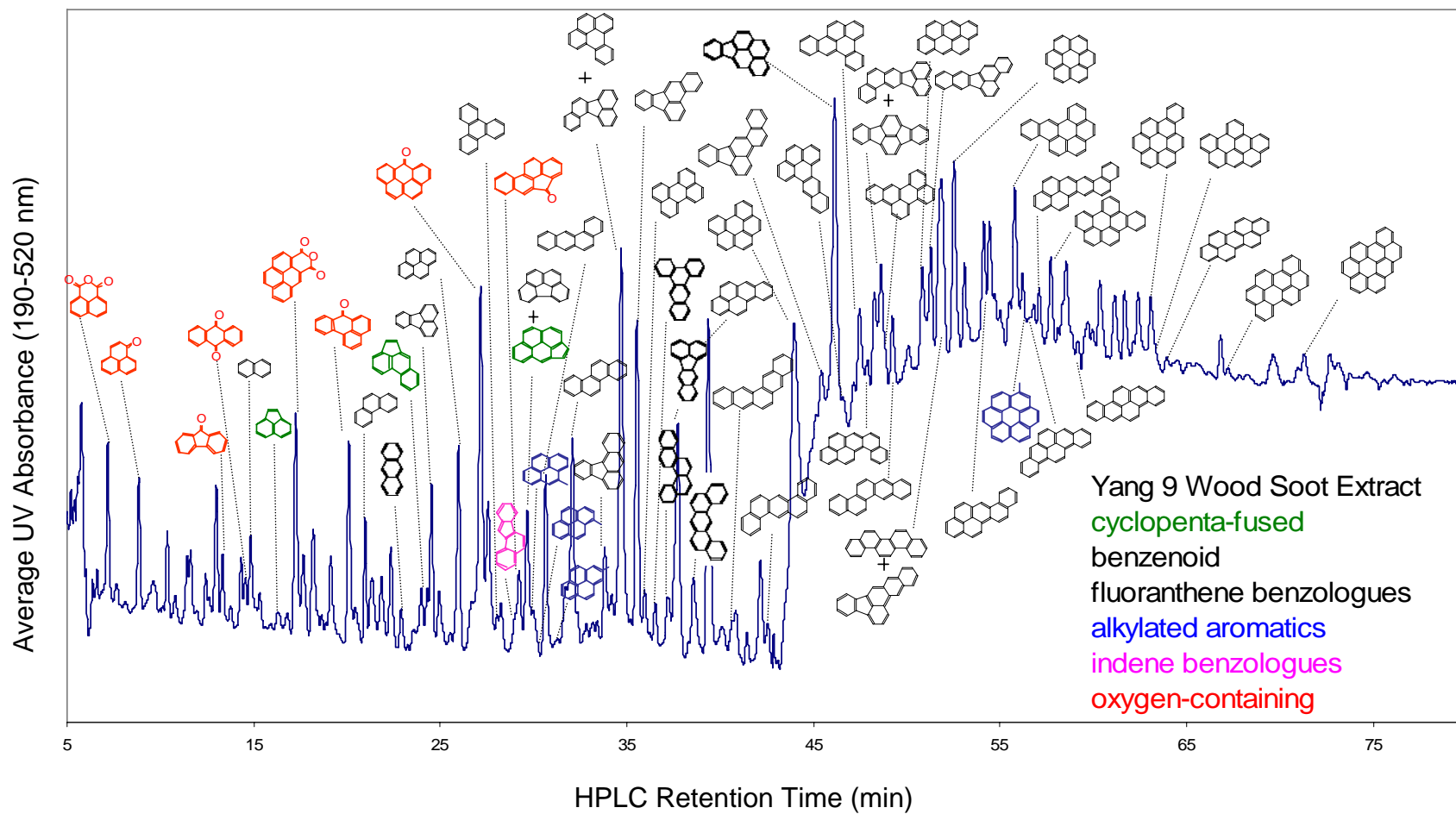


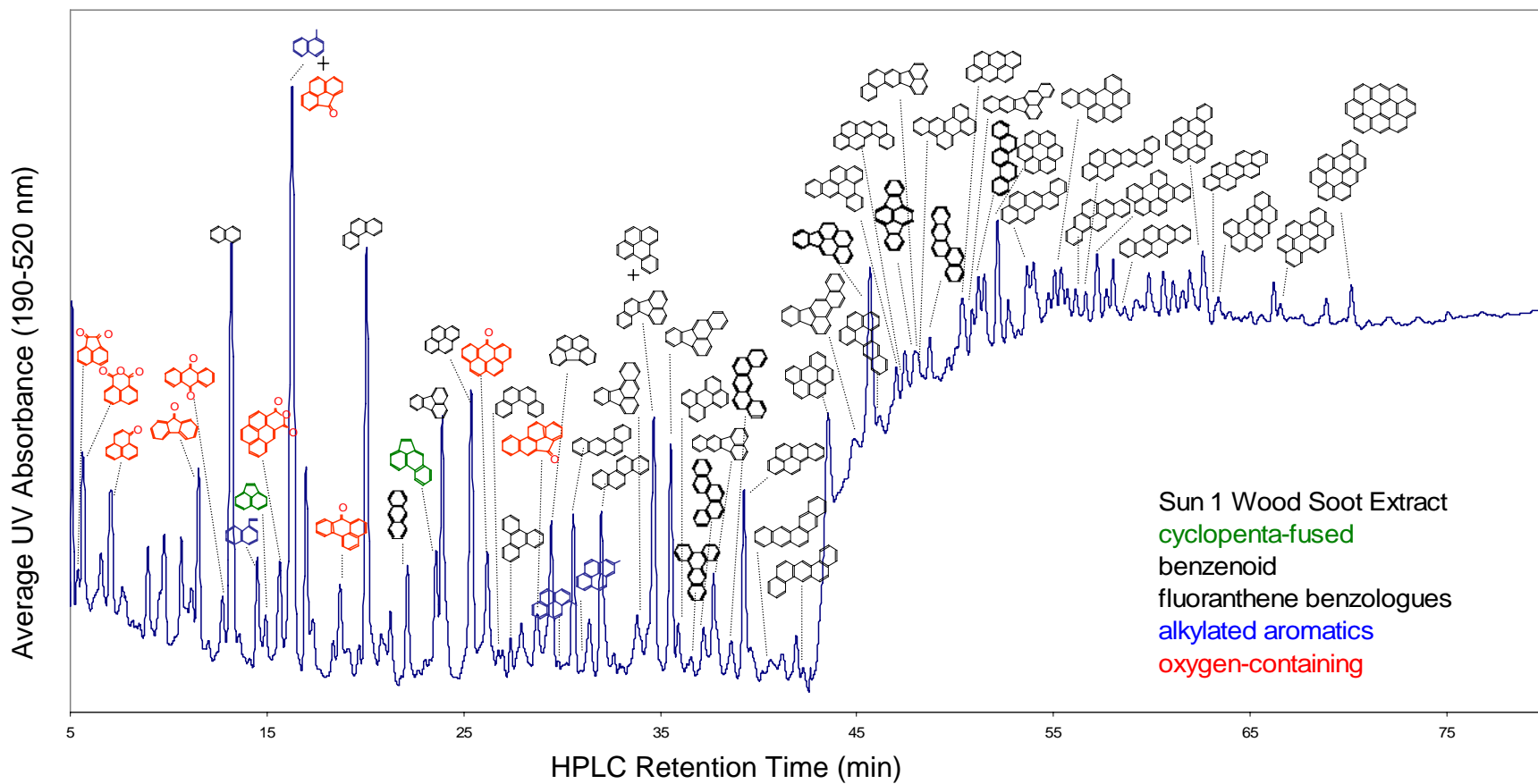
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