

# Chapter 1

## Introduction

Due to rapid growth of industrial development, population increasing and traffic density, people in Taiwan are facing serious air pollution problems (Yang, 2002). Volatile organic compounds (VOCs) were of interest in air pollution research due to their suspected role in the formation of ozone and photochemical oxidants associated with urban smog. However, with increasing awareness that many toxic air pollutants (TAPs) are known as suspected carcinogens and some are associated with acute and chronic health effects, a number of ambient monitoring programs have been conducted in America, Europe and Asia cities to identify and measure these compounds in urban air (Ho *et al.*, 2002). A large number of chemical compounds that damage the ambient air quality are formed during incomplete combustion of organic materials (Yang *et al.*, 2002). Since several species of PAHs are known to be animal and/or human carcinogens, it is important to evaluate the contributions of both particle-bound PAHs and gaseous-phase PAHs to the health-risk that associated with the exposure of the total PAH content (Tsai *et al.*, 2002). Ambient air PAHs in gas-phase and particle-phase had been performed at Taichung industrial site, Taiwan (Taichung Industrial Park, TIP) and suburban Taichung, Taiwan (Tunghai University Campus, THUC) in central Taiwan. Heavy traffic and stationary industries such as steel industries, metalworking industries, plastic industries, chemical petroleum industries and so on are around these two sampling sites.

However, there were some PAHs papers published in North and South Taiwan, respectively during past few years. However, there are lacks of the PAHs related papers in Central Taiwan area. In addition, there were many PAHs produced related sources such as steel industries, traffic vehicle, incinerator and the largest power plant (Taichung thermal power plant) in Asia were all located in Central Taiwan. The understand and monitor of these PAHs concentration distribution in central Taiwan had become an important issue for this related research field. The purpose of this research is to investigate and characterize chemical profiles of PAHs at both two sampling sites in Taichung. Comparisons of the PAHs concentration with other studies in different sites around the world were also investigated. Moreover, it is hoped that the results from this research will provide a baseline reference for a global database as well as for regulation to improve air quality in central Taiwan.

## Chapter 2

### Literature Review

#### 2.1 The characterization and distribution of PAHs

Atmosphere is a major pathway for transport and deposition of PAHs. Atmospheric deposition is an important mechanism controlling the fate of air-borne toxics and their transfer from the atmosphere to natural surfaces. Small particles contain higher concentration of PAHs per unit mass than large particles. It has been known that when PAHs compounds emitted in gaseous phases were condensed into particle phase, PAHs compounds were mostly distributed to small particles (Bae *et al.*, 2002). Although atmospheric PAHs are partitioned between particulate matter and gas phase, they are associated predominantly with particulate matter. These indicate that p-PAHs are considered to be a significant hazardous substance to human health through breathing. In view of this health concern, monitoring the level of p-PAHs in urban areas has become more important (Chetwittayachan *et al.*, 2002). It was found the gaseous-phase PAHs contained higher fractions of less-carcinogenic, low-molecular-weight PAHs homologues, whereas particle-bound PAHs contained higher fractions of more-carcinogenic, high-molecular-weight PAHs homologues (Tsai *et al.*, 2002). In practice there were much information on the multi-ringed heavier PAHs but have left the lighter vapor-phase PAHs components rather neglected. Although these lighter compounds have weaker carcinogenic/mutagenic properties, they are the

most abundant in the urban atmosphere and react with other pollutants to form more toxic derivatives (Park *et al.*, 2002). Because of the lowest boiling points and highest volatility, Nap is more abundant in the vapor phase. Therefore, its surface deposition will be relatively small in comparison with other PAHs, and Nap contributes to its larger level in air. The observed high levels of Nap in domestic environments of Taipei might be related to the popular use of camphor balls in the wardrobe (Li and Ro, 2000). This likely indicates that volatile PAHs, which can readily partition into the gas phase during atmospheric transport of aerosols, are probably not reliable tracers of combustion derived particulate matter and associated PAHs from source(s) to sink(s) (Dickhut *et al.*, 2000). Higher molecular weight compounds are associated primarily with particles and likely to be removed by dry deposition while lower molecular weight compounds are found primarily in gas phase and are subject to transformation or removal by photochemical degradation. Varying particle size distributions also affect removal of PAHs during transport in the atmosphere (Odabasi *et al.*, 1999). The particle/gas phase distribution varied widely. The gas phase percentage ranged from 1.1 to 99.4%, and generally decreased with increasing molecular weight. The amount of PAHs associated with the particulate phase increased with decreasing temperature, probably due to the temperature dependence of gas/particle partitioning (Odabasi *et al.*, 1999).

## 2.2 The effect of meteorological factors

Although washout, dry deposition and mixing way decrease the concentration of PAHs in the atmosphere during transport from urban areas, decomposition of these compounds via photo-oxidation is also suspected to reduce levels reaching non-urban areas (Odabasi *et al.*, 1999). This was because the washing out effect for particulates during rainy days and photochemical degradation during high solar radiation were minimized in wintertime (Ho and Lee 2002). In the atmosphere, PAHs will distribute between particulate and vapor phases, which predominantly depends on the physical characteristics of the compounds themselves and the environmental situation such as temperature and humidity (Liu *et al.*, 2001). The two-, three-, and four-ring PAHs were predominantly in vapor phase, while the five-ring PAHs were primarily associated with the particulate phase. The fraction of PAHs in vapor phase will increase with the increase of temperature (Liu *et al.*, 2001). This shows that wind speeds are an important factor on dry deposition velocity and, thus, dry deposition flux (Bae *et al.*, 2002). Bae *et al.*, (2002) indicated that the higher concentrations of atmospheric PAHs in winter than spring are mainly due to higher stationary and mobile source emission while the temperature effect cannot be neglected.

## 2.3 Epidemiological studies

### 2.3.1 Health effect of PAHs

In earlier time, following high dermal exposure, chimney sweeps developed skin cancers, especially scrotal cancer. Epidemiological studies were conducted among workers exposed at coke ovens in coal coking and coal gasification, in asphalt works, in foundries, in aluminum production plants, and from diesel exhaust (Partanen and Boffetta, 1994; Costantino *et al.*, 1995). In all these occupations, there were also exposures to other chemicals, making a direct correlation of cause to increased levels in lung cancer more problematic. There are only a few animal carcinogenic studies with oral administration of PAHs. BaA, BaP, DBA, and mixtures of PAHs (coal tar) were tested orally and were carcinogenic (WHO, 1998). Considering a number of the PAH species are known to be animal and/or human carcinogens, it is important to evaluate the contributions of both particle-bound PAHs and gaseous-phase PAHs to the health-risk that associated with the exposure of the total PAH content. It was found the gaseous-phase PAHs contained higher fractions of less carcinogenic low molecular weight PAH homologues, whereas particle-bound PAHs contained higher fractions of more carcinogenic high molecular weight PAH homologues. In principle, PAH homologues with high molecular weights are often more carcinogenic than those with low molecular weight (Tsai *et al.*, 2002; Park *et al.*, 2002). It is a well-known fact that PAHs are partitioned between particulate matter and gas phase in ambient air. Because of their biological properties, PAHs existence in the

surrounding air has a direct impact on the human population. For example, the lung cancer mortality is increasing in major countries of the world. Thus, survey of PAHs levels in indoor and outdoor air is important as a part of risk assessment and risk management to these chemicals (Liu *et al.*, 2001).

### ***2.3.2 Harm of BaP***

The implication of human exposure to mixtures of PAHs, rather than to individual substances, is important. Occupationally or environmentally, people are never exposed to a single PAH compound, but rather to a mixture of PAHs. In spite of this, BaP concentration is still a great concern because BaP has been shown to be a potent carcinogen in studies on laboratory animals, has been very extensively documented and is as readily as measured. In addition, BaP is often used as a marker for total PAH exposure in industry and in the environment (Lin *et al.*, 2002). PAHs have received increased attention in recent years in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo(a)pyrene (BaP) has been identified as being highly carcinogenic. To understand the extent of human exposure to BaP and other PAHs, reliable sampling and analytical methods are necessary (US EPA 1999).

## 2.4 PAHs profile for emission source

PAHs profiles for sources of relevance in other studies were listed in Table 2.4-1. The PAHs profiles for stationary sources, including steel industry, cement, power plant and incineration; mobile sources, including roadside soil particles, diesel and gasoline vehicle emission; combustion sources, including incomplete combustion, industrial oil burning, wood and coal combustion; indoor sources, including, camphor balls, incense burning and cooking-fuel. From previous studies (Yang *et al.*, 1998; Kulkarni and Venkataraman, 2000; Ho *et al.*, 2002; Park *et al.*, 2002; Caricchia *et al.*, 1999; Omar *et al.*, 2002; Li and Ro, 2000), the following PAHs have been identified as markers for various sources in atmospheres: steel industry – BaP, BaA, PER, BeP, COR and CYC; cement – AcPy, Acp and Ant; power plant – CYC and DBA; incineration – Pyr, PA, Flu, IND and CHR; diesel vehicle emission – AcPy, FL, Flu, PA, Pyr, BNT, CHR and BeP; gasoline vehicle emission – Flu, CHR, IND, BghiP, CYC and COR; roadside soil particles – PA, FL and Pyr; incomplete combustion and pyrolysis of fuels – FL, Pyr, PA, BghiP and IND; combustion sources – Nap, AcPy, Acp, Flu, PA and Ant; industrial oil burning – Pyr, CHR, Flu, BaP and CYC; wood burning – BaP and Flu; coal combustion – PA, Flu and Pyr; camphor balls – Nap; incense burning – FL, Pyr, BaP, BghiP; Cooking-fuel – Pyr and BaP.



Table 2.4-1

## Indicatory PAHs for various major sources

Category		Predominant PAH species	References
Stationary sources	Steel industry	BaP, BaA, PER, BeP, COR, CYC	[1]
	Cement	AcPy, Acp, Ant	[1]
	Power plant	CYC, DBA	[1]
	Incineration	Pyr, PA, Flu, IND, CHR	[1, 2]
Mobile sources	Diesel vehicle emission	AcPy, FL, Flu, PA, Pyr, CHR, BeP	[1, 2, 3, 5]
	Gasoline vehicle emission	Flu, CHR, IND, BghiP, CYC, COR	[1, 2, 3, 5, 6]
	Roadside soil particles	PA, FL, Pyr	[6]
Combustion sources	Incomplete combustion and pyrolysis of fuels	FLT, Pyr, Phen, BghiP, IND	[3]
	Combustion sources	Nap, AcPy, AcP, Flu, PA, Ant	[4]
	Industrial oil burning	Pyr, CHR, Flu, BaP, CYC	[1, 2]
	Wood burning	BaP, Flu	[2]
	Coal combustion	PA, Flu, Pyr	[2]
Indoor sources	Camphor balls	NaP	[7]
	Incense burning	FL, Pyr, BaP, BghiP	[7]
	Cooking-fuel	Pyr, BaP	[2]

References: [1] Yang *et al.*, 1998 [2] Kulkarni and Venkataraman, 2000 [3] Ho *et al.*, 2002 [4] Park *et al.*, 2002 [5] Caricchia *et al.*, 1999 [6] Omar *et al.*, 2002 [7] Li and Ro, 2000.

## 2.5 Statistics Methods

### 2.5.1 Factor Analysis

The basic assumption for receptor models is that the concentration of a pollutant at the receptor ( $X_i$ ) for a given sample is the linear sum of the products of the emission profile ( $a_i$ ) and contribution ( $S_i$ ) of  $n$ -sources, see eq 2.1. Note that  $a_i$  remains constant and  $S_i$  varies with time. Using the Z-score matrix described above, the correlation matrix  $C$  ( $n \times n$ ) is calculated. Factor analysis proceeds through the determination of the eigenvector (factor) matrix which is a matrix of weights each applicable to the variables,  $B$  ( $n \times n$ ), and the corresponding transposition,  $B^{-1}$  ( $n \times n$ ), matrix, which are used to calculate a diagonal table  $\Lambda$  ( $n \times n$ ) using the following equation 2.2: The matrix  $\Lambda$  ( $n \times n$ ) contains the eigenvalues of the corresponding eigenvectors, which are equal to the sum of the squares of the corresponding factor loadings. The number of extracted factors is equal to the number of variables. However, typically a smaller number  $p$ , of eigenvectors (factors) can explain a large fraction of the total variance. Therefore, the dimensionality of the system can be reduced from  $n$  to  $p$ . The virtually infinite number of mathematically equivalent solutions introduces an important limitation to the use of factor analysis. The orthogonal rotation of eigenvectors, where the right angle between the factors is equal to  $90^\circ$ , has been applied to overcome this problem. Oblique rotation was also used to split up correlated factors because the right angle between the factors can be varied and therefore they can take

up any position. Because the initial conclusions from factor loadings are not easily interpretable, these factors are orthogonally transformed using the VARIMAX method. This transformation (rotation) results in high loadings of certain variables on a given factor and relatively low loadings of the others. Therefore, this rotation produces a better correlation of factors with the measured species, allowing them to be attributed to specific sources of organic aerosol. The factor scores (FS) are the product of the component score coefficient matrix ( $W(p \times n)$ ) and the Z-score matrix ( $Z(n \times m)$ ). Since the Z-score is calculated using the mean concentrations, these initially calculated FS values do not correspond to the “real” factor scores.

To determine the “real” factor scores (source contributions), the “absolute zero factor score” must be calculated. This was achieved by separately scoring an extra day where ambient concentrations of elements are set at zero. The difference between the FS and the “absolute zero” FS is the actual factor score (AFS). Finally, by regressing daily concentrations of organic compounds on these AFS values, the source contributions are estimated as follows where  $M_j$  is the concentration of particle mass or element (in  $\text{ng m}^{-3}$ ) for the  $j$ -sample;  $AFS_{kj}^*$  is the rotated absolute factor score for  $k$ -source on sample  $j$ ;  $a_k$  is the regression coefficient of the AFS to organic compounds concentrations; and  $a^0$  is the intercept. The contribution of each factor-source to the total concentration of PAHs can be determined by multiplying the regression coefficients by the corresponding absolute factor score. A similar methodology was previously applied to apportion the sources of heavy metal, volatile organic compounds and PAHs in other studies (Yang *et al.*, 1998;

Dickhut *et al.*, 2000; Li and Ro 2000; Kavouras *et al.*, 2001; Ho *et al.*, 2002; Park *et al.*, 2002; Fang *et al.*, 2003).

$$Xi = \sum_{i=1}^n AiSi \dots\dots\dots (2.1)$$

$$B (nxm) \times C (nxn) \times B^{-1} (nxn) = \Lambda (nxn) \dots\dots\dots (2.2)$$

$$Mj = a^0 \times \sum_{k=1}^p ak(AFS)_{kj} \dots\dots\dots (2.3)$$

### 2.5.2 Hierarchical Cluster Analysis

Cluster analysis is an exploratory multivariate method that can be used to describe the relationships among variables. Classification of variables into groups using cluster analysis does not require prior information on the number and the properties of the groups. Several mathematical criteria can be used to examine the similarity (or difference) between variables and cases. The Euclidean distance defined as the length of the straight line between two points, the square of the Euclidean distance, and the Pearson correlation coefficient ( $R^2$ ) can be used in the classification of data. The Euclidean distance is used to explore similarities between cases, whereas Pearson correlation coefficient measures the similarities between variables. The initial outcome of hierarchical cluster analysis is a number of clusters that is equal to the number of variables. Afterward, a new cluster is formed based on the similarities between variables. This process is repeated as many times as required to form a single cluster. The similarities among the clusters decrease as clusters are merged into a single group. The average method is used to link clusters. Using different methods to measure similarities and link clusters and/or adding small

perturbations can examine the sensitivity and accuracy of cluster analysis. For this application, the Pearson correlation coefficient ( $R^2$ ) was used as a measure of the similarities between the variables, initially, and then between the clusters. The number and the structure of clusters formed using these methods are not affected with either the addition of small numbers of “bad” points or the use of a limited number of measurements. The statistical analysis SPSS 8.0 (Statistical Package for the Social Science) software was used to perform both the cluster and factor analysis by Kavouras *et al.*, (2001) and Ho *et al.*, (2002) to estimate source contribution on organic compound daily concentration.

## Chapter 3

### Experimental Methods

#### 3.1 Sampling program

Two sampling sites were selected to characterize the PAHs concentrations in ambient air in central Taiwan for this study. The location of sampling sites in Taichung city is given in Figure 3.1-1. Taichung Industrial Park (TIP) represents the typical large-scale multiple-industry in Taiwan. Taichung Industrial Park was developed on 580 hectares of land, and there are more than eight hundred factories at TIP sampling site, which include machine, steel, chemical, petroleum, plastic and electronics industry etc. The detailed classified and numbers of industries at Taichung industrial Park were shown in Table 3.1-1. The sampling site located on the roof of a pharmaceutical factory (15 m in height), which is located in the center of TIP. Another sampling site is selected in Tunghai University (THU) as a background site to compare to the neighboring industrial park. THU is located between Taichung City and Taichung County, which is surrounding by various trees and there are about 15,000 students and faculty members. Taichung Veterans General Hospital Incinerator and Taijunggang Road (the main line in Taichung City) are opposite of Tunghai University. The sampling site is located in Tunghai University Campus, the sampling heights were in the range of 1-1.5 m above ground level to simulate the breathing zone. THUC sampling site was also described in a previous study (Fang *et al.*, 2000).

48 h consecutive samplings for PAHs in ambient air were performed between August 2002 and March 2003 at TIP and THUC sampling sites simultaneously. A summary of sampling information (sampling date and meteorological conditions) is also provided in Figure 3.1-1. The range of temperature, relative humidity, average wind speed and atmospheric pressure during sampling period were 16-40 °C, 40-90%, 0.4-12.5 m/s and 1,002.8-1,024.9 hpa, respectively. Furthermore, the prevailing wind was blowing directly from north in this study.

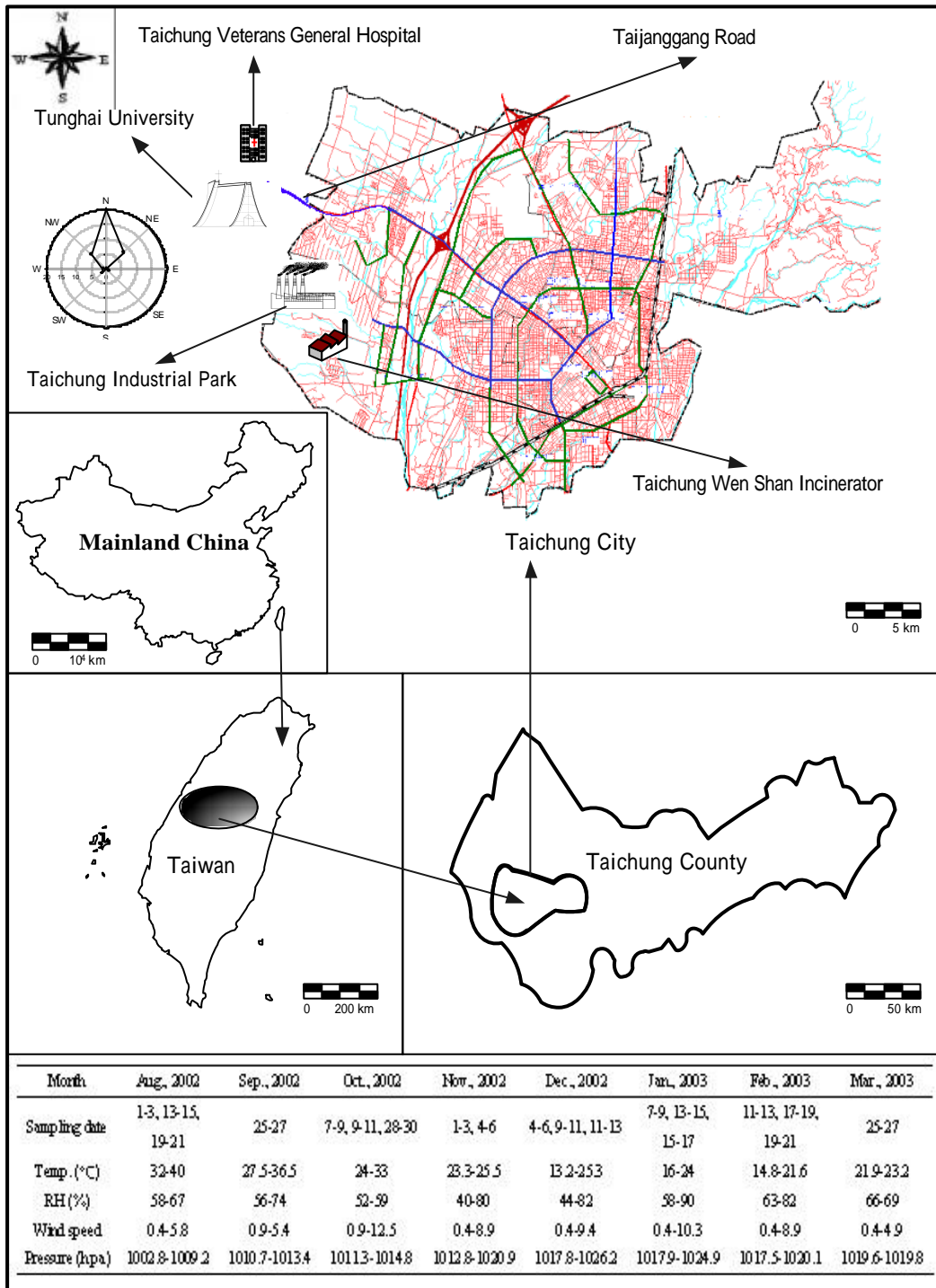


Figure 3.1-1. Sampling information and schematic of Taichung city sampling two sites (Taichung Industrial Park, TIP and Tunghai University Campus, THUC), which include Taichung Wen Shen Incinerator, Taichung Veterans General Hospital Incinerator and Taijanggal Road.



