DETERMINATION OF PAHs CONTENT IN SMOKE DURING GRILLING PROCESS USING MANGROVE CHARCOAL PRODUCED AT DIFFERENT CARBONIZATION TEMPERATURES

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A SPECIAL RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
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Abstract

Charcoal grilled products are one of the most important exported products of Thailand. However, grilled food products using charcoal may have a chance of carcinogenic contamination. Thus, the objective of this research was to study the effect of carbonization temperature on the chemical compositions of mangrove charcoal and PAHs contents generated in smoke during charcoal grilling. Firstly, mangrove charcoal was produced at carbonization temperatures of 500, 750 and 1000 °C. Then, yield and chemical compositions of the charcoal were determined. Finally, smoke generated during burning charcoals at 650 °C was collected to determine 16 major PAHs by Gas Chromatography/Mass Spectrometry (GC/MS). The results showed that charcoal produced at 500 °C presented the highest yield of about 28%, while the yields of charcoals produced at 750 and 1,000 °C were 23 and 22%, respectively. Regarding the chemical compositions, charcoals produced at 500 °C, 750 and 1,000 °C had, respectively, 21, 5 and 4 % of volatile matters and 69, 82 and 87% of fixed carbon. These results indicated that charcoals produced at lower carbonization temperatures possessed higher volatile matters, resulting in higher charcoal yields and lower fixed carbon. However, there were no significant differences in the yield, fixed carbon and volatile matters between charcoals produced at 750 and 1,000 °C. A total of 16 PAHs in the smoke produced during burning at 500, 750 and 1,000 °C was amounted at 4.52×10^3, 0.55×10^3 and 0.94×10^3 µg/g, respectively. Charcoal produced at 500 °C generated 4 PAHs, which are the carcinogen indicators in food according to Commission Regulation (EU) No 835/2011. In fact, charcoal produced at 500 °C possessed the highest concentrations of the volatile matters and the 16 PAHs. Nevertheless, no significant differences in 16 PAHs between charcoals produced at 750 and 1000 °C were observed. Therefore, it seemed that there is a relation between the volatile matters and total PAHs contents of charcoal.

Keywords: Carbonization/ Carcinogenic/ Charcoal/ Polycyclic Aromatic Hydrocarbon/ Volatile Matter

หัวข้อโครงการศึกษาวิจัยพิเศษ	การหาปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนในควันระหว่างการเผาถ่านที่ได้มาจากกระบวนการคาร์บอไนเซชันไม้โกงกางที่อุณหภูมิต่างๆ
หน่วยกิต	6
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ปีการศึกษา	2556

บทคัดย่อ

ปัจจุบันผลิตภัณฑ์ย่างแบบใช้ถ่านไม้เป็นหนึ่งในประเภทอาหารที่สร้างรายได้จากการส่งออกให้กับประเทศ หากแต่ผลิตภัณฑ์ชนิดนี้อาจมีโอกาสปนเปื้อนสารก่อมะเร็งได้ การศึกษาวิจัยในครั้งนี้จึงมุ่งเน้นที่จะศึกษาถ่าน ซึ่งเป็นหนึ่งในปัจจัยที่อาจส่งผลต่อการปนเปื้อน โดยวัตถุประสงค์ของงานวิจัยก็คือการศึกษาถึงผลของอุณหภูมิในกระบวนการคาร์บอไนซ์เซชันที่มีต่อองค์ประกอบของถ่านจากไม้โกงกาง และปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิดในควันซึ่งเกิดขึ้นในระหว่างการนำถ่านไปใช้ โดยทำการเผาไม้โกงกางให้กลายเป็นถ่านที่อุณหภูมิ 500 750 และ 1000 องศาเซลเซียส จากนั้นจึงหาร้อยละผลผลิตและสัดส่วนขององค์ประกอบในถ่าน นอกจากนี้ยังหาปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิด ด้วยการเก็บตัวอย่างควันจากการเผาถ่านโกงกางที่อุณหภูมิ 650 องศาเซลเซียส และนำมาวิเคราะห์ด้วยแก๊สโครมาโทกราฟี/แมสสเปกโตรมิทรี (GC/MS) พบว่าถ่านซึ่งผลิตที่อุณหภูมิ 500 องศาเซลเซียส มีร้อยละผลผลิตสูงที่สุด เท่ากับ 28 ขณะที่ถ่านซึ่งผลิตที่อุณหภูมิ 750 และ 1000 องศาเซลเซียส มีร้อยละผลผลิตเท่ากับ 23 และ 22 ตามลำดับ สำหรับสัดส่วนขององค์ประกอบภายในถ่าน พบว่าถ่านซึ่งผลิตที่อุณหภูมิ 500 750 และ 1000 องศาเซลเซียส มีร้อยละของสารระเหยเท่ากับ 21, 5 และ 4 และมีร้อยละของคาร์บอนคงตัวเท่ากับ 69, 82 และ 87 ตามลำดับ ซึ่งผลการทดลองเหล่านี้บ่งชี้ได้ว่าถ่านซึ่งผลิตที่อุณหภูมิคาร์บอไนเซชันต่ำจะให้ปริมาณร้อยละของสารระเหยสูง ส่งผลให้ถ่านมีปริมาณร้อยละผลผลิตสูงและคาร์บอนคงที่ต่ำ อย่างไรก็ตาม เมื่อพิจารณาสัดส่วนขององค์ประกอบในถ่านซึ่งผลิตที่อุณหภูมิ 750 และ 1000 องศาเซลเซียส พบว่า ปริมาณร้อยละของผลผลิต สารระเหย และคาร์บอนคงที่ของถ่านไม่แตกต่างกันอย่างมีนัยสำคัญ สำหรับการวิเคราะห์ปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิด

ในควันของถ่าน พบว่าถ่านซึ่งผลิตที่อุณหภูมิ 500 750 และ 1000 องศาเซลเซียส มีปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิด เท่ากับ 4.52×10^{3}, 0.55×10^{3} และ 0.94×10^{3} μg/g ตามลำดับ และพบว่าถ่านซึ่งผลิตที่ 500 องศาเซลเซียส มีสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอน 4 ชนิด ซึ่งเป็นตัวชี้วัดปริมาณสารก่อมะเร็งตามข้อกำหนดของสหภาพยุโรป (EU No 835/2011) ถ่านซึ่งผลิตที่อุณหภูมิ 500 องศาเซลเซียส ซึ่งให้ปริมาณร้อยละของสารระเหยสูง จะให้ปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิดสูงเช่นกัน และพบว่าปริมาณของสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิดในถ่านซึ่งผลิตที่อุณหภูมิ 750 และ 1000 องศาเซลเซียส ไม่แตกต่างกันอย่างมีนัยสำคัญ ดังนั้นจึงอาจกล่าวได้ว่าสารระเหยและปริมาณสารโพลิไซคลิกอโรมาติกไฮโดรคาร์บอนทั้ง 16 ชนิด ในถ่านมีความสัมพันธ์กัน

คำสำคัญ : กระบวนการคาร์บอไนเซชั่น/ ถ่าน/ สารก่อมะเร็ง/ สารโพลิไซคลิกอโรมาติก
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CHAPTER 1 INTRODUCTION

1.1 Research Rationale

Nowadays, grilled food is one of the most popular foods in Thailand and is another one exported food of Thailand such as processes chicken - Yakitori (Siamturakij, 2013; Thai Broiler Processing Exporters Association, 2012). However, the grilled food will be popular among the customers if they use charcoal as heat source for cooking. Due to, the product will have specific color and odor (Ratanapanon and Pornchalermpong, 2013).

Nonetheless, the grilled food using charcoal still has disadvantages that decrease the popularity in customers. That is the contamination of polycyclic aromatic hydrocarbons (PAHs) (Kangsadalampai, 2011; National Food Institute, 2011). PAHs consisting of two or more benzene ring. PAHs have only carbon and hydrogen in molecule structure. PAHs have more hundreds type but only 16 type are defined as carcinogens by United State Environmental Protection Agency (U.S. EPA). The EU regulation defines the maximum levels of Benzo[a]pyrene (agent of 16 PAHs) in smoke meat and smoke meat products at 0.005 ug/g wet weight (EU Regulation No. 208/2005) and PAH4 (Benzo[a]pyrene Chrysene Benzo[a]anthracene and Benzo[b]fluoranthene) at 0.03 ug/g wet weight (EU Regulation No 835/2011). However, in the present, there is no standard regulation for PAHs in grilled foods.

Many researchers found that PAHs were not detected in grilled product if they avoid used charcoal grilling in cooking process and the contamination of PAHs in grilled food may occur from incomplete combustion or high-temperature pyrolysis of charcoal (Farhadian et al., 2011; Olabemiwo, 2013; Yurchenko and Molder, 2005). The actual levels of PAHs in smoked foods depend on several variables in the smoking process, including type of smoke generator, combustion temperature, and degree of smoking (Farhadian et al., 2011; Yurchenko and Molder, 2005).

For other researches, the temperature used in carbonization affects to charcoal compositions which are moisture content volatile matter ash and fixed carbon (FAO, 1983). Volatile matter that found in charcoal has the relations in the same way with

PAHs and the carbonization temperature affect to the quantity of them. (Forest Products Research Division of Royal Forest Department, 1984; Zevenboven and Kilpinen, 2001; Fjellerup et al., 2005). Moreover, Viegas et al., 2012 found that the charcoal obtained from difference type of wood may effects on PAHs contents.

Therefore, in this study will interest the charcoal that is one of the main factors affect PAHs contaminant in grilled food. Mangrove wood was selected for the study because of it is a local wood and inexpensive. This study will focus on the difference of carbonization temperature that effect on charcoal compositions and PAHs contents in grilled food. For PAHs analysis, the charcoal samples were burned at 650 °C, then collect the smoke from charcoal burning and analyze by using GC-MS.

1.2 Hypothesis

Volatile matter which is components in charcoal might have the relationship with 16 PAHs occurring in smoke of charcoal.

1.3 Objective

To study the effect of carbonization temperature on composition of mangrove charcoal and PAHs content generated in smoke during charcoal grilling

1.4 Scopes

- Ten-year-old mangrove wood with 2 inch of diameter were used in charcoal making process which varied the carbonization temperature at 500, 750 and 1000 °C
- Components consisting of moisture content, volatile matter, ash and fixed carbon of mangrove charcoal obtained from various carbonization temperatures were analyzed by using ASTM method.
- Sixteen priority PAHs in smoke from combustion of 70 ± 2 g of mangrove charcoal at 650 °C were collected by absorption tube and determined by using Gas Chromatography-Mass Spectrometry (GC-MS)

1.5 Expected Benefit

To understand the relationship between charcoal compositions and PAHs content generated in smoke during charcoal combustion which may lead to a reduction of PAHs contamination on charcoal grilled food.

CHAPTER 2 THEORY AND LITERATURE REVIEW

2.1 Polycyclic aromatic hydrocarbon

2.1.1 What are polycyclic aromatic hydrocarbons?

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat. There are more than 100 different PAHs. PAHs generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes; however, not as the mixtures found in combustion products.

As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids. They can have a faint, pleasant odor. A few PAHs are used in medicines and to make dyes, plastics, and pesticides. Others are contained in asphalt used in road construction. They can also be found in substances such as crude oil, coal, coal tar pitch, creosote, and roofing tar. They are found throughout the environment in the air, water, and soil. They can occur in the air, either attached to dust particles or as solids in soil or sediment.

Although the health effects of individual PAHs are not exactly alike, the following 16 PAHs are considered as a group as follows: Naphthalene, Acenaphthylene, Acenaphthene, Anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Chrysene, Fluorene, Fluoranthene, Phenanthrene, Pyrene, Benzo[a]anthracene, Benzo[a]pyrene, Benzo[g,h,i]perylene, Dibenzo[a,h]anthracene, Indeno[1,2,3-c,d]pyrene

These 16 PAHs were chosen to be included in this profile because more information is available on these than on the others; they are suspected to be more harmful than some of the others, and they exhibit harmful effects that are representative of the PAHs; there is a greater chance that you will be exposed to these PAHs than to the others; and of all the PAHs analyzed, these were the PAHs identified at the highest concentrations at NPL hazardous waste sites More information can be found on the chemical and physical properties of PAHs in Table 2.1.

Table 2.1 Physical and chemical characteristics of some popular PAHs (Lee and Vu, 2010)

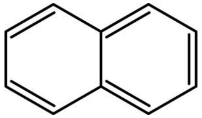
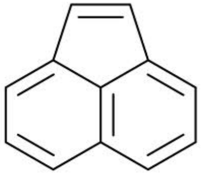
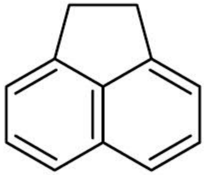
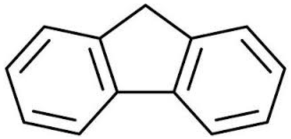
Characteristic	Chemical formula	Chemical structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg)
Naphthalene	$C_{10}H_8$		128.17	80.26	218	0.087
Acenaphthylene	$C_{12}H_8$		152.2	92-93	265-275	0.029
Acenaphthene	$C_{12}H_{10}$		154.21	95	96	$4.47x10^{-3}$
Fluorene	$C_{13}H_{10}$		166.2	116-117	295	$3.2x10^{-4}$

Table 2.1 Physical and chemical characteristics of some popular PAHs (Lee and Vu, 2010) (Cont.)

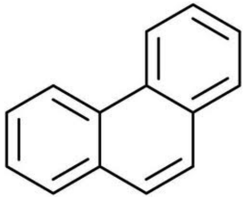
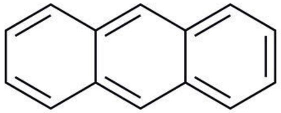
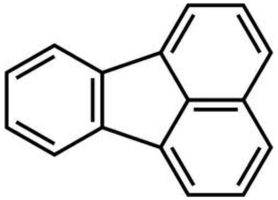
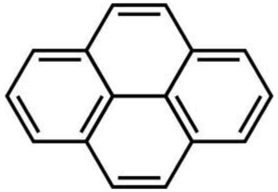
Characteristic	Chemical formula	Chemical structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg)
Phenanthrene	$C_{14}H_{10}$		178.2	100	340	$6.8x10^{-4}$
Anthracene	$C_{14}H_{10}$		178.2	218	340-342	$1.75x10^{-6}$
Fluoranthene	$C_{16}H_{10}$		202.26	110.8	375	$5.0x10^{-6}$
Pyrene	$C_{16}H_{10}$		202.3	156	393-404	$2.5x10^{-6}$

Table 2.1 Physical and chemical characteristics of some popular PAHs (Lee and Vu, 2010) (Cont.)

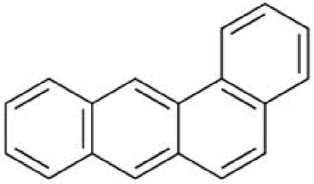
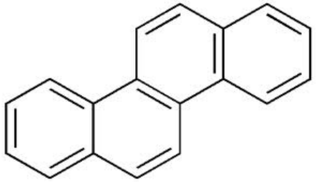
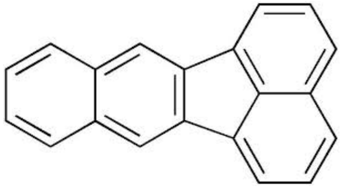
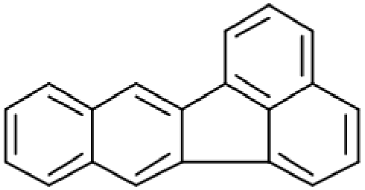
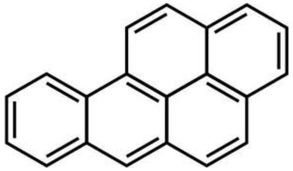
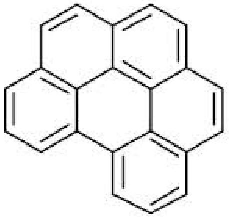
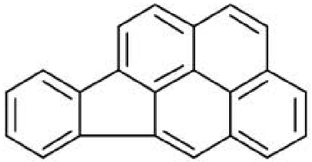
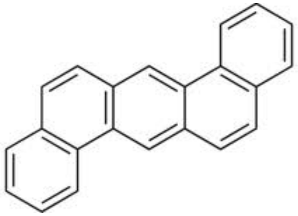
Characteristic	Chemical formula	Chemical structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg)
Benzo(a)anthracene	$C_{20}H_{12}$		228.29	158	438	$2.5x10^{-6}$
Chrysene	$C_{18}H_{12}$		228.28	254	448	$6.4x10^{-9}$
Benzo(b)fluoranthene	$C_{20}H_{12}$		252.3	168.3	No data	$5.0x10^{-7}$
Benzo(k)fluoranthene	$C_{20}H_{12}$		252.3	215.7	480	$9.59x10^{-11}$

Table 2.1 Physical and chemical characteristics of some popular PAHs (Lee and Vu, 2010) (Cont.)

Characteristic	Chemical formula	Chemical structure	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg)
Benzo(a)pyrene	$C_{20}H_{12}$		252.3	179-179.3	495	$5.6x10^{-9}$
Benzo(g,h,i)perylene	$C_{22}H_{12}$		276.34	273	550	$1.03x10^{-10}$
Indeno(1,2,3-c,d)pyrene	$C_{22}H_{12}$		276.3	163.6	530	$10.10x10^{-16}$
Dibenzo(a,h)anthracene	$C_{22}H_{14}$		278.35	262	No data	$1x10^{-10}$

PAHs containing up to 4 fused benzene rings are known as light PAHs and those containing more than four benzene rings are known as heavy PAHs. Heavy PAHs are more stable and more toxic than light ones.

PAHs of three rings or more have low solubilities in water and a low vapor pressure. As molecular weight increases, solubility and vapor pressure decrease. PAHs with two rings are more soluble in water and more volatile. Because of these properties, PAHs in the environment are found primarily in soil and sediment, as opposed to in water or air. However, PAHs are often found in particles suspended in water and air. PAHs are lipophilic in nature. Their presence has been reported in different edible oils from different countries.

2.1.2 How can polycyclic aromatic hydrocarbons affect health?

PAHs can be harmful to health under some circumstances. Several of the PAHs, including benzo[a]anthracene, benzo[j]fluoranthene, benzo[b]fluoranthene, chrysene, benzo[a]pyrene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene, have caused tumors in laboratory animals when they breathed these substances in the air, when they ate them, or when they had long periods of skin contact with them. Studies of people show that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can also develop cancer.

Mice fed high levels of benzo[a]pyrene during pregnancy had difficulty reproducing and so did their offspring. The offspring of pregnant mice fed benzo[a]pyrene also showed other harmful effects, such as birth defects and decreased body weight. Similar effects could occur in people, but we have no information to show that these effects do occur. Studies in animals have also shown that PAHs can cause harmful effects on skin, body fluids, and the body’s system for fighting disease after both short- and long-term exposure. These effects have not been reported in people.

The Department of Health and Human Services (DHHS) has determined that benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are known animal carcinogens. The International Agency for Research on Cancer (IARC) has determined the following: benzo[a]anthracene and benzo[a]pyrene are probably carcinogenic to humans; benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-c,d]pyrene are possibly carcinogenic to humans; and anthracene, benzo[g,h,i]perylene, benzo[e]pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to their carcinogenicity to humans.

EPA has determined that benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, chrysene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are probable human carcinogens and that acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to human carcinogenicity. Acenaphthene has not been classified for carcinogenic effects by the DHHS, IARC, or U.S. Environmental Protection Agency (EPA) (Table 2.2).

Table 2.2 17 priority PAHs were classified by the IARC in comparing those by the DHHS and the US-EPA (Lee and Vu, 2010)

PAHs	EPA	IARC	DHHS
Acenaphthene			
Acenaphthylene	Not classifiable		
Anthanthrene	Not classifiable	Not classifiable	
Benzo(a)anthracene	Probably Carcinogen	Probably Carcinogen	Animal Carcinogen
Benzo(a)pyrene	Probably Carcinogen	Probably Carcinogen	Animal Carcinogen
Benzo(b)fluoranthene	Probably Carcinogen	Possibly Carcinogen	Animal Carcinogen
Benzo(e)pyrene		Not classifiable	
Benzo(ghi)perylene	Not classifiable	Not classifiable	
Benzo(j)fluoranthene	Not included	Possibly Carcinogen	Animal Carcinogen
Benzo(k)fluoranthene	Probably Carcinogen	Possibly Carcinogen	
Chrysene	Probably Carcinogen	Not classifiable	
Dibenzo(ah)anthracene	Probably Carcinogen		Animal Carcinogen
Fluoranthene	Not classifiable	Not classifiable	
Fluorene	Not classifiable	Not classifiable	
Ideno(1,2,3-cd)pyrene	Probably Carcinogen	Possibly Carcinogen	Animal Carcinogen
Phenanthrene	Not classifiable		
Pyrene	Not classifiable	Not classifiable	

2.1.3 What recommendations has the federal government made to protect human health?

The federal government has set regulations to protect people from the possible health effects of eating, drinking, or breathing PAHs. EPA has suggested that taking into body each day the following amounts of individual PAHs is not likely to cause any harmful health effects: 0.3 milligrams (mg) of anthracene, 0.06 mg of acenaphthene, 0.04 mg of fluoranthene, 0.04 mg of fluorene, and 0.03 mg of pyrene per kilogram (kg) of body weight (one kilogram is equal to 2.2 pounds).

From what is currently known about benzo[a]pyrene, the federal government has developed regulatory standards and guidelines to protect people from the potential health effects of PAHs in drinking water. EPA has provided estimates of levels of total cancer-causing PAHs in lakes and streams associated with a risk of human cancer development. If the following amounts of individual PAHs are released to the environment within 24 hour period, EPA must be notified: 1 pound of benzo[b]fluoranthene, benzo[a]pyrene, or dibenzo[a,h]anthracene; 10 pounds of benzo[a]anthracene; 100 pounds of acenaphthene, chrysene, fluoranthene, or indeno[1,2,3-c,d]pyrene; or 5,000 pounds of acenaphthylene, anthracene, benzo[k]fluoranthene, benzo[g,h,i]perylene, fluorene, phenanthrene, or pyrene.

PAHs are generally not produced commercially in the United States except as research chemicals. However, PAHs are found in coal, coal tar, and in the creosote oils, oil mists, and pitches formed from the distillation of coal tars. The National Institute for Occupational Safety and Health (NIOSH) concluded that occupational exposure to coal products can increase the risk of lung and skin cancer in workers. NIOSH established a recommended occupational exposure limit, time-weighted average (REL-TWA) for coal tar products of 0.1 mg of PAHs per cubic meter of air (0.1 mg/m^3) for a 10-hour workday, within a 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends an occupational exposure limit for coal tar products of 0.2 mg/m^3 for an 8-hour workday, within a 40-hour workweek. The Occupational Safety and Health Administration (OSHA) have established a legally enforceable limit of 0.2 mg/m^3 averaged over an 8-hour exposure period (Table 2.3) (Agency for Toxic Substances and Disease Registry, 2009).