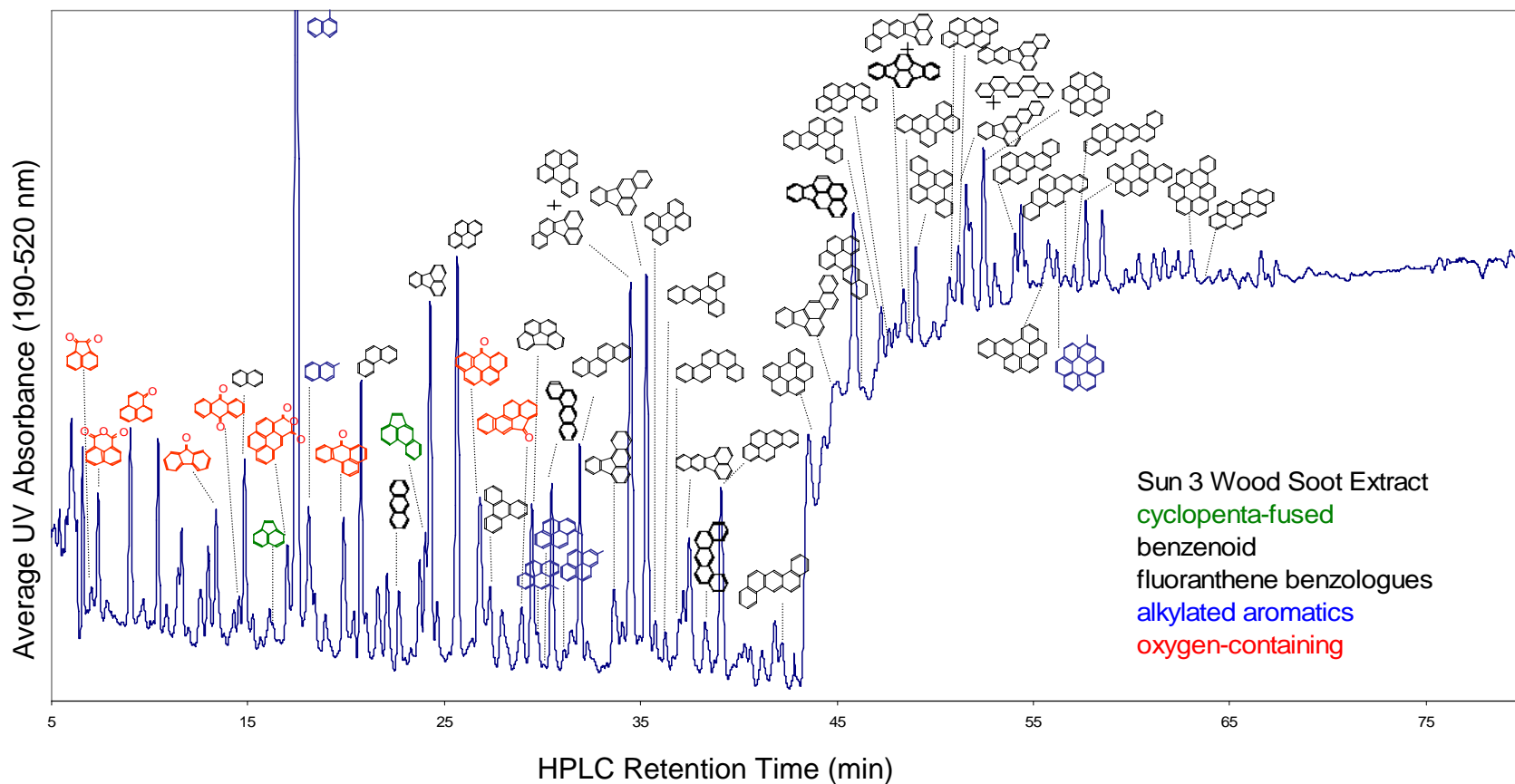
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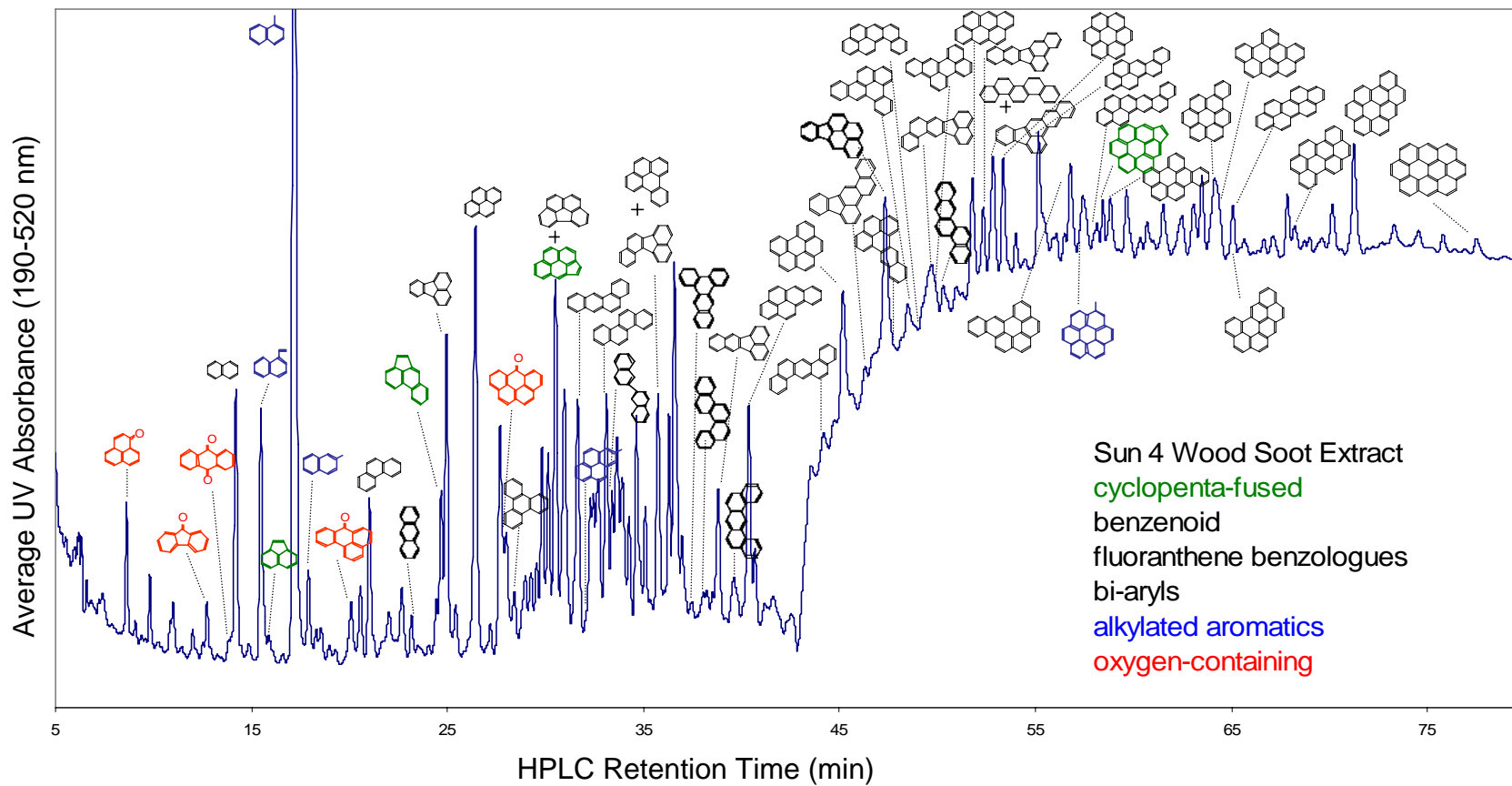