Table 3.1-1

The classified and number of industries at Taichung Industrial Park

NO.	Classification	Number
1	Mechanical industries	152
2	Metalworking industries	94
3	Plastics industries	72
4	Chemical industries	65
5	Printing industries	26
6	Electrical machinery industries	20
7	Steel industries	19
8	Other industries	309
Total		757

### 3.2 Sample collection

The sampling system and sampling procedure for ambient air samples were based on previous study (Fang *et al.*, 2002; Fang *et al.*, 2003). Airborne samples were collected using two PS-1 samplers (GPS1 PUF Sampler, General Metal Work) with a pump drawing air through a tissue quartz filter (2500 QAT-UP, Dimension 102 mm) to collect airborne particle-bound PAHs and total suspended particles. The filter was followed by a glass cartridge (Figure 3.3-1) containing a 5 cm long polyurethane foam (PUF diameter 6 cm) plug, which in turn was followed by 3 cm thick packing of XAD-16 resin (Amberlite), and finally by a 2 cm long PUF plug to collect the gas-phase PAHs. During sample transportation and storage, the PUF plug and resin were stored in a clean jar wrapped with aluminum foil, and quartz filters were placed in sealed CD boxes. Quartz filters were weighed before and after sampling to determine the amounts of particulate collected. Before sampling, quartz filters were baked in an oven at 450 °C for 8 h to remove organic impurities. The glass cartridges were cleaned by sequential Soxhlet extractions with distilled-deionized water, methanol, dichloromethane (DCM) and a mixture of DCM/n-hexane (50/50, v/v) for 24 h in turn and finally dried in a uncontaminated oven at 45 °C to remove residual solvent.

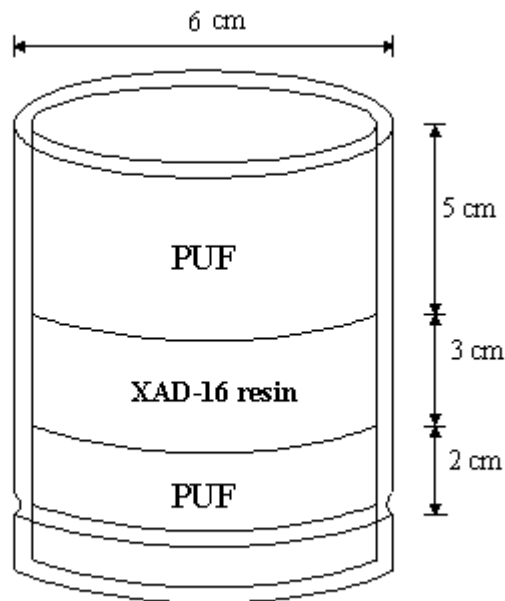


Figure 3.2-1. Glass cartridge (PUF/XAD-16/PUF).

### 3.3 Chemical analysis

The experimental flow chart was shown in figure 3.4-1. For PAH analysis of the samples: after final weighing, all quartz filters and glass cartridges were separately placed in appropriate Soxhlet extractors and extracted with DCM/n-hexane mixture (50/50, v/v) for 24 h. The extract was then concentrated under a rotary evaporator, cleaned and re-concentrated with ultra-pure nitrogen to exactly 1 ml using a procedure which was described previously by Lee *et al.*, (1995). All extracts were analyzed using a gas chromatograph/mass selective detector (GC/MSD) (GC3800, Varian with MS2000, Saturn). The analytical method was based on the USEPA Method TO-13 (U.S. EPA, 1999b).

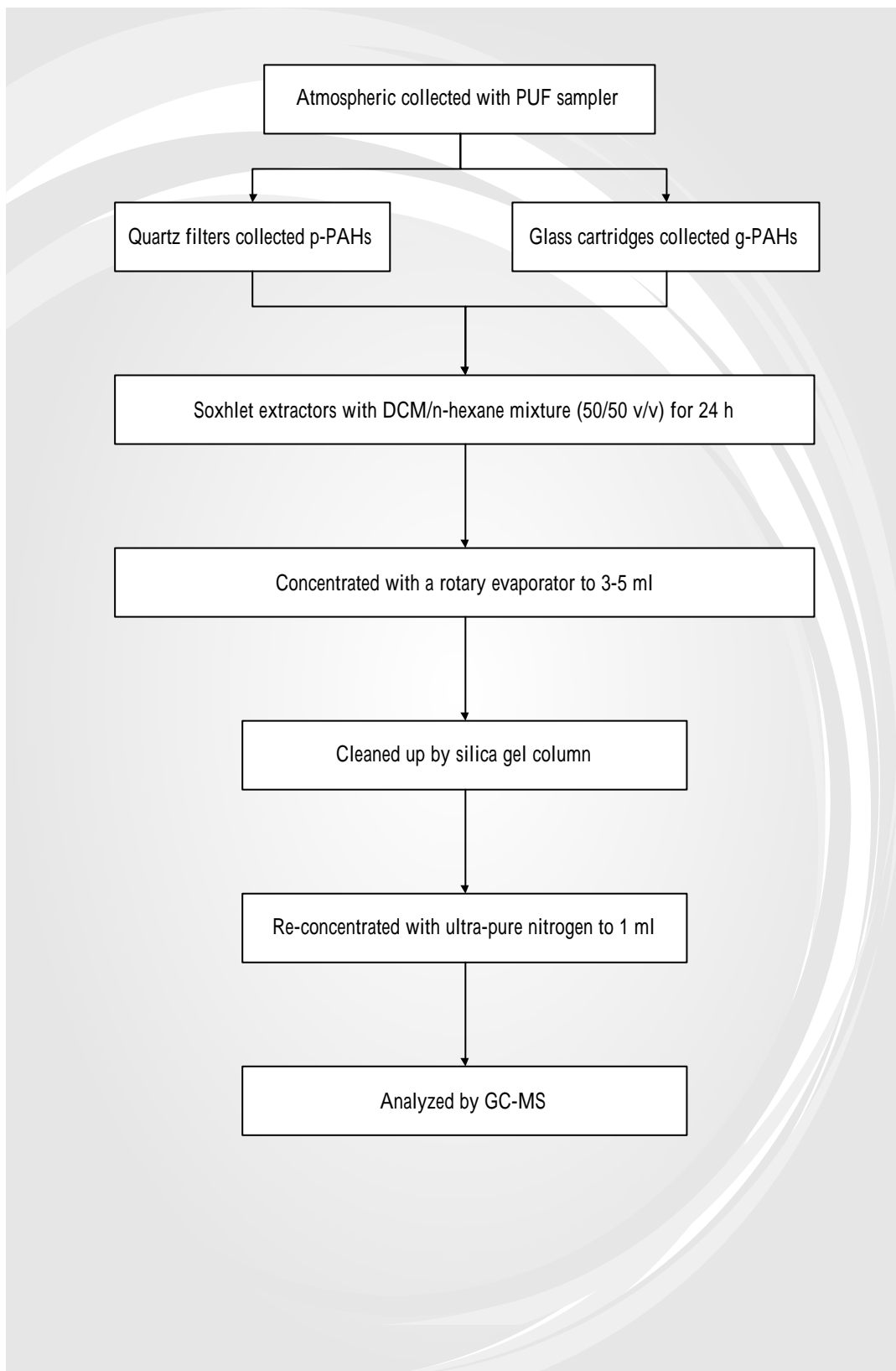


Figure 3.3-1. Experimental flow chart before PAHs sample analyzed.

### 3.4 Sampler device and analysis instrument

#### 3.4.1 PS-1 Sampler

The PS-1 (GPS1 PUF Sampler, General Metal Work) (Figure 3.2-1) consists of nine basic assemblies: dual chamber, sampling module, flow vent, magnehelic gage, voltage, elapsed time indicator, pump, 7-day skip timer, exhaust hose and aluminum shelter. The PS-1 sampler is a complete air sampling system designed to simultaneously collect suspended airborne particles at flow rate up to 280 liter per minute and flow rate was adjusted to 200 liter per minute in this study. The Quartz filter (diameter 10.2  $\mu\text{m}$ ) is used to filter the suspended particle in the study. The filters were first conditioned for 24 hrs under an electric chamber at humidity  $50 \pm 5\%$  and temperature  $25 \pm 5^\circ\text{C}$  prior to both on weight and off weighing. Filters were placed in sealed CD box during transport and storage process.



Figure 3.4-1. The structure of PUF Sampler used for PAHs collections.

### ***3.4.2 Weather Monitor***

The Weather Monitor II (#7440) is packed with important weather functions. It features a thoughtfully designed keyboard and display, with an intuitive, “user friendly” interface. Highs and lows are maintained for most functions and can be quickly viewed along with the time and date they occurred. User-programmable alarms can alert you to changes in weather conditions. There are even special alarms to announce rapid changes in barometric pressure or signal that temperature is approaching the dew point. A continuously displayed compass rose shows at a glance the current wind direction and speed in one of four units of measure: miles per hour, kilometers per hour, knots, or meters per second. The barometric trend arrow gives a visual indicator of rising, falling, or steady barometric pressure.



Figure 3.4-2. The illustration of Weather Monitor II.

### 3.4.3 Soxhlet extractor

An apparatus for cleaning samples which was using the distillation extraction method. In the Soxhlet apparatus (also called extractor, or chamber), the sample soaks in hot solvent that is periodically siphoned off, distilled and returned to the sample. The process continues until the siphoned-off solvent becomes clear. In the Soxhlet apparatus, the sample soaks in the solvent, while in the Dean-Stark apparatus, the solvent flows through the sample from top to bottom.



Figure 3.4-3. Soxhlet extractor for PAHs sample extracted.

### 3.4.4 Rotary evaporator

Rotary evaporators are used to remove solvents from reaction mixtures and can accommodate volumes as large as 3 liters. They are found in almost every organic laboratory. A typical rotary evaporator has a heatable water bath to keep the solvent from freezing during the evaporation process. The solvent is evaporated under vacuum, trapped by a condenser and is collected for easy reuse or disposal. Most labs use a simple water aspirator vacuum on their rotavaps, so a rotavap can not be used for air and water-sensitive materials unless special precautions are taken.



Figure 3.4-4. The structure of rotary evaporator for concentrated process.



### 3.4.5 Gas chromatograph / mass selective detector

All extracts were analyzed using a gas chromatograph/mass selective detector (GC/MSD) (GC 3800, Varian with MS 2000, Saturn) with an GC capillary column (30 m × 0.25 mm × 0.25 μm, DB-5). A computer-controlled automatic sampler (Model 8200) was used in conjunction with the GC/MS system. 1 μl of sample was injected in a splitless-mode. The injector and transfer line temperatures were 310 and 300 °C, respectively. The temperature program used was: 35 °C holds 3 min, then to 180 °C at 25 °C min<sup>-1</sup> and hold 2 min, then to 200 °C at 20 °C min<sup>-1</sup> and hold 2 min, then to 300 °C at 2 °C min<sup>-1</sup> and hold 6.4 min, total time 70 min.



Figure 3.4-5. GC 3800, Varian with MS 2000, Saturn.

### 3.5 Quality Control

Atmospheric PAHs sampling was used PS-1 sampler, PS-1 volumetric flow control was carried out before sampling. The GMW-40 Calibrator is used to calibrate the volumetric flow of PS-1. The processes of calibration are as follow:

1. Calibration of the PS-1 sampler is performed without a foam slug of filter paper in the sampling module.
2. Install the GMW-40 Calibrator on top of the 4" filter holder.
3. Connect an 8" water manometer to the calibrator.
4. Open the ball value fully.
5. Turn the system on by tripping the manual switch on the timer. Allow a few minutes for warm-up.
6. Adjust the voltage control screw to obtain a reading of 70 inches on the Magnehelic Gage.
7. With 70 inches on the dial gage as the first calibration point, record in and the manometer reading on data sheet.
8. Close the ball value slightly to readjust the dial gage down to 60 inches, record this figure and manometer reading on the data sheet.
9. Using the above procedure, adjust the ball value for readings at 50, 45, 40, 35, 30, 25, 20, 15, 10 and 5 inches and record on the data sheet.
10. Using these two sets of readings, plot a curve on the data sheet. This curve will be used for determining the actual flow rate in the field.
11. Readjust the voltage control fully clockwise to it is maximum setting. Open ball valve fully.

After each 48 h sampling, the filter and glass cartridges were stored at 4°C and analyzed within 15 days from collection. Quantification of PAHs were according to the retention times and peak areas of the calibration standards. The instruments were calibrated using at least five standard concentrations covering the concentration of interest for ambient air work. Correlation coefficient of the calibration curve was  $> 0.995$  for linear least-squares fit of the data. The detailed illustration was listed in appendix.

For the recovery test, at least 10% of the samples are analyzed in spiking with a known amount of PAHs to calculate recovery efficiencies. For example: First, detected the unknown BaP sample by GC/MS obtained the concentrations, then 1 mg L<sup>-1</sup> of BaP standard was added to unknown sample. Finally, found concentrations of BaP has 2.02 mg L<sup>-1</sup> and calculate recovery efficiencies. Recovery of BaP (%):  $(2.02 - 1) / 1 \times 100\% = 102\%$ . Method detection limit (MDL) was used to determine the lowest concentration level that can be detected to be statistically different from a blank. MDL was determined from selected the concentration slightly higher than lowest concentration of the standard line. Repeat this blank concentration for seven times to estimate the standard deviation. Then, the MDL was based on three times the standard deviation of the blank concentration.

The concentrations of the following PAHs were quantified in this study. Individual PAHs were according to their elution orders, recoveries (r) and method detection limits (mg L<sup>-1</sup>) for PAHs analysis were as followed: naphthalene (Nap, m/z 128, r 88%, 0.059 mg L<sup>-1</sup>), acenaphthylene (AcPy, m/z 152, r 93%, 0.091 mg L<sup>-1</sup>), acenaphthene (Acp, m/z 154, r 89%,

0.084 mg L<sup>-1</sup>), fluorene (Flu, m/z 166, r 91%, 0.072 mg L<sup>-1</sup>), phenanthrene (PA, m/z 178, r 85%, 0.171 mg L<sup>-1</sup>), anthracene (Ant, m/z 178, r 94%, 0.095 mg L<sup>-1</sup>), fluoranthene (FL, m/z 202, r 98%, 0.091 mg L<sup>-1</sup>), pyrene (Pyr, m/z 202, r 99%, 0.095 mg L<sup>-1</sup>), cyclopenta(c,d)pyrene (CYC, m/z 226, r 99%, 0.117 mg L<sup>-1</sup>), benzo(a)anthracene (BaA, m/z 228, r 95%, 0.116 mg L<sup>-1</sup>), chrysene (CHR, m/z 228, 101%, 0.531 mg L<sup>-1</sup>), benzo(b)fluoranthene (BbF, m/z 252, r 92%, 0.110 mg L<sup>-1</sup>), benzo(k)fluoranthene (BkF, m/z 252, r 101%, 0.329 mg L<sup>-1</sup>), benzo(e)pyrene (BeP, m/z 252, r 77%, 0.047 mg L<sup>-1</sup>), benzo(a)pyrene (BaP, m/z 252, r 86%, 0.183 mg L<sup>-1</sup>), perylene (PER, m/z 252, r 86%, 0.046 mg L<sup>-1</sup>), indeno(1,2,3,-cd)pyrene (IND, m/z 276, r 89%, 0.074 mg L<sup>-1</sup>), dibenzo(a,h)anthracene (DBA, m/z 278, r 91%, 0.054 mg L<sup>-1</sup>), benzo(b)chrycene (BbC, m/z 278, r 90%, 0.067 mg L<sup>-1</sup>), benzo(ghi)perylene (BghiP, m/z 276, r 95%, 0.093 mg L<sup>-1</sup>) and coronene (COR, m/z 300, r 99%, 0.117 mg L<sup>-1</sup>).

The characteristics of twenty one PAHs are shown in Table 3.5-1 and the concentrations of the following PAHs were quantified in this study and those PAHs were displayed according to their elution orders.

Table 3.5-1

The characteristic of twenty one PAHs (US EPA TO-13A)

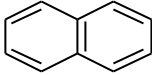
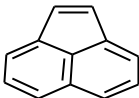
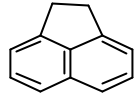
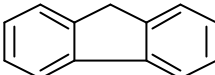
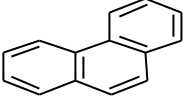
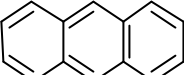
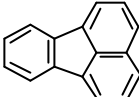
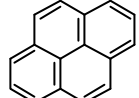
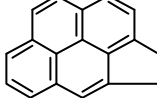
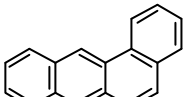
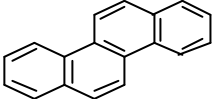
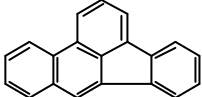
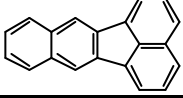
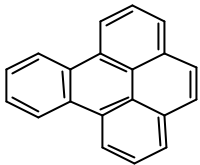
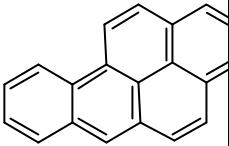
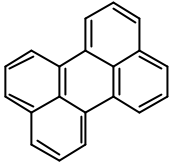
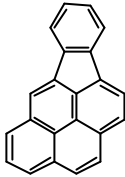
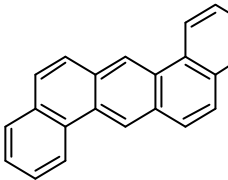
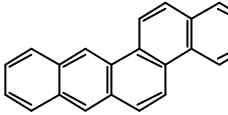
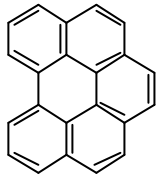
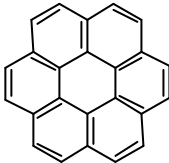
Compound	Abbr. <sup>a</sup>	MW <sup>b</sup>	Ring Structure	FP <sup>c</sup> (°C)	BP <sup>d</sup> (°C)
Naphthalene	Nap	128		81	218
Acenaphthylene	AcPy	152		93	270
Acenaphthene	Acp	154		96	279
Fluorene	Flu	165		117	294
Phenanthrene	PA	178		101	340
Anthracene	Ant	178		216	340
Fluoranthene	FL	202		111	383
Pyrene	Pyr	202		156	404
Cyclopenta[ <i>c,d</i> ]pyrene	CYC	228		N.A.	N.A.
Benz[ <i>a</i> ]anthracene	BaA	228		162	400
Chrysene	CHR	228		256	448
Benzo[ <i>b</i> ]fluoranthene	BbF	252		168	481
Benzo[ <i>k</i> ]fluoranthene	BkF	252		217	481

Table 3.5-1 (continued)

Compound	Abbr.	MW	Ring Structure	FP (°C)	BP (°C)
Benz[ <i>e</i> ]pyrene	BeP	252		179	493
Benzo[ <i>a</i> ]pyrene	BaP	252		177	496
Perylene	PER	252		278	NR
Indeno[1,2,3- <i>cd</i> ]pyrene	IND	276		N.A.	534
Dibenz[ <i>a,h</i> ]anthracene	DBA	278		270	535
Benzo[ <i>b</i> ]chrycene	BbC	278		294	N.A.
Benzo[ <i>g,h,i</i> ]perylene	BghiP	276		278	542
Coronene	COR	300		439	525

<sup>a</sup> Abbreviate. <sup>b</sup> Molecule Weight. <sup>c</sup> Fusing Point. <sup>d</sup> Boiling Point.

## Chapter 4

### Results and discussion

#### 4.1 PAHs in ambient air

Average TSP concentrations at TIP and THUC sampling sites were found to be  $87.5 \pm 38.5 \mu\text{g m}^{-3}$  and  $69.8 \pm 36.2 \mu\text{g m}^{-3}$ , respectively. In addition, the total PAHs concentrations at these sampling sites were found to be  $1434.5 \pm 1133.7 \text{ ng m}^{-3}$  and  $732.1 \pm 512.2 \text{ ng m}^{-3}$ , respectively.

PAHs can be classified by their numbers of aromatic ring as follows: 2-ring including Nap; 3-ring including AcPy, Acp, Flu, PA and Ant; 4-ring including FL, Pyr, BaA and CHR; 5-ring including CYC, BbF, BkF, BeP, BaP and PER; 6-ring including IND, DBA, BbC and BghiP; 7-ring including COR. PAHs having more aromatic rings, in general, represent higher molecular weights. PAHs can also be further classified into lower molecular weight (LMW containing 2- and 3-ringed PAHs), middle molecular weight (MMW containing 4-ring PAHs) and higher molecular weight PAHs (HMW containing 5-, 6- and 7-ringed PAHs) (Yang *et al.*, 1998).

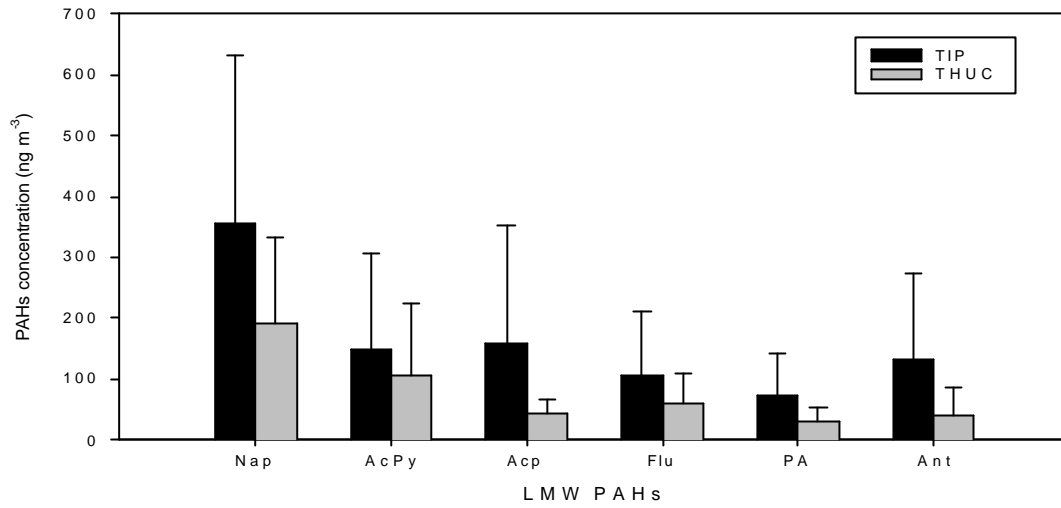
Profile of mean gas-phase PAHs (g-PAHs) and particle-phase PAHs (p-PAHs) were shown in Figure 4.1-1 and Figure 4.1-2, respectively. At TIP sampling site, most of the gas-phase PAHs concentrations were higher than those of the THUC sampling site. There are heavy traffic vehicle during working time and more than eight hundred factories are located at Taichung Industrial Park, which included 152 mechanical

industries, 94 metalworking industries, 72 plastic industries and 65 chemical and petroleum industries etc. This is the major reason for the high PAHs concentrations at TIP sampling site than THUC sampling site. Moreover, washout, dry deposition and mixing decrease the concentration of PAHs in the atmosphere during transport from urban areas, decomposition of these compounds via photo-oxidation is also suspected to reduce levels reaching non-urban areas (Odabasi *et al.*, 1999); BaA, IND and BghiP were three exceptions for these sampling sites. In the term of g-PAHs, LMW PAHs were the highest concentrations, and the order was MMW PAHs and HMW PAHs. Among LMW PAHs, Nap was the most abundant and the principal PAHs with average concentrations of 356.6 ng m<sup>-3</sup> and 27% of total gas-phase PAHs (1305.4 ng m<sup>-3</sup>) at TIP sampling site. Following that were Acp, AcPy, Ant, Flu and PA at 159.7, 147.5, 131.1, 106.4 and 73.6 ng m<sup>-3</sup>, respectively, while MMW PAHs had individual average concentrations all below 70 ng m<sup>-3</sup> and HMW PAHs had individual average concentrations all below 30 ng m<sup>-3</sup>. As for THUC sampling site, Nap was also found the abundant and principal, with average concentrations of 190.6 ng m<sup>-3</sup> and 29% of total gas-phase PAHs (646.2 ng m<sup>-3</sup>), followed by AcPy, Flu, Acp, Ant and PA at 104.7, 61.2, 41.8, 41.6 and 29.2 ng m<sup>-3</sup>, respectively, other MMW and HMW PAHs were within 30 and 20 ng m<sup>-3</sup>, respectively.