Table 2.3 Standards and Regulations for Polycyclic Aromatic Hydrocarbons (Agency for Toxic Substances and Disease Registry, 2009)

Agency	Focus	Level	Comments
American Conference of Governmental Industrial Hygienists (ACGIH)	Air: workplace	0.2 mg/m^3 for benzene-soluble coal tar pitch fraction	Advisory: TLV* (8 hour TWA**)
National Institute for Occupational Safety and Health (NIOSH)	Air: workplace	0.1 mg/m^3 for coal tar pitch volatile agents	Advisory: REL[+] (8 hour TWA)
Occupational Safety and Health Administration (OSHA)	Air: workplace	0.2 mg/m^3 for benzene-soluble coal tar pitch fraction	Regulation: (benzene soluble fraction of coal tar volatiles) PEL[++] (8 hour workday)
U.S. Environmental Protection Agency (U.S. EPA)	Water	0.0001 mg/L	MCL[+++] for benzo(a)anthracene
		0.0002 mg/L	MCL for benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene
		0.0003 mg/L	MCL for dibenz(a,h)anthracene
		0.0004 mg/L	MCL for indenol(1,2,3-c,d)pyrene

* TLV (Threshold limit value)

** TWA (Time weighted average): Concentration for a normal 8 hour workday and a 40 hour workweek to which nearly all workers may be repeatedly exposed

+ REL (Recommended exposure limit): Recommended airborne exposure limit for coal tar pitch volatiles (Cyclohexane extractable fraction) averaged over a 10 hour work shift

[++] PEL (Permissible exposure limit): The legal airborne permissible exposure limit (PEL) for coal tar pitch volatiles (Benzene soluble fraction) averaged over an 8 hour work shift

[+++] MCL: Maximum contaminant level

2.2 Charcoal

Charcoal is the solid residue remaining when wood is "carbonized" or "pyrolysed" under controlled conditions in a closed space such as a charcoal kiln. Control is exercised over the entry of air during the pyrolysis or carbonization process so that the wood does not merely burn away to ashes, as in a conventional fire, but decomposes chemically to form charcoal.

Air is not really required in the pyrolysis process. In fact, advanced technological methods of charcoal production do not allow any air to be admitted, resulting in a higher yield, since no extra wood is burned with the air and control of quality is facilitated. The pyrolysis process, once started, continues by itself and gives off considerable heat. However, this pyrolysis or thermal decomposition of the cellulose and lignin of which the wood is composed does not start until the wood is raised to a temperature of about 300 °C.

In the traditional charcoal kiln or pit some of the wood loaded into the kiln is burned to dry the wood and raise the temperature of the whole of the wood charge, so that pyrolysis starts and continues to completion by itself. The wood burned in this way is lost. By contrast, the success of sophisticated continuous retorts in producing high yields of quality charcoal is due to the ingenious way in which they make use of the heat of pyrolysis, normally wasted, to raise the temperature of the incoming wood so that pyrolysis is accomplished without burning additional wood, although some heat impact is needed to make up for heat losses through the walls and other parts of the equipment. The combustible wood gas given off by the carbonizing wood can be burned to provide this heat and to dry the wood. All carbonizing systems give higher efficiency when fed with dry wood, since removal of water from wood needs large inputs of heat energy.

The pyrolysis process produces charcoal which consists mainly of carbon, together with a small amount of tarry residues, the ash contained in the original wood, combustible gases, tars, a number of chemicals mainly acetic acid and methanol and a large amount of water which is given off as vapor from the drying and pyrolytic decomposition of the wood.

When pyrolysis is completed the charcoal, having arrived at a temperature of about 500 degree Celsius, is allowed to cool down without access of air; it is then safe to unload and it is ready for use.

The overwhelming bulk of the world's charcoal is still produced by the simple process briefly described above. It wastefully burns part of the wood charge to produce initial heat and does not recover any of the by-products or the heat given off by the pyrolysis process.

Other woody materials such as nut shells and bark are sometimes used to produce charcoal. Wood is, however, the preferred and most widely available material for charcoal production. Many agricultural residues can also produce charcoal by pyrolysis but such charcoal is produced as a fine powder which usually must be briquetted at extra cost for most charcoal uses. In any case, encouraging the wider use of crop residues for charcoal-making or even as fuel is generally an unwise agricultural practice, although the burning of sugar cane bagasse to provide heat in sugar production and the burning of cornstalks and coarse grasses as domestic fuel in some regions do provide an overall benefit where carried out as part of a rational agricultural policy.

On the grounds of availability, properties of the finished charcoal, and sound ecological principles, wood remains the preferred and most widely used raw material and there appears to be no reason why this should change in the future.

2.2.1 How wood is transformed into charcoal

The carbonization stage may be decisive in charcoal production even though it is not the most expensive one. Unless it is carried out as efficiently as possible, it puts the whole operation of charcoal production at risk since low yields in carbonization reflect back through the whole chain of production as increased costs and waste of resources.

Wood consists of three main components: cellulose, lignin and water. The cellulose and lignin and some other materials are tightly bound together and make up the material we call wood. The water is absorbed or held as molecules of water on the cellulose/lignin structure. Air dry or "seasoned" wood still contains 12-18% of adsorbed water. Growing, freshly cut or "unseasoned" wood contains, in addition, liquid water to give a total water content of about 40 to 100% expressed as a percentage of the oven dry weight of the wood.

The water in the wood has all to be driven off as vapor before carbonization can take place. To evaporate water requires a lot of energy so that using the sun to pre-dry the wood as much as possible before carbonization greatly improves efficiency. The water remaining in the wood to be carbonized, must be evaporated in the kiln or pit and this energy must be provided by burning some of the wood itself which otherwise would be converted into useful charcoal.

The first step in carbonization in the kiln is drying out of the wood at 100 °C or below to zero moisture content. The temperature of the oven dry wood is then raised to about 280 °C. The energy for these steps comes from partial combustion of some of the wood charged to the kiln or pit and it is an energy absorbing or endothermic reaction.

When the wood is dry and heated to around 280°C, it begins to spontaneously break down to produce charcoal plus water vapor, methanol, acetic acid and more complex chemicals, chiefly in the form of tars and non-condensable gas consisting mainly of hydrogen, carbon monoxide and carbon dioxide. Air is admitted to the carbonizing kiln or pit to allow some wood to be burned and the nitrogen from this air will also be present in the gas. The oxygen of the air is used up in burning part of the wood charged.

The spontaneous breakdown or carbonization of the wood above a temperature of 280°C liberates energy and hence this reaction is said to be exothermic. This process of spontaneous breakdown or carbonization continues until only the carbonized residue called charcoal remains. Unless further external heat is provided, the process stops and the temperature reach a maximum of about 400°C. This charcoal, however, will still contain appreciable amounts of tarry residue, together with the ash of the original wood. The ash content of the charcoal is about 3-5%; the tarry residue may amount to about 30% by weight and the balance is fixed carbon about 65-70%.

Further heating increases the fixed carbon content by driving off and decomposing more of the tars. A temperature of 500°C gives a typical fixed carbon content of about 85% and a volatile content of about 10%. The yield of charcoal at this temperature is about 33% of the weight of the oven dry wood carbonized - not counting the wood which was burned to carbonize the remainder. Thus the theoretical yield of charcoal varies with temperature of carbonization due to the change in its content of volatile tarry material. Table 2.4 shows the effect of final carbonization temperature on the yield and composition of the charcoal.

Table 2.4 Effect of carbonization temperature on yield and composition of charcoal (FAO, 1983)

Carbonisation Temperature (°C)	Chemical analysis of charcoal		Charcoal yield based on oven dry wood (0% moisture)
	% of fixed charcoal	% volatile material	
300	68	31	42
500	86	13	33
700	92	7	30

Low carbonization temperatures give a higher yield of charcoal but this charcoal is low grade, is corrosive due to its content of acidic tars, and does not burn with a clean smoke-free flame. Good commercial charcoal should have a fixed carbon content of about 75% and this call for a final carbonizing temperature of around 500 °C.

The yield of charcoal also shows some variation with the kind of wood. There is evidence that the lignin content of the wood has a positive effect on charcoal yield.
High lignin content gives a high yield of charcoal. Therefore, mature wood in sound condition is preferred for charcoal production. Dense wood also tends to give a dense, strong charcoal, which is also desirable. However, very dense woods sometimes produce a friable charcoal because the wood tends to shatter during carbonization. The friability of charcoal increases as carbonization temperature increases and the fixed carbon content increases as the volatile matter content falls. A temperature of 450 to 500°C gives an optimum balance between friability and the desire for high fixed carbon content.

The many variables possible in carbonization make it difficult to specify an optimum procedure - generally the best results will be obtained by using sound hardwood of medium to high density. The wood should be as dry as possible and usually be split to eliminate pieces more than 20 cm thick. Firewood which will be burned up inside the kiln or pit to dry out and start carbonization of the remainder can be of inferior quality and smaller in cross section. Its sole function is to produce heat to dry out and heat up the remainder to carbonizing temperature. One should try and reach a final temperature of around 500°C through the whole of the charge. With pits this is difficult since the air circulation and cooling effects are irregular and cold spots occur. These produce "brands" of uncarbonized wood. Trying to reach a final overall temperature of 500°C with a pit or kiln having poor and irregular air circulation usually results in burning part of the charcoal to ashes, while leaving other parts of the charge only partly carbonized.

2.2.2. Wood carbonization

Carbonization is a particular form of that process in chemical technology called pyrolysis that is the breakdown of complex substances into simpler ones by heating. Carbonization is the term used when complex carbonaceous substances such as wood or agricultural residues are broken down by heating into elemental carbon and chemical compounds which may also contain some carbon in their chemical structure. The term carbonization is also applied to the pyrolysis of coal to produce coke.

1. The stages in charcoal formation

As the wood is heated in the retort it passes through definite stages on its way to conversion into charcoal. The formation of charcoal under laboratory conditions has been studied and the following stages in the conversion process have been recognized.

- At 20 to 110°C, the wood absorbs heat as it is dried giving off its moisture as water vapor (steam). The temperature remains at or slightly above 100°C until the wood is bone dry.

- At 110 to 270°C, final traces of water are given off and the wood starts to decompose giving off some carbon monoxide, carbon dioxide, acetic acid and methanol. Heat is absorbed.

- At 270 to 290°C, this is the point at which exothermic decomposition of the wood starts. Heat is evolved and breakdown continues spontaneously providing the wood is not cooled below this decomposition temperature. Mixed gases and vapors continue to be given off together with some tar.

- At 290 to 400°C, as breakdown of the wood structure continues, the vapors given off comprise the combustible gases carbon monoxide, hydrogen and methane together with carbon dioxide gas and the condensable vapors: water, acetic acid, methanol, acetone, etc. and tars which begin to predominate as the temperature rises.

- At 400 to 500°C, at 400°C the transformation of the wood to charcoal is practically complete. The charcoal at this temperature still contains appreciable amounts of tar, perhaps 30% by weight trapped in the structure. This soft burned charcoal needs further heating to drive off more of the tar and thus raise the fixed carbon content of the charcoal to about 75% which is normal for good quality commercial charcoal. To drive off this tar the charcoal is subject to further heat inputs to raise its temperature to about 500°C, thus completing the carbonization stage.

2. Pyrolysis of biomass

Cellulose, hemicellulose, and lignin, the principal components of biomass, have different reaction kinetics. Hemicellulose is the most reactive constituent and lignin the least (Probstein and Hicks, 1982). Pyrolysis of whole biomass can be described in terms of the behavior of these components, each of which is discussed separately in the following sections. The reaction rates, products, and other thermal behavior of biomass pyrolysis are considered a combination of the behavior of its main components. Each component contributes to the behavior to an extent proportional to its weight percent contribution to the composition of the raw biomass. This is true in the absence of secondary reactions.

- Pyrolysis of cellulose

  The principal components of biomass, cellulose is the most widely studied. This is mainly because it is the major component of most biomass (43%). In addition, it is the least complicated, best defined component of biomass. Cellulose is the major source of the combustible volatiles that fuel flaming combustion. Cellulose also appears naturally almost in its pure state (e.g., cotton).

Numerous studies of pyrolytic thermal degradation of cellulose under various conditions have been reported and a simplified, two-pathway mechanism of its decomposition has been generally accepted (Figure 2.1).

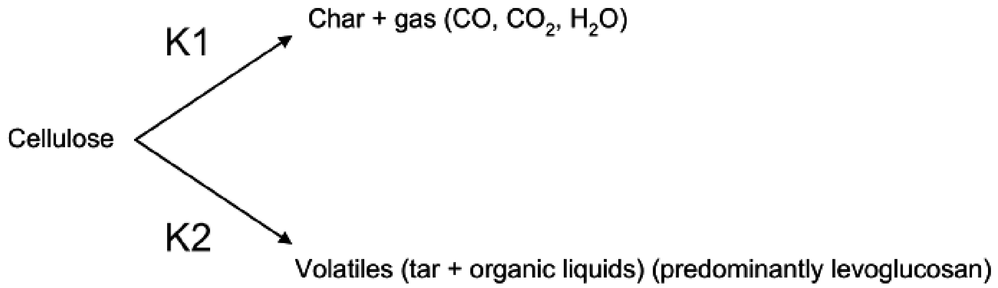


Figure 2.1 Simplified reaction model for cellulose decomposition (Sadaka, 2012)

Reaction 1 dominates at low temperatures while reaction 2 dominates at high temperatures. The existence of the two pathways is demonstrated by studies of the rates of weight loss of cellulose in nitrogen; the transition is found to occur at about 300 °C. Below this temperature, the following chemical reactions may occur: reduction of molecular weight, the appearance of free radicals, oxidation, dehydration, decarboxylation, and decarbonylation. The products are mainly CO, CO_2, H_2O, and a char residue.

The second pathway occurs at temperatures above 300 °C and involves decomposition of cellulose to tarry pyrolyzate containing levoglucosan as the major component (22-50%), which vaporizes and then decomposes with increasing temperature. As the temperature is increased from 300 °C to 500 °C, the amount of tarry products increases while the proportion of char component diminishes and the yields of levoglucosan remain almost constant.

The major products of pyrolysis of cellulose below 500 °C are char, tar (mainly levoglucosan), water, CO_2 and CO (Funakuzuri et al., 1986). The yield of light hydrocarbons, i.e., $C_1 - C_4$, is negligible below 500 °C but becomes considerable at high temperatures (Scott et al., 1988). Tar yield begins to drop as pyrolysis temperature is raised above 600 °C (Hajaligol et al., 1982). A rapid increase in total gas yield was recorded at almost the same temperature at which the tar yield begins to drop. This is an indication that primary tar cracking contributes to the total gas production at elevated temperatures.

- Pyrolysis of Hemicellulose

Glucoronoxylans (commonly referred to as xylan) are the most important hemicelluloses of hardwoods, and glucomannan is the predominant hemicellulose in softwoods. Xylan has been used in several studies (Koufopanos et al., 1989) to model the pyrolysis of hemicelluloses. Hemicelluloses are the most reactive major component of wood decomposing in the temperature range 200 - 260 °C. The thermal instability of hemicelluloses is probably due to their lack of crystallines. Decomposition of hemicellulose under Pyrolytic conditions is postulated to occur in two steps (Soltes and Elder, 1981). First is the breakdown of the polymer into water soluble fragments followed by conversion to monomeric units, and finally decomposition of these units to volatiles. Hemicelluloses produce more gases and less tar than cellulose, and no levoglucosan. They also produce more methanol and acetic acid than cellulose.

- Pyrolysis of Lignin

Lignin, the third major component of woody biomass, is a highly linked (3-D network polymer), amorphous, high molecular weight phenolic compound. Lignin serves as cement between the wood fibers and as a stiffening agent within them. Lignin is the least reactive component of biomass; higher temperatures are necessary for the pyrolysis of most lignin. The time required for complete pyrolysis of woody biomass at a given temperature is controlled by the pyrolysis rate of lignin at the operating conditions. Thermal decomposition of lignin occurs in the temperature range 280°C to 500°C, although some physical and/or chemical changes (e.g., depolymerization, loss of some methanol) may occur at lower temperatures (Koufopanos et al., 1989). Wenzel (1970) reported that, at a slow heating rate, lignin loses only about 50% of its weight when the pyrolysis is stopped at 800°C.

Pyrolysis of lignin yields more char and tar than cellulose. Soltes and Elder (1981) have reported a product composition of 51-66% char, 14-15% tar, 13-28% pyroligneous acid and about 12% gaseous products (consisting mainly of CO, CH_4 and C_2H_6). The tar residue is a mixture of phenolic compounds while the aqueous distillate contains, among other compounds, water, methanol, acetic acid, and acetone.

- Pyrolysis of Wood

Studies of the pyrolytic behavior of individual wood components have helped elucidate the different steps involved in the whole wood pyrolysis. Kinetic studies of wood pyrolysis indicated two distinct decomposition regimes. Rate data for the first and second (in time) regimes correlate very closely with those of pyrolysis of pure hemicellulose and cellulose, respectively. This may be interpreted to indicate decomposition of the major wood components is taking place separately.

Pyrolysis of wood takes place in a sequential manner with the least stable component, hemicellulose, decomposing first at temperatures of 200 °C to 280 °C and lignin, the most stable component, decomposing last at temperatures of 280 °C to 500 °C. It is not possible to define a strictly lower limit for the beginning of thermal decomposition of wood but the following sequence of events is generally observed at low heating rates:

- Up to 200 °C: Along with the removal of moisture, other volatile products such as acetic acid and formic acid are released. Non-condensable gases such as CO and CO_2 are also evolved.

- 200 - 280 °C: Further decomposition of the (char + wood) residue; decomposition is more vigorous with the release of pyroligneous acids, water, and non-condensable gases (CO, CO_2). Separation of tar is also observed.

- 280 - 500 °C: Release of combustible volatile products such as CO, CH_4, H_2, formaldehyde, formic acid, methanol, and acetic acid occur. Formation of char decreases in quantity but increases in carbon content. Release of condensable tar also continues.

- Above 500°C: Carbonization is complete. If the reaction products are not removed from the reaction zone as soon as they are formed, secondary reactions begin and char-gas reactions (Sadaka, 2010).

2.2.3 Properties of charcoal

Carbonization of wood gives rise to a complex range of products; solid, liquid and gaseous. Dozens of chemicals could be extracted from the liquid condensate if it were economically practical.

1. The quality of charcoal

The least demanding market for charcoal, quality-wise, is the domestic one. The reasons are that performance cannot be measured easily, the power of consumers as individuals to specify and obtain good quality charcoal is minimal and there is a certain trade-off possible between price and quality which the household consumer uses to obtain satisfactory results. However, this does not mean that quality control is not worthwhile. Provided it does not become unwieldy and bureaucratically counterproductive, a system of quality guidelines for household charcoal is a worthwhile step in ensuring maximum yield from the wood resource, nevertheless giving adequate household performance.

On the other hand, large users such as the charcoal iron industry know from their operating experience and research, the properties they seek in charcoal and have the means in the form of concentrated buying power and control over at least a part of their own charcoal production, to ensure that the charcoal they use conforms to their specification and produces pig iron at minimum overall cost.

Most of the specifications used to control charcoal quality have originated in the steel or chemical industry. When charcoal is exported, buyers tend to make use of these industrial quality specifications even though the main outlet of the imported charcoal may well be the domestic cooking or barbecue market. This factor should be borne in mind since industrial and domestic requirements are not always the same and an intelligent appraisal of actual market quality requirements may allow supply of suitable charcoal at a lower price or in greater quantities beneficial to both buyer and seller.

The quality of charcoal is defined by various properties and though all are interrelated to a certain extent, they are measured and appraised separately. These various quality factors are discussed below.

- Moisture content

Charcoal fresh from an opened kiln contains very little moisture, usually less than 1%. Absorption of moisture from the humidity of the air itself is rapid and there is, with time, a gain of moisture which even without any rain wetting can brings the moisture content to about 5 to 10%, even in well-burned charcoal. When the charcoal is not properly burned or where pyroligneous acids and soluble tars have been washed back onto the charcoal by rain, as can happen in pit and mound burning, the hygroscopitity of the charcoal is increased and the natural or equilibrium moisture content of the charcoal can rise to 15% or even more.

Moisture is an adulterant which lowers the calorific or heating value of the charcoal. Where charcoal is sold by weight, keeping the moisture content high by wetting with water is often practiced by dishonest dealers. The volume and appearance of charcoal is hardly changed by addition of water. For this reason bulk buyers of charcoal prefer to buy either by gross volume, e.g. in cubic meters, or to buy by weight and determine by laboratory test the moisture content and adjust the price to compensate. In small markets sale is often by the piece.

It is virtually impossible to prevent some accidental rain wetting of charcoal during transport to the market but good practice is to store charcoal under cover even if it had been bought on a volume basis, since the water it contains must be evaporated on burning and represents a direct loss of heating power. This occurs because the evaporated water passes off into the flue and is rarely condensed to give up the heat it contains on the object being heated in the stove.

Quality specifications for charcoal usually limit the moisture content to around 5-15% of the gross weight of the charcoal. Moisture content is determined by oven drying a weighed sample of the charcoal. It is expressed as a percentage of the initial wet weight.

There is evidence that charcoal with high moisture content (10% or more) tends to shatter and produce fines when heated in the blast furnace, making it undesirable in the production.

- Volatile matter other than water

  The volatile matter other than water in charcoal comprises all those liquid and tarry residues not fully driven off in the process of carbonization. If the carbonization is prolonged at high temperature, then the content of volatiles is low. When the carbonization temperature is low and time in the kiln is short, then the volatile matter content increases.

  These effects are reflected in the yield of charcoal produced from a given weight of wood. At low temperatures (300 °C) a charcoal yield of nearly 50% is possible. At carbonization temperatures of 500 – 600 °C volatiles are lower and retort yields of 30% are typical. At very high temperatures (around 1000 °C) the volatile content is almost zero and yields fall to near 25%. As stated earlier, charcoal can reabsorb tars and pyroligneous acids from rain wash in pit burning and similar processes. Thus the charcoal might be well burned but have high volatile matter content due to this factor. This causes an additional variation in pit burned charcoal in wet climates. The reabsorbed acids make the charcoal corrosive and lead to rotting of jute bags - a problem during transport. Also it does not burn cleanly.

  The volatile matter in charcoal can vary from a high of 40% or more down to 5% or less. It is measured by heating away from air, a weighed sample of dry charcoal at 900 °C to constant weight. The weight loss is the volatile matter. Volatile matter is usually specified free of the moisture content, i.e. volatile matter - moisture.

  High volatile charcoal is easy to ignite but may burn with a smoke flame. Low volatile charcoal is difficult to light and burns very cleanly. A good commercial charcoal can have a net volatile matter content - (moisture free) of about 30%. High volatile matter charcoal is less friable than ordinary hard burned low volatile charcoal and so produces less fines during transport and handling. It is also more hygroscopic and thus has higher natural moisture content.

- Fixed carbon content

  The fixed carbon content of charcoal ranges from a low of about 50% to a high or around 95%. Thus charcoal consists mainly of carbon. The carbon content is usually estimated as a "difference"; that is to say, all the other constituents are deducted from 100 as percentages and the remainder is assumed to be the % of "pure" or "fixed" carbon.

- Ash content

  Ash is determined by heating a weighed sample to red heat with access of air to burn away all combustible matter. This residue is the ash. It is mineral matter, such as clay, silica and calcium and magnesium oxides, etc., present in the original wood and picked up as contamination from the earth during processing.

  The ash content of charcoal varies from about 0.5% to more than 5% depending on the species of wood, the amount of bark included with the wood in the kiln and the amount of earth and sand contamination. Good quality lump charcoal typically has ash content of about 3%. Fine charcoal may have very high ash content but if material less than 4 mm is screened out the plus 4 mm residue may have an ash content of about 5-10%.