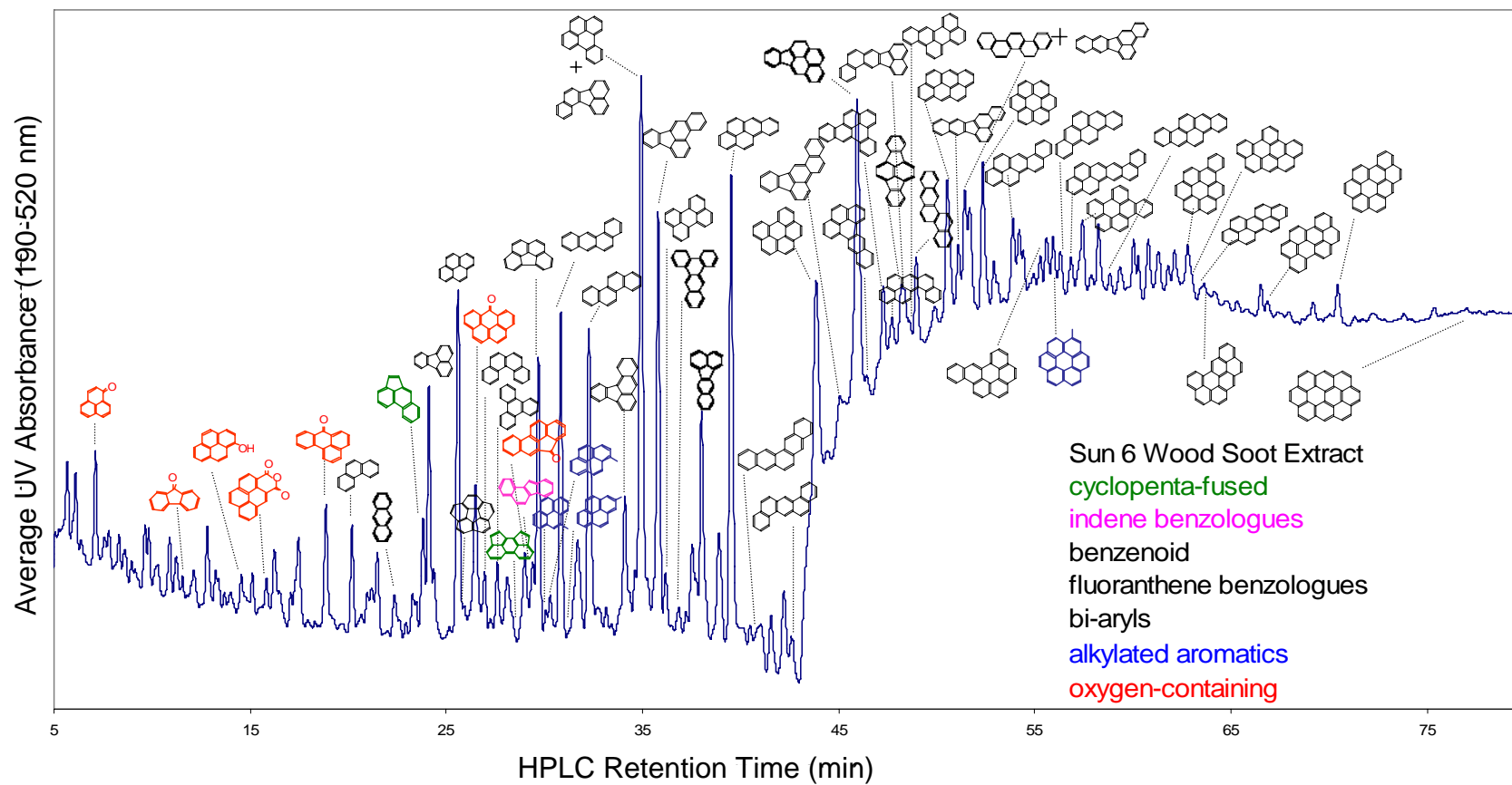
Note: 1-methylnaphthalene standard contaminated the sample.  
Hump at ~43 min. due to solvent change from ACN to DCM.