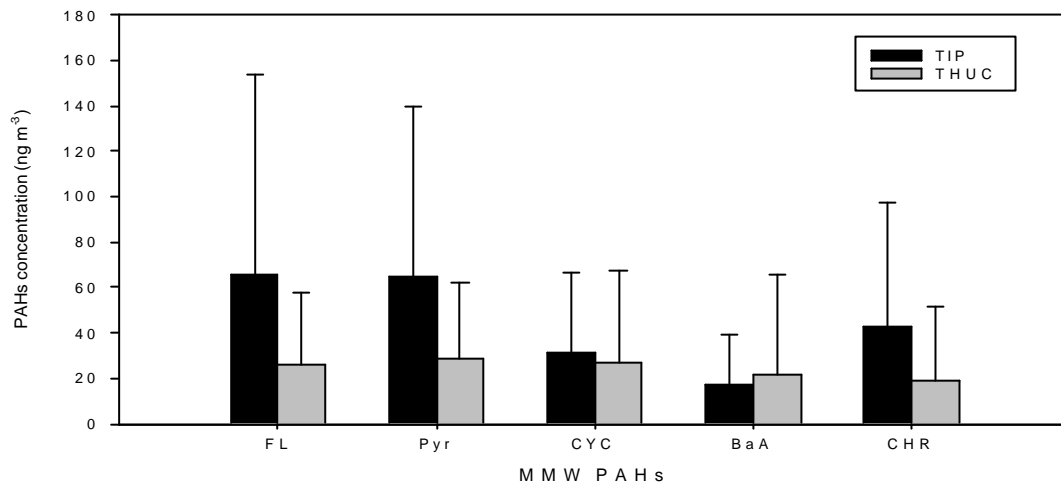
Different phenomenon can also be found in p-PAHs, the average total p-PAHs concentrations were 129.1 ng m<sup>-3</sup> and HMW PAHs are predominant in particle-phase PAHs. Following that for p-PAHs are LMW and MMW PAHs. Three highest concentrations were PER, COR and BbC; at 20.8, 18.3 and 11.9 ng m<sup>-3</sup>, respectively, at TIP sampling site.



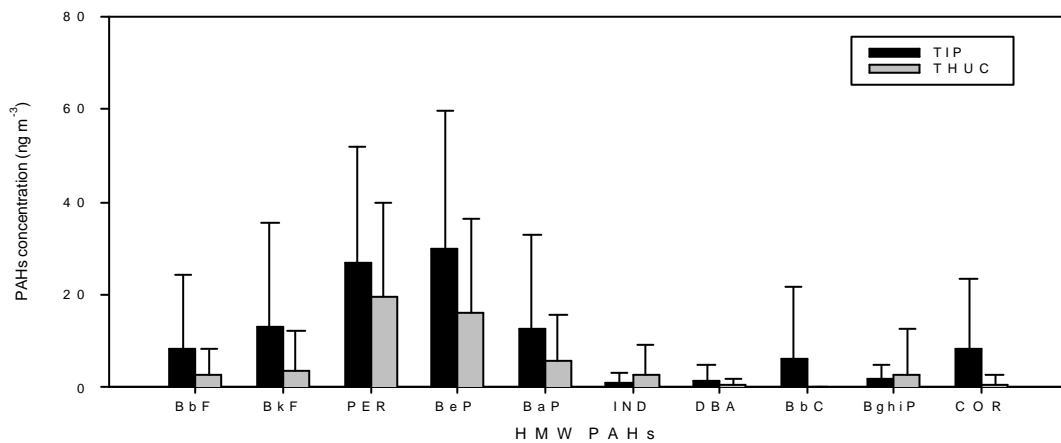
The result of the other average PAHs concentrations were all below 10 ng m<sup>-3</sup>. As for THUC sampling site, total p-PAHs concentrations was 85.9 ng m<sup>-3</sup>, and the other three highest p-PAHs concentrations for COR, BbC and PER were 12.8, 9.9 and 9.4 ng m<sup>-3</sup>, respectively. And the rest of the other PAHs concentrations were less than 5 ng m<sup>-3</sup>. The results indicated that LMW PAHs are predominant in g-PAHs and HMW PAHs are abundant in p-PAHs which were agreed with previous study (Yang *et al.*, 2002; Tsai *et al.*, 2002; Odabasi *et al.*, 1999; Lee *et al.*, 1995).



(a)

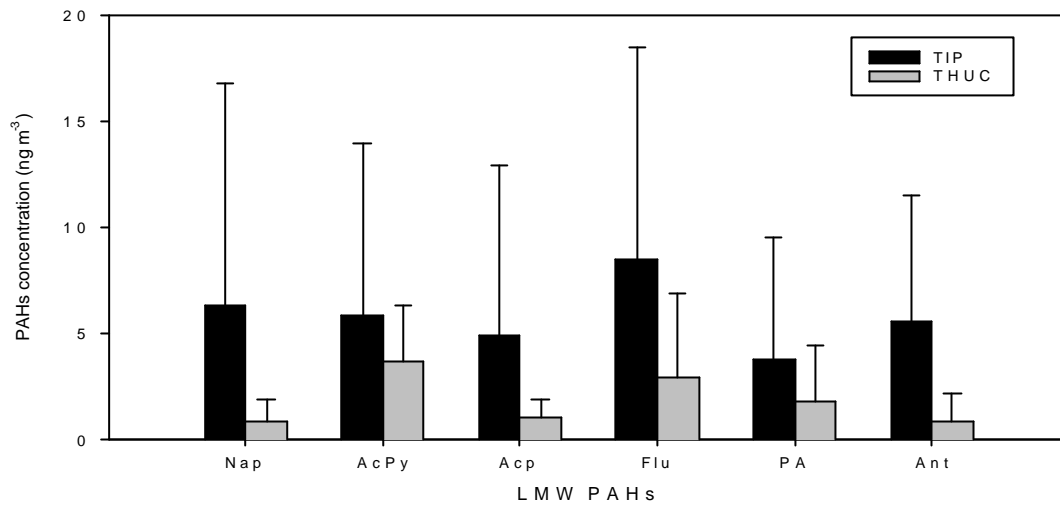


(b)

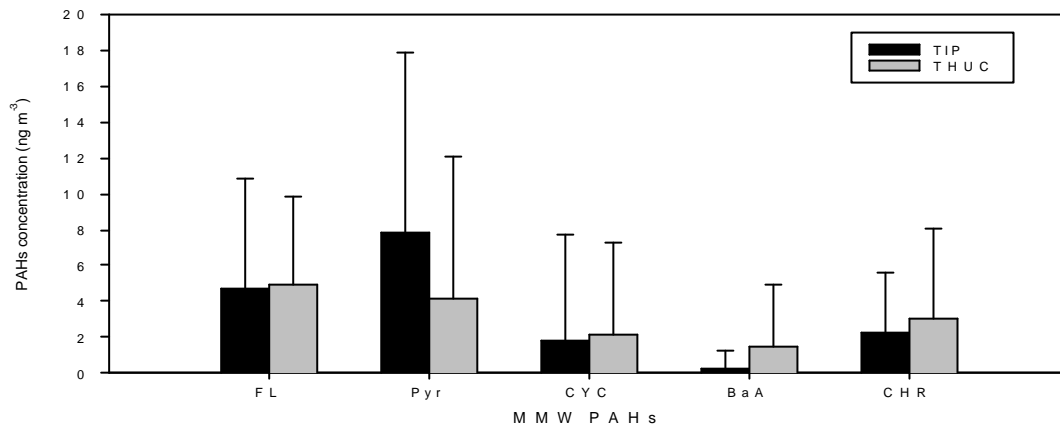


(c)

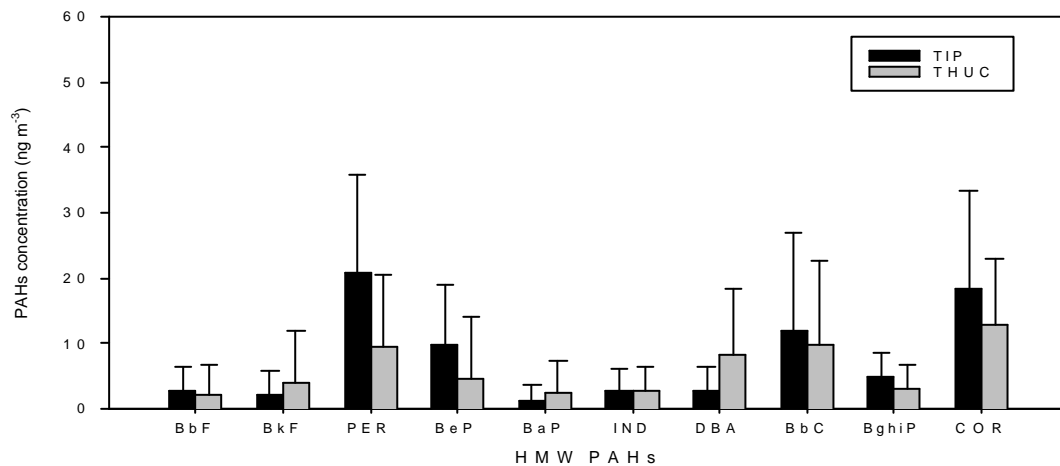
Figure 4.1-1 Profile of mean gas-phase individual (a) low molecular weight (b) middle molecular weight and (c) high molecular weight PAHs concentrations in ambient air at TIP and THUC sampling sites.



(a)



(b)



(c)

Figure 4.1-2 Profile of mean particle-phase individual (a) low molecular weight (b) middle molecular weight and (c) high molecular weight PAHs concentrations in ambient air at TIP and THUC sampling sites.

## 4.2 Effects of meteorological parameters

Pearson correlation matrix between PAHs and other meteorological parameters at TIP and THUC sampling sites were shown in Table 4.2-1. No significant correlations were observed between PAHs concentration and meteorological parameters such as wind speed, relative humidity and atmospheric pressure. Among the meteorological parameters the correlation between temperature and PAHs concentration were the highest. Temperature between g-PAHs and t-PAHs concentration showed a moderate level of negative correlation at two sampling sites. The correlation coefficients between temperature and g-PAHs were  $R_{THUC} = -0.459$  and  $R_{TIP} = -0.604$ , respectively, and the correlation coefficients between temperature and t-PAHs were  $R_{THUC} = -0.481$  and  $R_{TIP} = -0.607$ , respectively. This observation agreed with that reports which demonstrated that higher temperature is associated with lower PAHs concentration (Park *et al.*, 2002). However, temperature and p-PAHs had low negative correlation coefficients ( $R_{THUC} = -0.022$  and  $R_{TIP} = -0.216$ ) at TIP and THUC sampling site, respectively. TSP and PAHs also have moderate correlation at THUC and TIP sampling sites. It suggested that TSP and PAHs were come from the same source at both sampling sites. The highest position correlation of g-PAHs and t-PAHs ( $R_{TIP} = 0.997$  and  $R_{THUC} = 0.992$ ) are found in this study, which indicated that g-PAHs were the major portions of t-PAHs.

Table 4.2-1

Pearson correlation matrix between PAHs and other meteorological parameters

	1	2	3	4	5	6	7	8
(1) Temp.		0.08	-0.205	-0.754	-0.106	-0.459	-0.022	-0.481
(2) RH	0.08		0.055	0.152	-0.491	-0.352	-0.044	-0.372
(3) WS	-0.205	0.055		0.257	-0.368	-0.029	-0.328	-0.075
(4) P.	-0.754	0.152	0.257		-0.441	0.211	-0.034	0.215
(5) TSP conc.	0.014	-0.258	-0.637	-0.239		0.548	-0.078	0.559
(6) g-PAHs	-0.604	-0.54	-0.202	0.17	0.564		-0.347	0.992
(7) p-PAHs	-0.216	0.35	-0.388	-0.07	0.421	0.26		-0.223
(8) t-PAHs	-0.607	-0.502	-0.227	0.161	0.583	0.997	0.33	

Note: Value in row i and column j of the upper triangle were the correlation between compound i and compound j for the meteorological parameters and pollutant concentrations at THUC sampling site; value in row i and column j of the lower triangle give the correlation between compound i and j for the meteorological parameters and pollutant concentrations at TIP sampling site.

RH <sup>a</sup>: Relative humidity.

WS <sup>b</sup>: Wind speed.

P <sup>c</sup>: Atmospheric pressure.

g-PAHs <sup>d</sup>: gas-phase PAHs.

p-PAHs <sup>e</sup>: particle-phase PAHs.

t-PAHs <sup>f</sup>: total PAHs (gas + particle phase).

### 4.3 PAHs source identification using factor analysis

The determination of indicatory PAHs from emission sources is the first step for apportionment of PAHs contribution to the ambient air. We screen the category source at both sampling sites base on Table 2.4-1. The PAHs profiles for stationary sources, including steel industry, cement industry, power plant and incineration; mobile sources, including diesel and gasoline vehicle emission. From previous studies (Yang *et al.*, 1998; Kulkarni and Venkataraman, 2000; Ho *et al.*, 2002; Caricchia *et al.*, 1999; Omar *et al.*, 2002), the following PAHs have been identified as markers for various sources in atmospheres: steel industry – BaP, BaA, PER, BeP, COR and CYC; cement plant – AcPy, Acp and Ant; power plant – CYC and DBA; incineration – Pyr, PA, Flu, IND and CHR; diesel vehicle emission – AcPy, FL, Flu, PA, Pyr, CHR and BeP; gasoline vehicle emission – Flu, CHR, IND, BghiP, CYC and COR.

Principal component analysis (PCA) is the oldest and most widely used multivariate statistical technique in the atmospheric sciences. The principle of PCA is to transform the original set of variables into a smaller set of linear combinations that account for most of the variance of the original set. The primary function of this analysis is the reduction of the number of variables while retaining the original information as much as possible, and thus variables with similar characteristics can be grouped into factors (Ho *et al.*, 2002). Source groupings were determined using PCA with varimax rotation and retention of principal components having eigenvalues  $> 1$  of the complete the data set of PAHs concentrations. Factor analysis in this study was carried out using the statistical analysis

SPSS 8.0 software.

Figure 4.3-1 shows the factor loading of three retained factors that account for PAHs data at TIP and THUC sampling sites. At TIP sampling site, Factor 1 (PC1) explained 28.775% of the variance of data and has high loading for Nap (0.746), Flu (0.815), PA (0.803) and Pyr (0.771); moderate loading for AcPy (0.663) and Acp (0.647) which were identified as the “Diesel vehicle emission”. The main sources of these PAHs are the primary emission from diesel exhaust, that also can attributed to diesel truck active frequently at TIP sampling site. Factor 2 (PC2) presents 27.577% of the variance and a close association between Ant (0.831), FL (0.795), CYC (0.747), BaA (0.776), CHR (0.932), BeP (0.934) and PER (0.841); moderate loading for Nap (0.556), AcPy (0.518), Acp (0.615) and BkF (0.508). Clearly, PC2 is related to exhaust emissions from “Industry source”. There are more than eight hundred factories are located at Taichung Industrial Park, which included 152 mechanical industries, 94 metalworking industries, 19 steel industries etc., which are major factor in this. Factor 3 (PC3) had 16.545% of variance and no high loading.

As for THUC sampling site, three factors were also obtained and analyzed. PC1, PC2 and PC3 were associated with “Incineration source”, “Gasoline vehicle emission” and “Industry source / Power plant”, respectively. The data were recorded as PC1 had high loading for Flu (0.774), PA (0.800), Ant (0.891), Pyr (0.928), CHR (0.789) and BbF (0.851), PC2 had high loading for IND (0.861) and BghiP (0.815); moderate loading for COR (0.576), while PC3 showed high loading for CYC (0.715), BaA (0.862), PER (0.93) and DBA (0.785), respectively.

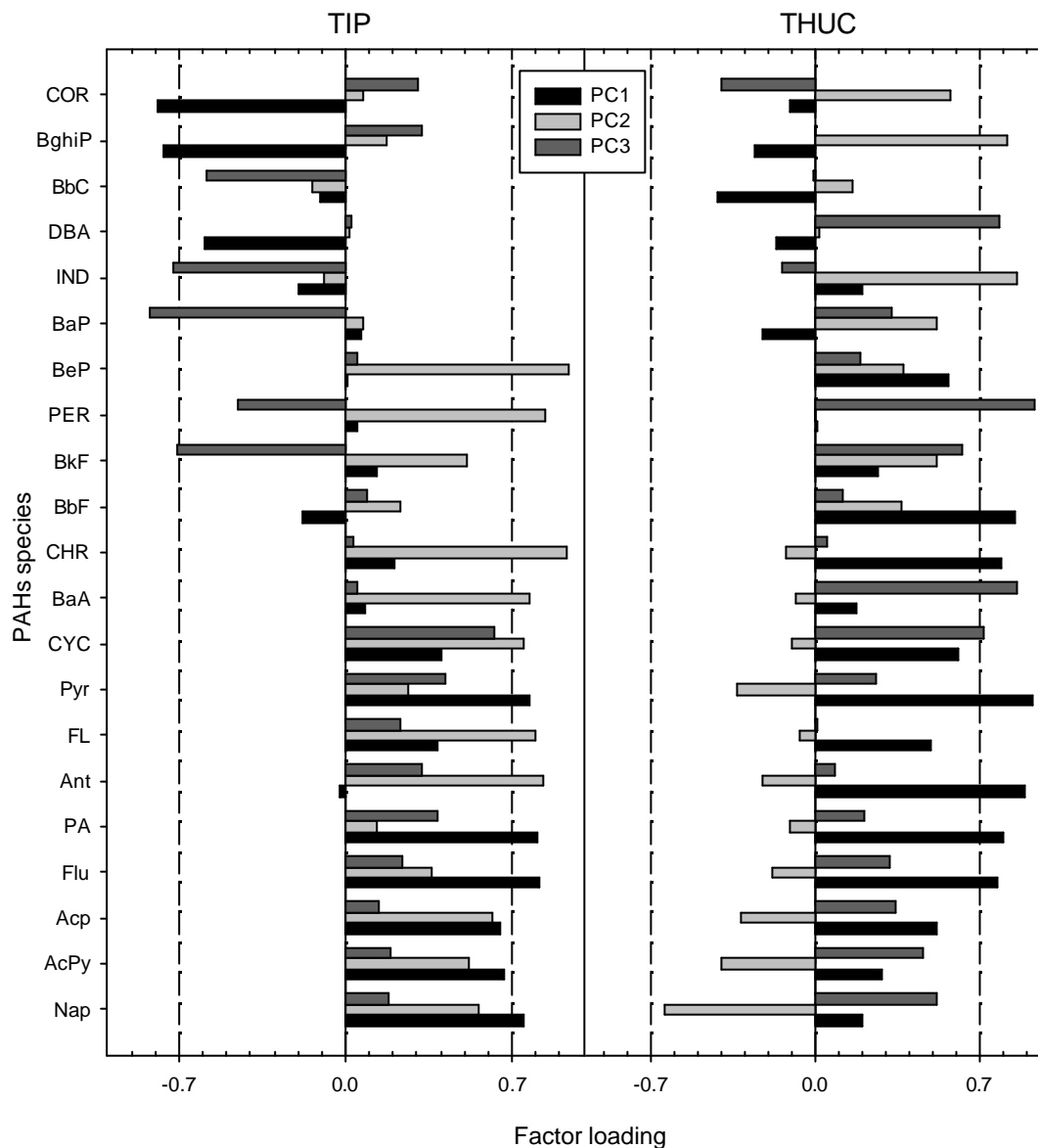


Figure 4.3-1 Principal components analysis of ambient air PAHs concentration at TIP and THU sampling sites. PC1, PC2 and PC3 presents 28.8%, 27.6% and 16.5% of the variance at TIP sampling site; 28.7%, 19.6% and 17.7% of the variance at THU sampling site, respectively.



#### 4.4 Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is a way of identifying meaningful aggregations. The primary function of cluster analysis is to uncover the interrelationship among variable (Ho et al., 2002). The Euclidean distance defined as the length of the straight line between two points, the square of the Euclidean distance, and the Pearson correlation coefficient ( $R^2$ ) can be used in the classification of data. The Euclidean distance is used to explore similarities between cases, whereas Pearson correlation coefficient measures the similarities between variables (Kavouras et al., 2001). Therefore, Ward's method and Euclidean square distances were applied for hierarchical cluster analysis in this study.

Figure 4.4-1 and 4.4-2 depicts the HCA results at TIP and THUC sampling site, there are two large clusters can be separated at two sampling sites. At TIP sampling site, the first cluster (Cluster 1) was composed of BbC, BghiP, CYC, CHR, BeP, PER, FL and COR. These PAHs are come from Industry emission source. AcPy, Acp, PA, Pyr, Flu and Ant were included in second cluster (Cluster 2), these PAHs are diesel vehicle source. At THUC sampling site, BbC, DBA, BghiP, BaA, PER, CYC, Flu, Ant, FL, CHR, PA, BeP, Acp, Pyr and COR were included in Cluster 1 and 2, these PAHs have both sources (Gasoline vehicle and stationary source), and Cluster 3 (Nap and AcPy) is represented combustion sources, respectively. The result of source identification by HCA was agreed with PCA, and it provided a useful method for identification PAHs sources during varied meteorological condition and emission sources.