2. Pyroligneous acid

The watery condensate of the vapors leaving the retort is known as pyroligneous acid. Water insoluble tars condense at the same time and separate from the watery phase on standing. The composition of pyroligneous acid is extremely complex and only the major constituents can be mentioned. The yield is important for determining the economics of recovery and varies with the type of wood carbonized.

For guidance the following are typical yields obtained from pyroligneous acid produced by carbonizing northern hemisphere deciduous hardwoods.

- Acetic acid is the most valuable product in terms of total cash return that can be recovered from the pyroligneous acid. Although the amount of acetic acid marketed as a by-product of wood distillation nowadays is rather insignificant the acid from wood distillation is sought after for certain uses because it is fairly pure. The method used to recover the acid from the condensate is usually by solvent extraction of the crude acid liquor using ethyl acetate after the soluble tars and the methanol/acetone have been separated. The acetic acid passes into the ethyl acetate phase. The ethyl acetate is recovered in a still and returned to the extraction column. The acetic acid is purified by distillation. Several grades may be produced which vary in their purity and acid content.

- Methanol and acetone, Because of the low prices ruling for these products made by the petro-chemical route and the high cost of separating them as pure grades from the pyroligneous acid it is usual to recover them as a mixture which also contains methyl acetone. The mixture is sold as a solvent for use in the paint industry.

  The mixed solvent is recovered by distilling the water phase after the insoluble tar has been decanted. The liquid is distilled in a primary still and the acetic acid, methanol, acetone, etc. is vaporized. The soluble tars remain in the still. The vapors are fractionated in a column and the crude mixed methanol solvent fraction (about 85% methanol) is separated from the mixture of acetic acid and water. This latter mixture is purified as described above by solvent extraction of the acetic acid. The crude methanol cut could be further purified but price does not allow it as a rule and it is sold as mixed solvent.

- The tars or insoluble tar is a useful product in veterinary medicine as an antiseptic and as a wood preservation agent and caulking compound. When produced from softwood distillation it is usually called Stockholm tar. It's recovery by decantation from the condensate is simple. Aromatic substances valuable in medicine and perfumery can be separated from this tar by complex chemical processes. If this tar were produced in the developing world it would probably find local markets at a reasonable price.

  The soluble tar is more difficult to market. This material is a complex mixture of highly condensed yet water miscible substances for which very few uses seem to exist. It has been used as an admixture with clay in brick making to produce porous bricks and of course can be burned as a fuel.

> The tars from wood distillation must be recognized as pollutants of the environment and hence cannot be allowed to escape into streams. Waste liquors of all kinds from by-product recovery must be run into closed shallow ponds and the water allowed to evaporate leaving behind the tarry residues. These, after they have accumulated can be burned to remove the risk they pose to stream life, fish, water supplies and so on. This method works well in areas where the net evaporation exceeds the net precipitation, i.e. where charcoal is being made in a semi-arid climate but is an obvious failure in the humid tropics.

Alternatively the tars and all the volatile material except the water component can be burned as fuel. In many ways this is the best way of using the material rather than investing in by-product recovery schemes. Because of the large amount of energy needed to evaporate the water it is best to burn the mixture of gas and condensable as hot uncondensed gas as close as possible to the carbonizing equipment.

2.2.4 Charcoal output evaluation

The charcoal output was evaluated in terms of yield, production rate and production efficiency. This section will discuss the methods used to determine these factors.

- Yield

  The charcoal output yield can be evaluated either by volume or by weight of charcoal output/wood input. For large scale kilns, it is more convenient to evaluate the output yield based on volume. In this study, the evaluation was based on weight since only small and medium scale kilns were used. In addition, for scientific purposes, the only sure measurement is weight as weight accurately reflects the conversion loss through the process. The charcoal output yield can be calculated from the relation:

$$\%\text{Yield} = \frac{\text{Weight of lump charcoal output (freshly recovered)}}{\text{Oven dried weight of wood input - weight of brands}} \times 100 \qquad \text{Eq.2.1}$$

  The weight of wood input (including firewood used at the firing port) is based on oven dried weight which can be calculated from the actual weight of wood input.

$$\text{Oven dried weight of wood} =$$
$$\text{Weight of green wood} - ((\text{Moisture content} / 100) \times \text{Weight of green wood}) \quad \text{Eq.2.2}$$

In the experiment, the moisture content of green wood was determined by averaging the moisture content of at least 10 pieces of green wood selected randomly from the wood loaded.

$$\%\text{Moisture content} = \frac{\text{Green wood weight - Oven dried wood weight}}{\text{Oven dried wood weight}} \times 100 \quad \text{Eq.2.3}$$

Output from charcoal kilns included lump charcoal, fine and ash, and brands. The brands resulted from the incomplete conversion of wood to charcoal. Most of the brands were at the bottom end of wood standing on the kiln floor. It is assumed that the lump charcoal immediately taken from the charcoal kiln has no moisture content.

- Production Rate

  The charcoal output production rate can be calculated from the relation:

$$\text{Production rate, kg/hr} = \frac{\text{Lump charcoal weight, kg}}{\text{Total operating hour}} \quad \text{Eq.2.4}$$

(Note: total operating time counts from start firing until kiln closing).

2.2.5 Charcoal quality evaluation

This section will discuss the methods by which the charcoal quality was evaluated. Sampling methods for specimens to be used in the determination of moisture content and density, proximate analyses, heat of combustion and the water boiling test will be discussed.

- The moisture content of the lump charcoal was determined by drying it in an oven at 105 ± 2 °C until constant weight was obtained. Then the moisture content was calculated as follows:

$$\%\text{Moisture content} = \frac{\text{Charcoal weight - Oven dried weight of charcoal}}{\text{Oven dried weight of charcoal}} \times 100 \qquad \text{Eq.2.5}$$

- Proximate analysis

  The lump charcoal was ground into powder for the determination of moisture, volatile matter, and ash content according to the method described in ASTM D 1762-64. The fixed carbon content was the amount of carbon that is not volatile in the furnace at a temperature of 950 °C for 15 minutes, less the amount of ash remaining after the charcoal was completely combusted in the furnace at a temperature of 750 °C for 6 hours. Three replicates were done for each sample. The amount of fixed carbon was then calculated from the relation:

$$\%\text{Fixed carbon} = 100 - \%\text{Volatile matter} - \%\text{Ash} \qquad \text{Eq.2.6}$$

2.3 Factors affecting on PAHs content in smoke when applied the charcoal in grill process

This section will discuss about charcoal standard and review the others researches that studied about factors affecting on PAHs content.

2.3.1 Charcoal standard for grilling process (TISI. 658/2547)

This standard covers only charcoal obtained from burning wood and used for grilling process. The desired features of charcoal are as follows:

- Generalization: charcoal must be uniformly of black, no soil debris and wood (from incomplete combustion) contaminate.
- Moisture: not more than 8% by weight
- Heat energy: not less than 7,000 calorie/gram
- Ash: not more than 3% by weight
- Volatile: not more than 8% by weight
- Usability: no light flakes and has a little smoke

2.3.2 Literature reviews - factors affecting on PAHs contents

1. Formation of PAHs

The formation of PAHs during charcoal grilling at high temperature may be due to the incomplete combustion of charcoal or transformation of some food components such as triglyceride and cholesterol. In contrast, with electric grilling only minor amount of PAHs and no carcinogenic PAHs were observed (Masuda et al., 1996; Lijinsky and Ross, 1967).

The formation of PAHs can be attributed to incomplete combustion of wood or gasoline, or food processing such as grilling and smoking. Although the exact mechanism of PAHs formation was not well understood, some authors postulated that they might be formed through free radical reaction, intramolecular addition or polymerization of small molecules (Pitts, 1983; Perez et al., 1986; U.S. EPA, 1987).

The possible sources of PAHs in food are environmental contamination, as well as thermal treatment of varying severity which is used in the preparation and manufacturing of foods (Guillen, 1994), the absorption and deposition of particulates during food processing such as smoking, grilling, boiling and toasting, the pyrolysis of fats and the incomplete combustion of charcoal (Larsson et al., 1983; Guillen, 1994; Moret et al., 1997).

The formation of various PAHs profiles during smoking can be dependent upon temperature, time, smoke composition, moisture content of wood and the presence of oxygen (Fretheim et al., 1980). The actual levels of PAHs in smoked foods depend on several variables in the smoking process, including type of smoke generator, combustion temperature, and degree of smoking (Larsson, 1982; Moret et al., 1997).

Cooking toxicants (HAs) and (PAHs) were significantly produced through meat grilling process at high temperature (Ferguson, 2010; Jagerstad and Skog, 2005). Incomplete charcoal pyrolysis is, by itself, responsible for the formation of HAs and PAHs contaminating grilled food in this way (Viegas et al., 2012).

2. Temperature

Temperature of smoke generally plays a very important role, because the amount of PAHs in smoke formed during pyrolysis increases linearly with the smoking temperature within the interval 400 – 1000 °C (Simko, 2002).

3. Fat dripping

During grilling, the fat drippings did not fall on the charcoal, and hence, the PAHs formed did not come up with smoke, and thus the adherence of PAHs to the meat surface might not be possible. To prevent formation of PAHs during charcoal grilling, the direct contact of meat with the cooking flame or grilling at high temperature should be avoided (Chen and Lin, 1997).

The natural meat and fish juices that are released during the grilling and fall from the muscle food into the charcoal can suffer pyrolysis and lead to the formation of HAs and PAHs, which, being dragged by the smoke, are deposited on the surface of the food (Costa et al., 2009; Hassan et al., 2010).

Fat dripping from salmon samples grilled in wood charcoal lead to flame formation, increasing release of smoke that carries HAs and PAHs, and increasing the temperature near the surface during the flashing (Sinha et al., 1995).

4. Other review

Charcoal grilling produces highest PAH levels. Among the commercial meat products, charcoal-barbecued chicken contained highest levels of total PAHs (Chung et al., 2011). Direct exposition of meat products to smoke brings about higher concentrations of PAHs as compared to indirect methods, when PAHs are partially eliminated by condensation in tars (Simko, 2002).

2.3.3 Literature reviews - other factors that may affect the charcoal compositions and PAHs contents in smoke of charcoal

1. Tar

The biomass during heating are broken down resulting in a gas consisting mainly of CO_2, H_2O, CH_4, CO, H_2, tar and char. Tar is the name for the group of species that are liquid at room temperature although they are gaseous at pyrolysis temperature (Weerdhof, 2012). As the temperature is increased, liquid and gases products is increased at the expense of char. Cellulose and hemicellulose are converted mainly into liquids while the other product classes, gases and char, are mainly due to lignin degradation (Branca et al., 2003). As the temperature is increased, liquid and gases products is increased at the expense of char. Cellulose and hemicellulose are converted mainly into liquids (Tar) while the other product classes, gases and char, are mainly due to lignin degradation (Branca et al., 2003). The residual tar content of the char was determined by analytical flash pyrolysis of the char combined with GC/MS analysis of the produced volatiles. The analyses showed that at a pyrolysis end-temperature of 600 °C no residual volatile tar compounds were detectable. This implies that pyrolysis of wood char at temperatures above 600 °C will not result in further release of tar compounds from the char (Fjellerup et al., 2005).

Tar is formed during the pyrolysis process by the thermal breakdown of the polymers cellulose, hemicellulose and lignin. The tar consists of various organic compounds, which can condense and thus be troublesome for the subsequent processes. The tar decomposition depends also on the tar class; class 2 tars are easier to crack than class 3 and 4. The fourth class is the aromatics such as benzene, naphthalene, acenaphthylene, anthracene phenanthrene and pyrene. This class is formed above 750 °C (Fjellerup et al., 2005).

Tar is a mixture of mainly aromatics such as benzene, toluene, phenol, pyridines, thiophenes and 2-4 ring PAHs such as naphtalene and anthracene. These are formed during pyrolysis or gasification of solid fuels. Depending on the fuel and the process conditions (temperature and gas phase) and reactor type the amounts of phenolic compounds *versus* hydrocarbon aromatics and PAHs can vary widely. For example, Simell et al. (1996) distinguishes “low temperature tar” which is formed at temperatures below 650 °C and consists mainly of the primary decomposition products of the fuel, and “high temperature tar”, mainly mono- and polycyclic aromatic compounds, formed by secondary reactions between primary pyrolysis products (Zevenhoven and Kilpinen, 2001).

The tar is converted by two secondary reactions into secondary gasses and char.

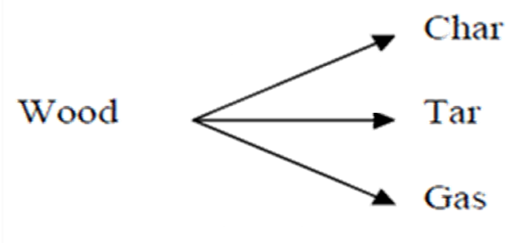


Figure 2.2 The wood is converted via three parallel reactions into char, tar and gas in primary reactions (Weerdhof, 2012)

For the secondary reactions, tars produced during the decomposition of the virgin fuel can decompose further. Several authors suggest a transformation of tar to char and gas following two independent reactions. Tar decomposition is suggested to be catalyzed by the solid matrix of the fuel resulting in char creation on the pore walls (Weerdhof, 2012).

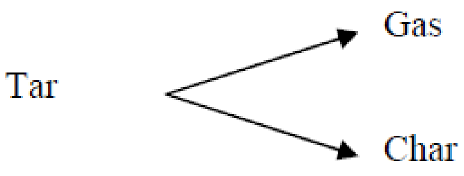


Figure 2.3 Tar is converted to gas and char in secondary reaction (Weerdhof, 2012)

2. Pyrolysis of cellulose

Cellulose is the major source of the combustible volatiles that fuel flaming combustion (Sadaka, 2012). Thermal degradation of cellulose normally starts around 350 °C. During pyrolysis the polymer chains can be broken down into smaller polymers (Weerdhof, 2012). Pyrolysis of cellulose is essentially complete above 600 °C (Funazukuri et al., 1986) and thermal decomposition of tar and some liquid fractions begin, resulting in a considerable increase in gaseous products (Sadaka, 2012).

3. Pyrolysis of hemicelluloses

Compared to cellulose, hemicellulose is a more branched polymer. The thermal degradation of hemicellulose starts around 270 °C (Weerdhof, 2012). Hemicelluloses produce more gases and less tar than cellulose. They also produce more methanol and acetic acid than cellulose (Sadaka, 2012).

4. Pyrolysis of lignin

Lignin has also a relatively large carbon content compared to cellulose and hemicellulose, and is as a result the most charring biomass component. The thermal degradation of lignin starts around 390 °C (Weerdhof, 2012).

Lignin is the least reactive component of biomass; higher temperatures are necessary for the pyrolysis of most lignin. The time required for complete pyrolysis of woody biomass at a given temperature is controlled by the pyrolysis rate of lignin at the operating conditions. Pyrolysis of lignin yields more char and tar than cellulose (Sadaka, 2012).

2.4 Gas Chromatography / Mass Spectrometry (GC/MS)

Gas chromatography coupled to mass spectrometry is a versatile tool to separate, quantify and identify unknown (volatile) organic compounds and permanent gases. By combining sensitivity and a high resolving power, complex mixtures can be analyzed. The information obtained can be used for detection of impurities, contamination control and improvement of, for example, semiconductor manufacturing processes.

1. General uses

   - Identification and quantitation of volatile and semivolatile organic compounds in complex mixtures

   - Determination of molecular weights and (sometimes) elemental compositions of unknown organic compounds in complex mixtures.

- Structural determination of unknown organic compounds in complex mixtures both by matching their spectra with reference spectra and by a priori spectral interpretation

2. Common applications

- Quantitation of pollutants in drinking and wastewater using official U.S. Environmental Protection Agency (EPA) methods

- Quantitation of drugs and their metabolites in blood and urine for both pharmacological and forensic applications

- Identification of unknown organic compounds in hazardous waste dumps

- Identification of reaction products by synthetic organic chemists

- Analysis of industrial products for quality control

3. Analysis time

In addition to sample preparation time, the instrumental analysis time usually is fixed by the duration of the gas chromatographic run, typically between 20 and 100 min. Data analysis can take another 1 to 20 hr (or more) depending on the level of detail necessary.

4. Limitations

- General

  Only compounds with vapor pressures exceeding about 10–10 torr can be analyzed by gas chromatography mass spectrometry (GC-MS). Many compounds with lower pressures can be analyzed if they are chemically derivatized (for example, as trimethylsilyl ethers). Determining positional substitution on aromatic rings is often difficult. Certain isomeric compounds cannot be distinguished by mass spectrometry (for example, naphthalene versus azulene), but they can often be separated chromatographically.

- Accuracy

  Qualitative accuracy is restricted by the general limitations cited above. Quantitative accuracy is controlled by the overall analytical method calibration. Using isotopic internal standards, accuracy of ±20% relative standard deviation is typical.

- Sensitivity and Detection Limits

  Depending on the dilution factor and ionization method, an extract with 0.1 to 100 ng of each component may be needed in order to inject a sufficient amount.

2.4.1 Gas chromatography (GC)

Gas Chromatography is used to separate volatile compounds in a mixture. The separated compounds can be identified and quantified. To achieve the identification of different compounds, three steps can be distinguished

1. Injection

Depending on the sample (gas, liquid or solid), compounds in a mixture need to be volatilized or extracted from the matrix by one of the injection techniques listed in Table 2.5.

2. Separation

After injection of a mixture, separation is achieved in the capillary column. This column is coated with a fluid or a solid support, the stationary phase. An inert gas, also called the mobile phase, is flowing through the column. Depending on the phase equilibrium between the stationary and mobile phase, compounds travel with different velocities through the column. The mixture becomes separated, and as a result, individual compounds reach the detector with a different retention time. By choosing a column, which separates on boiling point, polarity, size or stereochemistry, a wide range of compounds can be separated.

3. Detection

Many different detectors (Table 2.6) can be used for detection of the separated compounds. The mass spectrometer (Figure 2.4) combines a high sensitivity with the unique property of being able to determine the molecular composition. Below, only the mass spectrometer will be discussed in more detail. The other detectors are dedicated tools to analyze specific compounds (see also Table 2.6) (MiPlaza, 2009).

Table 2.5 Injection techniques and their applications

Injection Technique	Used for
Split	High concentration samples (liquid/gas) Only small amounts of sample required
Split-less	Trace analysis (liquid/gas)
Thermal Desorption	Trace analysis (gases) and solid samples Desorption of volatile compounds in a solid matrix
Headspace	Volatile compounds in difficult matrices For collection of vapors above dirty samples
Solid Phase Micro Extraction (SPME)	Volatile compounds in difficult matrices with pre-concentration

Table 2.6 Detection techniques and their applications

Detector	**Used for**
Mass spectrometer (MS)	Identification of unknown compounds
Flame Ionization Detector (FID)	Compounds containing Carbon
Thermal Conductivity Detector (TCD)	Universal detection for gases without Carbon
Nitrogen Phosphorous Detector (NPD)	Selective detection of Nitrogen and Phosphor containing compounds
Electron Capture Detector (ECD)	Selective detection of halogen containing compounds
Atomic Emission Detector (AED)	Selective detection of elemental composition

2.4.2 Mass Spectrometry (MS)

Compounds enter the ion source and are ionized and fragmented by using a high energy electron bombardment. The ions are extracted from the source with an electric field and fed into the mass analyzer (see Figure 2.4). By applying electric fields, ions with a certain mass to charge ratio can reach the electron multiplier. The fragmentation pattern measured is characteristic for each molecule, making identification possible (Figure 2.5) (MiPlaza, 2009).

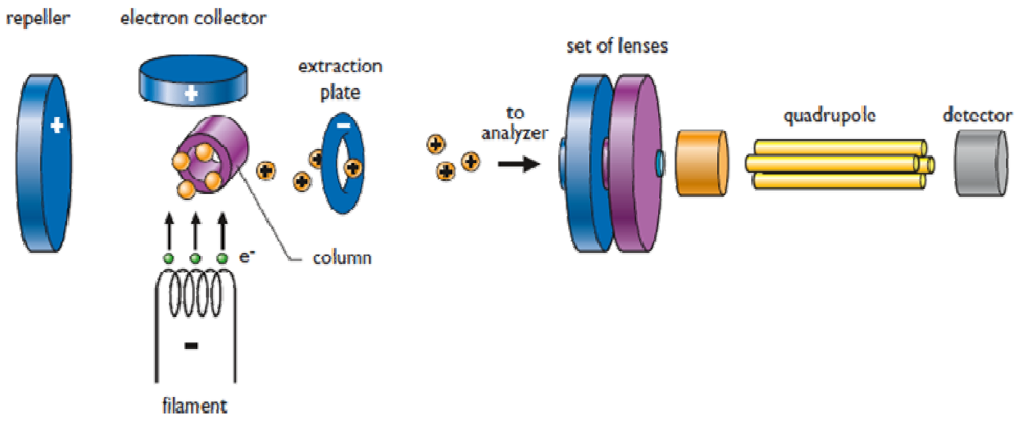


Figure 2.4 Schematical drawing of an electron impact ionization source and a quadrupole mass spectrometer. The compounds to be analyzed are represented by the orange spheres (MiPlaza, 2009)

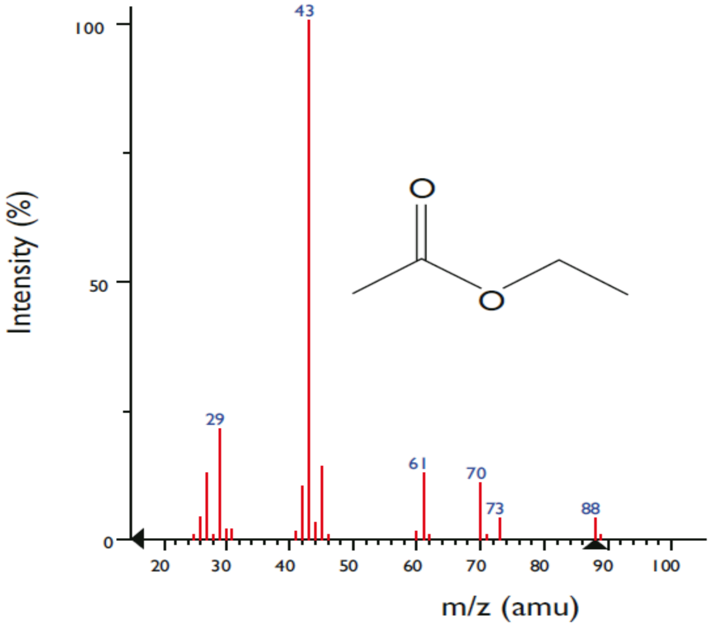


Figure 2.5 Mass spectrum depicting the characteristic fragmentation pattern of ethyl acetate ($C_4H_8O_2$) with at Mw=88.05 g/mol the molecular ion (MiPlaza, 2009)

2.4.3 Qualitative

There are three ways of examining GC-MS data. First, the analyst can go through the gas chromatogram (as reproduced by the mass spectrometer) and look at the mass spectra scanned at each GC peak maximum. This has the advantage of being relatively quick but the disadvantage of missing components of the mixture that are not fully resolved by the GC column.