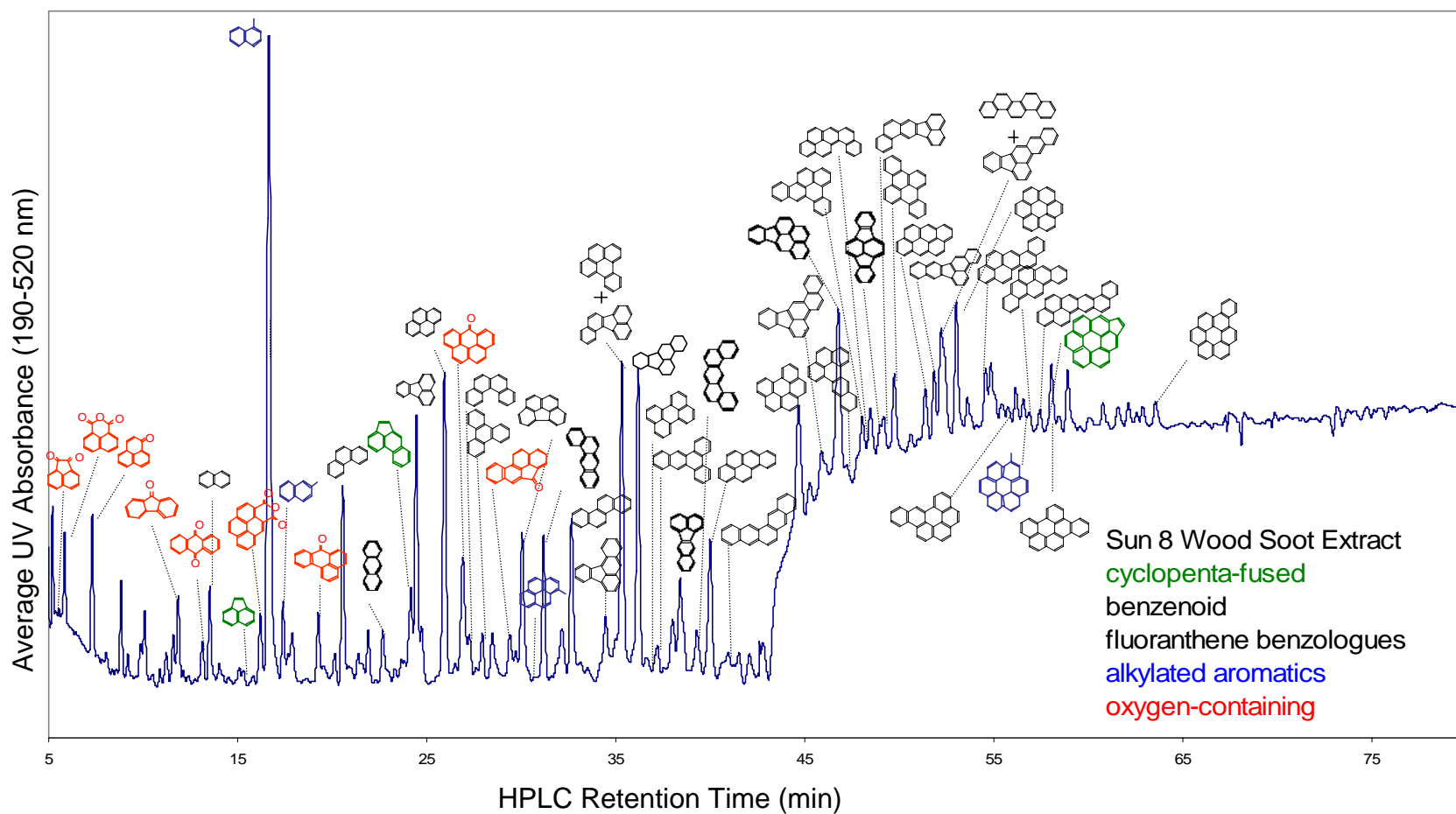
Note: 1-methylnaphthalene standard contaminated the sample.  
Hump at ~43 min. due to solvent change from ACN to DCM.



Note: 1-methylnaphthalene standard contaminated the sample.  
Hump at ~43 min. due to solvent change from ACN to DCM.

















Note: Hump at ~43 min. due to solvent change from ACN to DCM


















Note: 1-methylnaphthalene standard contaminated the sample.  
 Hump at ~43 min. due to solvent change from ACN to DCM.

## APPENDIX B – YIELD

Compound	Structure	Formula	MW	Yang 6	Yang 3	Yang 10	Yang 1	Yang 2	Yang 8	Yang 9	Sun 1	Sun 3	Sun 4	Sun 6	Sun 8
OXYGENATED PAH															
2-Naphthaldehyde		C <sub>11</sub> H <sub>8</sub> O	156	N.D.	N.D.	0.0042	N.D.	N.D.	0.0008	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1-Naphthaldehyde		C <sub>11</sub> H <sub>8</sub> O	156	N.D.	N.D.	0.0023	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenzofuran		C <sub>12</sub> H <sub>8</sub> O	168	N.D.	N.D.	0.0030	N.D.	N.D.	0.0016	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Acenaphthenequinone		C <sub>12</sub> H <sub>6</sub> O <sub>2</sub>	182	0.0009	0.0048	0.0016	N.D.	N.D.	N.D.	N.D.	0.0007	0.0013	N.D.	N.D.	0.0001
Naphthalene-1,8-dicarboxylic anhydride		C <sub>12</sub> H <sub>6</sub> O <sub>3</sub>	198	0.0049	0.0239	0.0089	N.D.	0.0007	0.0018	0.0037	0.0030	0.0026	N.D.	N.D.	0.0014
Phenalenone		C <sub>13</sub> H <sub>8</sub> O	180	0.0065	0.0302	0.0094	0.0087	0.0005	0.0056	0.0033	0.0032	0.0042	0.0031	0.0063	0.0027
9-Flourenone		C <sub>13</sub> H <sub>8</sub> O	180	0.0034	0.0104	0.0190	0.0076	0.0016	0.0054	0.0022	0.0042	0.0033	0.0016	0.0015	0.0022
Anthraquinone		C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	208	0.0048	N.D.	N.D.	0.0029	0.0003	0.0017	0.0013	0.0016	0.0010	0.0005	N.D.	0.0005
4H-cyclopenta[def]phenanthren-4-one		C <sub>15</sub> H <sub>8</sub> O	204	N.D.	0.0223	0.0068	0.0026	N.D.	0.0029	N.D.	0.0005	N.D.	N.D.	N.D.	N.D.
1-Hydroxypyrene		C <sub>16</sub> H <sub>10</sub> O	218	N.D.	0.0024	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0016	N.D.
Benzanthrone		C <sub>17</sub> H <sub>10</sub> O	230	0.0088	0.0394	0.0103	0.0029	0.0003	0.0022	0.0034	0.0013	0.0020	0.0015	0.0045	0.0009
4-Oxa-benzo[cd]pyrene-3,5-dione		C <sub>18</sub> H <sub>8</sub> O <sub>3</sub>	272	0.0075	0.0159	0.0143	0.0039	N.D.	0.0009	0.0046	0.0017	0.0016	N.D.	0.0019	0.0012
6H-benzo[cd]pyren-6-one		C <sub>19</sub> H <sub>10</sub> O	254	0.0234	0.1658	0.0186	0.0098	0.0010	0.0048	0.0095	0.0021	0.0038	0.0019	0.0086	0.0025
Cyclopenta[def]chrysene-4-one		C <sub>19</sub> H <sub>10</sub> O	254	0.0059	0.0160	N.D.	0.0021	0.0001	0.0008	0.0017	0.0008	0.0013	N.D.	0.0046	0.0008