## Dendrogram using Ward Method

### Rescaled Distance Cluster Combine

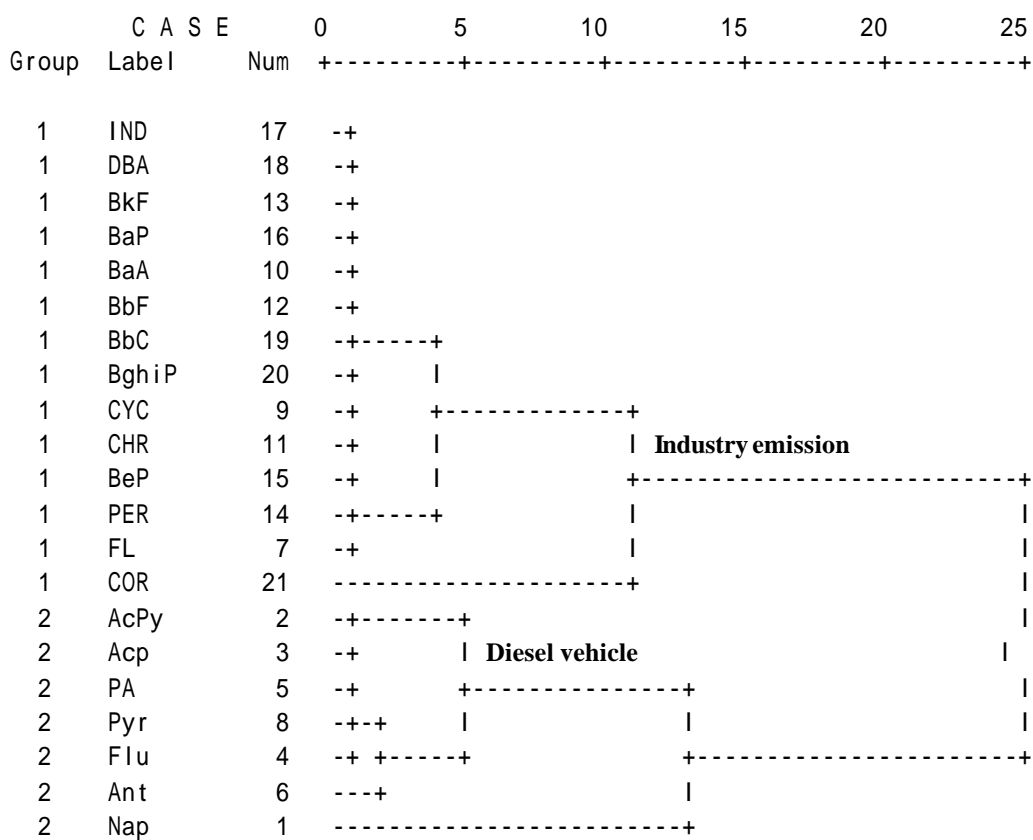


Figure 4.4-1 Hierarchical cluster analysis of polycyclic aromatic hydrocarbons (PAHs) at TIP sampling site.

## Dendrogram using Ward Method

### Rescaled Distance Cluster Combine

Group	C A S E	0	5	10	15	20	25
		Num	+-----+-----+-----+-----+-----+				
1	BbF	12	-+				
1	BaP	16	-+				
1	BkF	13	-+				
1	IND	17	-+				
1	BbC	19	-+-----+				
1	DBA	18	-+				
1	BghiP	20	-+				
1	BaA	10	-+	+-----+			
2	PER	14	-++				
2	CYC	9	-+				
2	Flu	4	-++-----+				
2	Ant	6	-+	<b>Stationary source</b>			<b>Gasoline vehicle</b>
2	FL	7	-+			+-----+	
2	CHR	11	-+				
2	PA	5	-+				
2	BeP	15	-++				
2	Acp	3	-+				
2	Pyr	8	-+				
2	COR	21	------+				
3	Nap	1	------+				+-----+
3	AcPy	2	------+	<b>combustion</b>			

Figure 4.4-2 Hierarchical cluster analysis of polycyclic aromatic hydrocarbons (PAHs) at THUC sampling site.

#### 4.5 Comparison of PAHs concentration in Europe, America and Asia

Table 4.5-1 was showed the results of comparison of atmospheric PAHs concentrations with other studies in Europe, America and Asia areas. In general, the results indicated that special sampling sites such as indoor Hangzhou, urban Hangzhou, traffic Tainan, indoor temple and industrial park (TIP) possessed extreme high t-PAHs average concentrations, which were recorded as 10,569.5, 9,775.8, 8,110, 6,258 and 1,434.5 ng m<sup>-3</sup>, respectively. At the traffic, rural, urban and suburban sampling site, Asia countries have higher t-PAHs concentrations than Europe and America. Urban Hangzhou (China) had the highest t-PAHs concentrations (averaged 9,775.8/10,569.5 ng m<sup>-3</sup>, Outdoor/Indoor) during 1999. Urban Tainan (Taiwan) had the second high t-PAHs concentration (averaged 1520 ng m<sup>-3</sup>) between 1991 and 1992. Following urban Hong Kong had the third high t-PAHs concentrations (averaged 1083.8 ng m<sup>-3</sup>). The t-PAHs concentration at suburban Taichung (THUC, Taiwan) was found to be 732.1 ng m<sup>-3</sup> which is about similar the average PAHs concentrations in the other Asia countries (including, traffic, urban, suburban and rural sampling site, excepted traffic Tainan), and is about 3.5 times higher than Europe and America counties (including, traffic, urban and rural sampling sites).

As for p-PAHs concentration, semi open temple sampling site have the highest p-PAHs concentration, which were recorded as 490 ng m<sup>-3</sup>. The industrial sampling site in the world, Inchon (Korea) has the highest p-PAHs concentration (average 410/101 ng m<sup>-3</sup>, winter/spring). Following that for p-PAHs concentrations are Taichung (Taiwan), Naples (Italy) and

Mumbai (India) which were recorded as 129.1, 39.5 and 38.8 ng m<sup>-3</sup>, respectively. However, concentration of p-PAHs at area of suburban in Taichung, Taiwan (THUC) were recorded as 85.9 ng m<sup>-3</sup> which is about 1.4 times higher than the other sampling sites (urban, rural and residential) of Asia area, and is about 7.8 times higher than the other sampling sites of America and Europe areas.

There are different in number and species in the various studies, these compare cannot represent each site genuine PAHs concentrations. Therefore, this study also compare individual PAH which has the highest toxic environmental factors (TEFs) such as DBA and BaP, this is based in the report of WHO (1998). The highest t-BaP concentration at Tainan temple was 102.1 ng m<sup>-3</sup>, followed that were indoor Hangzhou (11.7 ng m<sup>-3</sup>), suburban Tainan (10.3 ng m<sup>-3</sup>), urban Hangzhou (9.4 ng m<sup>-3</sup>), industrial Taichung (7.6 ng m<sup>-3</sup> in this study), suburban Taichung (3.6 ng m<sup>-3</sup> in this study), urban Seoul (2.55 ng m<sup>-3</sup>) and indoor Taipei (2.4 ng m<sup>-3</sup>), respectively. The other t-BaP concentrations studies were all below 2 ng m<sup>-3</sup>. As for t-DBA concentrations, the highest concentrations were also occurred at Tainan temple (22.8 ng m<sup>-3</sup>). Followed by industrial Taichung (7.0 ng m<sup>-3</sup> in this study), suburban Taichung (5.1 ng m<sup>-3</sup> in this study), indoor Taipei (3.5 ng m<sup>-3</sup> incense-burning room), urban Taipei (3.3 ng m<sup>-3</sup>), indoor Taipei (2.9 ng m<sup>-3</sup>), suburban Tainan (2.4 ng m<sup>-3</sup>) and traffic tunnel in Gothenburg (1.6 ng m<sup>-3</sup>), respectively. The t-BaP concentrations were all below 1 ng m<sup>-3</sup> for the rest of the other studies.

As for p-BaP concentrations, the six highest concentrations were traffic Copenhagen (4.4 ng m<sup>-3</sup>), traffic Naples (3 ng m<sup>-3</sup>), Industrial Naples (2.75 ng m<sup>-3</sup>), urban Seoul (2.55 ng m<sup>-3</sup>), Industrial Taichung (2.3 ng m<sup>-3</sup>)

and industrial Mumbai ( $2 \text{ ng m}^{-3}$ ), respectively. And the other studies revealed that p-BaP concentrations were all below  $2 \text{ ng m}^{-3}$ . In term of p-DBA concentrations, TIP and THUC sampling sites had highest concentrations which were recorded as  $2.7$  and  $3.2 \text{ ng m}^{-3}$ , respectively.

Table 4.5-1

Comparison of atmospheric PAHs concentrations ( $\text{ng m}^{-3}$ ) at different sites around the world

Location	Survey year	p-PAHs	p-BaP	p-DBA	t-PAHs	t-BaP	t-DBA	Particle size
<i>(a) Asia</i>								
Urban Seoul, Korea <sup>[1]</sup>	1998 - 1999	26.3	2.55	0.55	86	2.55	0.55	TSP ( $\Sigma$ 16 PAHs)
Urban Seoul, Korea <sup>[2]</sup>	2000	66	0.61	-	-	-	-	TSP ( $\Sigma$ 15 PAHs)
Inchon, Korea (Industrial city) <sup>[2]</sup>	2000	255.5	0.73	-	-	-	-	TSP ( $\Sigma$ 15 PAHs)
Rural Yangsuri, Korea <sup>[2]</sup>	2000	96.6	0.17	-	-	-	-	TSP ( $\Sigma$ 15 PAHs)
Rural Yangpyoung, Korea <sup>[2]</sup>	2000	195	0.53	-	-	-	-	TSP ( $\Sigma$ 15 PAHs)
Urban Hong Kong, China <sup>[3]</sup>	1999 - 2000	-	-	-	1083.8	0.49	0.19	TSP ( $\Sigma$ 20 PAHs)
Urban Hangzhou, China <sup>[4]</sup>	1999	-	-	-	9775.8	9.4	-	( $\Sigma$ 12 PAHs)
Indoor Hangzhou, China <sup>[4]</sup>	1999	-	-	-	10569.5	11.7	-	( $\Sigma$ 12 PAHs)
Urban Kuala Lumpur, Malaysia <sup>[5]</sup>	1998 - 1999	6.3	0.42	0.005	-	-	-	PM <sub>10</sub> ( $\Sigma$ 17 PAHs)
Rural Kuala Lumpur, Malaysia <sup>[5]</sup>	2000	0.3	0.005	0.003	-	-	-	PM <sub>10</sub> ( $\Sigma$ 17 PAHs)
Residential Mumbai, India <sup>[6]</sup>	1996 - 1997	24.5	1.9	-	-	-	-	PM <sub>10</sub> ( $\Sigma$ 7 PAHs)
Industrial Mumbai, India <sup>[6]</sup>	1996 - 1997	38.8	2	-	-	-	-	PM <sub>10</sub> ( $\Sigma$ 7 PAHs)
Temple in Tainan, Taiwan <sup>[7]</sup>	1996	-	-	-	6258	102.1	22.8	TSP ( $\Sigma$ 21 PAHs)
Suburban Tainan, Taiwan <sup>[7]</sup>	1996	-	-	-	231	10.3	2.4	TSP ( $\Sigma$ 21 PAHs)
Urban Tainan, Taiwan <sup>[7]</sup>	1996	-	-	-	541	-	-	TSP ( $\Sigma$ 21 PAHs)
Traffic Tainan, Taiwan <sup>[8]</sup>	1991 - 1992	-	-	-	8110	-	-	TSP ( $\Sigma$ 21 PAHs)
Urban Tainan, Taiwan <sup>[8]</sup>	1991 - 1992	-	-	-	1520	-	-	TSP ( $\Sigma$ 21 PAHs)
Rural Tainan, Taiwan <sup>[8]</sup>	1991 - 1992	-	-	-	972	-	-	TSP ( $\Sigma$ 21 PAHs)

Table 4.5-1 (continued)

Urban Taipei, Taiwan <sup>[9]</sup>	1995 - 1996	-	-	-	209	1.7	3.3	TSP ( $\Sigma$ 15 PAHs)
Indoor Taipei, Taiwan <sup>[9]</sup>	1995 - 1996	-	-	-	267	1.7	2.9	TSP ( $\Sigma$ 15 PAHs)
Indoor Taipei, Taiwan (Incense-burning) <sup>[9]</sup>	1995 - 1996	-	-	-	348	2.4	3.5	TSP ( $\Sigma$ 15 PAHs)
Steel and iron plants in Taiwan <sup>[10]</sup>	1998 - 1999	-	-	-	1020	0.38	0.22	TSP ( $\Sigma$ 21 PAHs)
Industrial Taichung, Taiwan (TIP) (This study)	2002 - 2003	129.1	2.3	2.7	1434.5	7.6	7	TSP ( $\Sigma$ 21 PAHs)
Suburban Taichung, Taiwan (THUC) (This study)	2002 - 2003	85.9	1.3	3.2	732.1	3.6	5.1	TSP ( $\Sigma$ 21 PAHs)
Location	Survey year	p-PAHs	p-BaP	p-DBA	t-PAHs	t-BaP	t-DBA	Particle size
<i>(b) Europe and America</i>								
Residential Naples, Italy <sup>[11]</sup>	1996 - 1997	22.7	0.9	0.48	-	-	-	TSP ( $\Sigma$ 17 PAHs)
Traffic Naples, Italy <sup>[11]</sup>	1996 - 1997	54.8	3	0.35	-	-	-	TSP ( $\Sigma$ 17 PAHs)
Industrial Naples, Italy <sup>[11]</sup>	1996 - 1997	39.5	2.75	0.44	-	-	-	TSP ( $\Sigma$ 17 PAHs)
Rome, Italy <sup>[12]</sup>	1993 - 1998	6.88	1.38	0.22	-	-	-	PM <sub>10</sub> ( $\Sigma$ 7 PAHs)
Rural Chicago, America <sup>[13]</sup>	1995	-	-	-	428	1.6	-	TSP ( $\Sigma$ 14 PAHs)
Urban Baltimore, America <sup>[14]</sup>	1997	2.13	0.124	0.013	22.12	0.124	0.013	TSP ( $\Sigma$ 23 PAHs)
Chesapeake Bay in Baltimore, America <sup>[14]</sup>	1997	0.85	0.05	0.006	9.2	0.05	0.006	TSP ( $\Sigma$ 23 PAHs)
Traffic Copenhagen, Denmark <sup>[15]</sup>	1992 - 1993	77.36	4.4	-	-	-	-	TSP ( $\Sigma$ 21 PAHs)
Park in Copenhagen, Denmark <sup>[15]</sup>	1992 - 1993	22	1.4	-	-	-	-	TSP ( $\Sigma$ 21 PAHs)
Traffic London, England <sup>[16]</sup>	1991 - 1992	-	-	-	111.01	1.95	0.13	TSP ( $\Sigma$ 18 PAHs)
Traffic tunnel in Gothenburg, Sweden <sup>[17]</sup>	2000	152.6	1.28	0.44	1181.3	1.3	1.6	TSP ( $\Sigma$ 29 PAHs)

[1] Park et al., 2002 [2] Bae et al., 2002 [3] Lee et al., 2001 [4] Liu et al., 2001 [5] Omar et al., 2002 [6] Kulkarni and Venkataraman, 2000 [7] Lin et al., 2002 [8] Lee et al., 1995 [9] Li and Ro, 2000 [10] Yang et al., 2002 [11] Caricchia et al., 1999 [12] Menichini et al., 1999 [13] Odabasi et al., 1999 [14] Dachs et al., 2002 [15] Nielsen et al., 1996 [16] Brown et al., 1996 [17] Wingfors et al., 2001.



## Chapter 5

### Conclusions and Suggestions

#### 5.1 Conclusions

The average t-PAHs concentration at TIP and THUC sampling sites of central Taiwan were found to be  $1,434.5 \pm 1,133.7 \text{ ng m}^{-3}$  and  $732.1 \pm 512.2 \text{ ng m}^{-3}$ , respectively. The results indicated that LMW PAHs are predominant in g-PAHs and HMW PAHs are abundant in p-PAHs. Temperature is the most important factor for the particle/gas phase PAHs distribution. This study has identified the sources of PAHs at both sampling sites in Taichung by methods of PCA and HCA. Results also demonstrated that the major sources of PAHs came from diesel vehicle emission and steel industries at TIP sampling site. Moreover, incineration and gasoline vehicle were the major contribution at THUC sampling site. The major sources of Nap, AcPy, Acp, Flu, PA and Pyr are diesel vehicle emission exhausts, FL, CYC, BaA, CHR, Ant, PER and BeP are came from industries sources at TIP sampling site. As for THUC sampling site, the sources of Flu, PA, Ant, Pyr, CHR and BbF came from incinerator, IND, BghiP and COR are the result of gasoline vehicle emission, CYC, BaA, PER and DBA are contributed by industrial stationary sources and power plant. Either p-PAHs or t-PAHs concentrations in Asia, Europe and America countries can be found that PAHs concentration in Asia was higher than Europe and America during the past decade. Most important of all, the most toxic PAHs such as BaP and DBA are also had higher in

Asia countries than Europe and America countries.

## 5.2 Suggestions

The major suggestions for this study are as follows:

1. TIP sampling site are surrounded Taichung Wen Shan Incinerator, Taichung Veterans General Hospital Incinerator and local industrial waste incinerators. Thus the major contribution for PAHs come from incinerator source are expected.
2. Heavy traffic including gasoline and diesel engine vehicle during working hours at locally and the main traffic road line “Taichung Cong Rd.” nearby leading to high PAHs concentrations at both sampling sites.
3. There are higher PAHs concentrations such as BaP and DBA which have high toxic factor in Asia than America and Europe countries is the most important issue for future study.
4. PCA for identifying PAHs sources is a useful and general method for many related studies. However, there was very little research which combines PCA and HCA methods in identifying the PAHs sources, especially in Asia area. Thus, we combined these two methods and successfully in identifying PAHs sources in Taiwan area.

5. We collected and compared all the PAHs characterize related study at difference countries and region. The comparison of the PAHs data is important information for the future study references.