The second approach is to look at each mass spectrum in turn, in essence stacking up the mass spectra one behind the other and examining them individually. This has the advantage of completeness but the disadvantage of tedium. The third approach is to look at the intensity of one particular mass as a function of time.

This third approach makes use of the three-dimensional nature of GC-MS data. Two of these dimensions are the mass versus intensity of the normal mass spectrum; the third dimension is the GC retention time over which the mass spectral data are acquired. This idea is illustrated in Figure 2.6. The x axis represents GC retention time, the y-axis represents intensity, and the z-axis represents mass (or more properly, m/z ratios). As shown in Figure 2.6, a mass spectrum is displayed in the y–z plane. Because a mass spectrum is scanned every 1 to 3 sec, it is also possible to examine the data in the x–y plane. This is a plot of the intensity of one selected mass as a function of time. This plot is called a mass chromatogram (Hites and Biemann*,* 1970).

An example may make this concept clear. At the retention time marked with an asterisk in Figure 2.6, the abbreviated mass spectrum extending into the foreground (the y–z plane) was observed. This happens to be the mass spectrum of methyl stearate; note the relatively abundant ion at m/z 298, which is this compound's molecular weight. The mass chromatogram of m/z 298 is shown in the x–y plane in Figure 2.6. Note that this mass chromatogram shows one peak, which corresponds to the retention time of methyl stearate. In other words, of all the hundreds of mass spectra taken during this GC-MS experiment, m/z 298 is present in only a very few spectra. Only compounds with m/z 298 in their mass spectra will show up in the mass chromatogram of that mass.

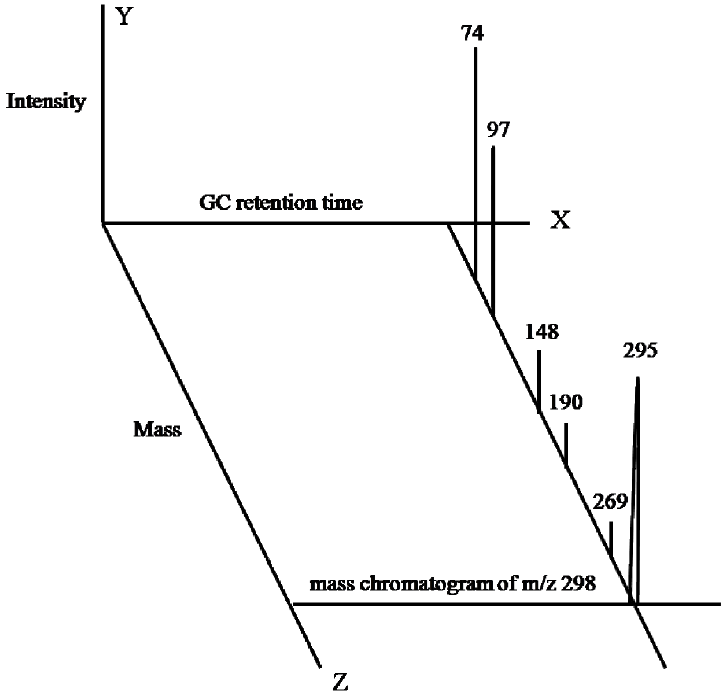


Figure 2.6 A diagram demonstrating the three-dimensional nature of GC-MS data. The abbreviated mass spectrum extending onto the foreground is that of methyl stearate; the mass chromatogram of m/z 298 (the molecular ion of methyl stearate) is also shown (Hites and Biemann, 1970)

Mass chromatograms can be thought of as a very selective gas chromatographic detector, in this case, one that responds only to methyl stearate. Other compounds can be selectively detected by picking other masses. For example, m/z 320 would be a good mass to use for the selective detection of a tetrachlorodibenzo-p-dioxin because this is its molecular weight. If a mass that is present in the mass spectra of a class of compounds is selected, that compound class can be selectively detected. For example, m/z 149 is present in the mass spectra of alkyl phthalates for alkyl chain lengths greater than two carbon atoms. Thus, the mass chromatogram of m/z 149 would selectively show all the phthalates in a sample.

Mass chromatograms are also useful for determining whether a given mass belongs in a given mass spectrum. For example, if the liquid phase from a GC column is beginning to thermally decompose, all of the mass spectra taken during a GC-MS experiment with that column might show a moderately abundant ion at m/z 207. However, the mass chromatogram of m/z 207 will not show peaks because the source of this ion is bleeding continuously from the column and is not a discrete compound. In fact, the mass chromatogram of 207 will probably track the temperature program of the GC column. Using this approach, it is easy to distinguish between the ions that really belong in a given mass spectrum and those from background. By looking at sets of mass chromatograms, it is possible to determine whether various ions come from the same compound even if the compounds are not completely resolved by the GC column. If ions belong together (that is, they come from the same GC peak), the mass chromatograms for all these ions will be super imposable in time. In fact, these mass chromatograms should all have the same peak shape because they all came from the same GC peak. If the mass chromatograms are not super imposable in time or in shape, the corresponding ions are probably from different compounds, which may have come out of the GC column at slightly different retention times.

Because GC-MS experiments are somewhat complicated, there is always a possibility for something to go wrong. To prevent this, stringent quality assurance procedures are necessary. The following is a nonexhaustive list of some of these problems and what can be done about them.

First, because the analyst is often working at ultra trace levels (a few nanograms, for example), it is possible for a compound that was not originally in the sample to sneak in during the analytical procedure. In particular, sample contamination can come from solvents and glassware. The former problem can be prevented by using high-quality (and expensive) solvents, the latter by heating the glassware to 450 °C after solvent and acid washing. The most common contaminant is probably di(2-ethylhexyl)phthalate. Its mass spectrum is shown in Figure 2.5. Note the important ions at m/z l49, l67, and 279. It pays to remember this spectrum; it was once published as that of a natural product (Kintz et all., 1991). Phthalates are extremely common as plasticizers. They are particularly abundant (5 to 20%) in polyvinylchloride-based plastic products such as Tygon tubing.

Second, if components in the sample decompose before or after workup, the analyst will not obtain accurate results. Under these conditions, it is possible to identify (and quantitate) a compound that was not originally in the sample or the analyze of interest could have vanished from the sample. Thus, both false positives and false negatives can result from sample decomposition. This can happen while the sample is waiting to be analyzed or during the analysis itself. For example, a GC injection port held at 250 to 300 °C can cause thermal decomposition of some compounds. One useful procedure is to add (or spike) the analyze into a sample at a known concentration. If there is a substantial loss of this compound or the suspicious formation of another compound, sample decomposition may be a problem.

Third, if the GC column or GC-MS interface is not working properly, the whole GC-MS experiment is in jeopardy. Cold spots are a common problem, as are catalytic surfaces that selectively remove some compounds from the GC gas stream. These problems can be identified using a mixture of standard compounds of varying polarities and acidities.

Fourth, either the mass spectrometer itself or the data system may not be working properly. In this case, incorrect isotope ratios, mass discrimination (ions at higher masses appear less abundant than they should), or mass assignment errors could occur. The key to identifying these problems is to run an overall mass spectrometer performance standard. The one recommended (mandated in many cases) by the EPA is decafluorotriphenylphosphine, the mass spectrum of which is shown in Figure 2.8. This compound is a good standard. It is easy to run by GC-MS, and it has ions up to about m/z 450. The abundances for the various ions, as required by the EPA, are published in the Federal Register and in various other official EPA methods. These requirements change from time to time, but they are available from the EPA.

To ensure qualitative identification of an organic compound using GC-MS, several criteria should be met: First, the mass spectra of the unknown compound and of the authentic compound must agree over the entire mass range of the spectra. It is particularly important to compare the patterns within narrow mass ranges (for example, from m/z 50 to 60 in Figure 2.7); these patterns should agree almost exactly. In this case, the spectrum of the authentic compound might come from a library of reference spectra or from the actual compound itself. In the latter case, the compound could be purchased or synthesized. Second, the GC retention times of the unknown compound and of the authentic compound must agree within about ±1 to 2 sec. It is often convenient to do this experiment by coinjecting the unknown mixture and the authentic compound. The GC peak in question should increase in size by the correct factor. Third, a compound cannot be considered fully identified in a mixture unless two other questions are addressed: Is the identification plausible? Why is it present in a given sample? If identification is implausible or if there is no reason for a compound to be present in a sample, the identification could be wrong or the compound could be a contaminant.

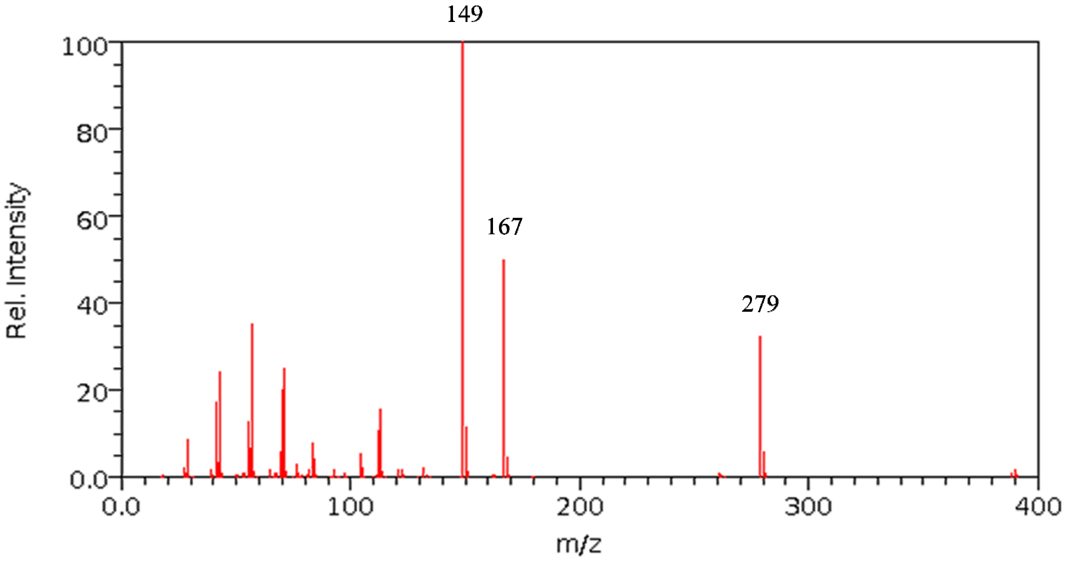


Figure 2.7 Mass spectrum of Di (2-ethylhexyl) phthalate, a very common experimental contaminant (Hites and Biemann, 1970)

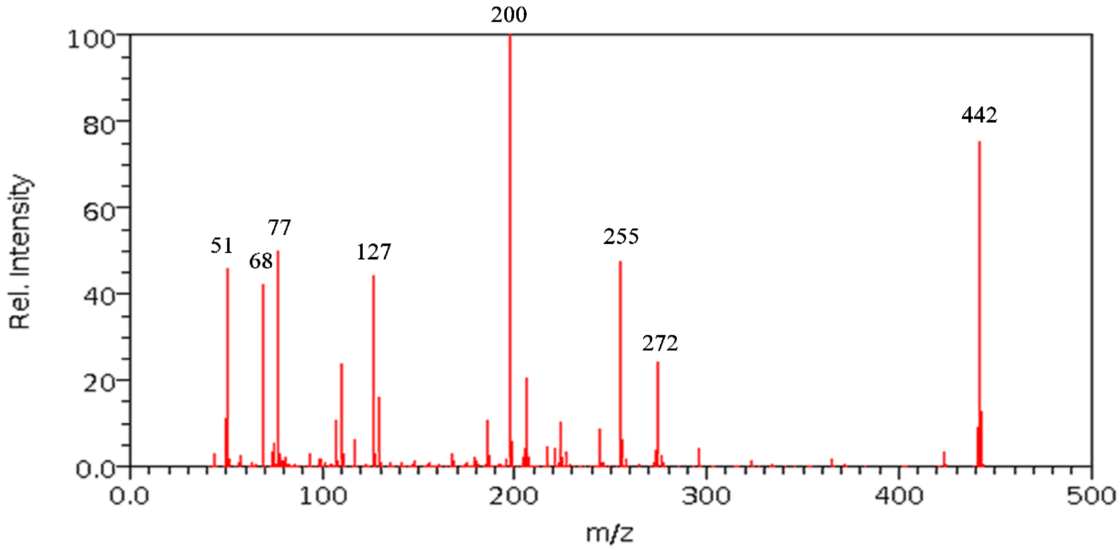


Figure 2.8 Mass spectrum of decafluorotriphenylphosphine, an EPA-mandated standard (Hites and Biemann, 1970)

2.4.4 Quantitative

GC-MS can also be used to measure the concentration of one or more analytes in a complex mixture. Quantitation can be based on peak areas from mass chromatograms or from selected ion monitoring. The latter requires more explanation (Sweely et all., 1996).

With the selected ion monitoring technique, the mass spectrometer is not scanned over all masses; instead, the instrument jumps from one selected mass to another. The advantage of this approach is that the mass spectrometer spends much more time at a given mass, the signal-to-noise ratio at that mass improves, and the overall sensitivity of the experiment increases by a factor of 100 to 1000. For example, the mass spectrometer might integrate for 500 msec at mass $m1$, jump to mass m^2 in 10 msec, integrate for 500 msec at that mass, and jump back to $m1$ in 10 msec, repeating this cycle for the duration of the GC run. In essence, the intensities of the two masses are recorded as a function of GC retention time, with measurements made every 1.02 sec. In practice, rather than only two masses, 5 to 10 masses are usually monitored simultaneously for 100 to 200 msec each. In this manner, the GC-MS response of 5 to 10 compounds, depending on the specificity of the selected masses, can be measured.

The difference between mass chromatograms and selected ion monitoring is significant. With the latter technique, the responses from only a few preselected masses are recorded. With mass chromatograms, all of the masses are scanned; thus, no pre-selection is required. This is the necessary tradeoff for higher sensitivity. Clearly, the mass spectrum of the analyze must be known so that the masses that uniquely characterize it can be selected. This information can be obtained from the literature (or from a library of reference spectra) or from the laboratory. Each selected set of masses can be monitored for the duration of the complete GC run or for only selected GC retention times (often called time windows). Selected ion monitoring is almost fully software driven; thus, it is very flexible. Different sets of masses, different time windows, and different integration times can be easily set up.

To convert the peak areas to mass of analyze, whether from mass chromatograms or from selected ion monitoring, the peak areas must be calibrated. The two main strategies are based on external and internal standards. With external standards, the area of one or more mass chromatogram is calibrated with a known amount of the analyze injected into the GC-MS in a different experiment. Detection limits of a few nanograms can be achieved with this technique. However, the strategy that gives the most accurate quantitative results is the use of internal standards, which are known amounts of compounds added to the sample before isolation of the analytes begins. After sample extraction and cleanup, only the ratio of response between the analyte and the internal standard must be measured. This ratio multiplied by the amount of the internal standard gives the amount of the analysis injected into the GC-MS system. This can be converted to concentration using the correct dilution factors.

The best internal standards are chemically very similar to the analyze; thus, any losses of the analyze during the analytical procedure are duplicated by losses of the internal standard, so it is a self-correcting system. Homologues of the analyze can be used as internal standards, but the very best are isotopically labeled versions of the analyze. Using isotopically labeled standards and selected ion monitoring, it is possible to get sensitivities of less than 1 pg. Depending on the relationship of the internal standard to the analyze, the precision and accuracy of most analyses are improved by at least a factor of 2 to 3 over external calibration. The tradeoff is complexity and cost. Ideally, an internal standard for each analyze in a mixture should be used, and isotopic standards can sometimes cost several hundred dollars for a few milligrams.

The chromatogram is divided into retention time windows; each of them successively monitors one or two target compounds. Each target compound is characterized by one quantitation ion and two “qualifier” ions. The abundance ratios between qualifiers and the quantitation ions allow a check of the identity of the suspected allergen, according to the following formula:

$$Q = 100 - \frac{\sum_{i=1}^{i=n}\left(100 * \left| r_i - r_i' \right|\right)\left(\mathrm{In}[100r_i + 1]\right)^2}{21.3 * \sum_{i=1}^{i=n} r_i} \qquad \text{Eq.2.7}$$

Where n is the number of ions per compound, r_i is the reference peak area ratio, and r_i' is the observed peak area ratio.

A Q-value between 90 and 100 indicates a positive recognition of the target peak. A lower value indicates that either the quantitation ion belongs to another compound or coelutes with another analyze (Debonneville et al., 2004).

CHAPTER 3 MATERIALS AND METHODS

3.1 Raw Materials

Mangrove woods were purchased from a local area in Khao Yeesarn, Samutsongkhram. Age of Mangrove woods was controlled at 10 years and has diameter in the range of 1.5-2.0 inches. Mangrove woods must keep in the area without moisture before using in charcoal making process.

3.2 Chemical Reagents

3.2.1 Polynuclear Aromatic Hydrocarbons 16 Solution, Sigma-Aldrich, USA

3.2.2 Diethyl Ether ($(C_2H_2)_2O$), AR grade, RCI Labscan, Thailand

3.2.3 Dichloromethane (CH_2Cl_2), AR grade, RCI Labscan, Thailand

3.2.4 Hexanes ($CH_3(CH_2)_4CH_3$), AR grade, RCI Labscan, Thailand

3.2.5 Cyclohexane (C_6H_{12}), AR grade, RCI Labscan, Thailand

3.2.6 Sodium Sulphate Anhydrous (Na_2SO_4), AR grade, Carlo Erba, Germany

3.3 Equipments

3.3.1 Furnace, Model 2-160 series 2, NEY, USA

3.3.2 Soxhlet Extractors (Set 50/42), Pyrex, UK

3.3.3 Heating mantles, Model MM-500 ml, FALC, Italy

3.3.4 Cellulose Extraction Thimbles (33×80 mm), Whatman, England

3.3.5 Cooling, Model Cool Ace series CA-111, EYELA, Japan

3.3.6 Rotary Evaporator, Model R210, Buchi, Switzerland

3.3.7 PUF Cartridges, Model ORBO-1500 small PUF/XAD/PUF, Supelco, USA

3.3.8 Hot Air Oven, ULM 800, Memmert, Germany

3.3.9 Gas Chromatography/Mass Spectrophotometer, Series 5975C, Agilent, USA

3.4 Determination of carbonization temperature on charcoal composition

3.4.1 Preparation of mangrove charcoal using different carbonization temperatures

Making charcoal process or carbonization in this study would be used furnace to shift the wood to be the charcoal. The process occurs in furnace could divided into two phase. The first phase was to increase furnace temperature until its reach setting temperature. Then, the temperature in furnace would be controlled to constant along given time. The carbonization temperature in this study was defined to three temperatures that are 500, 750 and 1,000 °C.

For carbonization process, the woods were contained in ceramic box with the cover to make it be the close system. Then, put the box into furnace and set temperature rate at 20 °C/min. The furnace's temperature would increase until it reaches 500, 750 and 1,000 °C. After that, the furnace would be control temperature for 1 hour.

Figure 3.1 Mangrove wood in ceramic box

Figure 3.2 Ceramic box with the cover in furnace

Figure 3.3 Mangrove charcoal obtained from carbonization

Note: After charcoal making process was complete, waiting for the furnace's temperature decreases to 100 °C, and then bring charcoal left to cool in desiccators before store in aluminum foil vacuum bag. All this procedure was conducted 2 times for the experiment.

3.4.2 Characterization of charcoal composition

1. Yield

Mangrove wood was weigh into ceramic box for 70 ± 1 grams, then burn the wood until the wood become to charcoal. Then, the dried charcoal was weigh and calculated the yield follow Equation 3.1.

$$\%\text{Yield} = \frac{\text{Weight of charcoal output}}{\text{Weight of mangrove wood input}} \times 100 \qquad \text{Eq.3.1}$$

2. Moisture content (ASTM D 3173-95)

Mangrove charcoal was weigh into moisture can for 4 ± 1 grams, then oven the charcoal to displace the moisture until the weight was constant. Then, the dried charcoal was weigh and calculated the moisture content follow Equation 3.2.

$$\%\text{Moisture Content} = \frac{\text{Charcoal weight - Oven dried weight of charcoal}}{\text{Oven dried weight of charcoal}} \times 100 \qquad \text{Eq.3.2}$$

3. Volatile matter (ASTM D 3175-95)

The oven dried mangrove charcoal was weigh into crucible for 4 ± 1 grams, and then close the lid. After that, the charcoal was burned to displace the volatile matter at 950 °C for 7 minute. The charcoal was allowed to cool in desiccators and repeat again until the weight was constant, and then calculate the volatile matter follow Equation 3.3.

$$\%\text{Volatile Matter} = \frac{\text{Charcoal weight - Oven dried weight of charcoal}}{\text{Oven dried weight of charcoal}} \times 100 \qquad \text{Eq.3.3}$$

4. Ash (ASTM D 3174-95)

The oven dried mangrove charcoal was weigh into crucible for 4 ± 1 grams. The charcoal was burned without the lid in furnace at 650 °C until the weight was constant, and then calculated the ash follow Equation 3.4.

$$\%\text{Ash} = \frac{\text{Oven dried weight of charcoal output (Ash)}}{\text{Weight of charcoal input}} \times 100 \qquad \text{Eq.3.4}$$

5. Fixed carbon

Fixed carbon could be calculated from the result of the difference follows Equation 3.5

$$\%\text{Fixed carbon} = 100 - \%\text{Volatile matter} - \%\text{Ash} \qquad \text{Eq.3.5}$$

3.5 Determination of carbonization temperature of charcoal on PAHs content in smoke during grilling

3.5.1 Smoke collection during charcoal burning

70 g of mangrove charcoal was weigh into ceramic box without the cover to make it be the open system. Then, the mangrove charcoal was burned in furnace at 650 °C for 2 hours (around 92% of charcoal was burned) by setting heating rate at 20 °C/min. During heating the charcoal, the 30 cm length of rubber tube which was heat resistant would connected with tunnel of furnace and the other end would connected with the Polyurethane foam (PUF) and XAD resin packed into a tube or PUF/XAD cartridge (Figure 3.4) for collecting the smoke that occurred from charcoal burning.

In addition, the other end of PUF/XAD cartridge would connect with the air pump used for control the air flow rate at 1.5 m^3 per minute as shown in Figure 3.5. During smoke collecting process, the PUF/XAD tube was wrapped in aluminum foil to protected from light.