Note: Yield (mg/mg soot)

N.D. – Not detected

Compound	Structure	Formula	MW	Yang 6	Yang 3	Yang 10	Yang 1	Yang 2	Yang 8	Yang 9	Sun 1	Sun 3	Sun 4	Sun 6	Sun 8
CYCLOPENTA-FUSED and ETHYNYL-SUBSTITUTED PAH															
Acenaphthylene		C <sub>12</sub> H <sub>8</sub>	152	0.0018	0.0054	0.0131	0.0040	0.0004	0.0016	0.0009	0.0014	0.0004	0.0009	N.D.	0.0004
Acephenanthrylene		C <sub>16</sub> H <sub>10</sub>	202	0.0026	0.0261	0.0112	0.0071	0.0001	0.0059	0.0010	0.0020	0.0017	0.0031	0.0053	0.0018
Cyclopent[hi]acephenanthrylene		C <sub>18</sub> H <sub>10</sub>	226	N.D.	0.0112	0.0011	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0009	N.D.
Cyclopenta[cd]pyrene		C <sub>18</sub> H <sub>10</sub>	226	N.D.	0.0343	0.0103	0.0058	0.0002	0.0069	0.0008	N.D.	N.D.	0.0051	N.D.	N.D.
Cyclopenta[b,c]coronene		C <sub>26</sub> H <sub>12</sub>	324	N.D.	0.0111	N.D.	0.0012	N.D.	N.D.	N.D.	N.D.	N.D.	0.0011	N.D.	0.0001
1-Methylnaphthalene		C <sub>11</sub> H <sub>10</sub>	142	0.0218	N.D.	0.0126	N.D.	0.0058	N.D.	N.D.	0.0285	0.0549	0.1279	N.D.	0.0432
2-Methylnaphthalene		C <sub>11</sub> H <sub>10</sub>	142	N.D.	N.D.	0.0060	N.D.	0.0023	N.D.	N.D.	N.D.	0.0071	0.0054	N.D.	0.0028
1-Ethynylnaphthalene		C <sub>12</sub> H <sub>8</sub>	152	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0038	N.D.	0.0108	N.D.	N.D.
2-Ethynylnaphthalene		C <sub>12</sub> H <sub>8</sub>	152	N.D.	N.D.	0.0031	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
4-Methylpyrene		C <sub>17</sub> H <sub>12</sub>	216	0.0006	0.0044	0.0013	0.0012	N.D.	0.0005	0.0011	0.0001	0.0001	N.D.	0.0010	0.0001
1-Methylpyrene		C <sub>17</sub> H <sub>12</sub>	216	0.0004	0.0060	0.0012	0.0012	N.D.	0.0004	0.0002	N.D.	0.0001	N.D.	0.0020	N.D.
2-Methylpyrene		C <sub>17</sub> H <sub>12</sub>	216	0.0011	0.0088	0.0011	0.0007	N.D.	0.0003	0.0002	0.0002	0.0002	0.0002	0.0010	N.D.
3-Ethynylpyrene		C <sub>18</sub> H <sub>10</sub>	226	0.0006	0.0039	0.0006	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2,2'-Binaphthalene		C <sub>20</sub> H <sub>14</sub>	254	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0092	N.D.	N.D.
Methyl coronene		C <sub>25</sub> H <sub>14</sub>	314	N.D.	0.0004	N.D.	0.0005	N.D.	N.D.	0.0002	N.D.	0.00005	0.0002	0.0004	0.0001

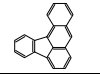
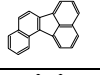
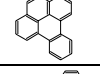
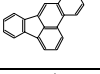
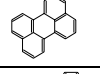
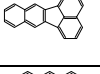
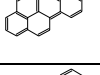
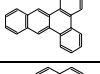
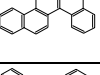
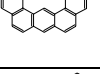
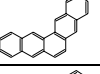
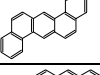
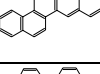
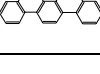
Note: Yield (mg/mg soot)

N.D. – Not detected

Compound	Structure	Formula	MW	Yang 6	Yang 3	Yang 10	Yang 1	Yang 2	Yang 8	Yang 9	Sun 1	Sun 3	Sun 4	Sun 6	Sun 8
2- to 4-RING PAH															
Naphthalene		C10H8	128	0.0059	0.0198	0.0263	0.0105	0.0066	0.0057	0.0048	0.0152	0.0065	0.0124	N.D.	0.0034
Phenanthrene		C14H10	178	0.0075	0.0167	0.0245	0.0115	0.0012	0.0074	0.0021	0.0061	0.0039	0.0032	0.0043	0.0033
Anthracene		C14H10	178	0.0030	0.0063	0.0114	0.0070	0.0002	0.0042	0.0012	0.0025	0.0020	0.0012	0.0029	0.0014
Fluoranthene		C16H10	202	0.0106	0.0449	0.0193	0.0144	0.0005	0.0125	0.0030	0.0033	0.0052	0.0065	0.0100	0.0044
Pyrene		C16H10	202	0.0137	0.0533	0.0257	0.0194	0.0005	0.0148	0.0043	0.0042	0.0064	0.0100	0.0152	0.0052
Benzo[a]fluorene		C17H12	216	0.0003	N.D.	0.0028	N.D.	0.0002	N.D.	0.0014	N.D.	N.D.	N.D.	0.0072	N.D.
Benzo[c]phenanthrene		C18H12	228	N.D.	N.D.	0.0025	N.D.	0.0002	N.D.	N.D.	0.0004	N.D.	N.D.	0.0034	0.0007
Triphenylene		C18H12	228	0.0020	0.0130	0.0034	0.0014	0.0004	0.0008	0.0006	0.0003	0.0016	0.0009	0.0032	0.0006
Benz[a]anthracene		C18H12	228	0.0086	0.0557	0.0116	0.0071	0.0003	0.0048	0.0027	0.0015	0.0022	0.0044	0.0104	0.0017
Chrysene		C18H12	228	0.0128	0.0640	0.0131	0.0074	0.0006	0.0050	0.0044	0.0020	0.0030	0.0035	0.0126	0.0026
Benzo[ghi]fluoranthene		C18H10	226	0.0069	0.0298	0.0072	0.0037	0.0001	0.0010	0.0019	0.0015	0.0020	0.0008	0.0087	0.0021
Corannulene		C20H10	250	0.0009	0.0023	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0016	N.D.


