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## **Appendix –**

### **21 PAHs of the calibration curve**

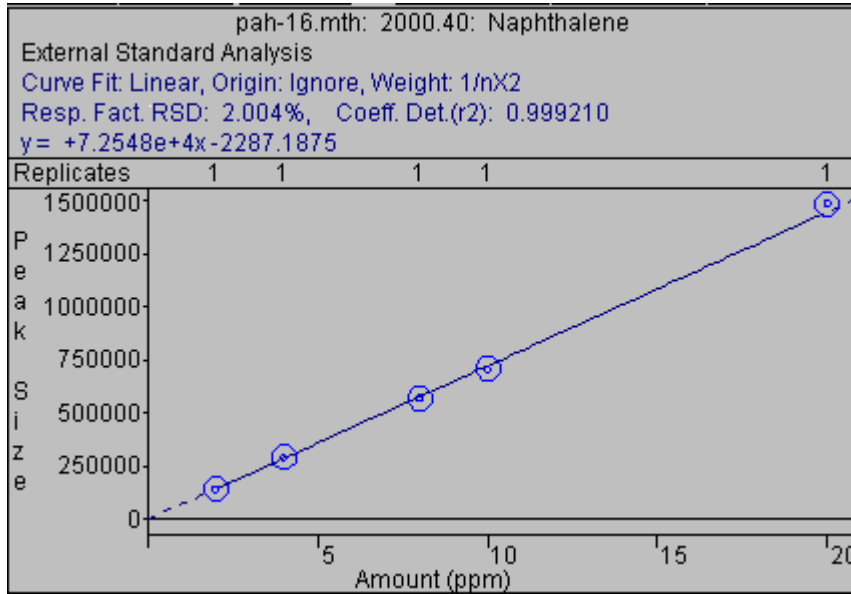


Figure A-1. The calibration curve of NaP

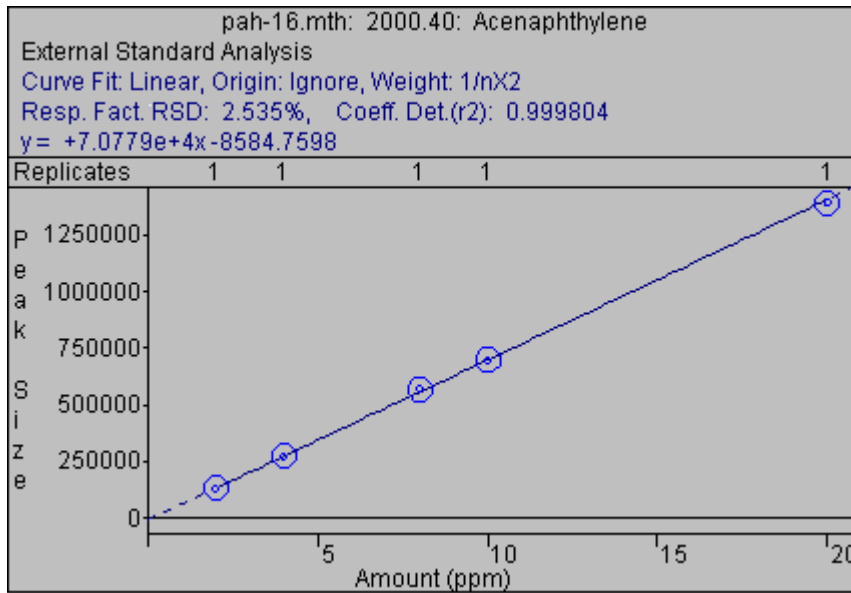


Figure A-2. The calibration curve of AcPy

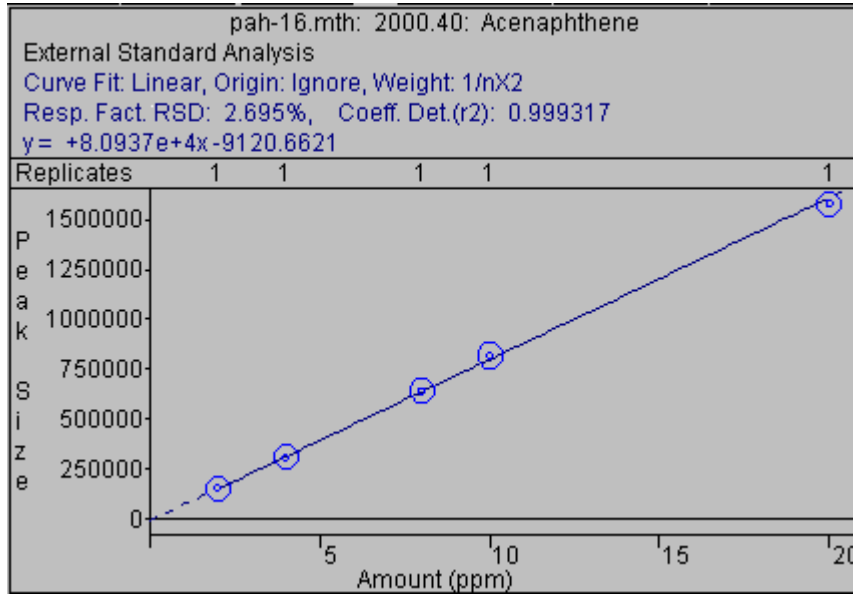


Figure A-3. The calibration curve of Acp

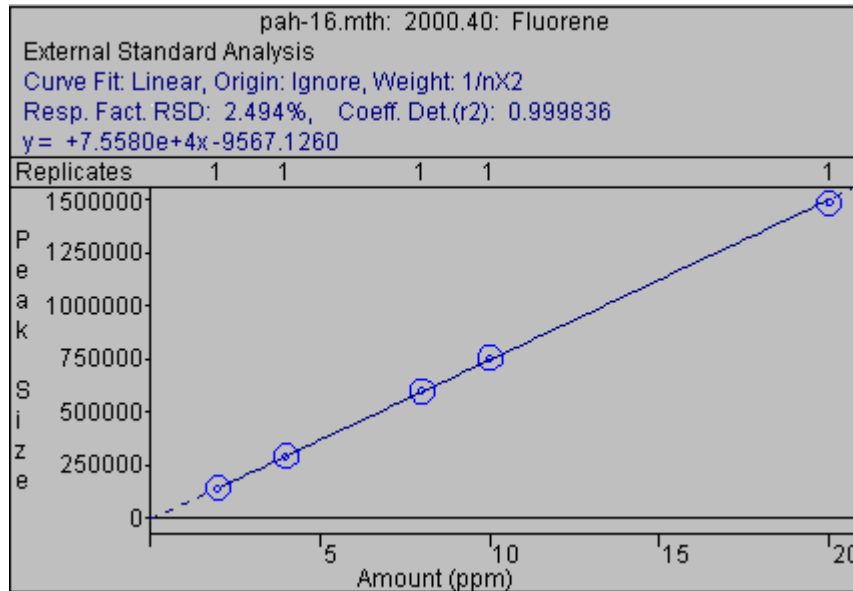


Figure A-4. The calibration curve of Flu

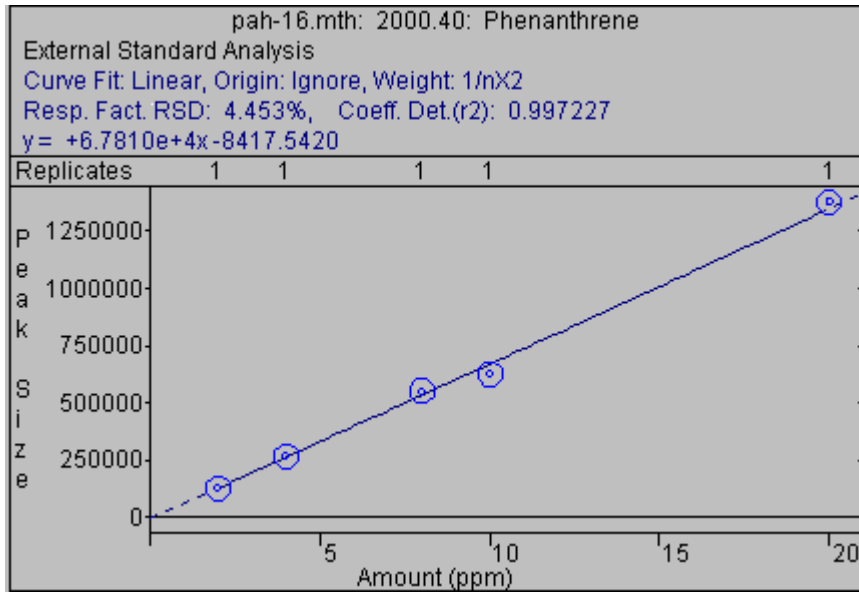


Figure A-5. The calibration curve of PA

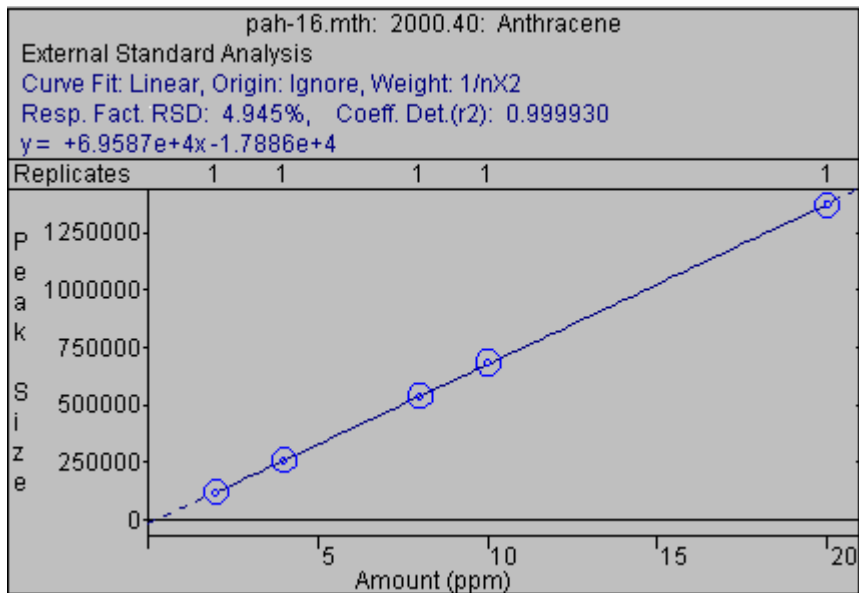


Figure A-6. The calibration curve of Ant

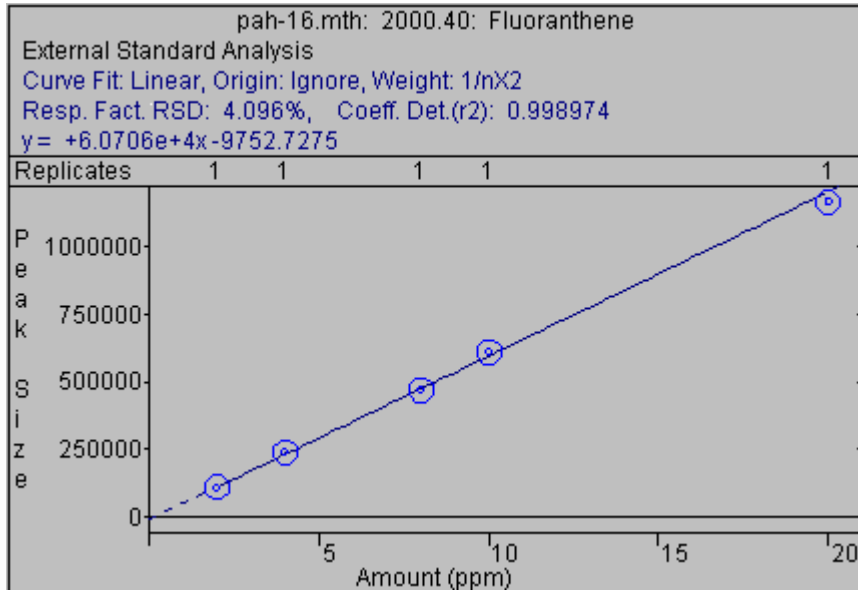


Figure A-7. The calibration curve of FL

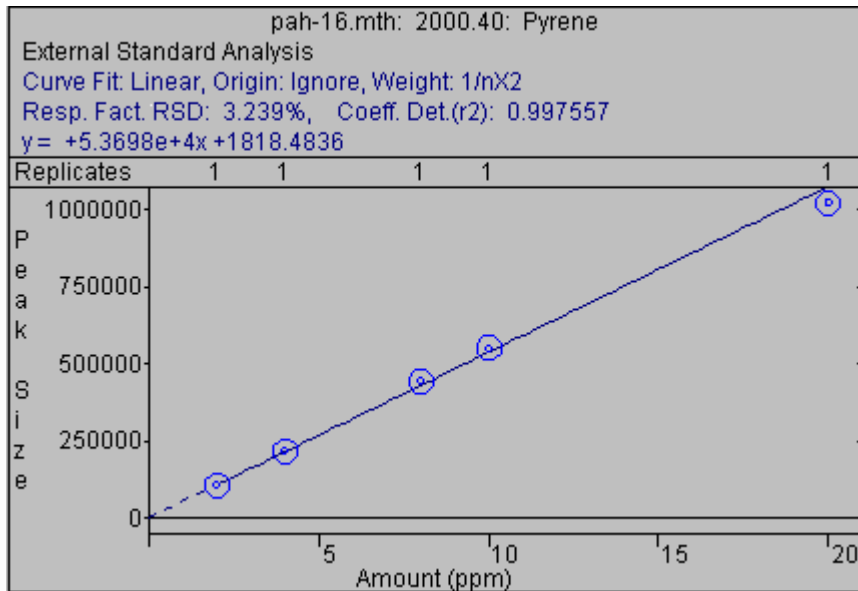


Figure A-8. The calibration curve of Pyr

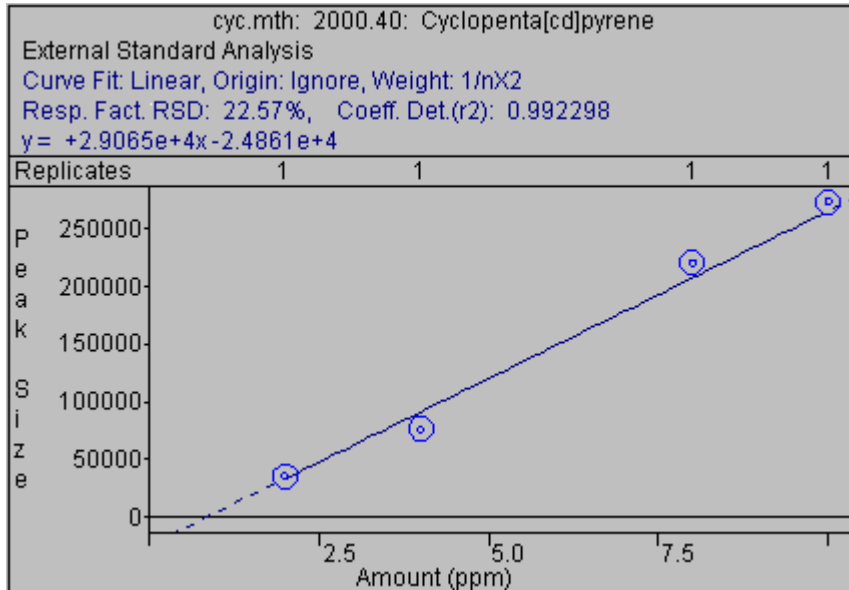


Figure A-9 The calibration curve of CYC

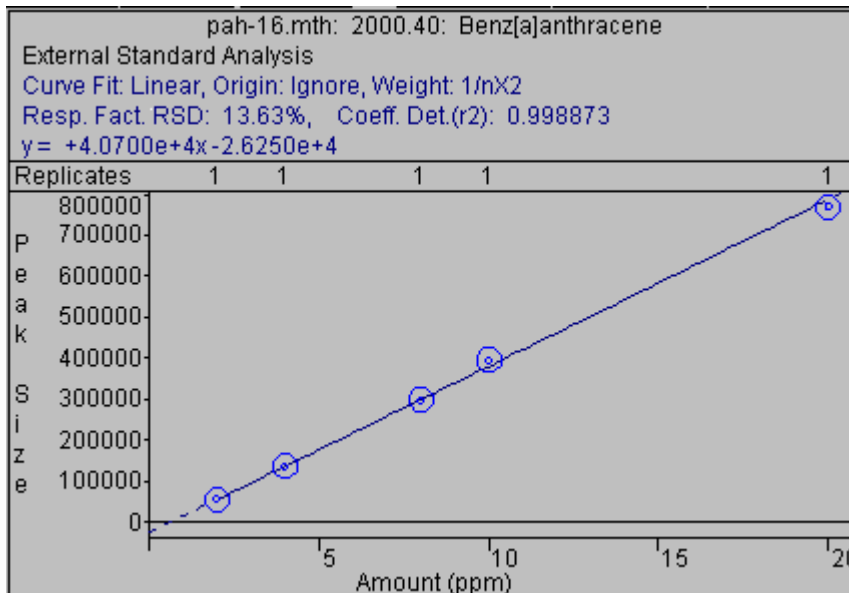


Figure A-10. The calibration curve of BaA



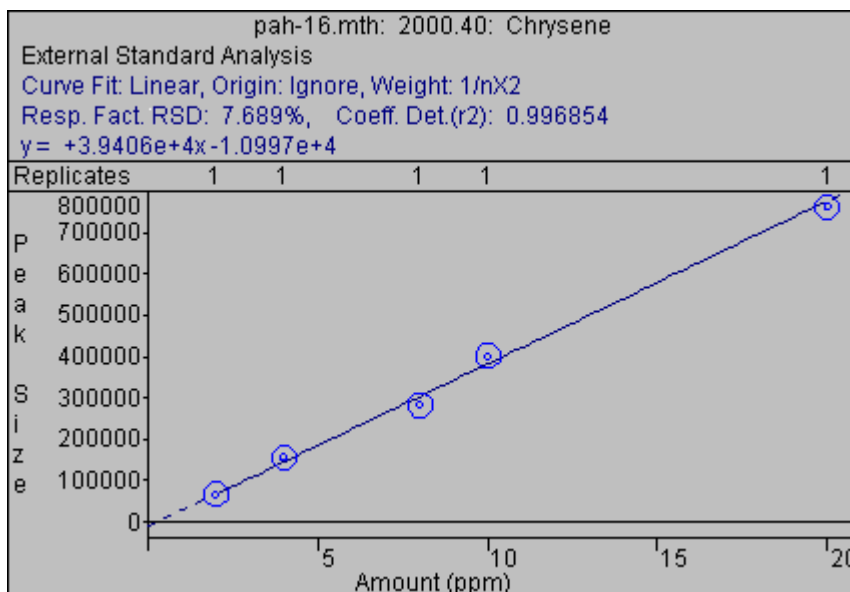


Figure A-11. The calibration curve of CHR

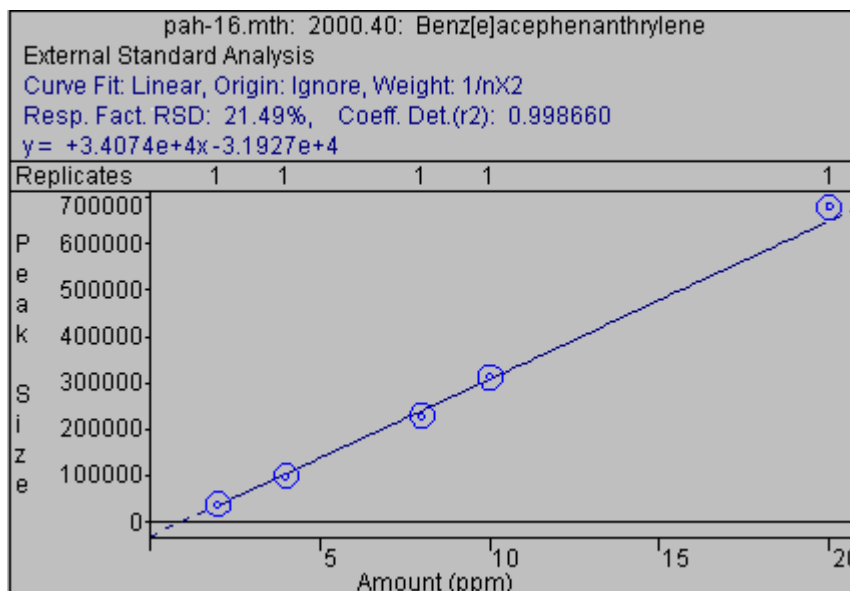


Figure A-12. The calibration curve of BbF

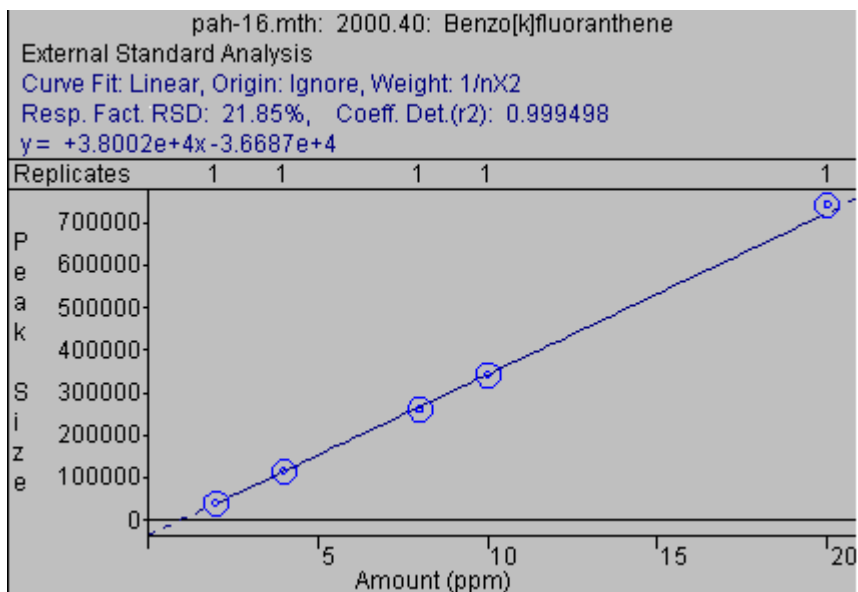


Figure A-13. The calibration curve of BkF

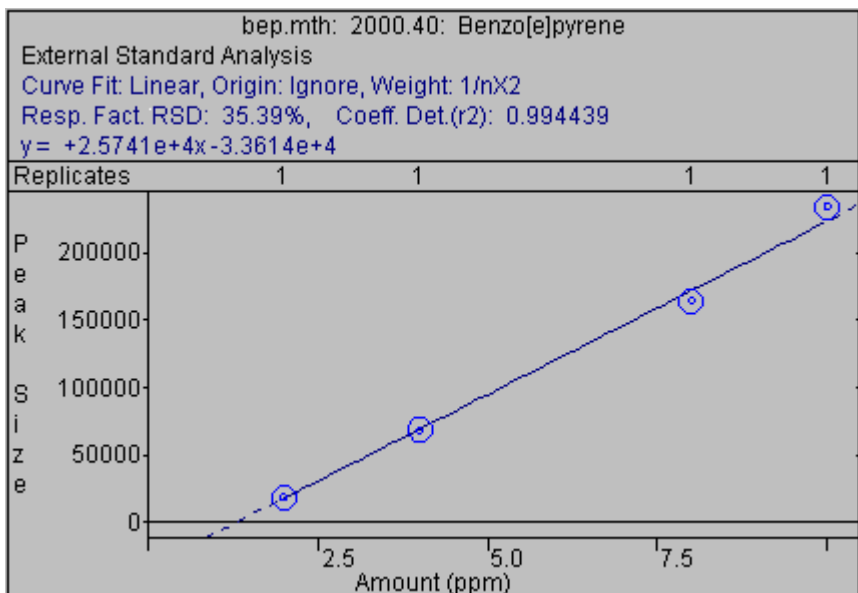


Figure A-14. The calibration curve of BeP

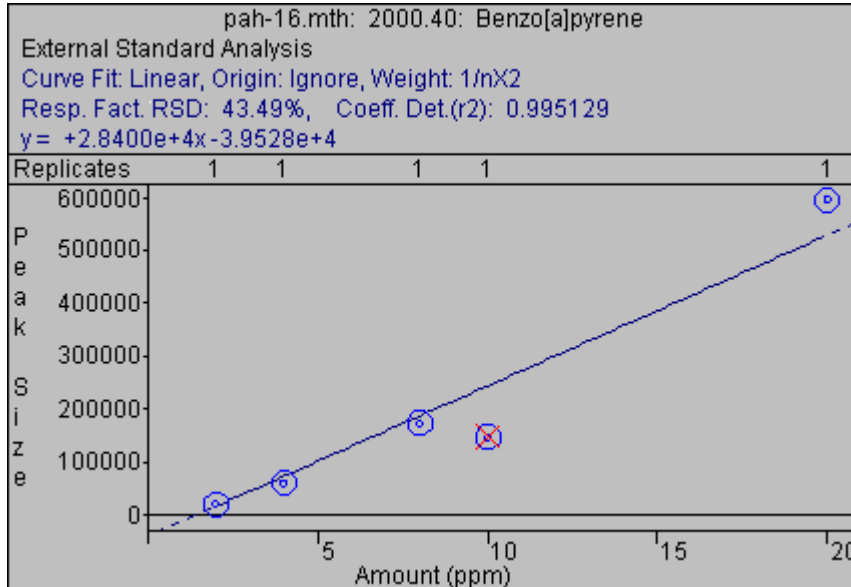


Figure A-15. The calibration curve of BaP

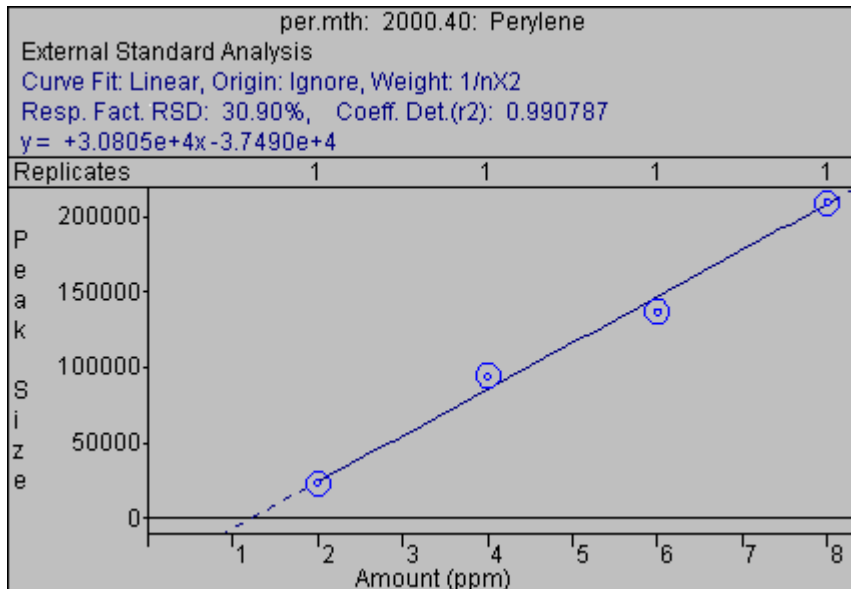


Figure A-16. The calibration curve of PER

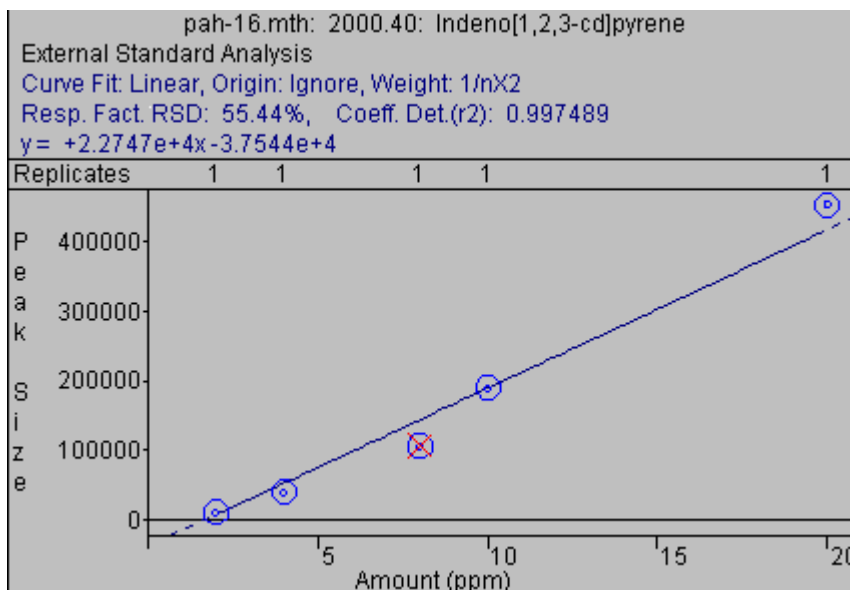


Figure A-17. The calibration curve of IND

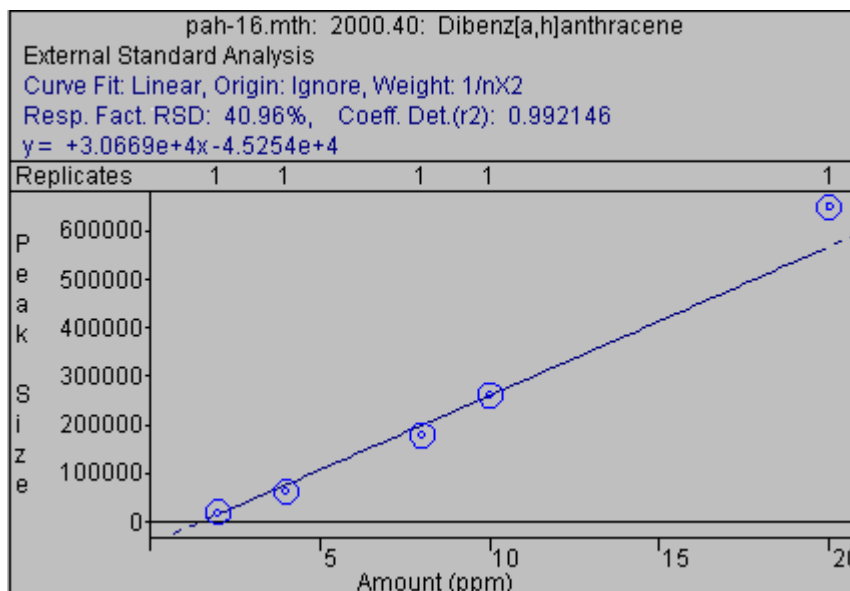


Figure A-18. The calibration curve of DBA

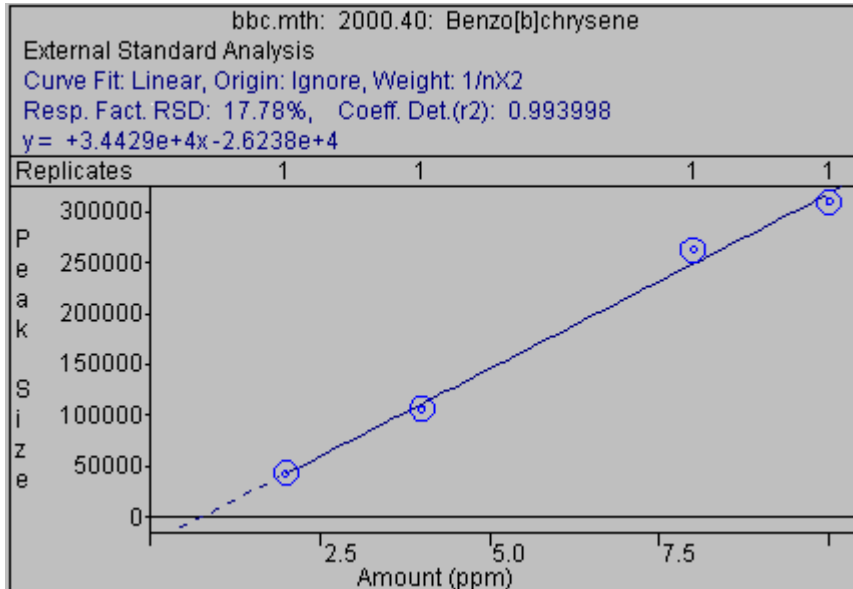