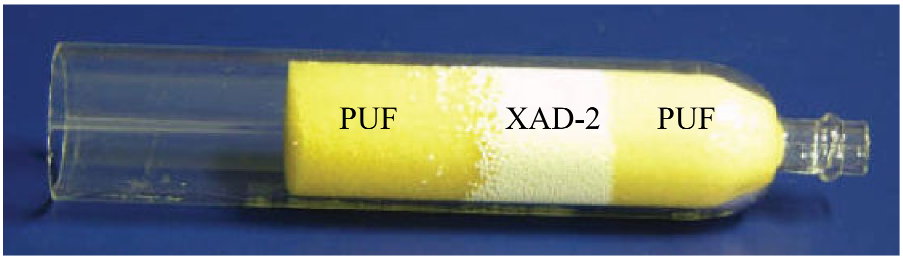


Figure 3.4 PUF/XAD cartridge compositions

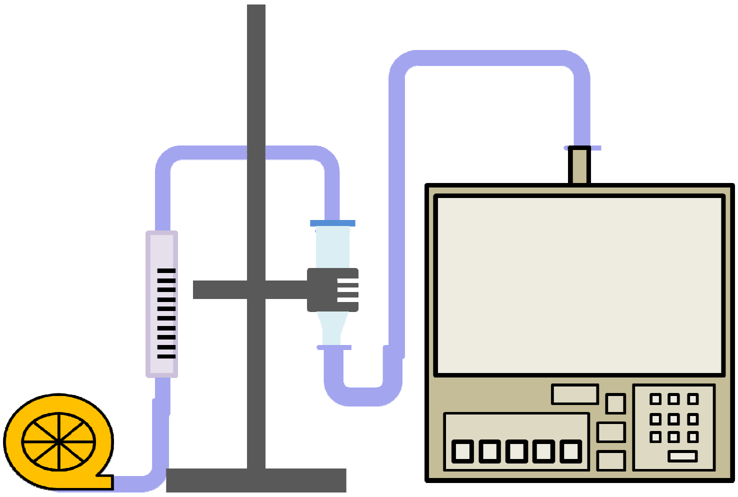


Figure 3.5 Smoke collection system

Note: After the smoke collection was finished, the PUF/XAD cartridge must keep away from light and the cartridge's temperature must not more than 4 °C until it was extracted.

3.5.2 Analysis of PAHs in smoke

1. Solvent extraction

The PUF and XAD resin were put in extraction thimble, then place in the Soxhlet apparatus (Figure 3.6). 350 ml of 10 percent diethyl ether in hexane was added to the PUF apparatus and 350 ml of dichloromethane to the XAD apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour. Allow to cool and then disassemble the apparatus.

The extract was concentrated using a rotary evaporator (the conditions were shown in Table 3.1). The solvent volume was evaporated until below 1 ml. During the operation, the internal wall of the concentrator flask must be rinsed down several times with cyclohexane, the solvent level in flask must be kept below the water level of the bath. The extract must never be allowed to become dry. Bring the final volume back to 3.0 ml with cyclohexane, then transfer the extract to a Teflon®-sealed screw-cap amber vial, label the vial, and store at 4 ± 2 °C.

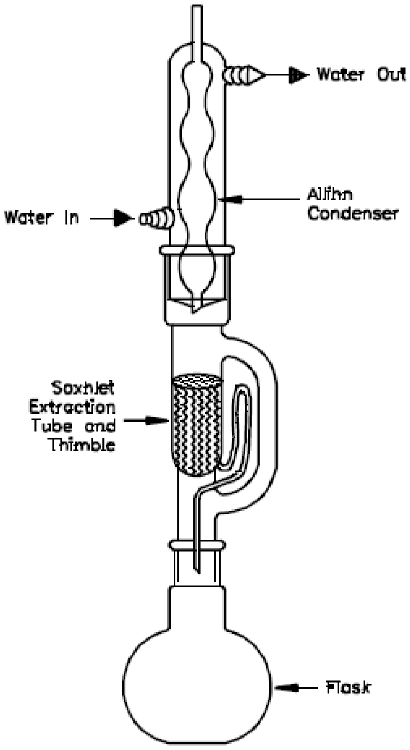


Figure 3.6 Soxhlet extraction apparatus with Allihn condenser

Table 3.1 Rotary evaporator conditions

Solvent	**Conditions**
Dichloromethane (CH_2Cl_2)	Bath temperature: 57 °C Boiling temperature: 37 °C Pressure: 921 mbar Cooling H_2O max: 20 °C
Hexane (C_6H_{14})	Bath temperature: 60 °C Boiling temperature: 40 °C Pressure: 360 mbar Cooling H_2O max: 20 °C

2. GC-MS analysis

The following were the GC-MS analytical conditions, as also outlined in Table 3.2. The results of the analysis were expressed in form of chromatogram which had retention time used to specify the kinds of PAHs as shown in Figure 3.7 and Table 3.3.

The standard curve of 16 PAHs were in the range of 0.0 - 2.0 µg/µL and had R-squared of about 0.99. The standard curves of each type of PAHs were show in Appendix A.

Table 3.2 GC-MS conditions for PAHs analysis (TO-13A, 1999)

Activity	**Conditions**
Gas Chromatography	
Column	DB-5 crosslinked, 5% phenyl methyl silicone (30 m x 0.32 mm, 1.0 µm film thickness)
Carrier Gas	Helium, velocity between 28-30 cm^3/sec at 250 °C
Injection Volume	2 µL, Grob-type, splitless
Injector Temperature	290 °C
Temperature Program	
Initial Column Temperature	70 °C
Initial Hold Time	4 ± 0.1 min.
Program	10 °C/min to 300 °C and hold 10 min.
Final Temperature	300 °C
Final Hold Time	10 min or until all compounds of interest have eluted
Mass Spectrometer	
Transfer Line Temperature	290 °C
Electron Energy	70 volts (nominal)
Ionization Mode	EI
Mass Range	Selected ion monitoring (SIM) mode, dwell for a longer time over a smaller mass range

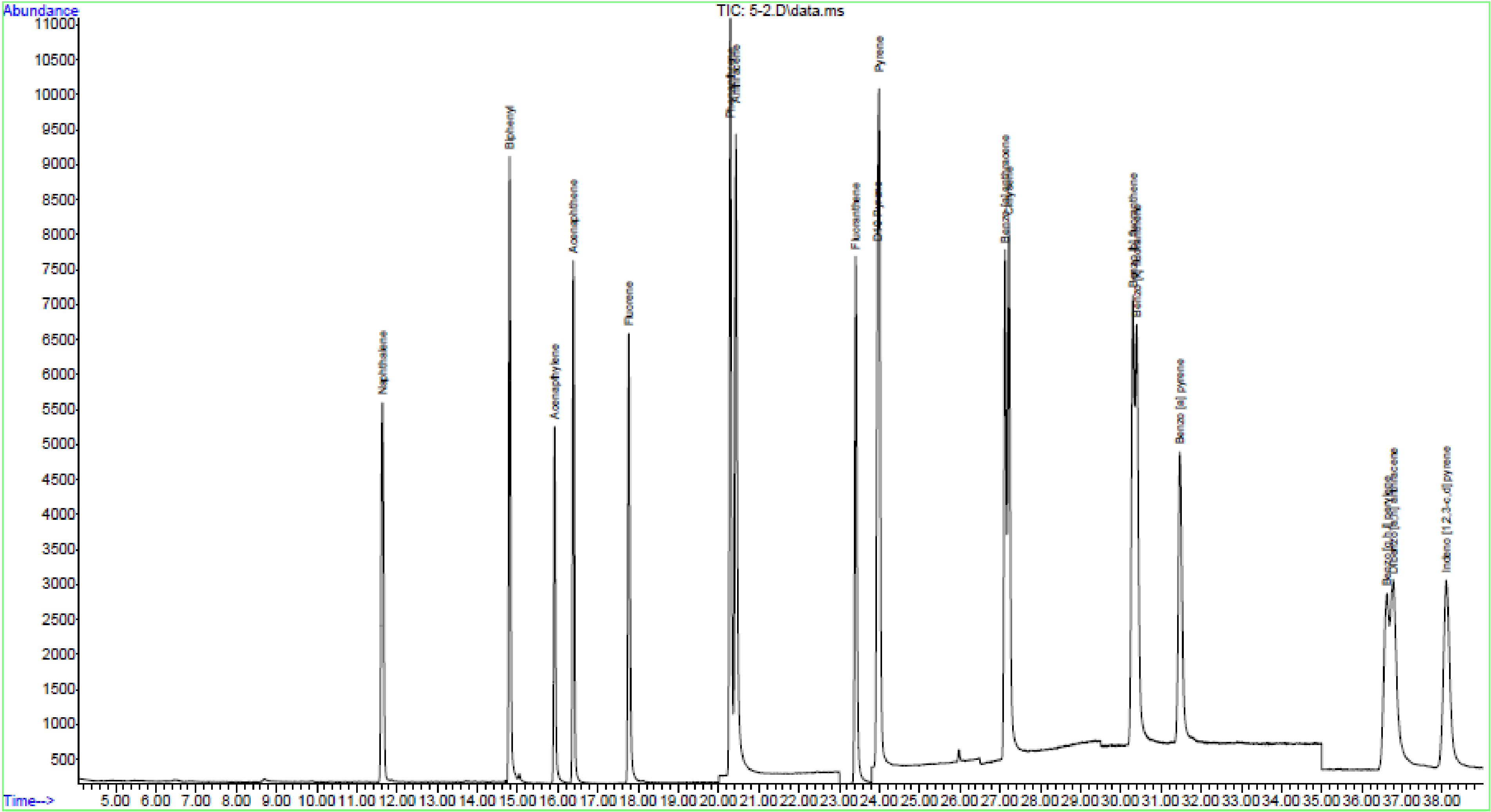


Figure 3.7 Chromatogram of 16 PAHs standard

Table 3.3 Retention time of 16 PAHs (TO-13A, 1999)

No.	Compound	Retention time
1	Naphthalene	11.614
2	Acenapthylene	15.921
3	Acenaphthene	16.390
4	Fluorene	17.766
5	Phenanthrene	20.291
6	Anthracene	20.425
7	Fluoranthene	23.421
8	Pyrene	24.006
9	Benzo[a]anthracene	27.135
10	Chrysene	27.136
11	Benzo[b]fluoranthene	30.335
12	Benzo[k]fluoranthene	30.365
13	Benzo[a]pyrene	31.493
14	Benzo[g,h,i]perylene	36.653
15	Dibenzo[a,h]anthracene	37.046
16	Indeno[1,2,3-c,d]pyrene	38.156

However, the experiments were used Q-value (can calculate according to Eq.3.6) to determine the reliability of the results acquired which the results, that were choose, must has Q-value more than 90.

$$Q = 100 - \frac{\sum_{i=1}^{i=n}\left(100 * \left| r_i - r_i' \right|\right)\left(\mathrm{In}\left[100 r_i + 1\right]\right)^2}{21.3 * \sum_{i=1}^{i=n} r_i} \qquad \text{Eq.3.6}$$

Where n was the number of ions per compound, r_i was the reference peak area ratio, and r_i' was the observed peak area ratio (Debonneville et al., 2004).

Note: All the procedure of PAHs analysis would conduct 2 times for this experiment.

CHAPTER 4 RESULTS AND DISCUSSIONS

This research was aimed to study the difference of carbonization temperatures used for making the mangrove charcoal on yield and chemical compositions of charcoal and on PAHs contents in smoke during charcoal grilling. This chapter was divided into three parts which were the study of the different carbonization temperature on charcoal chemical compositions, the analysis of the 16 PAHs concentration in smoke during charcoal grilling and the relationship between charcoal chemical compositions and 16 PAHs in smoke of mangrove charcoal.

4.1 Effect of carbonization temperature on charcoal chemical compositions

This section was the comparison of percentage of charcoal compositions consisting of moisture content volatile matter ash and fixed carbon in mangrove charcoal produced at different carbonization temperatures (500 750 and 1000 °C). In this study, the carbonization temperature was selected above 500 °C to produce a charcoal because the main components of wood which were cellulose hemicelluloses and lignin could be degraded completely (Sadaka, 2012; Koufopanos et al., 1989; Hajaligol et al., 1982). From the experimental results in Table 4.1, it was found that the percentage of moisture content and volatile matter of mangrove charcoal at carbonization temperature of 1000 °C were less than the mangrove charcoal at carbonization temperature of 750 and 500 °C. On the other hand, the percentage of fixed carbon tends to be increased when the carbonization temperature was increased. Furthermore, the percentages of ash of mangrove charcoal at all carbonization temperatures were similar. Moreover, the percentage of all components of mangrove charcoal that used carbonization temperature at 750 and 1000 °C were similar.

500 °C 750 °C 1000 °C

Figure 4.1 Mangrove charcoals produced at carbonization temperature of 500, 750 and 1000 °C

Table 4.1 The percentage of moisture content, volatile matter, ash, and fixed carbon of mangrove charcoals produced at carbonization temperature of 500, 750 and 1000 °C

Charcoal compositions	Carbonization temperature (°C)		
	500	750	1000
Yield (%)	28.89+0.62 ^{A}	23.38+0.35 ^{B}	22.17 ^{B}
Moisture content (%)	1.55 ± 0.40 ^{A}	0.68 ± 0.07 ^{B}	0.81 ± 0.01 ^{AB}
Volatile matter (%)	21.05 ± 0.86 ^{A}	5.55 ± 0.03 ^{B}	4.90 ± 0.15 ^{B}
Ash (%)	9.40 ± 1.34 ^{A}	11.52 ± 5.21 ^{A}	7.55 ± 0.26 ^{A}
Fixed carbon (%)	69.55 ± 0.48 ^{A}	82.93 ± 5.18 ^{B}	87.55 ± 0.11 ^{B}

Note: Statistical analysis was shown in Appendix B.

The percentages of yield of charcoal at high carbonization temperature were less than the charcoal at low carbonization temperature. Because the amount of water evaporation and ignition or decomposition of three main components in mangrove wood (300-500 °C cellulose, 200-260 °C hemicelluloses, 280-500 °C of lignin) would better occur if the process was using the high carbonization temperature (Sadaka, 2012). During the decomposition of three main wood components at different carbonization temperatures, the products would be in form of solid (Charcoal) liquid (Tar) and gas (Volatile matter and others) in the different quantity which might affect to the different weight of charcoal. At high carbonization temperature, the charcoal yield presented low and less moisture content and volatile matter than the charcoal at lower carbonization temperature. However, lignin, which is one of the main wood components, was the most difficult to burn. When the decomposition of lignin (280-500 °C of lignin) was occurred, it would provide the mainly carbon to charcoal. This carbon was the part of charcoal that could be flammable. It was called "Fixed carbon". The burning the wood using high temperature affect to the high proportion of fixed carbon in charcoal (Water and volatile matter were driven off by heating) (FAO, 1983; Fjellerup et al., 2005; Weerdhof, 2012: Sadaka, 2012).

The difference of charcoal's components could separate the quality of charcoal. The charcoal at high carbonization temperature (low moisture content and volatile matter, high fixed carbon) would have more purity. In addition, the volatile in charcoal could be easy to ignition. The volatile did not provide the heat energy to environment because it would evaporate out to the atmosphere in form of smoke. However, the ignition of volatile could help to flammable the fixed carbon, which during burning the heat energy would emit to environment (FAO, 1983; Forest Products Research Division of Royal Forest Department, 1984).

Moreover, the percentage of yield, moisture content, volatile matter, ash and fixed carbon of mangrove charcoal at carbonization temperature of 750 °C was not significantly different from the charcoal at carbonization temperature of 1000 °C. The percentages of charcoal compositions seem alike between the charcoal using carbonization temperature of 750 and 1000 °C. The wood components were likely to be completed decomposition (the same type of wood was resulted in the similar of charcoal compositions) if the high carbonization temperature (above 500 °C) was used (Sadaka, 2012). However, the percentages of ash of charcoal at all carbonization temperature were not significantly different because ash could not to light a fire. Ash is inorganic that was residue from burning. The same types of wood would provide the same quantity of ash.

4.2 Effect of carbonization temperature of charcoal on PAHs content in smoke during grilling

Grilling using charcoal for providing the heat energy should consider about the contamination of 16 PAHs. The charcoal was assumed that it is the one of main factor to making 16 PAHs contamination occur. Thus, in this section PAHs were analyzed 16 by collecting smoke during burning 70 ± 1 g of charcoal at 650 °C for 2 hours (the charcoal in this step was burned around 90%). The experimental results of this section were shown in Table 4.2

According to the United States Environmental Protection Agency (USEPA), 16 PAHs have chosen as priority pollutants due to their presence in the atmosphere and carcinogenicity. For Commission regulation (EU), benzo[a]pyrene and the sum of 4

PAHs (benzo[a]pyrene, chrysene, benzo[a]anthracene and benzo[b]fluoranthene) were used as indicators in food. Maximum levels of benzo[a]pyrene and the sum of 4 PAHs were set respectively at 0.005 µg/g (EU Regulation No. 208/2005) and 0.03 µg/g (EU Regulation No. 835/2011) in smoked meat and smoked meat products.

When considering the experimental results, the charcoal produced at carbonization temperature of 500 °C have the total concentration of 4 PAHs in smoke over the EU standard that was 0.29 ± 0.03 mg/g or about 0.29×10^3 µg/g (Considering in case of all of PAHs adhere onto the food), but the total concentration of 4 PAH in smoke of charcoal at carbonization temperature of 750 and 1000 °C were not found. In addition, it was found that benzo[a]pyrene occurred only in charcoal at carbonization temperature of 500 °C which was equal 0.04 mg/g (The experimental results would consider only the results that have Q-value more than 90) (Debonneville et al., 2004).

For the total concentration of 16 PAHs in smoke from charcoal, it was found that all charcoal using carbonization temperature of 500, 750 and 1000 °C produced the total concentration of 16 PAHs over the standard which were 5.94 ± 0.62, 0.51 ± 0.19 and 0.94 ± 0.66 mg/g of charcoal, respectively.

Note: The concentrations of PAHs in this experiment were detected only in smoke from charcoal during grilling, not detected in grilled food.

Table 4.2 Concentrations of PAHs in smoke from charcoal which used carbonization temperature of 500 750 and 1000 °C

Target compounds	Concentration of PAHs at each carbonization temperature (mg/g of charcoal)		
	500 °C	750 °C	1000 °C*
Naphthalene	1.94 ± 1.67	0.42 ± 0.41	0.94
Acenapthylene	0.33	N/A	N/A
Acenaphthene	N/A	N/A	N/A
Fluorene	N/A	N/A	N/A
Phenanthrene	1.08 ± 0.91	0.04 ± 0.03	N.D.
Anthracene	0.31 ± 0.22	0.01	N.D.
Fluoranthene	1.18	N/A	N/A

Table 4.2 Concentrations of PAHs in smoke from charcoal which used carbonization temperature of 500 750 and 1000 °C (Cont.)

Target compounds	Concentration of PAHs at each carbonization temperature (mg/g of charcoal)		
	500 °C	750 °C	1000 °C*
Pyrene	0.79 ± 0.90	0.05 ± 0.01	N/A
Benzo[a]anthracene	0.11 ± 0.14	N/A	N/A
Chrysene	0.09 ± 0.10	N/A	N/A
Benzo[b]fluoranthene	0.05	N/A	N/A
Benzo[k]fluoranthene	N.D.	N.D.	N/A
Benzo[a]pyrene	0.04	N/A	N/A
Benzo[g,h,i]perylene	0.01	N/A	N/A
Dibenzo[a,h]anthracene	N/A	N/A	0.001
Indeno[1,2,3-c,d]pyrene	0.0098	N/A	N/A
Total 16 PAHs	5.94 ± 0.62	0.51 ± 0.19	0.94 ± 0.66
PAH4	0.29 ± 0.03	N/A	N/A

Note: * There is only one experimental result due to the limitation of furnance
(N/A) = not available (N.D.) = not detection

4.3 The relationship between charcoal compositions and 16 PAHs in smoke of mangrove charcoal.

Furthermore, the analysis of charcoal compositions (Experiment 4.1 and 4.2) would help to know the effect of carbonization temperature on quality of charcoal. This section would consider the relationship between volatile matter and 16 PAHs in charcoal at various carbonization temperatures (500, 750 and 1000 °C).

From Table 4.2, the type and concentration of PAHs which remaining in charcoal were unequal and tended to decrease the concentration of PAHs along the carbonization temperature increased. This trend was similar with volatile matter that found in charcoal (Table 4.1) Fjellerup et al. (2005) found that, when cellulose and hemicelluloses in wood was decomposed from heat, the tar would residue in charcoal in form of liquid at room temperature. When tar was heat, it would be in form of volatile matter. The volatile matter that Fjellerup et al. (2005) detected was methyl derivatives of aromatics such as toluene, indene, methylacenaphthylene, methylnaphthalene, etc. and polycyclic aromatic hydrocarbon such as naphthalene, acenaphtalene, phenanthrene, pyrene, fluoranthrene, and other aromatic hydrocarbon. Also, the quantity of tar remained in charcoal that used the carbonization temperature over 600 °C would have the trend to decrease follow the carbonization temperature increased. It did same with the experimental 4.1 and 4.2 that are the trend of volatile matter and PAHs in charcoal tends to decrease when carbonization temperature were increased.

Therefore, volatile matter that found in charcoal had the relations in the same way with PAHs and the carbonization temperature affected the quantity of them. (Forest Products Research Division of Royal Forest Department, 1984; Fjellerup et al., 2005; Zevenboven and Kilpinen, 2001). However, the disintegration of tar that gave the aromatic hydrocarbon might react to be other PAHs. It did not have any research indicated about the mechanism of PAHs formation. There has only hypothesis for PAHs that might be formed through free radical reaction, intramolecular addition or polymerisation of small molecules (Pitts, 1983; Perez et al., 1986).

In addition, the smoke from mangrove charcoal using carbonization temperature of 750 and 1000 °C had resembled types and quantity of PAHs. Because, the combustion of wood components was complete at temperature above 500 °C which made the components of charcoal and quantity of 16 PAHs were alike (Sadaka, 2012).

CHAPTER 5 CONCLUSIONS AND RECOMMENDATION

The aim of this research was to study the effect of carbonization temperature on yield and composition of mangrove charcoal and PAHs content generated in smoke during charcoal grilling.

The results showed that the different carbonization temperatures affected the yield and chemical composition of mangrove charcoal. Yields of charcoals produced at 500, 750 and 1,000 °C were 28, 23 and 22%, respectively. In term of chemical composition, charcoals produced at 500 °C, 750 and 1,000 °C had 1.55, 0.68 and 0.81% for moisture content, 21.05, 5.55 and 4.90% for volatile matter, 9.40, 11.52 and 7.55% for ash and 69.55, 82.93 and 87.55% for fixed carbon, respectively.

The results of yield and chemical composition indicated that charcoal produced at low carbonization temperature presented a high volatile matter, resulting in a high charcoal yield and low fixed carbon. However, there was no significant difference of yield, fixed carbon and volatile matter between charcoal produced at 750 and 1,000 °C.

For total 16 PAHs generated in smoke during charcoal grilling, the different carbonization temperatures affected the concentration and type of PAHs. Charcoals produced at 500, 750 and 1,000 °C generated respectively 4.52×10^3, 0.55×10^3 and 0.94×10^3 μg/g. In addition, charcoals produced at 500 °C generated 4 PAHs which are the carcinogen indicators in food according to Commission Regulation (EU) No 835/2011.

In conclusion, it seemed that there was a relation between volatile matter and total PAHs content of charcoal, as the results showed that charcoal produced at 500 °C which had the high volatile matter generated the highest concentration of 16 PAHs. In addition, no significance of 16 PAHs between charcoals produced at 750 and 1000 °C which had no significant difference in volatile matter was found.