Note: Yield (mg/mg soot)

N.D. – Not detected

Compound	Structure	Formula	MW	Yang 6	Yang 3	Yang 10	Yang 1	Yang 2	Yang 8	Yang 9	Sun 1	Sun 3	Sun 4	Sun 6	Sun 8
5-RING PAH															
Benzo[ <i>a</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0075	0.0371	0.0036	0.0026	0.0002	0.0014	0.0014	0.0008	0.0013	N.D.	0.0045	0.0012
Benzo[ <i>j</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0100	0.0518	0.0107	0.0018	0.0001	0.0041	0.0024	0.0005	0.0013	0.0003	0.0046	0.0005
Benzo[ <i>e</i> ]pyrene		C <sub>20</sub> H <sub>12</sub>	252	0.0211	0.0779	0.0119	0.0109	0.0010	0.0020	0.0065	0.0029	0.0049	0.0037	0.0176	0.0051
Benzo[ <i>b</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0172	0.0892	0.0127	0.0075	0.0008	0.0040	0.0047	0.0024	0.0045	N.D.	0.0128	0.0040
Perylene		C <sub>20</sub> H <sub>12</sub>	252	0.0049	0.0240	0.0043	0.0023	0.0002	0.0012	0.0017	0.0010	0.0010	N.D.	0.0031	0.0006
Benzo[ <i>k</i> ]fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	0.0120	0.0552	0.0091	0.0047	0.0005	0.0028	0.0045	0.0009	0.0018	0.0022	0.0062	0.0012
Benzo[ <i>a</i> ]pyrene		C <sub>20</sub> H <sub>12</sub>	252	0.0253	0.1334	0.0199	0.0126	0.0007	0.0060	0.0072	0.0024	0.0031	0.0047	0.0191	0.0026
Dibenz[ <i>a,c</i> ]anthracene		C <sub>22</sub> H <sub>14</sub>	278	0.0020	0.0114	0.0016	0.0004	0.0001	0.0006	0.0006	0.0002	0.0005	0.0003	0.0010	0.0005
Benzo[ <i>c</i> ]chrysene		C <sub>22</sub> H <sub>14</sub>	278	0.0027	N.D.	0.0035	0.0007	0.00004	0.0006	0.0011	0.0006	0.0007	0.0004	N.D.	N.D.
Dibenz[ <i>a,j</i> ]anthracene		C <sub>22</sub> H <sub>14</sub>	278	0.0041	0.0246	0.0041	0.0028	0.0002	0.0011	0.0014	0.0006	0.0009	0.0010	N.D.	0.0007
Pentaphene		C <sub>22</sub> H <sub>14</sub>	278	0.0025	0.0109	N.D.	N.D.	0.0001	0.0007	0.0008	0.0003	N.D.	N.D.	0.0011	0.0002
Dibenz[ <i>a,h</i> ]anthracene		C <sub>22</sub> H <sub>14</sub>	278	0.0020	0.0070	0.0014	0.0014	N.D.	0.0004	0.0008	0.0002	0.0007	0.0006	0.0020	N.D.
Benzo[ <i>b</i> ]chrysene		C <sub>22</sub> H <sub>14</sub>	278	0.0047	0.0167	0.0038	0.0010	0.0002	0.0024	0.0013	0.0006	N.D.	0.0007	0.0039	N.D.
Picene		C <sub>22</sub> H <sub>14</sub>	278	0.0088	0.0126	N.D.	0.0021	0.0002	0.0012	0.0014	0.0010	0.0014	0.0009	0.0047	0.0015

Note: Yield (mg/mg soot)

N.D. – Not detected

Compound	Structure	Formula	MW	Yang 6	Yang 3	Yang 10	Yang 1	Yang 2	Yang 8	Yang 9	Sun 1	Sun 3	Sun 4	Sun 6	Sun 8
6-RING PAH															
Benzo[ghi]perylene		C <sub>22</sub> H <sub>12</sub>	276	0.0321	0.1322	0.0314	0.0130	0.0018	0.0069	0.0100	0.0027	0.0032	0.0054	0.0163	0.0034
Indeno[1,2,3-cd]pyrene		C <sub>22</sub> H <sub>12</sub>	276	0.0329	0.1506	0.0272	0.0123	0.0016	0.0063	0.0093	0.0030	0.0043	0.0042	0.0177	0.0039
Indeno[1,2,3-cd]fluoranthene		C <sub>22</sub> H <sub>12</sub>	276	0.0051	0.0198	0.0035	0.0007	0.0001	0.0005	0.0005	0.0005	0.0007	N.D.	0.0027	0.0005
Anthanthrene		C <sub>22</sub> H <sub>12</sub>	276	0.0072	0.0440	0.0058	0.0067	0.0003	0.0022	0.0023	0.0011	0.0013	0.0024	0.0064	0.0010
Naphtho[1,2-b]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0097	0.0270	0.0026	0.0031	0.0003	0.0007	0.0012	0.0004	0.0007	0.0007	0.0022	0.0007
Naphtho[2,3-e]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0015	0.0078	0.0021	0.0011	0.0002	0.0007	0.0006	0.0004	0.0003	0.0010	0.0016	0.0004
Dibenzo[a,e]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0031	0.0386	0.0084	0.0040	0.0005	0.0019	0.0027	0.0009	0.0016	0.0011	0.0046	0.0013
Naphtho[1,2-a]pyrene		C <sub>24</sub> H <sub>14</sub>	302	N.D.	0.0099	N.D.	0.0010	N.D.	N.D.	0.0012	0.0004	0.0009	0.0003	0.0011	0.0003
Naphtho[2,1-k]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0042	0.0199	0.0039	0.0021	0.0003	0.0023	0.0020	0.0004	0.0007	0.0009	0.0021	0.0007
Benzo[b]perylene		C <sub>24</sub> H <sub>14</sub>	302	0.0024	0.0290	0.0026	N.D.	N.D.	0.0005	0.0006	0.0002	0.0005	0.0006	0.0020	N.D.
Dibenzo[e,l]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0010	0.0025	N.D.	0.0009	0.0001	N.D.	N.D.	N.D.	0.0018	N.D.	N.D.	0.0017
Naphtho[2,3-b]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0015	0.0069	N.D.	N.D.	0.0003	N.D.	0.0006	N.D.	0.0005	0.0006	0.0015	0.0005
Dibenzo[b,k]fluoranthene		C <sub>24</sub> H <sub>14</sub>	302	0.0024	0.0192	0.0051	0.0023	0.0005	0.0014	0.0020	0.0003	0.0009	0.0009	0.0018	0.0008
Naphtho[2,1-a]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0060	0.0292	0.0062	0.0042	0.0005	0.0027	0.0026	0.0009	0.0011	0.0028	0.0036	0.0009
Dibenzo[a,h]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0006	0.0040	0.0014	N.D.	N.D.	N.D.	0.0002	0.0002	N.D.	N.D.	0.0006	N.D.
Dibenzo[a,i]pyrene		C <sub>24</sub> H <sub>14</sub>	302	0.0017	0.0184	0.0030	0.0005	0.0001	0.0006	0.0005	0.0001	0.00004	N.D.	0.0018	0.0003
Naphtho[2,3-a]pyrene		C <sub>24</sub> H <sub>14</sub>	302	N.D.	0.0017	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Note: Yield (mg/mg soot)