Figure A-19. The calibration curve of BbC

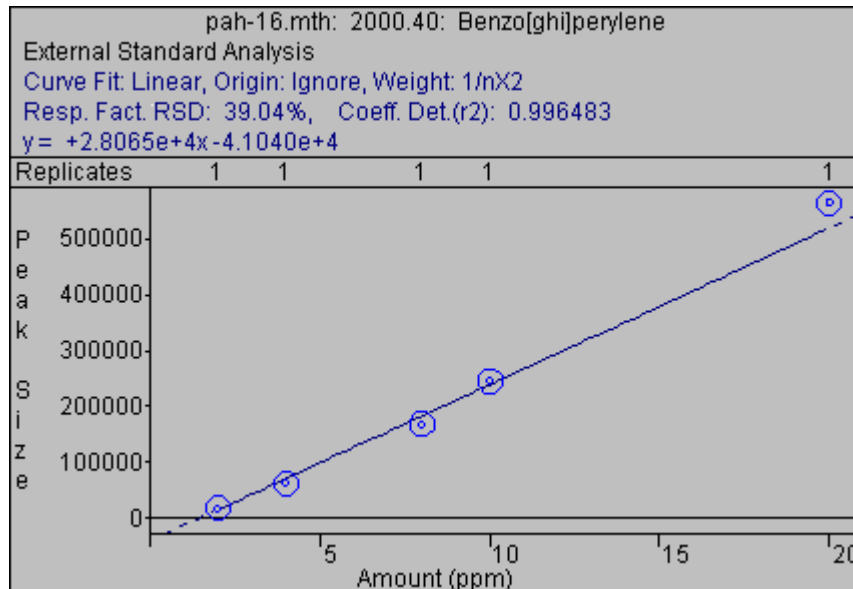


Figure A-20. The calibration curve of BghiP

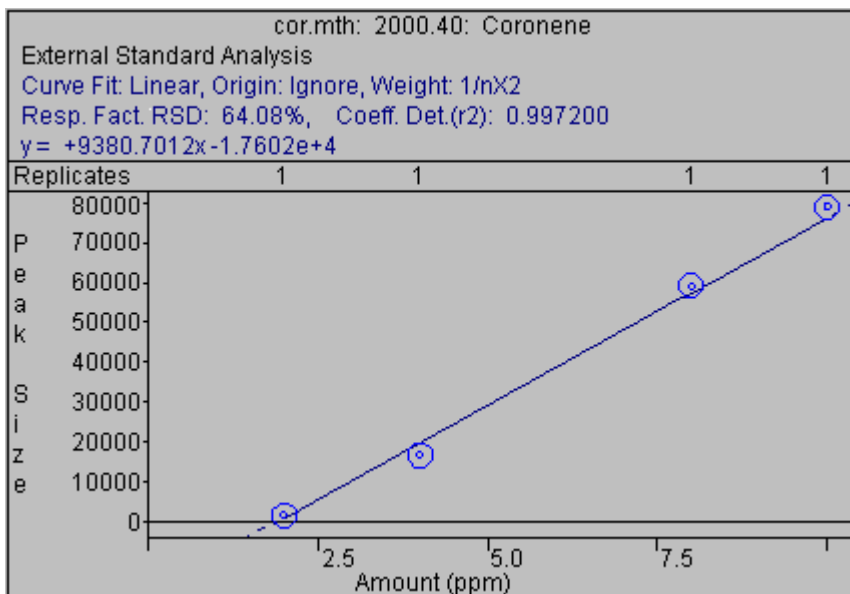


Figure A-21. The calibration curve of COR

## **Appendix –**

### **Mass spectrum of 21 PAHs**

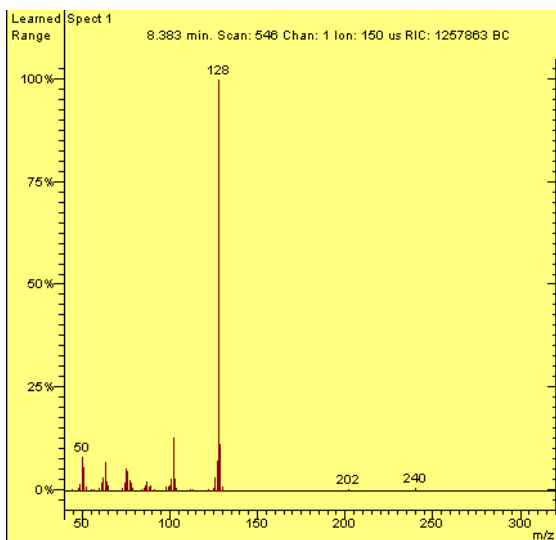


Figure B-1. Mass spectrum of Nap

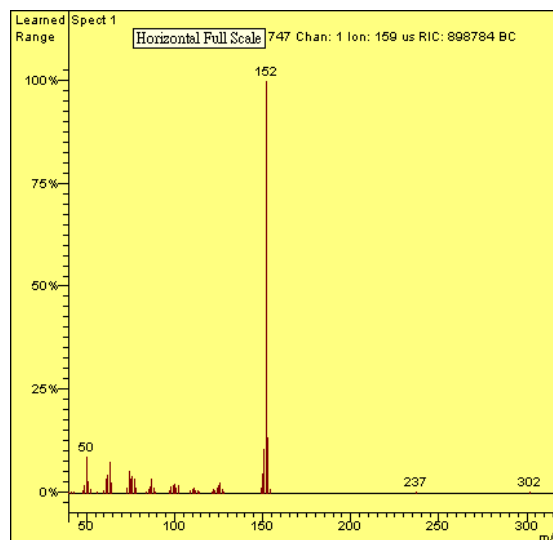


Figure B-2. Mass spectrum of AcPy

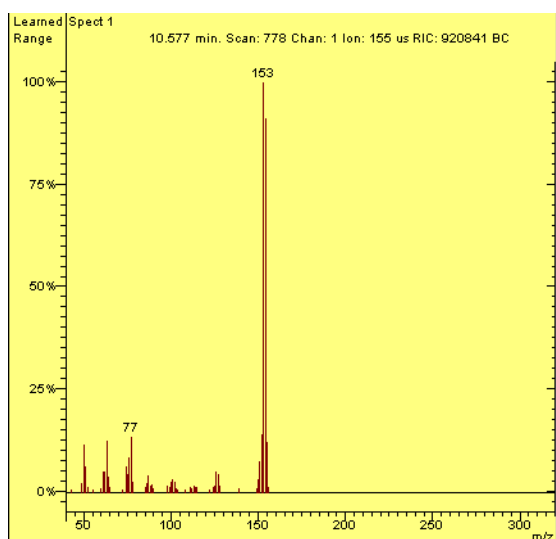


Figure B-3. Mass spectrum of Acp

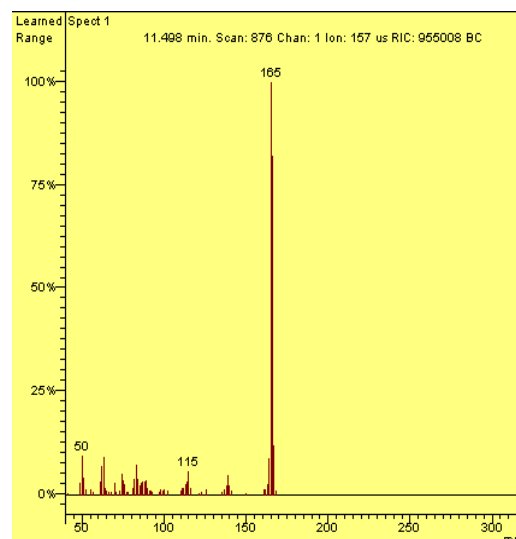


Figure B-4. Mass spectrum of Flu

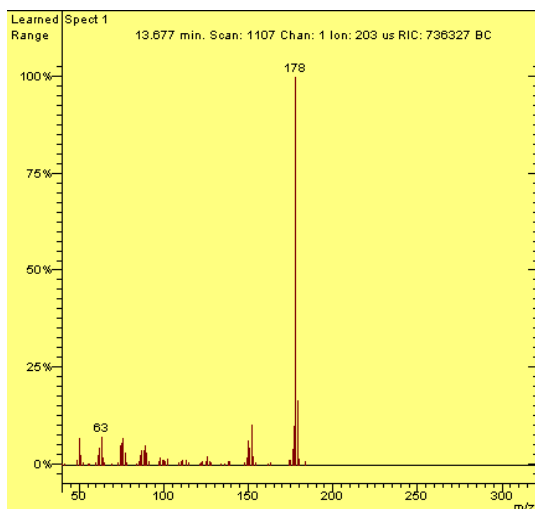


Figure B-5. Mass spectrum of PA

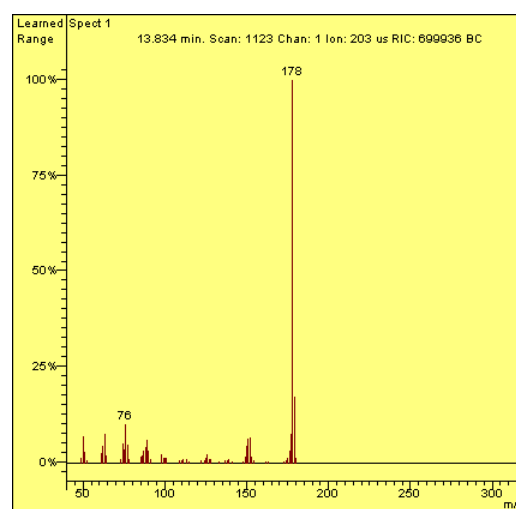


Figure B-6. Mass spectrum of Ant



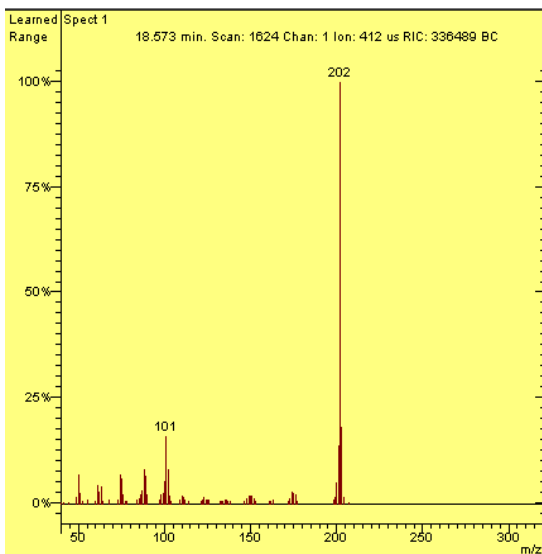


Figure B-7. Mass spectrum of FL

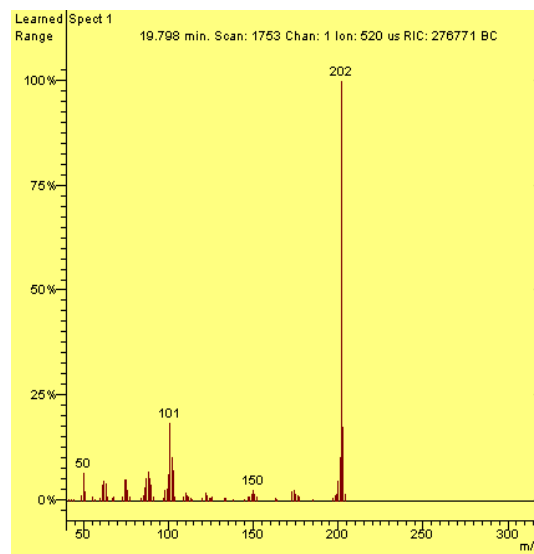


Figure B-8. Mass spectrum of Pyr

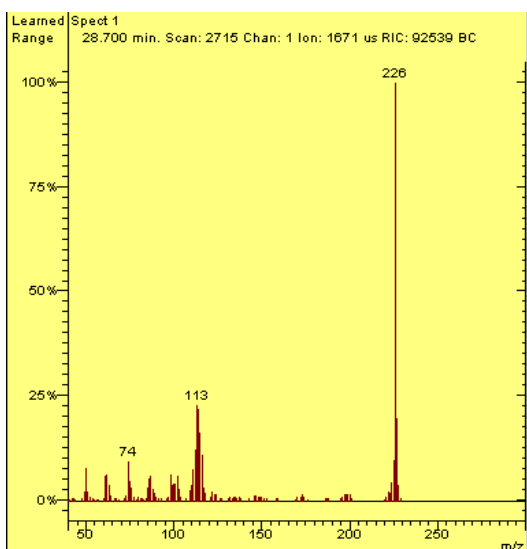


Figure B-9. Mass spectrum of CYC

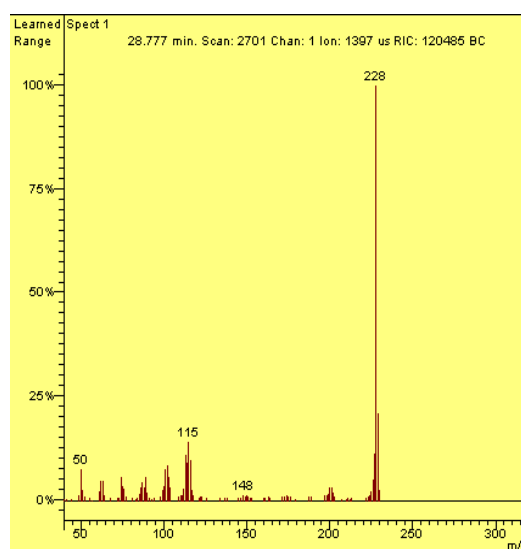


Figure B-10. Mass spectrum of BaA

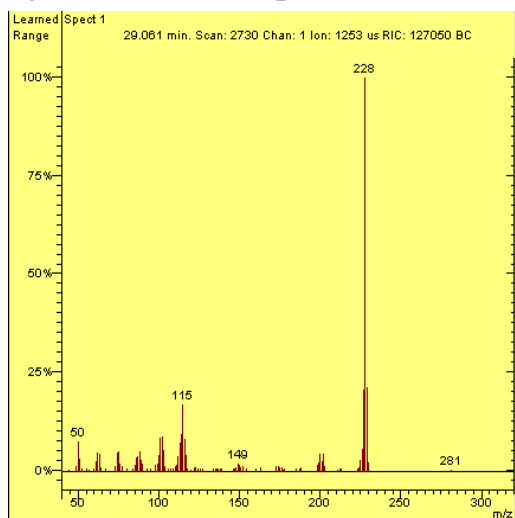


Figure B-11. Mass spectrum of CHR

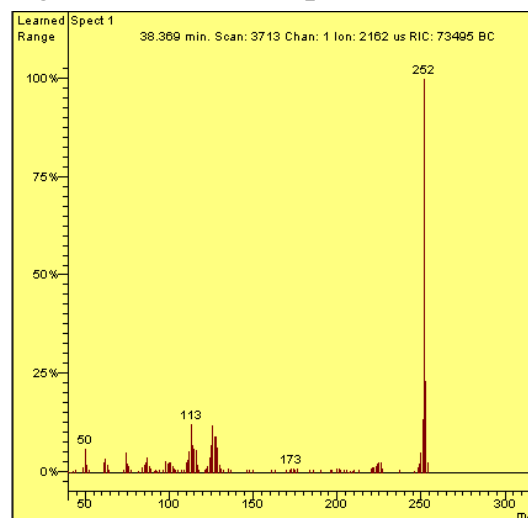


Figure B-12. Mass spectrum of BbF

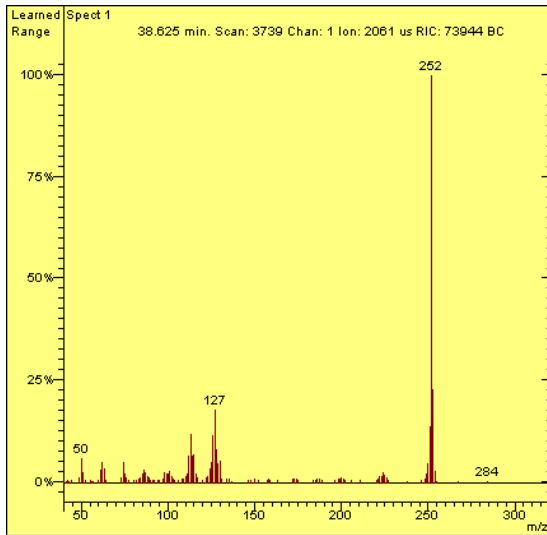


Figure B-13. Mass spectrum of BkF

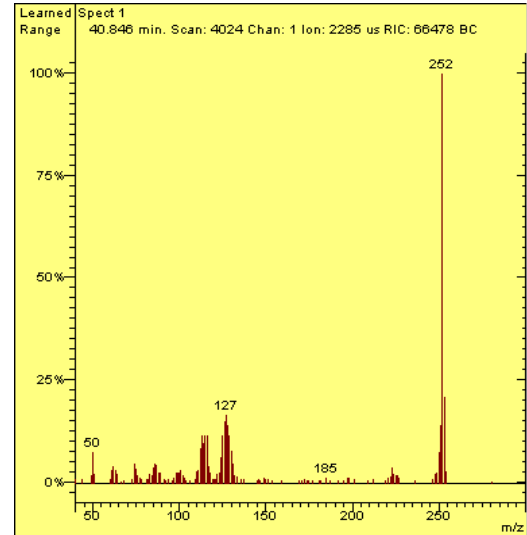


Figure B-14. Mass spectrum of BeP

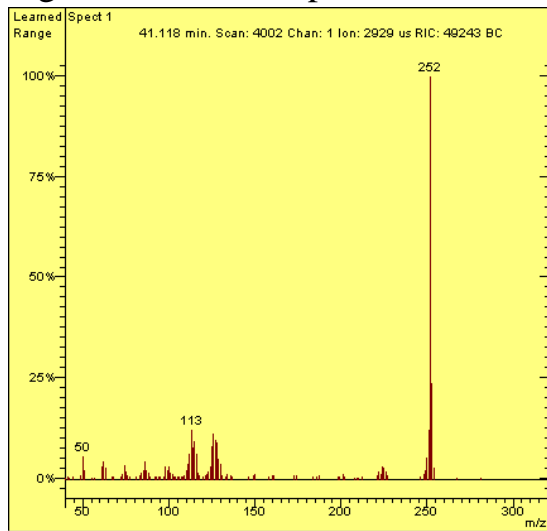


Figure B-15. Mass spectrum of Bap

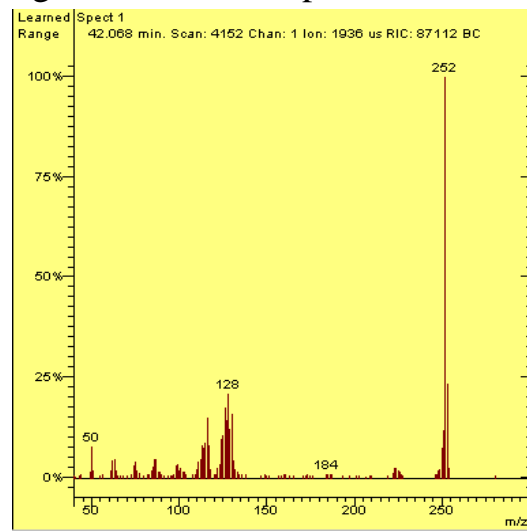


Figure B-16. Mass spectrum of PER

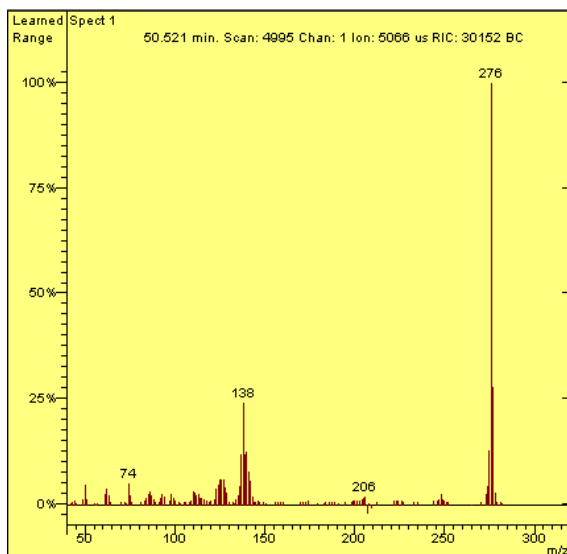


Figure B-17. Mass spectrum of IND

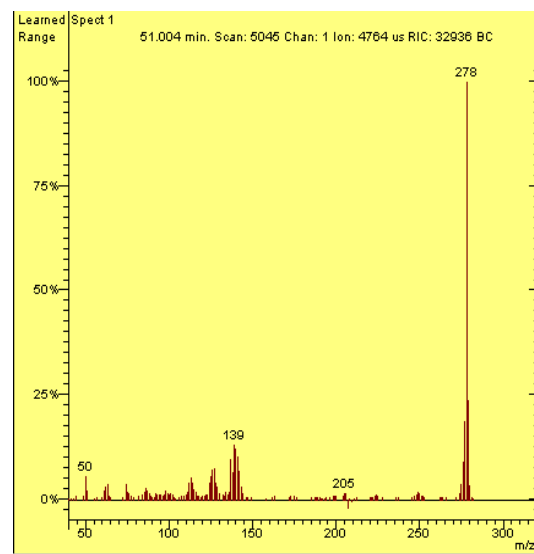


Figure B-18. Mass spectrum of DBA