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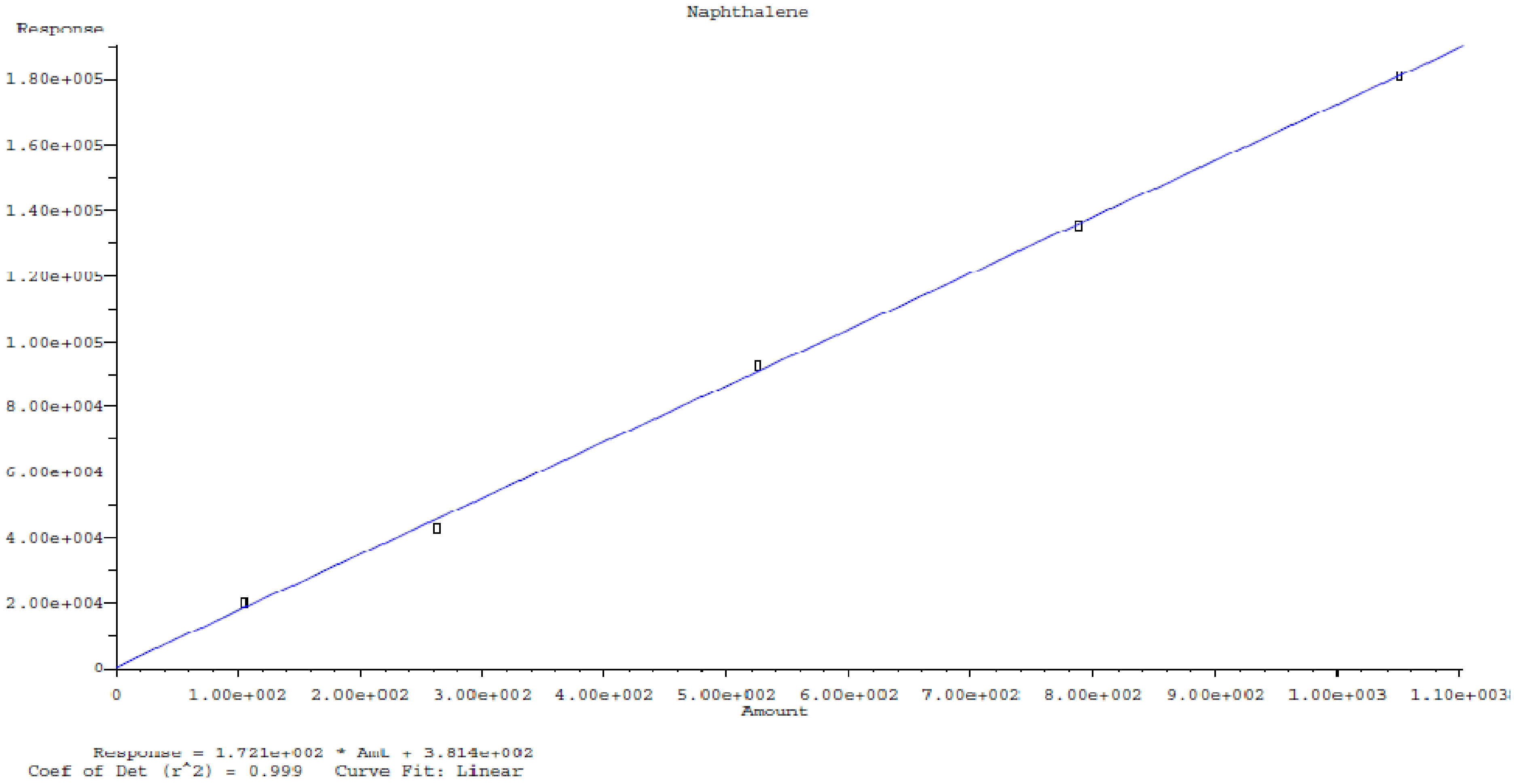
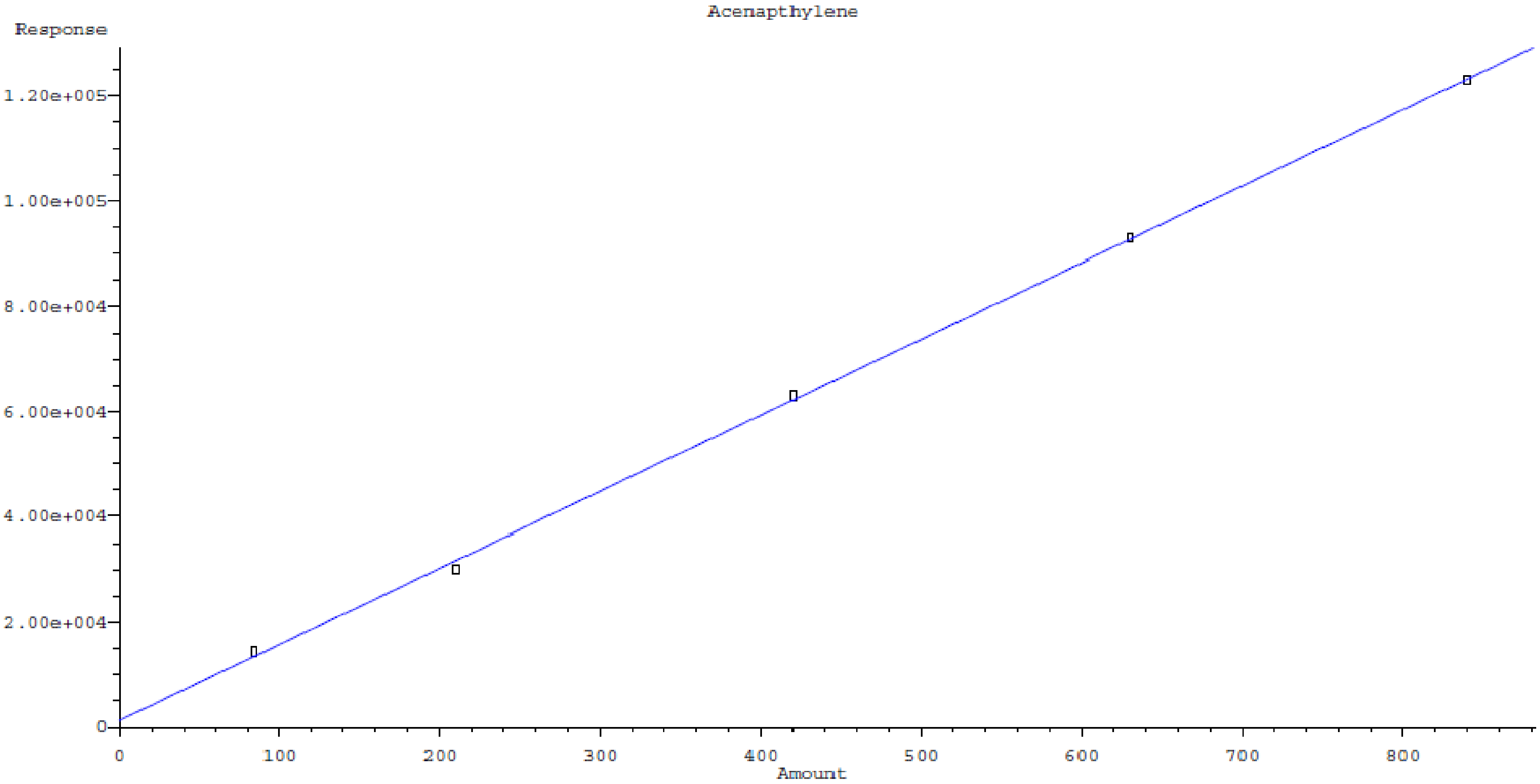
APPENDIX A
Standard Curve



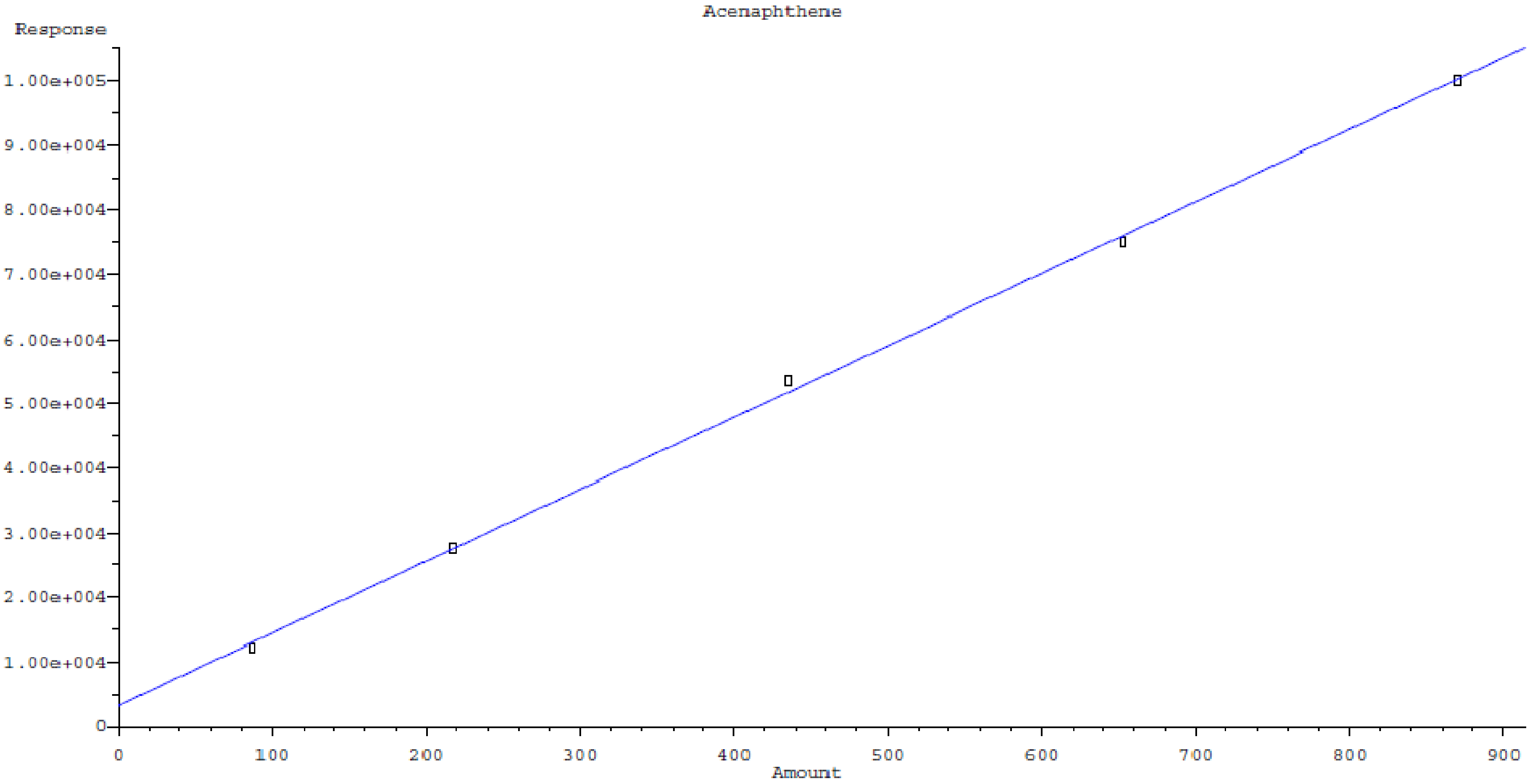
```
    Response = 1.721e+002 * Amt + 3.814e+002
Coef of Det (r^2) = 0.999   Curve Fit: Linear
```

Figure A.1 Standard curve of Napthalene



```
      Response = 1.451e+002 * Amt + 1.339e+003
Coef of Det (r^2) = 0.999   Curve Fit: Linear
```

Figure A.2 Standard curve of Acenapthylene



```
      Response = 1.115e+002 * Amt + 3.310e+003
Coef of Det (r^2) = 0.999   Curve Fit: Linear
```

Figure A.3 Standard curve of Acenaphthene

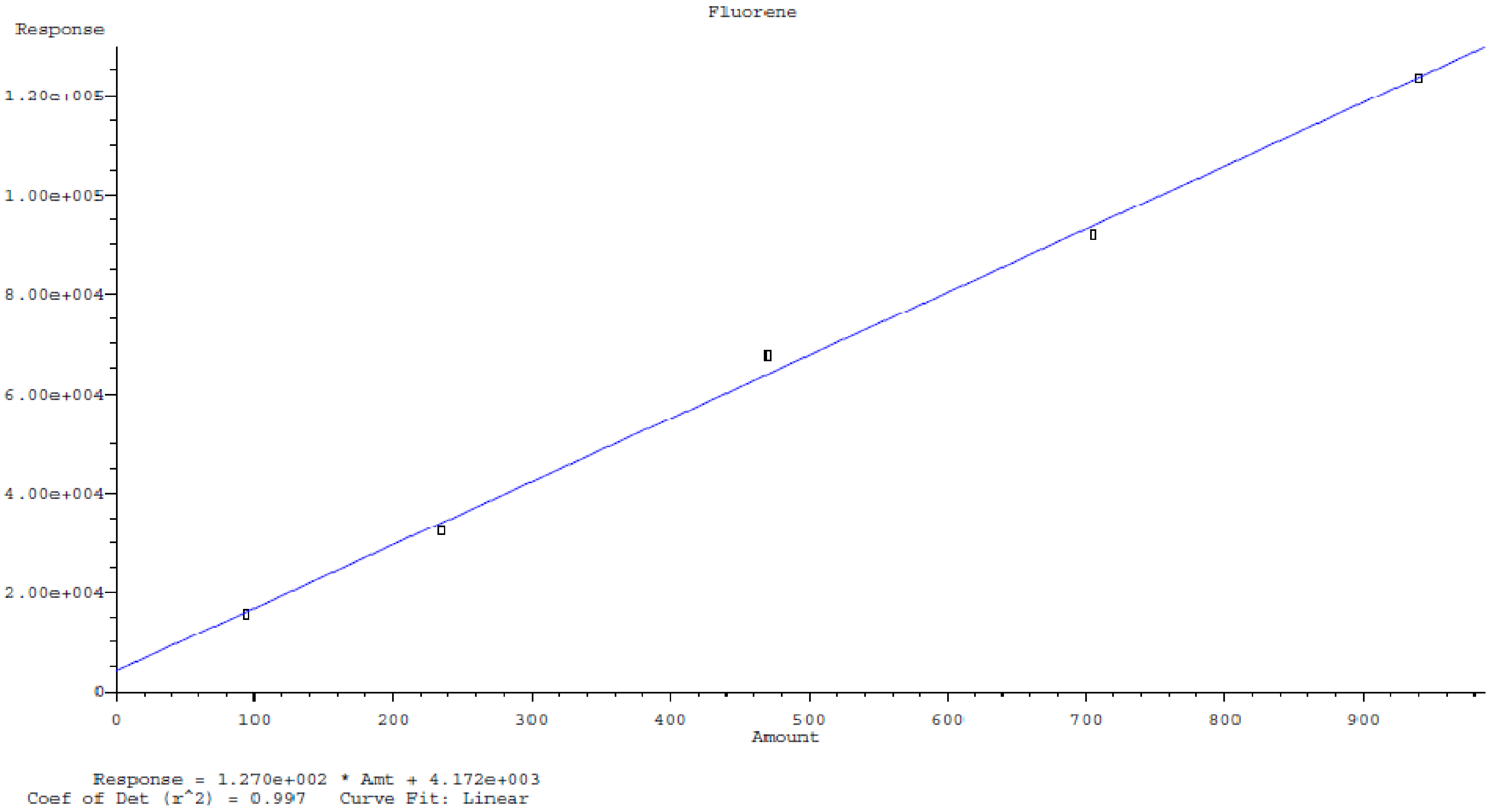
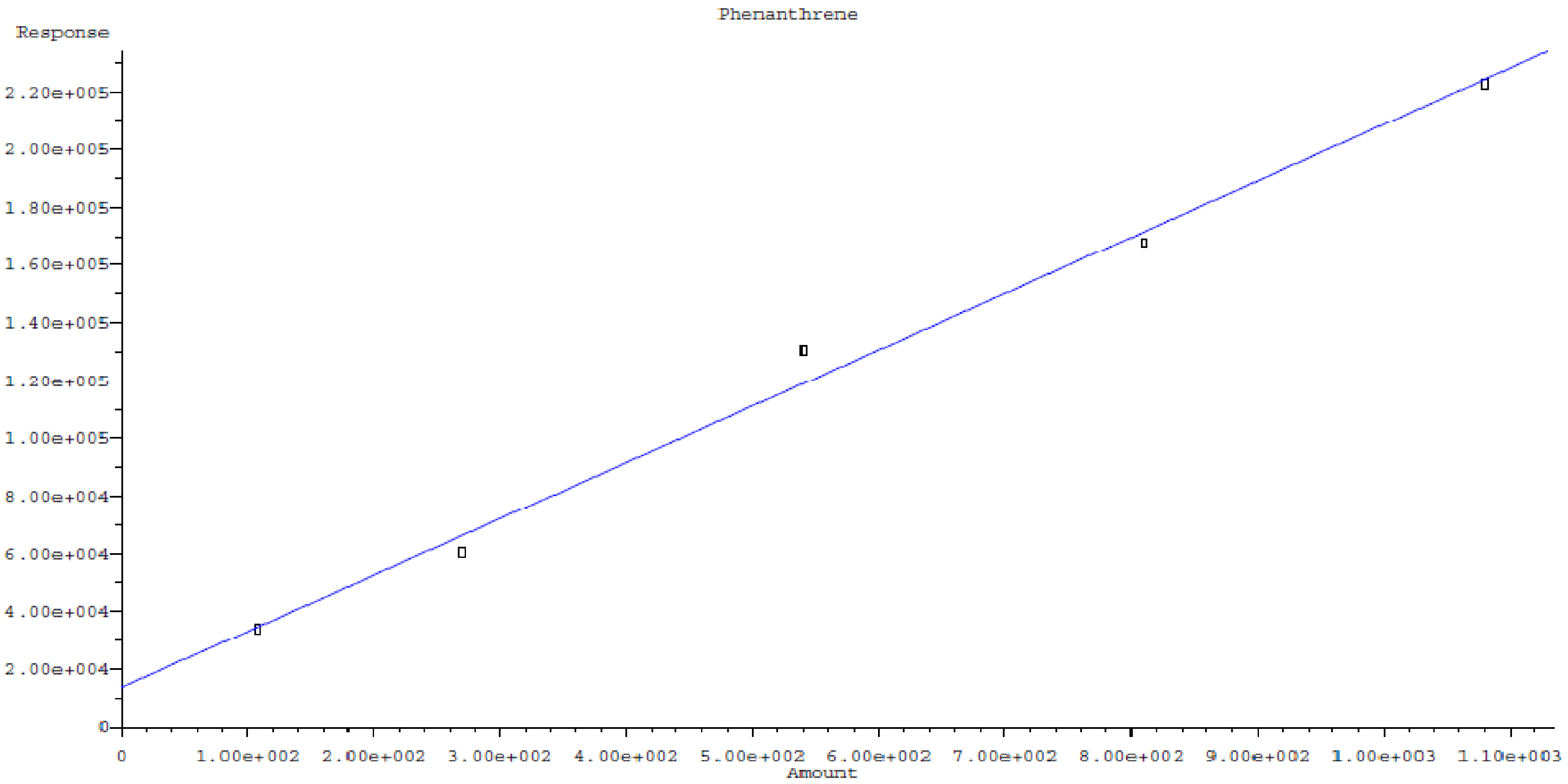
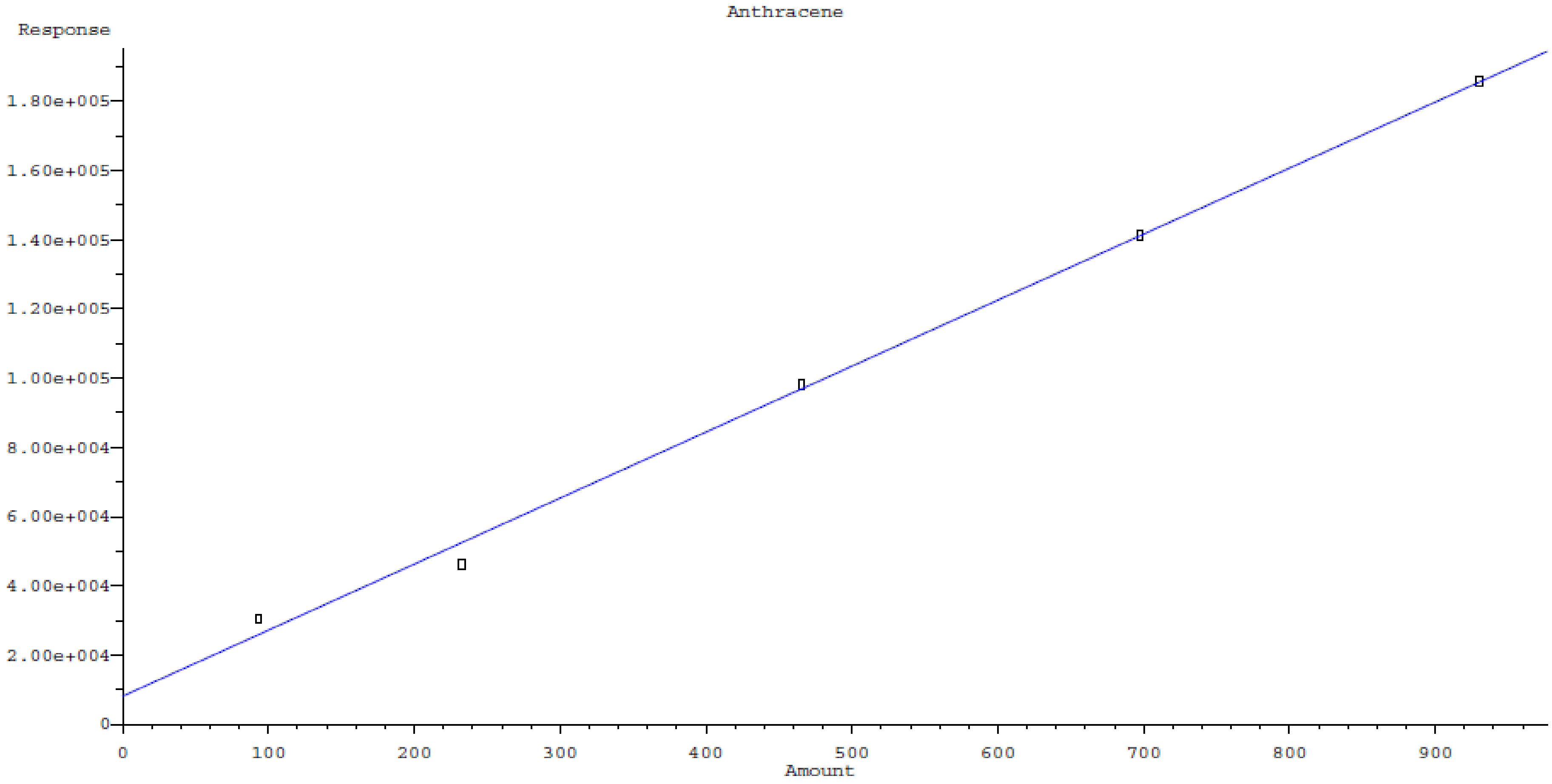


Figure A.4 Standard curve of Fluorene



```
     Response = 1.950e+002 * Amt + 1.359e+004
Coef of Det (r^2) = 0.992    Curve Fit: Linear
```

Figure A.5 Standard curve of Phenanthrene



Response = 1.908e+002 * Amt + 8.111e+003
Coef of Det (r^2) = 0.996   Curve Fit: Linear