N.D. – Not detected

Compound	Structure	Formula	MW	Yang 6	Yang 3	Yang 10	Yang 1	Yang 2	Yang 8	Yang 9	Sun 1	Sun 3	Sun 4	Sun 6	Sun 8
7- to 10-RING PAH															
Coronene		C24H12	300	0.0159	0.0788	0.0170	0.0059	0.0019	0.0041	0.0049	0.0020	0.0033	0.0027	0.0079	0.0025
Dibenzo[b,ghi]perylene		C26H14	326	0.0058	0.0345	0.0206	0.0080	0.0010	0.0044	0.0018	0.0005	0.0009	0.0005	0.0004	0.0001
Dibenzo[e,ghi]perylene		C26H14	326	0.0067	0.0316	0.0101	0.0059	0.0011	0.0024	0.0022	0.0013	0.0019	0.0019	0.0035	0.0015
Dibenzo[cd,lm]perylene		C26H14	326	N.D.	N.D.	N.D.	0.0024	0.0001	0.0005	0.0002	0.0002	0.0001	0.0001	0.0006	N.D.
Benzo[a]coronene		C28H14	350	0.0059	0.0248	0.0071	0.0056	0.0013	0.0034	0.0016	0.0012	0.0009	0.0034	0.0045	0.0006
Phenanthro[5,4,3,2-efghi]perylene		C28H14	350	N.D.	N.D.	0.0044	0.0016	0.0007	0.0006	0.0008	N.D.	N.D.	0.0016	0.0009	N.D.
Benzo[ghi]naphtho[8,1,2-bcd]perylene		C28H14	350	N.D.	0.0170	N.D.	N.D.	N.D.	N.D.	N.D.	0.0003	N.D.	0.0013	0.0008	N.D.
Benzo[pqr]naphtho[8,1,2-bcd]perylene		C28H14	350	0.0076	0.0424	N.D.	0.0022	0.0003	0.0012	0.0003	0.0003	N.D.	0.0011	0.0010	N.D.
Phenanthro[2,3-a]pyrene		C28H16	352	0.0030	0.0288	0.0035	0.0016	0.0005	0.0011	0.0011	0.0003	0.0004	0.0005	0.0016	0.0004
Naphtho[8,1,2-abc]coronene		C30H14	374	0.0035	0.0238	N.D.	0.0061	0.0008	0.0043	0.0019	0.0008	N.D.	0.0039	0.0026	N.D.
Ovalene		C32H14	398	N.D.	0.0046	N.D.	0.0011	0.0002	0.0009	N.D.	0.0001	N.D.	0.0007	0.0002	N.D.
Dibenzo[a,j]coronene		C32H16	400	N.D.	0.0011	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Note: Yield (mg/mg soot)

N.D. – Not detected

## APPENDIX C- HEALTH EFFECTS OF WOOD COMBUSTION

Health Effects of Woodsmoke Air Pollution Bay Area Air Quality Management District Dec-04

### Scientific Studies on Health Effects of Woodsmoke and Particulate Matter Air Pollution

[Editors Note 2004: This reference document combines studies of symptoms associated with households using wood heat (Indoor Air Quality), studies relating outdoor concentrations of woodsmoke to adverse health effects in the whole population (Ambient Air Quality), and laboratory studies of physiological responses to woodsmoke.