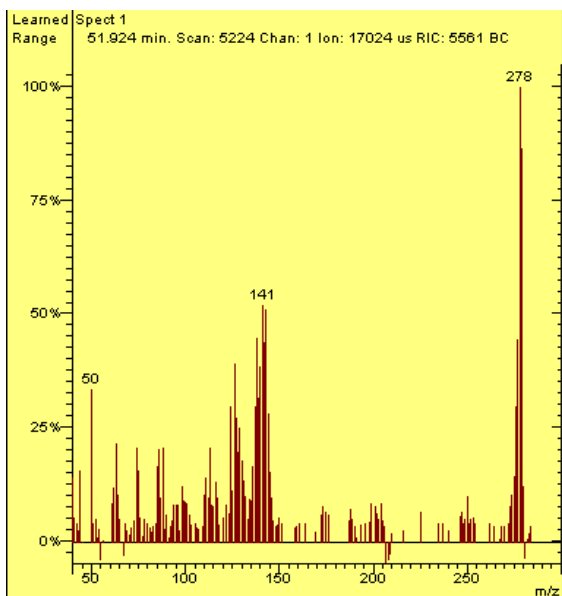


Figure B-19. Mass spectrum of BbC

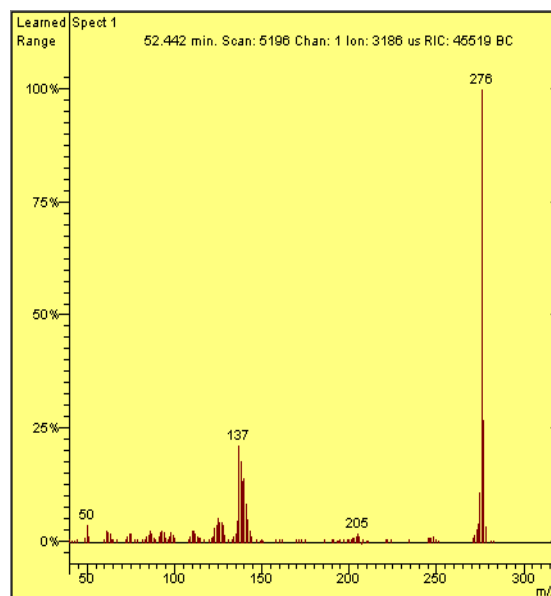


Figure B-20. Mass spectrum of BghiP

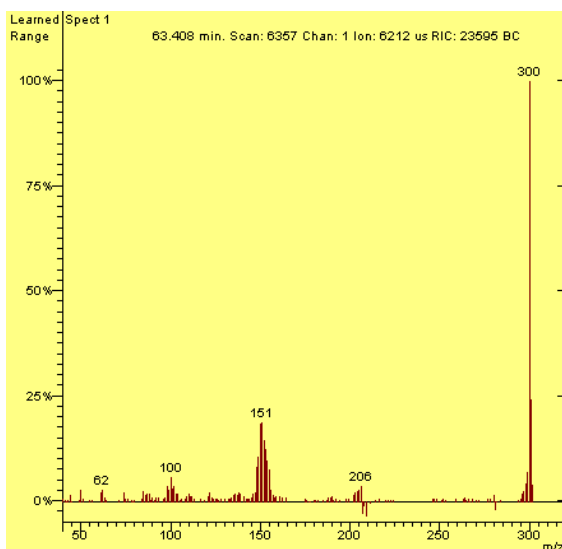


Figure B-21. Mass spectrum of COR

## **Appendix –**

### **Total ion chromatogram of 21 PAHs**

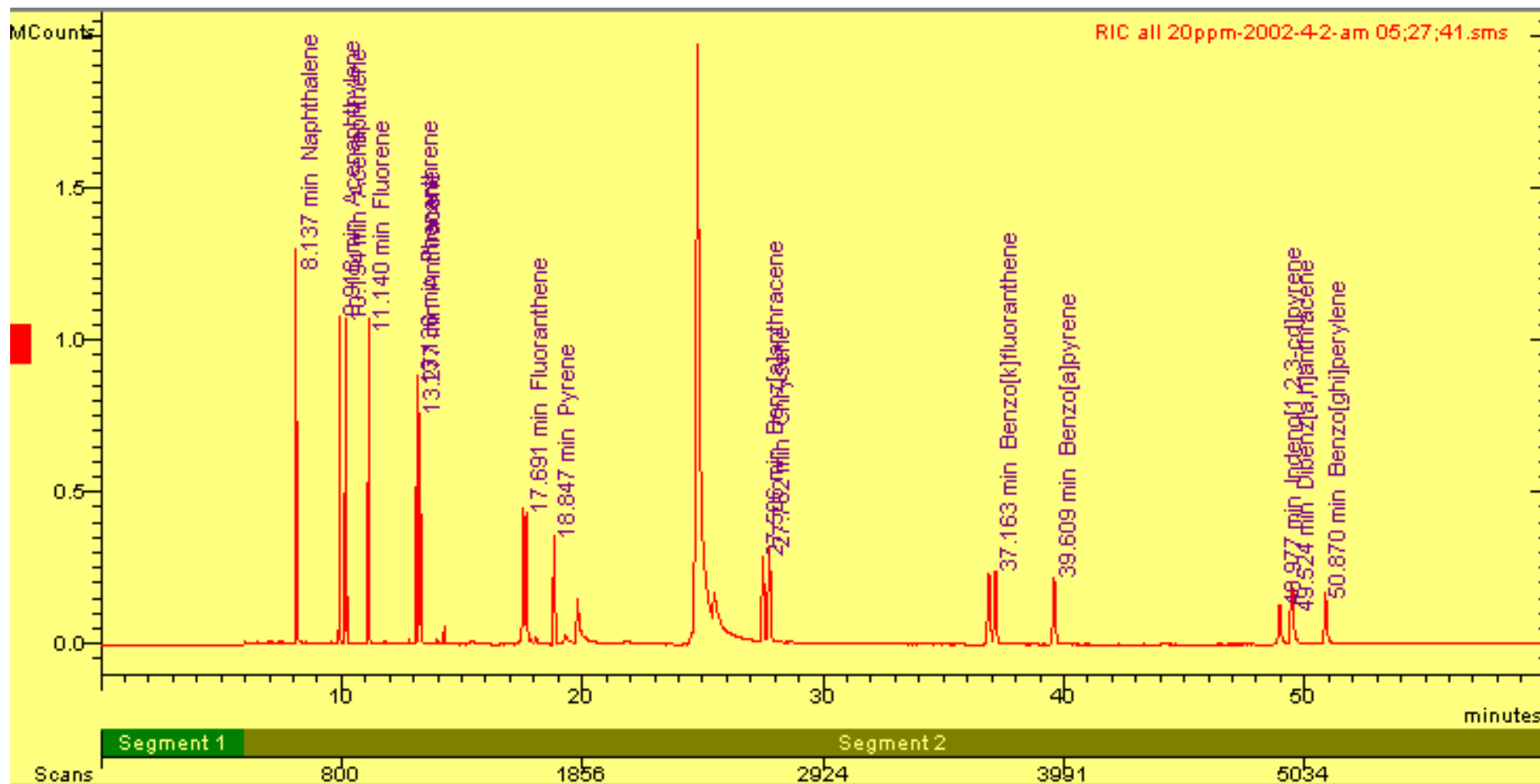


Figure C-1. Total ion chromatogram (TIC) of 16 species PAHs

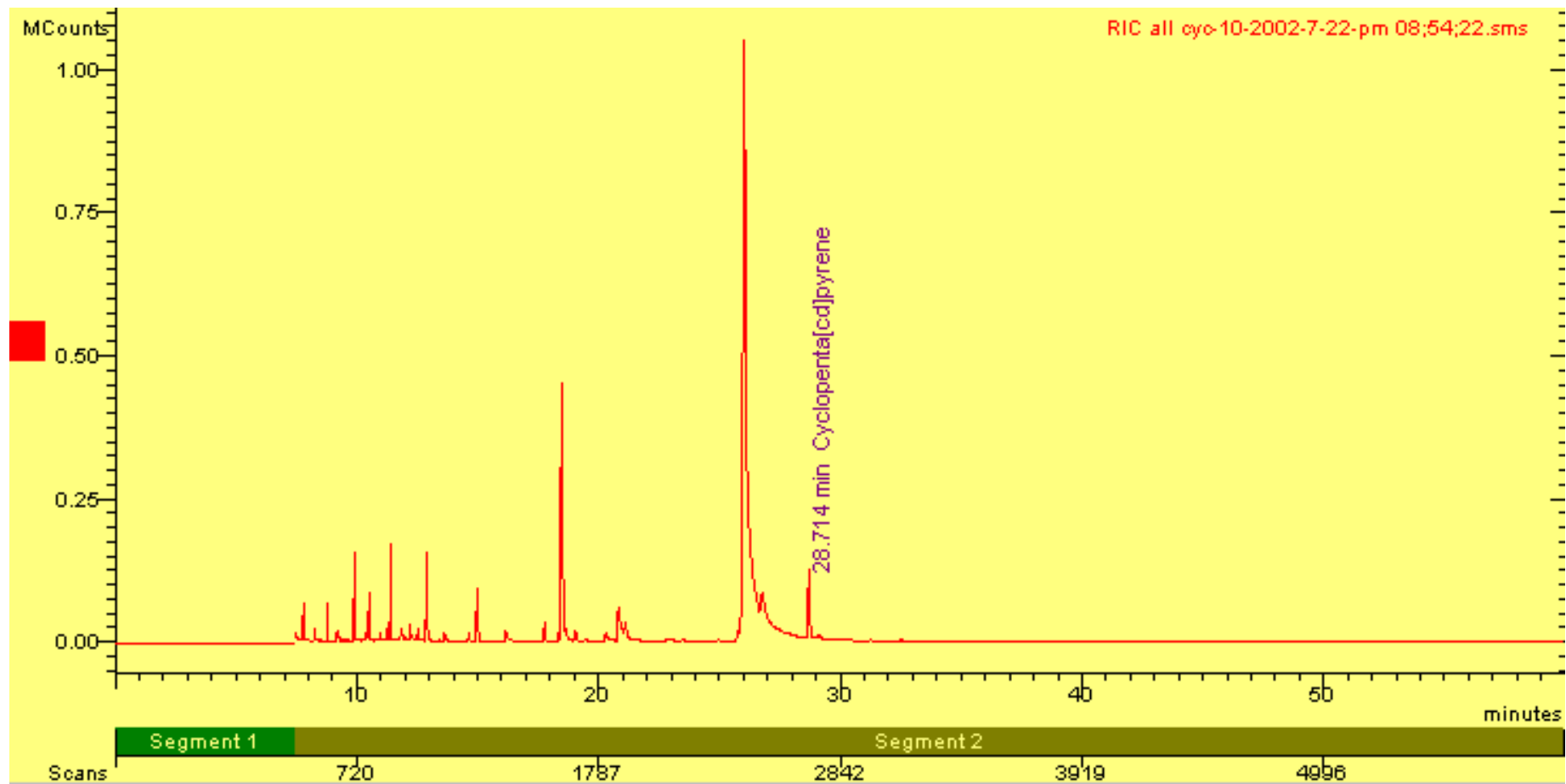


Figure C-2. Total ion chromatogram (TIC) of CYC

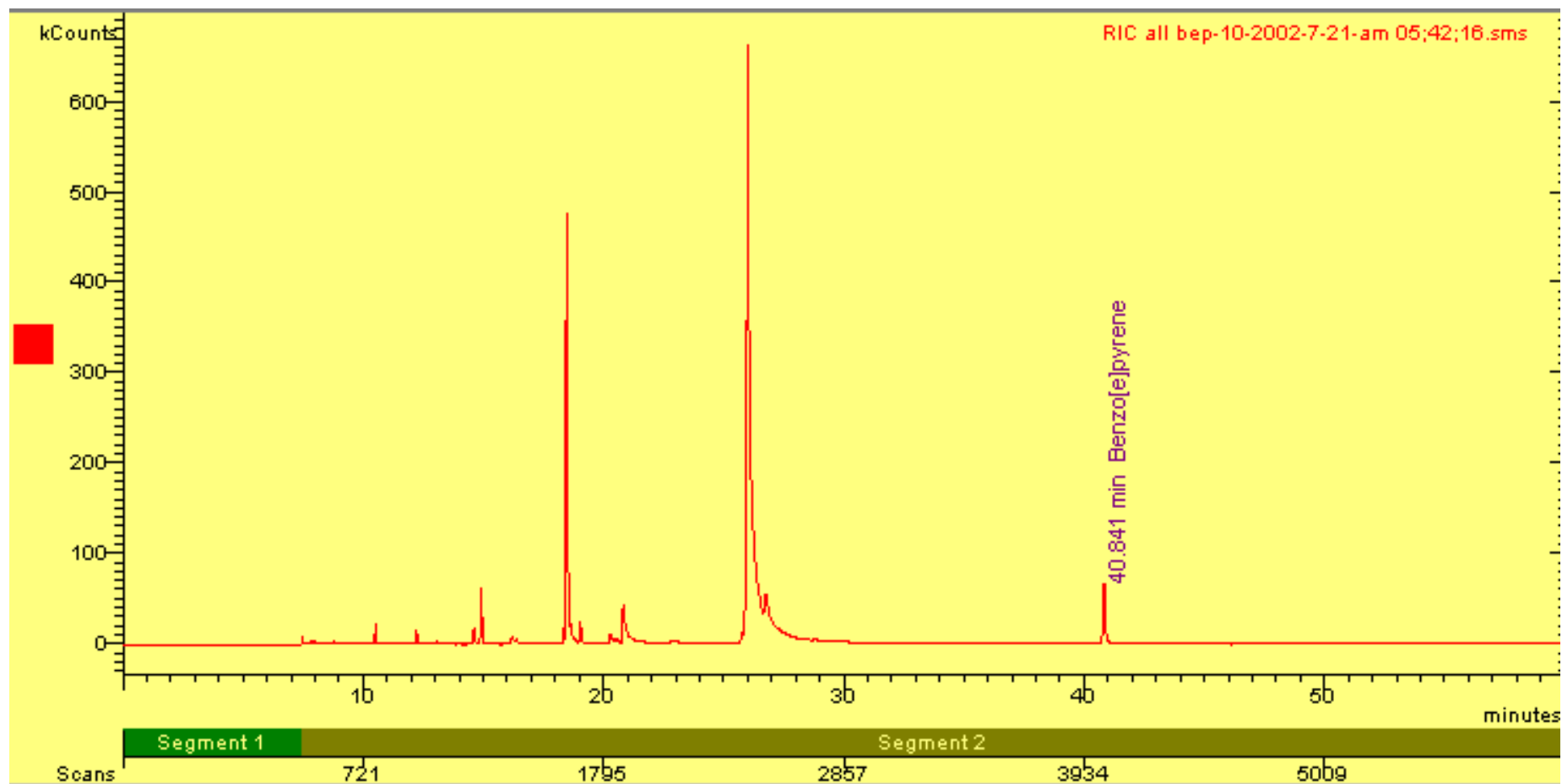


Figure C-3. Total ion chromatogram (TIC) of BeP

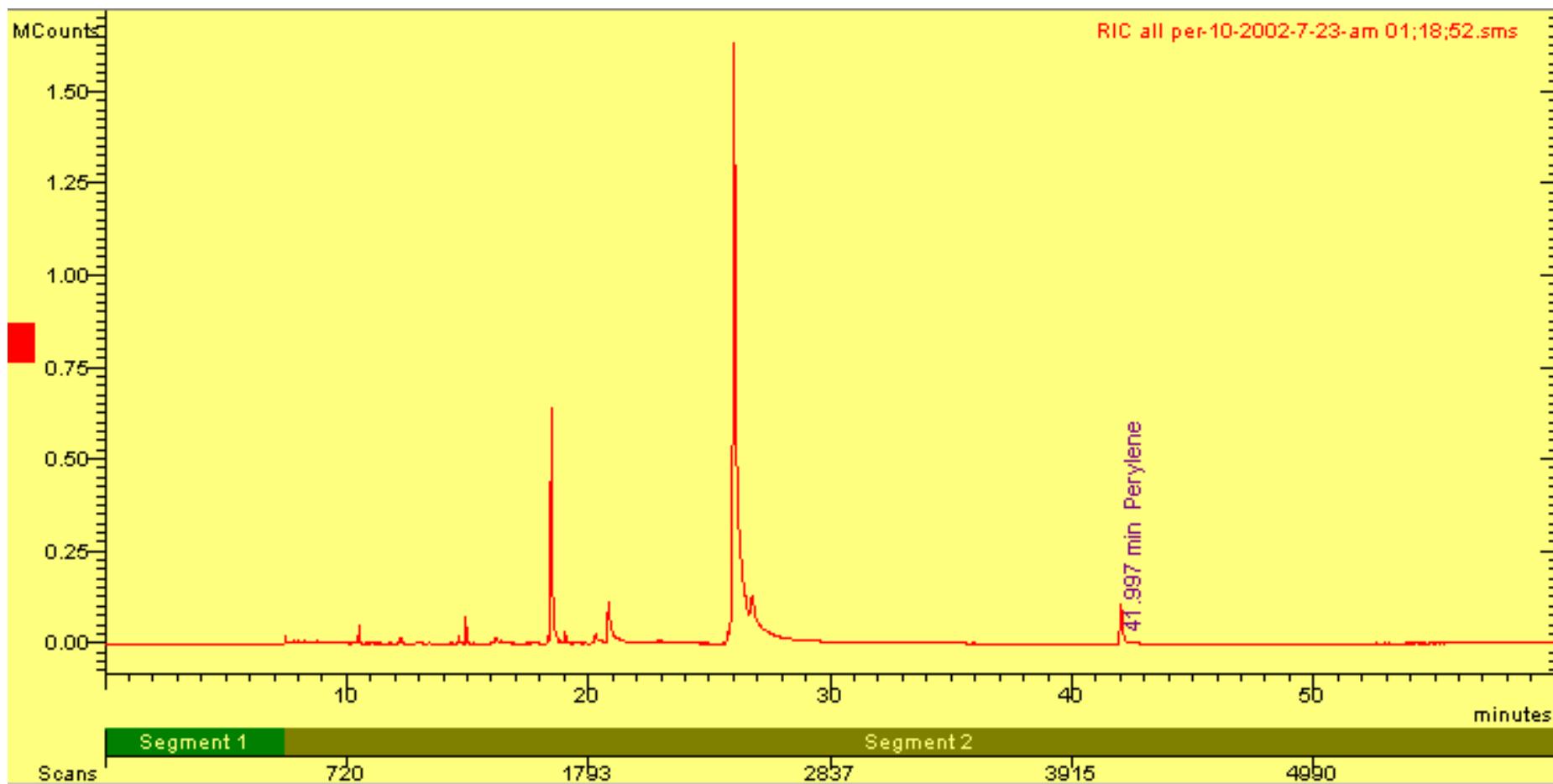


Figure C-4. Total ion chromatogram (TIC) of PER



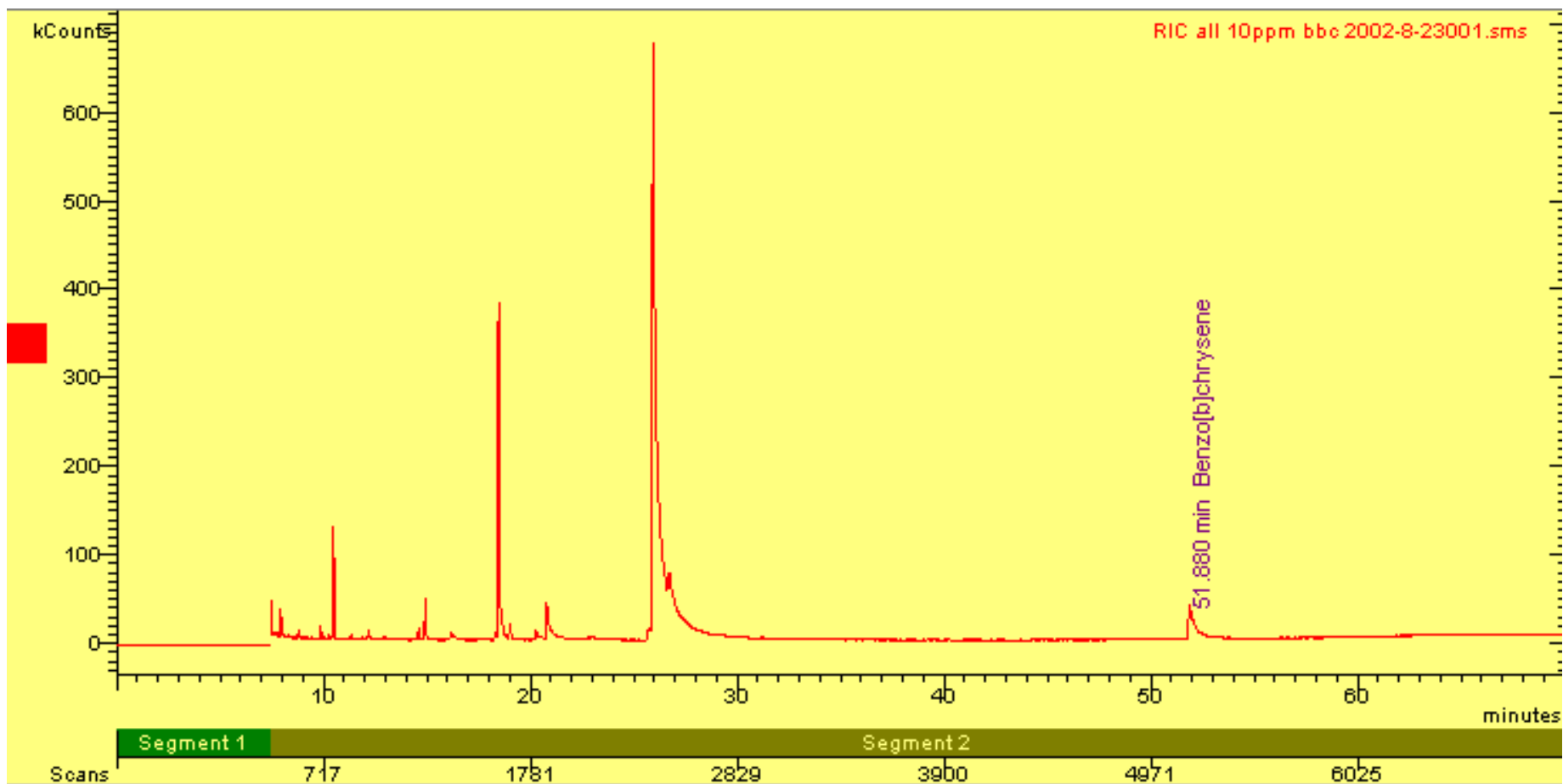


Figure C-5. Total ion chromatogram (TIC) of BbC

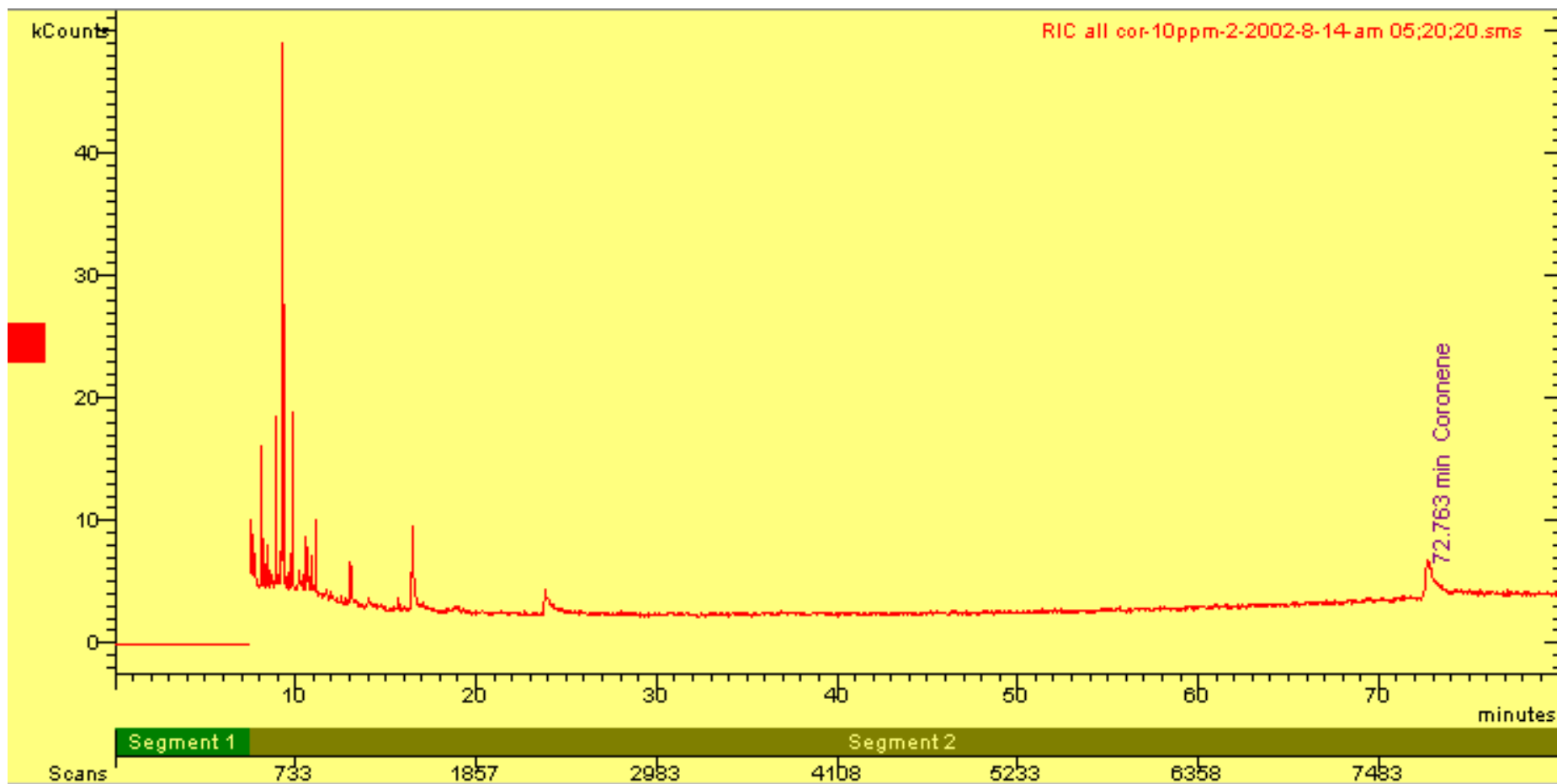


Figure C-6. Total ion chromatogram (TIC) of COR

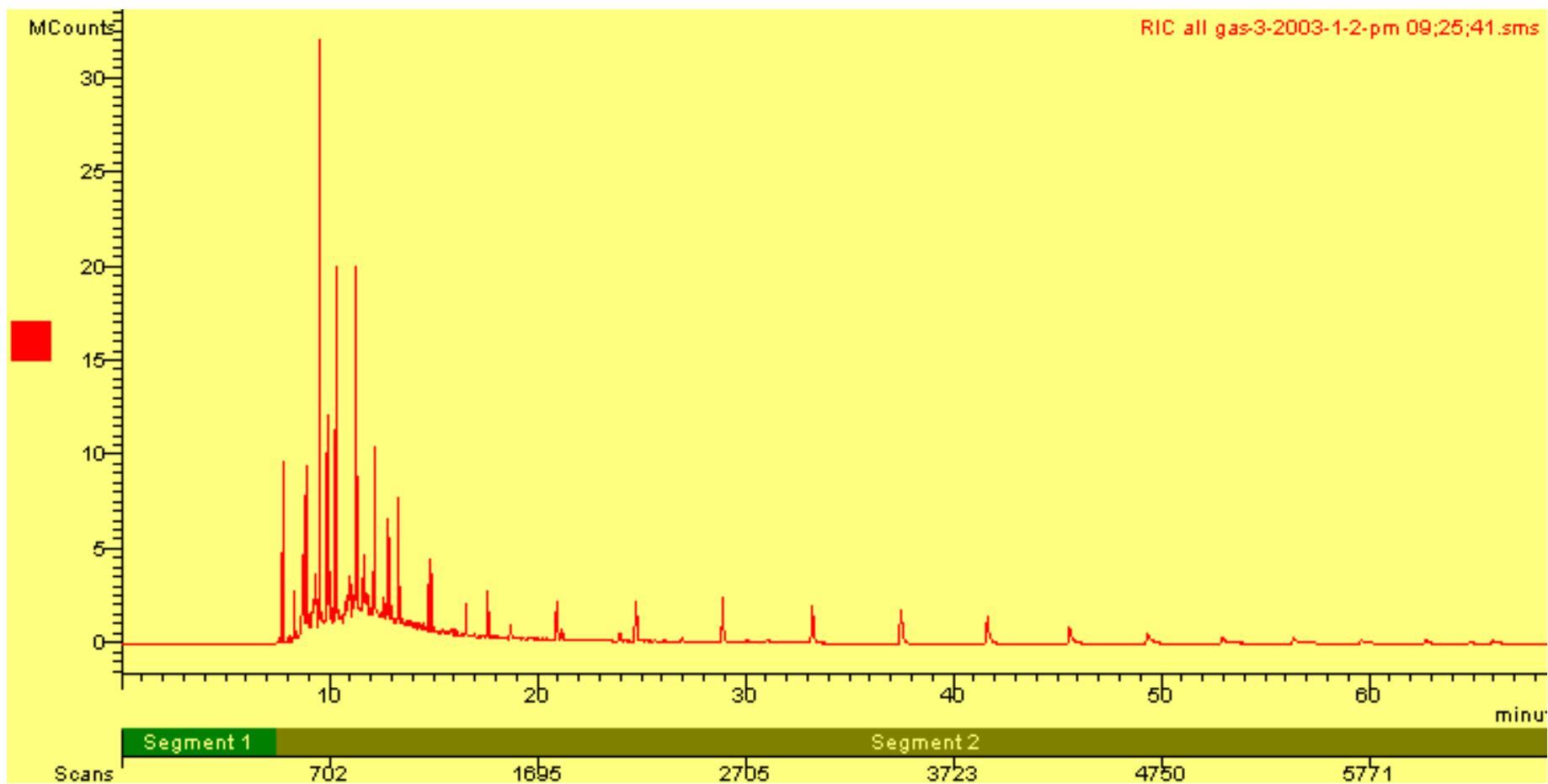


Figure C-7. Total ion chromatogram (TIC) of atmospheric gas-phase PAHs unknown sample

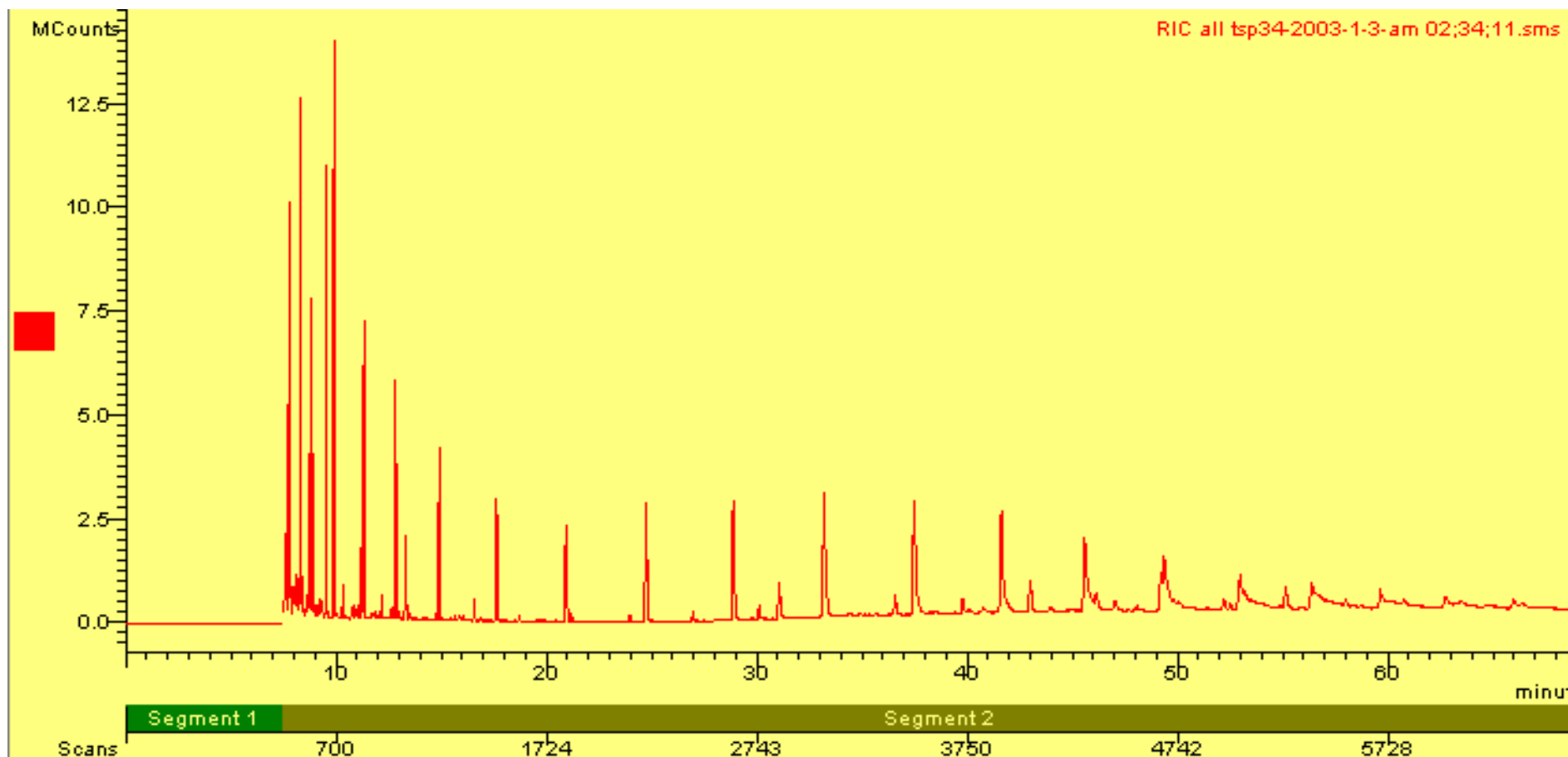


Figure C-8. Total ion chromatogram (TIC) of atmospheric particle-phase PAHs unknown sample

**Appendix –**

**Comment Answer**

## 口試委員意見回覆

鄭曼婷 教授

1. 論文摘要不需有分析方法之介紹。

回覆：在中英文摘要中已移除分析方法之介紹。

2. 論文中需提及所採樣之樣品數。

回覆：在中英文摘要已經加入樣品數 (N = 19) 之描述

3. 建議 PAHs 特徵值之探討可以列入未來探討對象。

回覆：謝謝教授建議，未來將會深入探討。

4. 台中與台北 PAHs 數據比較中，台北偏低是否有其他因子的影響。

回覆：台北 PAHs 的採樣方式是採用小型個人採樣器，而且他們的主題主要是針對室內室外 PAHs 的相關性，所以並沒有考慮到對於都會區型態 PAHs 的濃度特性，而我們是針對區域性大氣濃度的特徵以 PS-1 採樣器採樣。所以台中所得到的濃度要比台北來得高。

5. 建議可以比較台中地區其他研究之 PAHs 數據。

回覆：目前台灣中部 PAHs 之文獻並不多，若將來有新的文獻發表將會列入討論。

6. 建議未來是否可以量化汽油車輛以及柴油車輛對大氣 PAHs 之貢獻量。

回覆：謝謝教授建議，未來將會尋找適合的模式或統計方式估算出各個來源 PAHs 的貢獻量。