Figure A.6 Standard curve of Anthracene

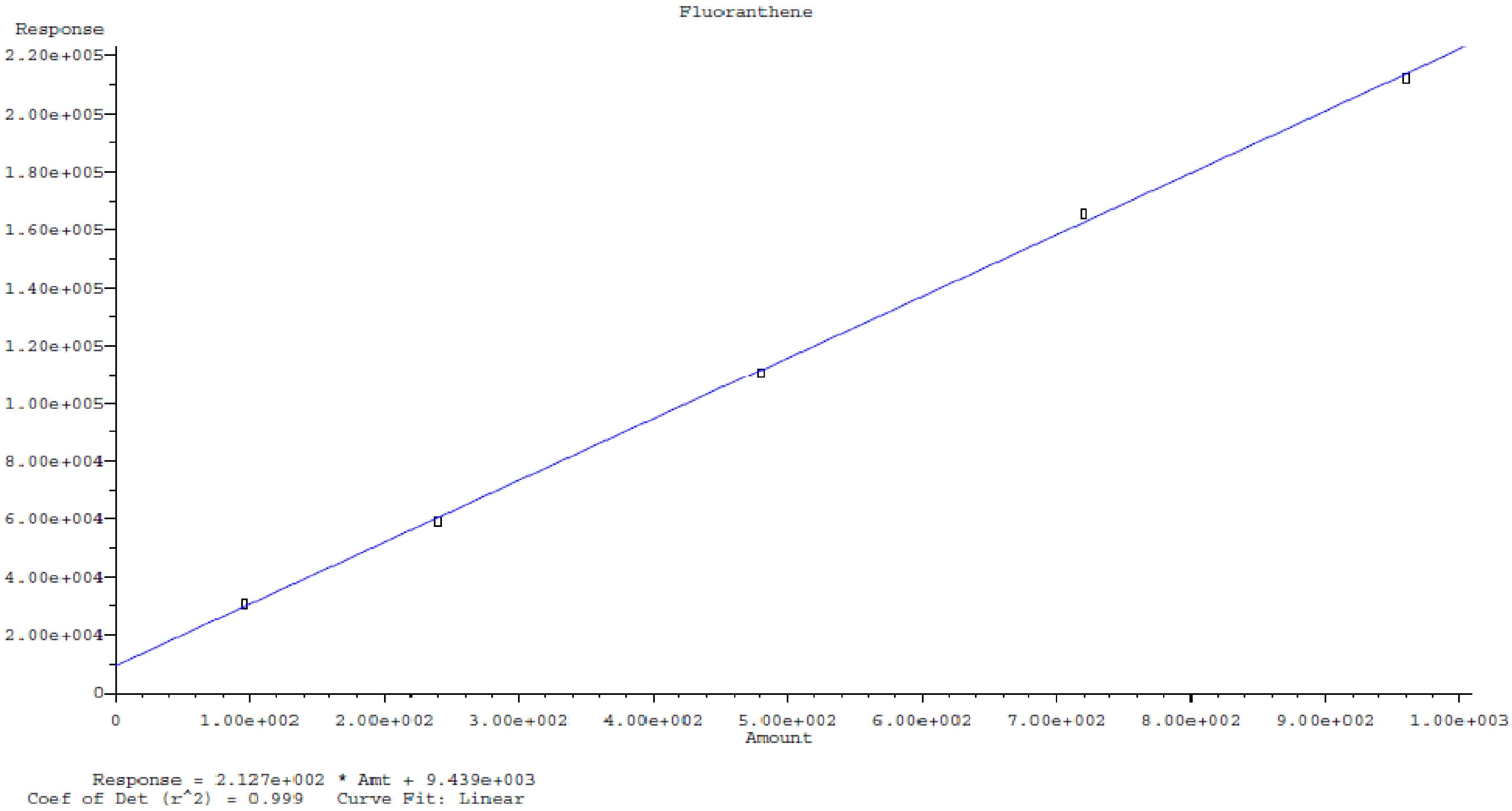
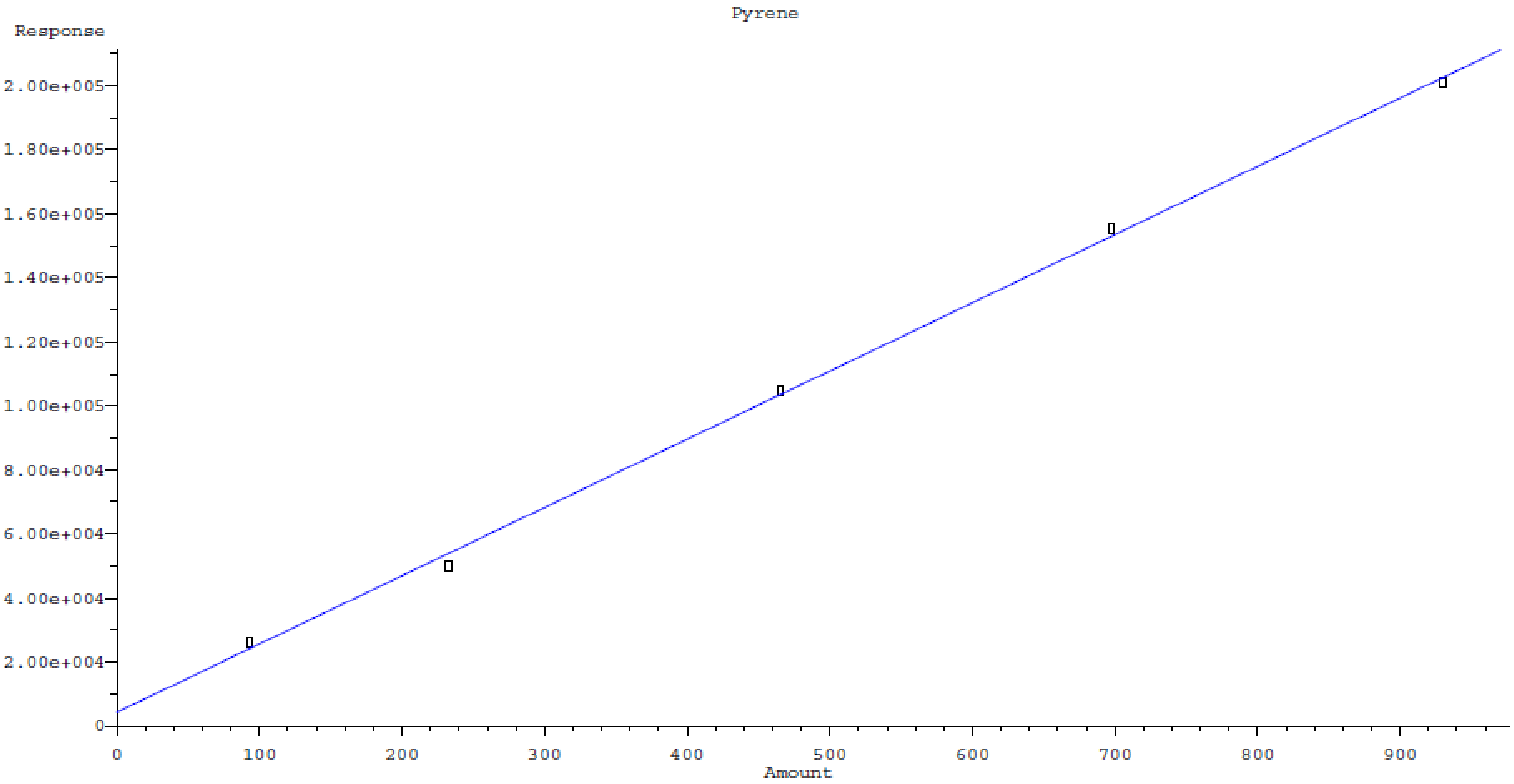


Figure A.7 Standard curve of Fluoranthene



```
     Response = 2.131e+002 * Amt + 4.339e+003
Coef of Det (r^2) = 0.999   Curve Fit: Linear
```

Figure A.8 Standard curve of Pyrene

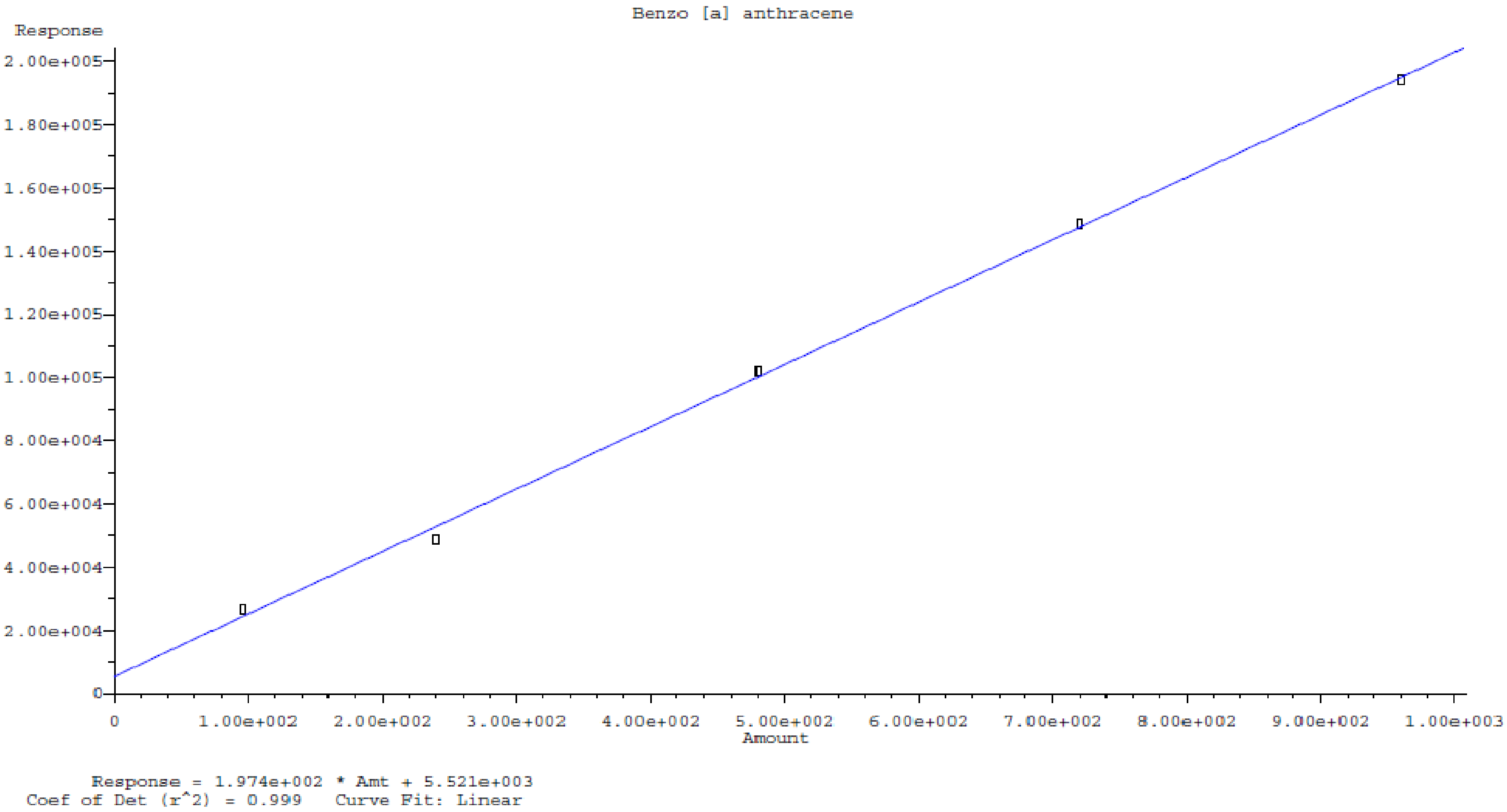
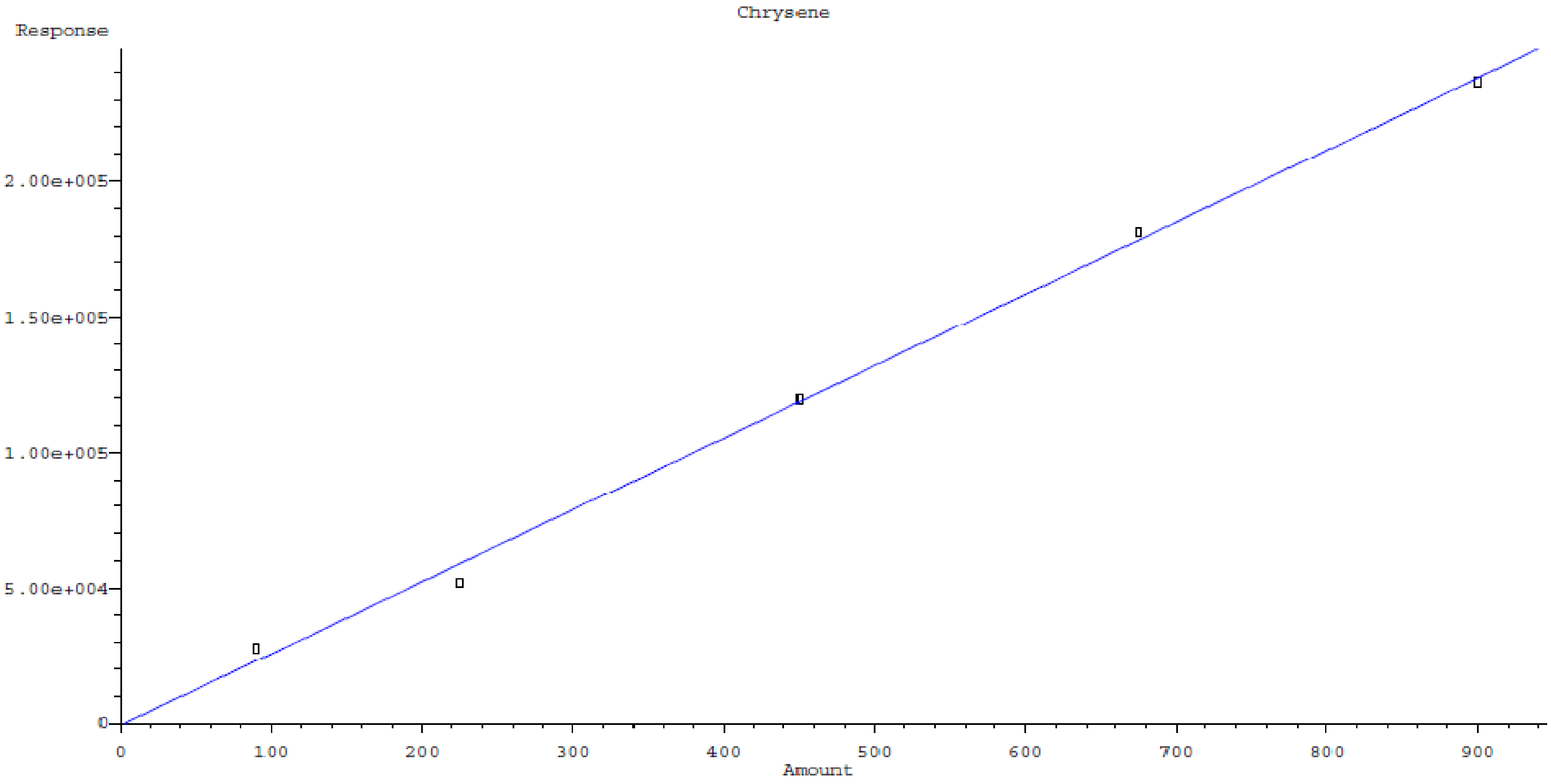


Figure A.9 Standard curve of Benzo [a] anthracene



```
   Response = 2.653e+002 * Amt - 8.043e+002
Coef of Det (r^2) = 0.997   Curve Fit: Linear
```

Figure A.10 Standard curve of Chrysene

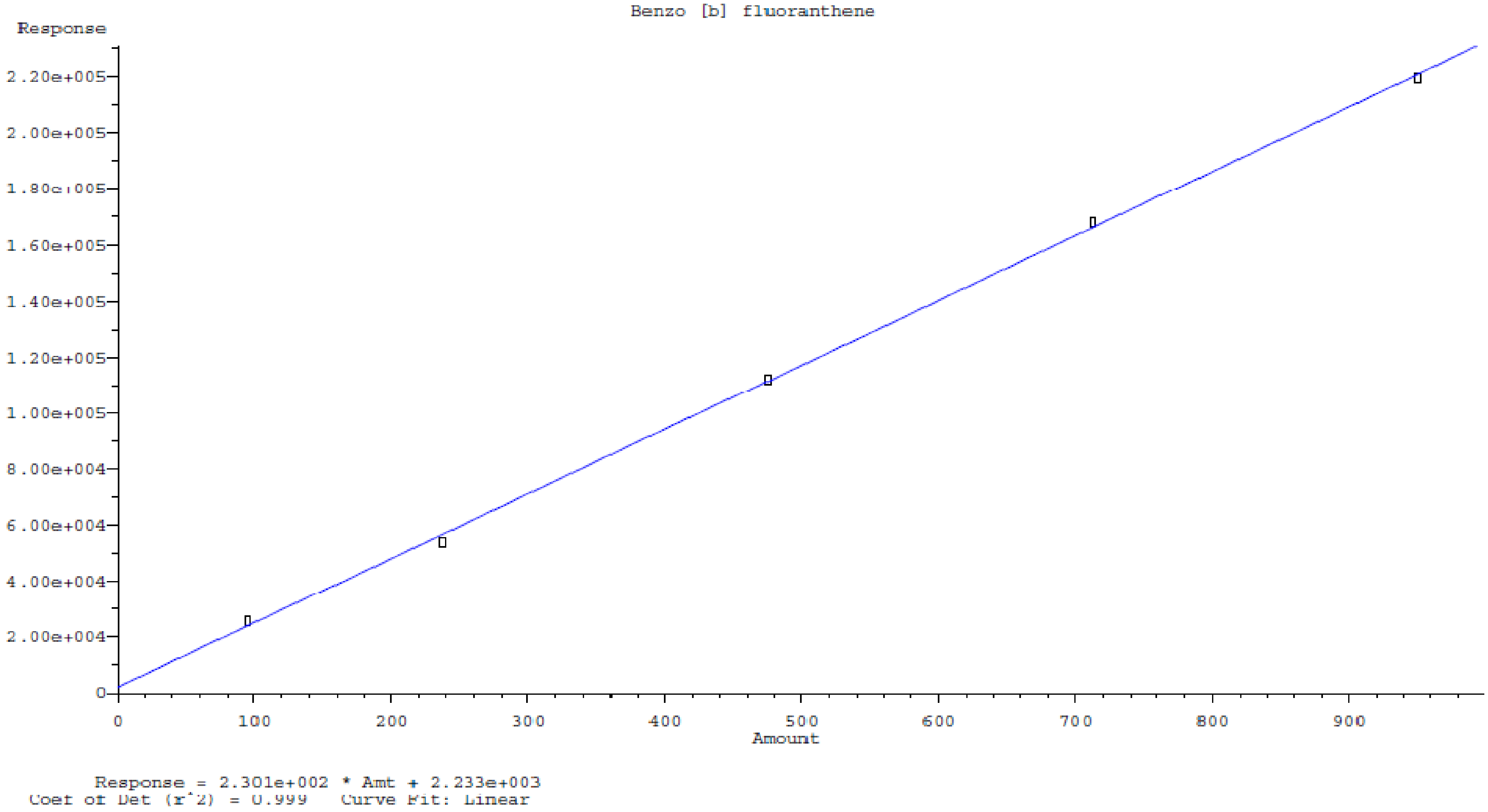


Figure A.11 Standard curve of Benzo [b] fluoranthene

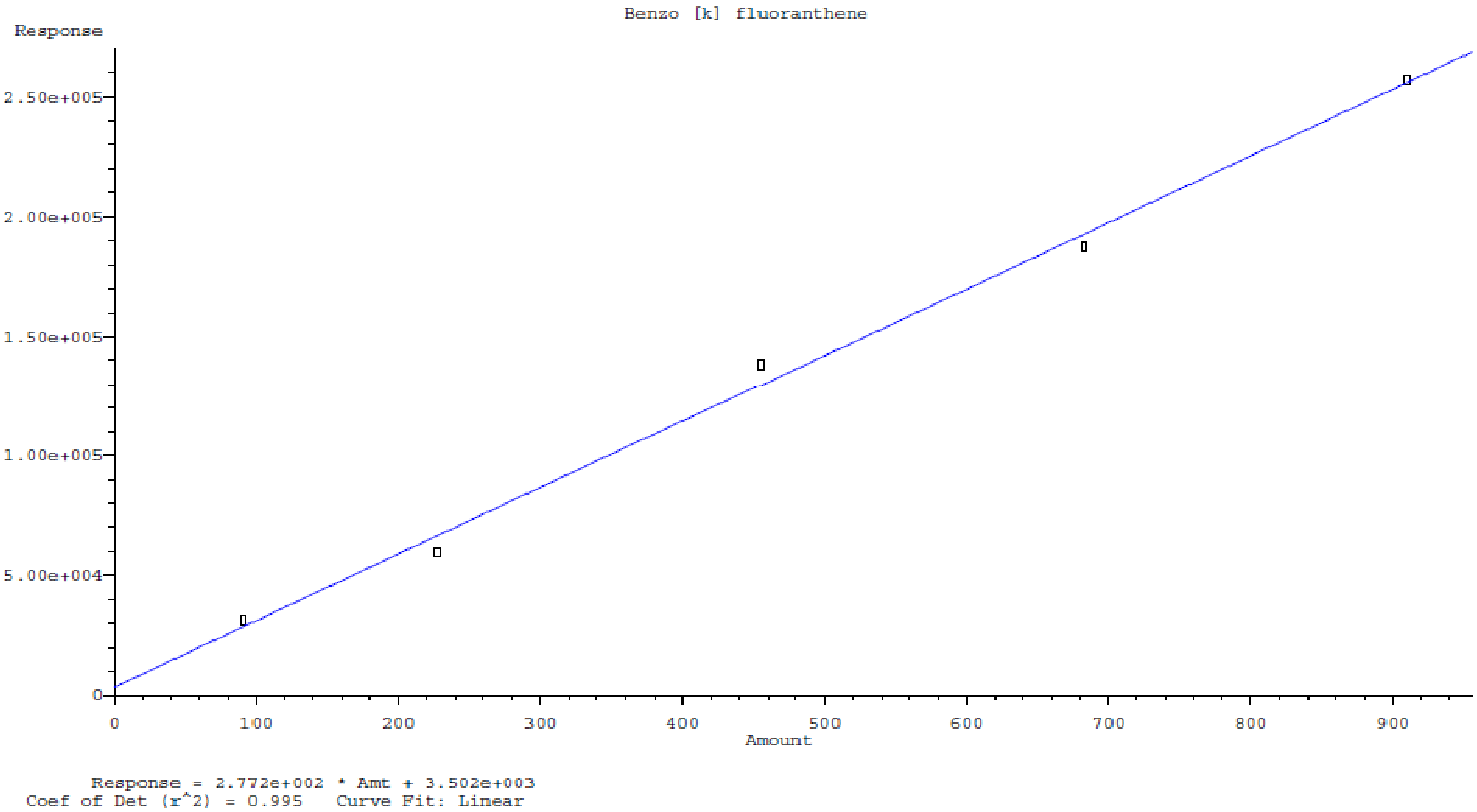
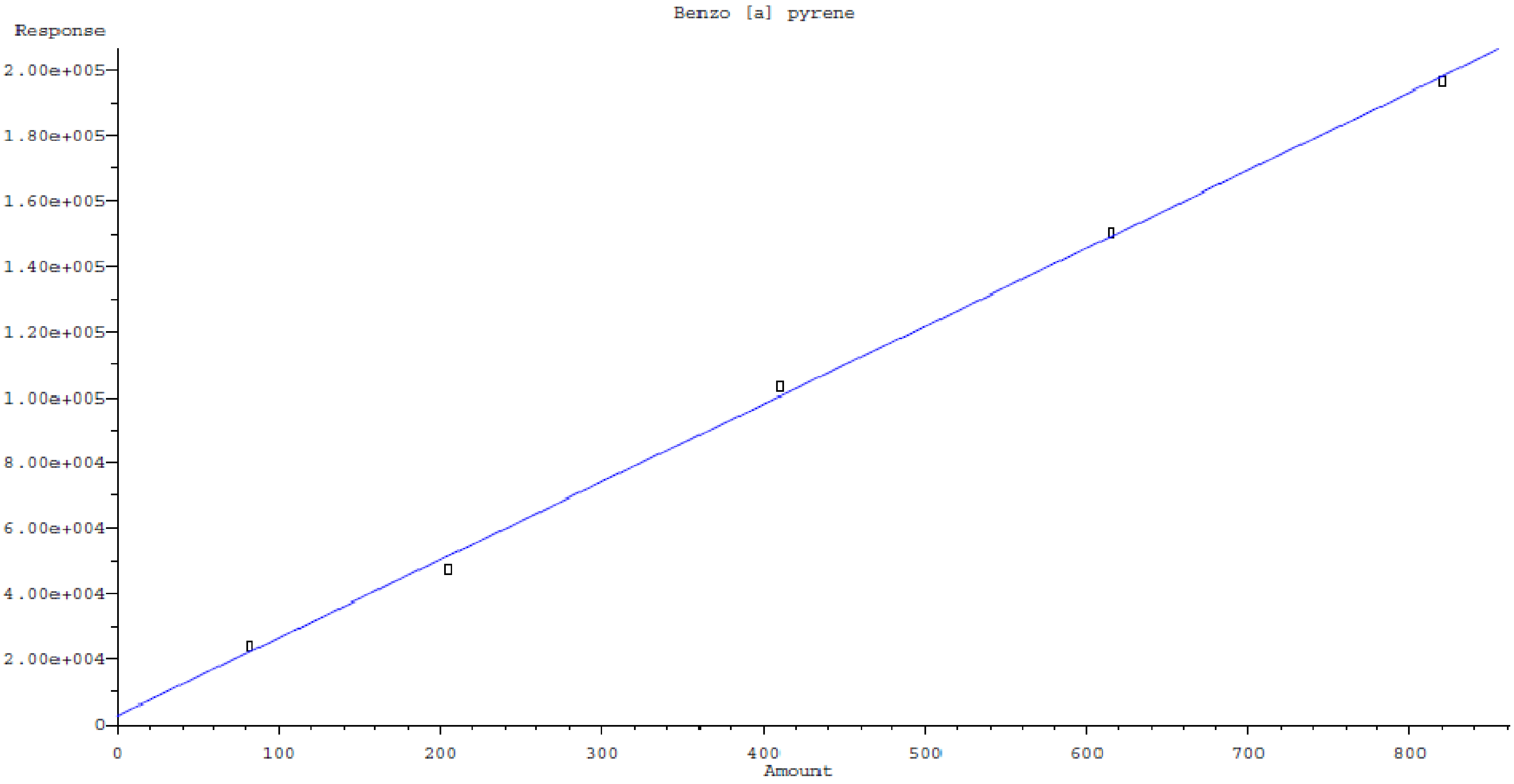