Authors by Date	Summary of Findings
Gauderman et al. 2004	New findings from the Children's Health Study in the New England Journal of Medicine confirm reduced lung function growth in children exposed to higher levels of air pollution (including PM 2.5) from ages 10 to 18.
Samet, J, et al 2004	The study assessed the effects of five major outdoor-air pollutants on daily mortality rates in 20 of the largest cities and metropolitan areas in the U.S. from 1987 to 1994. There is consistent evidence that the levels of fine particulate matter in the air are associated with the risk of death from all causes and from cardiovascular and respiratory illnesses.
Brook, RD, et al, 2004	A panel of experts conducted a comprehensive review of almost 200 scientific studies on air pollution and cardiovascular disease – including heart attacks, abnormal hear rhythms, strokes, hardening of the arteries. The American Heart Association issued a scientific statement on air pollution, concluding “because a number of studies have demonstrated associations between particulate air pollution and adverse cardiovascular effects even when levels of ambient PM2.5 were within current standards, even more stringent standards for PM2.5 should be strongly considered by the EPA.”
Gullett et al., 2003	Emissions from residential fireplace and woodstove appliances burning fuels available from the San Francisco Bay area were sampled for polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs), polychlorinated biphenyls (PCBs), hexachlorobenzene (HxCBz), particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs, and the monosaccharide levoglucosan. A total of 32 PAH compounds, ranging in concentration from 0.06 to 7 mg/kg, amounted to between 0.12 and 0.38% of the PM mass, depending on the wood and facility type.
Dubick MA, et al. 2002	This study investigated antioxidant status in lavage fluid, lung, liver, heart and kidney in a rat model to simulate an inhalation injury as might be encountered by firefighters and burn victims. Data suggest that smoke inhalation, independent of burn injury, induces an oxidant stress that persists for at least the first 48 h after smoke exposure.
Zelikoff et al, 2002	The toxicology of inhaled woodsmoke. This is a "mini-review article (which) brings together many of the human and animal studies performed over the last three decades in an attempt to better defined the toxicological impact of inhaled woodsmoke on exposed children and adults..."
Tesfaigzi et al, Jan 2002	This study of health effects of subchronic exposure to low levels of wood smoke in rats suggests that exposure to wood smoke caused minor but significant changes in pulmonary function. Further studies are needed to establish whether exposure to wood smoke exacerbates asthma-like symptoms that resemble those described for children living in homes using wood stoves for heating and cooking.
MahalanabiS D et al. 2002	We evaluated the risk factors for childhood pneumonia with particular reference to indoor air-pollution associated with solid fuel use for cooking (e.g. coal, wood, dung), using a case-control study in a children's hospital in Calcutta. Solid fuel use (and other factors) were associated with high risk of pneumonia
Kim J, Hanley JA.	This study was to determine the role of environmental pollutants in the etiology of nasal polyposis, 55 patients in rural northeastern Quebec. Forty-five (82%) of the cases, but only 14 (25%) of the controls, reported using woodstoves, yielding a crude odds ratio (OR) of 13.1. There is a strong association between the use of woodstoves as a principal source of heating and the development of nasal polyposis.
Kim O, et al. 2002	In this study in Thailand, smoke samples, in both gas and particulate matter (PM) phases, of the three domestic stoves were collected using U.S. EPA modified method 5 and were

	analyzed. The study compared emissions of polycyclic aromatic hydrocarbons (PAH), toxicity, and mutagenicity from domestic cooking using sawdust briquettes, wood, and kerosene. The total toxicity emission factor was the highest from sawdust, followed by kerosene and wood fuel. The tests could be used for a quick assessment of potential health risks.
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Stone, 1995	Rats were exposed to no pollution or 800 ug/m3 woodsmoke for 1 hour, then to golden staph bacteria. The bacteria were more virulent in animals which breathed the woodsmoke. This was attributed to suppression in activity of the rats' macrophages, immune cells that roam the body, looking to engulf and destroy foreign particles.
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Koenig et al., 1993	Significant association in Seattle (where the majority of particulate air pollution originates from woodsmoke) between outdoor fine particle pollution and decreased lung function (measured by spirometry) in asthmatic children aged 8-11.
Lal et al., 1993	Rats exposed to woodsmoke suffered “bronchiolitis, hyperplasia and hypertrophy of bronchiolar epithelial lining cells, some necrosed lining cells desquamated into lumens, congestion of parenchymatous blood vessels, oedema, hyperplasia of lymphoid follicles, peribronchiolar and perivascular infiltration of polymorphonuclear cells, and mild emphysema”. Conditioned worsened with accumulated exposure. The results indicate progressive pathomorphological pulmonary lesions with subsequent exposure to wood smoke in controlled conditions.”
Dean et al., 1992	Case of methemoglobinemia, sudden onset of cyanosis, irritability, metabolic acidosis, and a lethal methemoglobin level of 71.4% in a 10 week old infant. Family history revealed a wood-burning stove which emitted pine tar fumes as the potential environmental methemoglobin-producing source. The infant’s cradle was situated five feet from the stove. The baby was treated and recovered.
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Daigler et al., 1991	A comparison of patients in New York with physician-diagnosed otitis media (n = 125, 74% response), and controls (n = 237, 72% response) showed exposure to a woodburning stove was significantly associated (P<.05 with increased otitis (an inflammation of the middle ear marked by pain, fever, dizziness, and abnormalities of hearing.)
Heumann et al., 1991	Children with the highest exposure to wood smoke had a significant decrease in lung function, measured by FEV1 and FVC. 410 children aged 8-11 in Klamath Falls, Oregon.
Lewtas et al., 1991	Mutagenicity testing of air containing smoke emitted from woodheaters in Boise, Idaho, US, using the Ames test on salmonella and tumor initiation assays in mice found that woodsmoke was 12 times more carcinogenic than an equal concentration of cigarette smoke.

Morris et al., 1990	58 Navajo children under 2 years with diagnosed pneumonia or bronchiolitis were compared with matched control children. Use of a wood burning stove was associated with a 4 times higher risk of lower respiratory tract infection (P<.001).
Johnson, 1990	Particle pollution from woodsmoke in the air was associated with significant decreases in lung function in children aged 8-11. 495 subjects in Montana.
Browning, et al., 1990	No statistically significant differences, but a pattern of increased symptoms and chronic illness in children aged 1-5 in the area with high wood smoke.
Butterfield, et al., 1989	Significant correlation (P<.01), between woodstove use and frequency of wheeze, severity of wheeze, frequency of cough and waking up at night with cough, based on 59 subjects aged 1 to 5.5 years.
Boone et al., 1989	“Woodsmoke prove to be a major source of indirect genotoxins in homes. The increase is probably due to higher concentrations of polycyclic aromatic hydrocarbons in the wood smoke aerosol ...” USA.
van Houdt et al., 1986	“The use of wood stoves caused an increase of indoor mutagenicity in 8 out of 12 homes.”
Honicky et al., 1985	Moderate and severe respiratory symptoms were significantly greater ( P<.001) in 34 children, aged 1-7 years in houses with woodstoves than in 34 children houses without. Conclusion: “Present findings suggest that indoor heating with wood-burning stoves may be a significant etiologic factor in the occurrence of symptoms of respiratory illness in young children.” Michigan, US.
Tuthill, 1984.	Risk of respiratory symptoms increased by 10%, but this was not statistically significant. Study of children aged 5-11, 258 with woodstoves, 141 without. Exposure to formaldehyde from any source, including wood burning, significantly increased risk.
Alfheim et al, 1984	“Whereas wood heating in an “airtight” stove was found to cause only minor changes in the concentration of PAH and no measurable increase of mutagenic activity of the indoor air, both these parameters increased considerably when wood was burned in an open fireplace, yielding PAH concentrations comparable to those of ambient urban air. Woodburning in the closed stove did, however, result in increased concentrations of mutagenic compounds and PAH on particles sampled in the vicinity of the house.”

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