## 張鎮南 教授

1. 氣相與固相之 PAHs 濃度相差甚大，在分析過程中分析濃度是否有超出檢量線範圍？

回覆：是的，大氣當中氣相 PAHs 濃度的確比固相 PAHs 濃度高出許多，所以再注入 GC / MS 分析前會將氣相 PAHs 樣品稀釋至適當濃度，以求得準確的濃度值。

## 方國權 教授

1. 建議未來可以將 DBA 列為管制對象。

回覆：謝謝教授建議。

2. 台北是否有使用相同採樣器之 PAHs 研究。

回覆：目前文獻記載只有李芝珊 教授的研究，未來若有發現將會加入討論。

3. 建議可以將最新的發表著作 (International Journal of Environment and Pollution) 列入文獻當中。

回覆：謝謝教授建議，新著作已加入文獻當中。

## 黃啟裕 教授

1. 在圖列表中 Figure B-1 至 Figure B-21 有筆誤。

回覆：謝謝教授指正，論文當中已經修正。

2. P. 4 第 11 行 (Odabasi et al., 1999) 的文獻有所矛盾。

回覆：謝謝教授指正，已刪除此段不合理句子。

3. 論文中應提及 SPSS 8.0 之全名。

回覆：謝謝教授指正，於 P. 13 第 7 行已加入 SPSS 8.0 全名 ( Statistical Package for the Social Science )。

4. 建議可以將論文中的縮寫列表方便查詢。

回覆：謝謝教授建議，於圖表列後以置入縮寫對照表。

5. P. 20 第一段句子要加入動詞。

回覆：謝謝教授指正，此段句子已加入動詞，修正後之句子如下：

An apparatus for cleaning samples “which was” using the distillation extraction method.

6. 建議加入實際樣品之質譜圖。

回覆：謝謝教授建議，已於附錄 P. 83-84 加入大氣氣相以及固相 PAHs 樣品之質譜圖。

7. 應將 3.4 這一節移至 3.1。

回覆：已將原來 3.4 小節實驗流程移為 3.1 小節。

8. 建議各國比較可以找其年代接近的文獻。

回覆：謝謝教授建議，未來有可能的話將盡量比較年代接近之數據來做比較。



## 張士昱 博士

1. 建議未來採樣點設置可以增加背景測站。

回覆：謝謝教授建議，未來的實驗規劃將納入考慮。

2. 溫度對 PAHs 濃度有相當的影響，在採樣過程溫度是否會降低 PS-1 採樣器內所收集樣品的濃度。

回覆：再運送樣品的過程中會以小冰櫃運送採樣樣品，採樣器原本的設計就有一個可以遮雨擋陽光的蓋子，所以採樣期間並不會受到降雨以及光降解的影響，至於採樣器內的溫度礙於採樣器本身的設計並無法改善，只能夠縮短樣品置於採樣器中不必要的時間。

3. 光降解作用對 PAHs 濃度有很大的影響，在採樣過程是否有保存裝置。

回覆：是的，採樣過程中樣品均有使用鋁箔紙包裹採樣樣品避免陽光照射產生光降解作用。

4. XAD-2 與 XAD-16 差異為何？

回覆：XAD-16 是新一代的吸附劑，效果比 XAD-2 好很多，故採用 XAD-16 作為氣相 PAHs 樣品的收集。

5. 採樣器流量控制對所收集到的濃度影響相當大，其流量控制過程應有所提及。

回覆：是的已於 3.5 節 P. 26 中重新描述 PS-1 採樣器之流量校正過程。

6. PS-1 採樣器所測得的 TSP 濃度應有所表示。

回覆：是的，已於 4.1 節 P. 31 提及 TSP 濃度之描述。

7. P. 26 第 15 行 MDL 算式有誤。

回覆：是的，已訂正錯誤。

8. 建議未來可以參考 MTBE 之數值作為排放來源的指標。

回覆：謝謝建議，未來將會納入探討。

9. 光化學作用對大氣 PAHs 濃度影響甚大，建議未來可以將臭氧等光化學指標  
作為未來探討的一部份。

回覆：謝謝建議，未來將會納入探討。