Figure A.12 Standard curve of Benzo [k] fluoranthene



Response = 2.380e+002 * Amt + 2.748e+003
Coef of Det (r^2) = 0.998   Curve Fit: Linear

Figure A.13 Standard curve of Benzo [a] pyrene

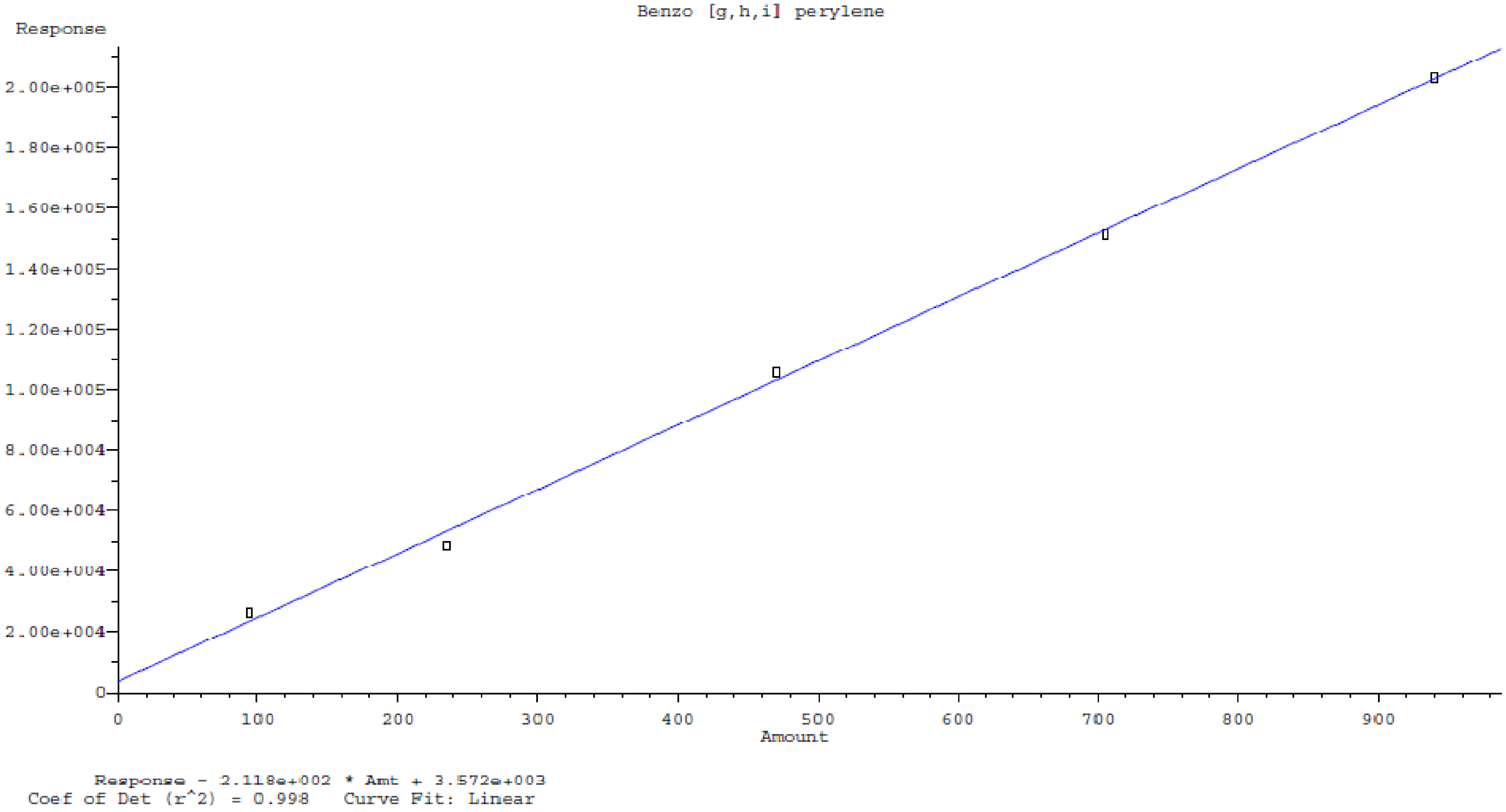


Figure A.14 Standard curve of Benzo [g,h,i] perylene

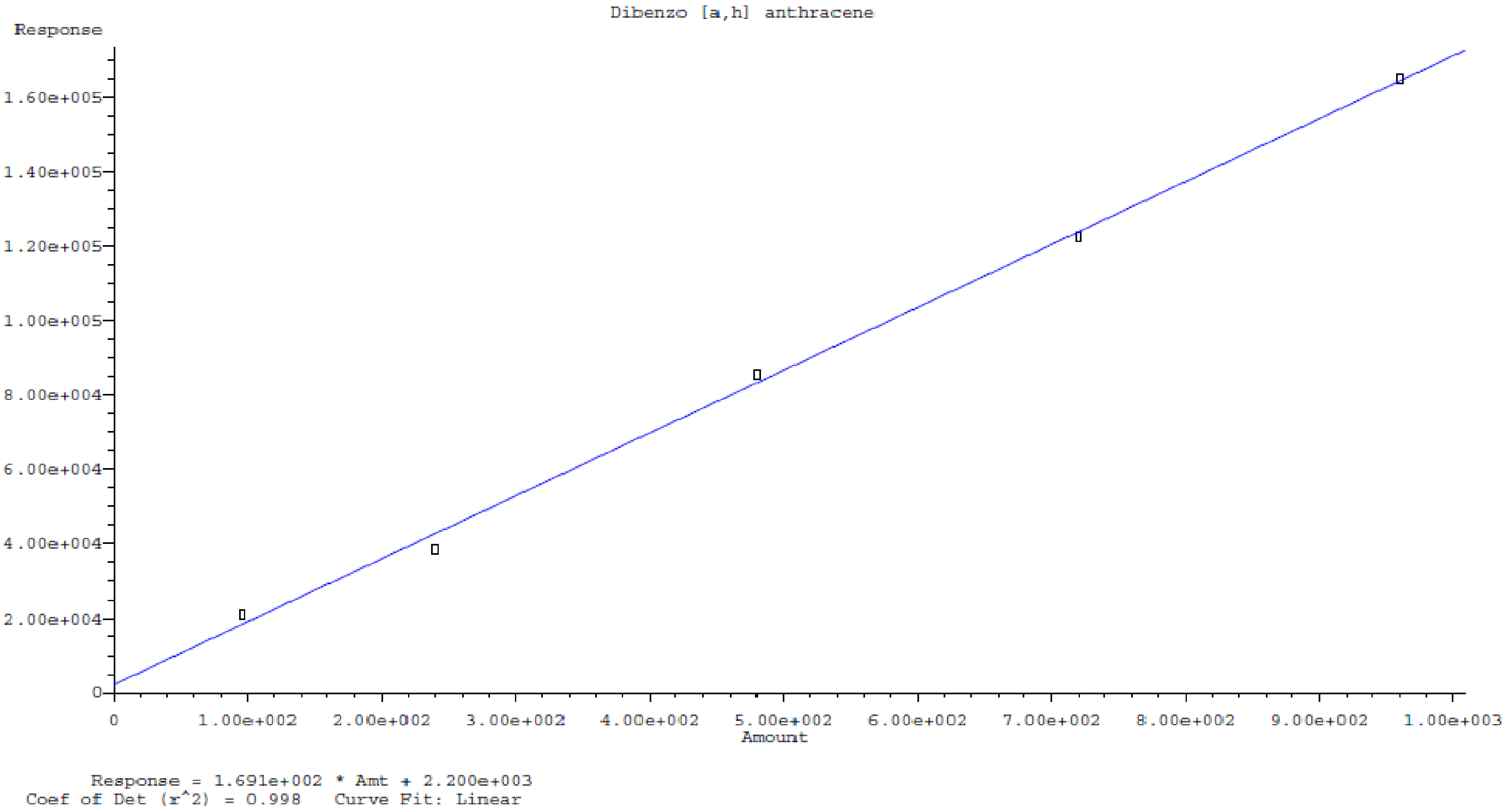


Figure A.15 Standard curve of Dibenzo [a,h] anthracene

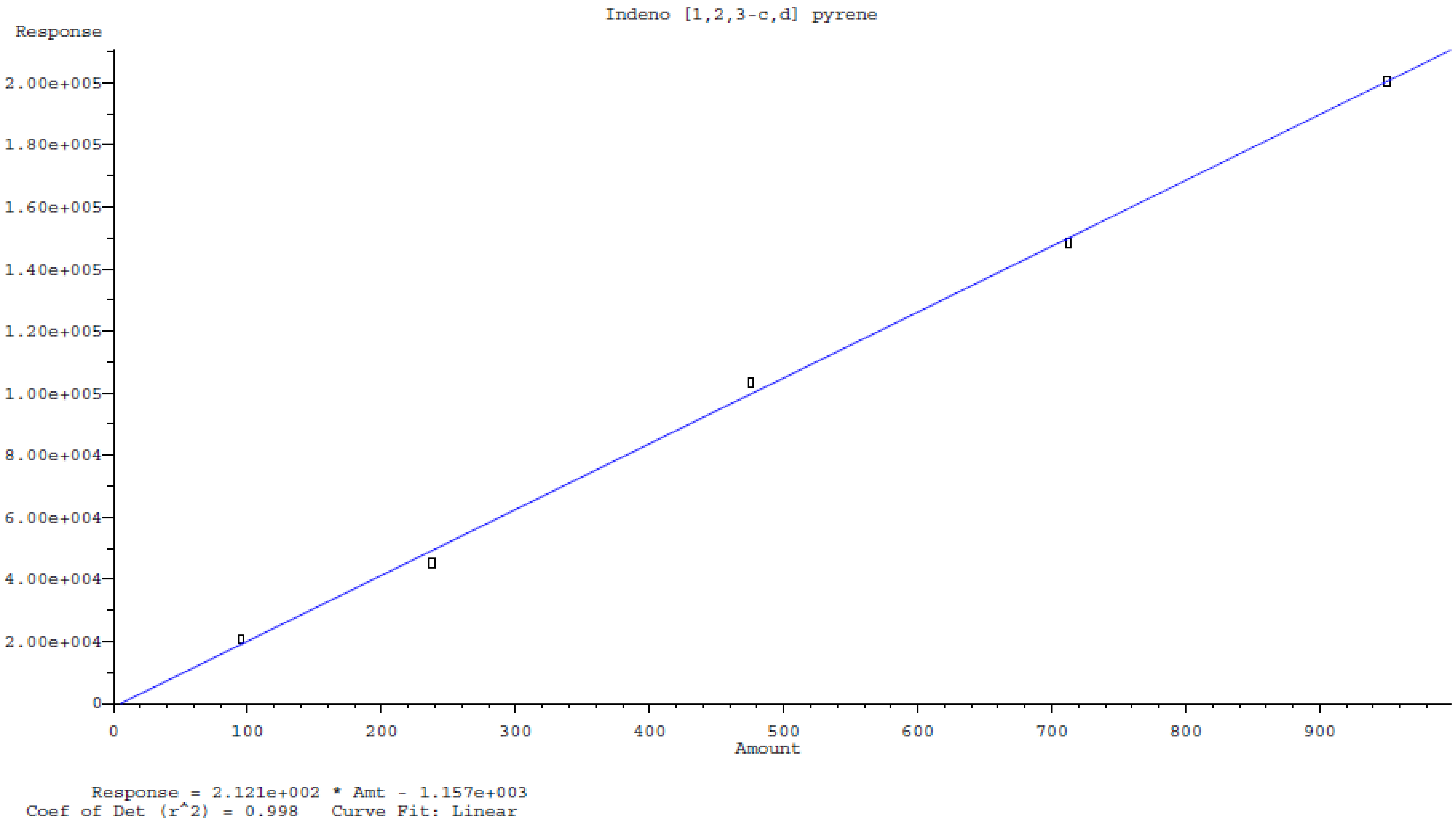


Figure A.16 Standard curve of Indeno [1,2,3-c,d] pyrene

APPENDIX B

Statistical Analysis

Table B.1 ANOVA table of volatile matter, moisture content, ash, fixed carbon and yield of mangrove charcoal at carbonization temperature of 500 750 and 1000 °C

One-Way ANOVA

		Sum of Squares	Df	Mean Square	F	Sig.
VOLATILE	Between Groups	334.541	2	167.271	654.508	.000
	Within Groups	.767	3	.256		
	Total	335.308	5			
MOISTURE	Between Groups	.877	2	.438	7.797	.065
	Within Groups	.169	3	.056		
	Total	1.046	5			
ASH	Between Groups	15.787	2	7.894	.816	.521
	Within Groups	29.032	3	9.677		
	Total	44.819	5			
FIXED	Between Groups	349.521	2	174.760	19.340	.019
	Within Groups	27.108	3	9.036		
	Total	376.629	5			
YIELD	Between Groups	51.403	2	25.702	153.153	.001
	Within Groups	.503	3	.168		
	Total	51.907	5			

Table B.2 Duncan table of volatile matter of mangrove charcoal at carbonization temperature of 500 750 and 1000 °C

Duncan

TEMP	N	Subset for alpha = .05	
		1	2
1000.00	2	4.8950	
750.00	2	5.5450	
500.00	2		21.0500
Sig.		.289	1.000

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 2.000

Table B.3 Duncan table of moisture content of mangrove charcoal at carbonization temperature of 500 750 and 1000 °C

Duncan

TEMP	N	Subset for alpha = .05	
		1	2
750.00	2	.6750	
1000.00	2	.8100	.8100
500.00	2		1.5450
Sig.		.609	.053

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 2.000

Table B.4 Duncan table of ash of mangrove charcoal at carbonization temperature of 500 750 and 1000 °C

Duncan

TEMP	N	Subset for alpha = .05
		1
1000.00	2	7.5550
500.00	2	9.4000
750.00	2	11.5250
Sig.		.290

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 2.000

Table B.5 Duncan table of fixed carbon of mangrove charcoal at carbonization temperature of 500 750 and 1000 °C

Duncan

TEMP	N	Subset for alpha = .05	
		1	2
500.00	2	69.5500	
750.00	2		82.9250
1000.00	2		87.5500
Sig.		1.000	.222

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 2.000

Table B.6 Duncan table of yield of mangrove charcoal at carbonization temperature of 500 750 and 1000 °C

Duncan

TEMP	N	Subset for alpha = .05	
		1	2
1000.00	2	22.1700	
750.00	2	23.3800	
500.00	2		28.8950
Sig.		.060	1.000

Means for groups in homogeneous subsets are displayed.

[a] Uses Harmonic Mean Sample Size = 2.000

APPENDIX C

Experimental Data

Table C.1 Moisture content of mangrove charcoal at each carbonization temperature

Carbonization temperature (°C)	500		750		1000	
	1	2	1	2	1	2
Moisture can (g)	8.0328	7.9527	7.9694	7.9898	7.8055	7.8023
Moisture can + charcoal1 (g)	13.5800	13.0905	13.5455	13.3923	13.4899	13.4767
Charcoal (before) (g)	5.5472	5.1378	5.5761	5.4025	5.6844	5.6744
Moisture can + charcoal2 (g)	13.5100	12.9964	13.5050	13.3586	13.4431	13.4312
Charcoal (after) (g)	5.4772	5.0437	5.5356	5.3688	5.6376	5.6289
Moisture content (%)	1.2619	1.8315	0.7263	0.6238	0.8233	0.8018
Average	1.5467		0.6750		0.8126	
STD	0.4028		0.0725		0.0152	

Table C.2 Volatile matter of mangrove charcoal at each carbonization temperature

Carbonization temperature (°C)	500		750		1000	
	1	2	1	2	1	2
Crucible (g)	19.7933	19.2865	22.0917	22.3127	19.1819	23.0083
Crucible + charcoal (g)	25.0309	24.3953	27.6319	27.6853	24.4296	28.2324
Charcoal (before) (g)	5.2376	5.1088	5.5402	5.3726	5.2477	5.2241
Crucible + charcoal (g)	23.9602	23.2886	27.3254	27.3861	24.1668	27.9821
Charcoal (after) (g)	4.1669	4.0021	5.2337	5.0734	4.9849	4.9738
Volatile matter (%)	20.4426	21.6626	5.5323	5.5690	5.0079	4.7913
Average	21.0526		5.5506		4.8996	
STD	0.8627		0.0260		0.1532	

Table C.3 Ash of mangrove charcoal at each carbonization temperature

Carbonization temperature (°C)	500		750		1000	
	1	2	1	2	1	2
Crucible (g)	22.5453	21.9456	20.0289	21.2505	21.3600	23.8463
Crucible + charcoal (g)	28.1774	27.1682	25.6304	26.8202	26.3986	29.1947
Charcoal (g)	5.6321	5.2226	5.6015	5.5697	5.0386	5.3484
Crucible + ash (g)	23.1280	22.3869	20.8807	21.6871	21.7312	24.2602
Ash (g)	0.5827	0.4413	0.8518	0.4366	0.3712	0.4139
Ash (%)	10.3461	8.4498	15.2066	7.8388	7.3671	7.7388
Average	9.3979		11.5227		7.5529	
STD	1.3408		5.2098		0.2628	

Table C.4 Fixed carbon of mangrove charcoal at each carbonization temperature

Carbonization temperature (°C)	500		750		1000	
	1	2	1	2	1	2
Fixed carbon (%)	69.2114	69.8876	79.2611	86.5922	87.6250	87.4700
Average	69.5495		82.9266		87.5475	
STD	0.4781		5.1839		0.1096	

Table C.5 The concentration of 16 PAHs and Q-value obtained from analysis the smoke from mangrove charcoal at each carbonization temperature by using GC/MS

Target compounds		Concentration of PAHs at each carbonization temperature (OC)									
		500/1		500/2		750/1		750/2		1000/1*	
		mg/g	Q-value	mg/g	Q-value	mg/g	Q-value	mg/g	Q-value	mg/g	Q-value
Naphthalene	NAP	0.7570	100	3.1158	99	0.7027	100	0.1281	98	0.9376	99
Acenapthylene	ACP	0.1258	81	0.3287	92	0.0023	1	0.0183	44	0.0155	1
Acenaphthene	ACY	0.0365	62	0.0452	1	0.0420	42	N/A	90	0.0477	87
Fluorene	FLR	0.1267	77	0.1422	60	0.0054	67	0.0134	88	0.0131	13
Phenanthrene	PHE	1.7307	99	0.4390	99	0.0183	96	0.0667	99	N.D.	
Anthracene	ANT	0.4661	99	0.1512	94	N/A	66	0.0051	97	N.D.	
Fluoranthene	FLT	1.1813	98	0.1471	88	3.7714	86	0.0120	82	0.0069	9
Pyrene	PYR	1.4276	97	0.1512	97	0.0530	99	0.0389	98	0.0088	82
Benzo[a]anthracene	BaA	0.2129	96	0.0152	100	0.0056	75	0.0003	72	N/A	62
Chrysene	CHR	0.1597	96	0.0123	98	0.0040	68	0.0018	74	0.0018	28
Benzo[b]fluoranthene	BbF	0.0517	96	0.0047	81	0.0006	69	0.0003	59	0.0003	1
Benzo[k]fluoranthene	BkF	N.D.		N.D.		N.D.		N.D.		N/A	56
Benzo[a]pyrene	BaP	0.0363	99	0.0132	73	0.0005	61	0.0192	75	0.0149	78
Benzo[g,h,i]perylene	BgP	0.0088	96	0.0005	59	N/A	52	N/A	52	N/A	52
Dibenzo[a,h]anthracene	DhA	N/A	95	N/A	12	N/A	1	N/A	53	0.0008	100
Indeno[1,2,3-c,d]pyrene	IcP	0.0098	96	0.0023	56	0.0011	55	0.0006	55	0.0007	1

* There is only one experimental result due to the limitation of machine

(N/A) = not available (N.D.) = not detection

CURRICULUM VITAE

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