

## CHAPTER III

### MATERIAL AND METHODS

#### 3.1 Instruments

##### Analysis

1. Gas Chromatograph-Mass Spectrometer (GC-MS) : model GC 8000 series, AS 800 Autosampler and Mass Spectrometer Model MD 800 from Fison Instrument.

##### 2. GC-MS Conditions

Column	:	DB-1HT capillary column, 30 m length ; ID 0.25 mm, film thickness 0.1 $\mu\text{m}$ Temp. limit -60°C to 400°C
Carrier Gas	:	Helium purity 99.999 %, flow rate of 45 cm/sec
Oven	:	60 °C(1 min) to 150 °C ramp at 20 °C/min, hold for 3 minutes then ramp at 8 °C/min to 200 °C(3 min) ,then ramp at 8 °C/min to 310 °C, 8 min final time.
Injection temperature	:	250 °C
Injection technique	:	splitless
GC-MS interface temperature	:	250 °C
Mass analyser	:	quadopole
Ionization mode of MS	:	EI <sup>+</sup>
Source temperature of MS	:	250 °C
Mass scan type:full scan	:	50-400 amu at 400 amu/sec
Solvent delay	:	3.75 min

3. High Vacuum Pump, Edwards, Model E2m2 20035.

Extraction and Concentration.

1. Soxhlet : 200 mL

2. Heating Mantle

3. Rotary Evaporator: Eyela Rotary Vacuum Evaporator,  
Tokyo Rikakikai Co.,Ltd.

4. Water Vacuum Pump: Eyela, Aspirator A-3S, Tokyo Rikakikai Co.,Ltd.

5. Filter Paper : Whatman No.4, Circle 150 mm., Whatman  
International Limited

6. Water Bath : Thermolyne, Lybron Corporation,  
Subsidiary of Sybron Corporation Dubuque,  
Iowa, USA.

### Sampling

1. High Volume Air Sampler :

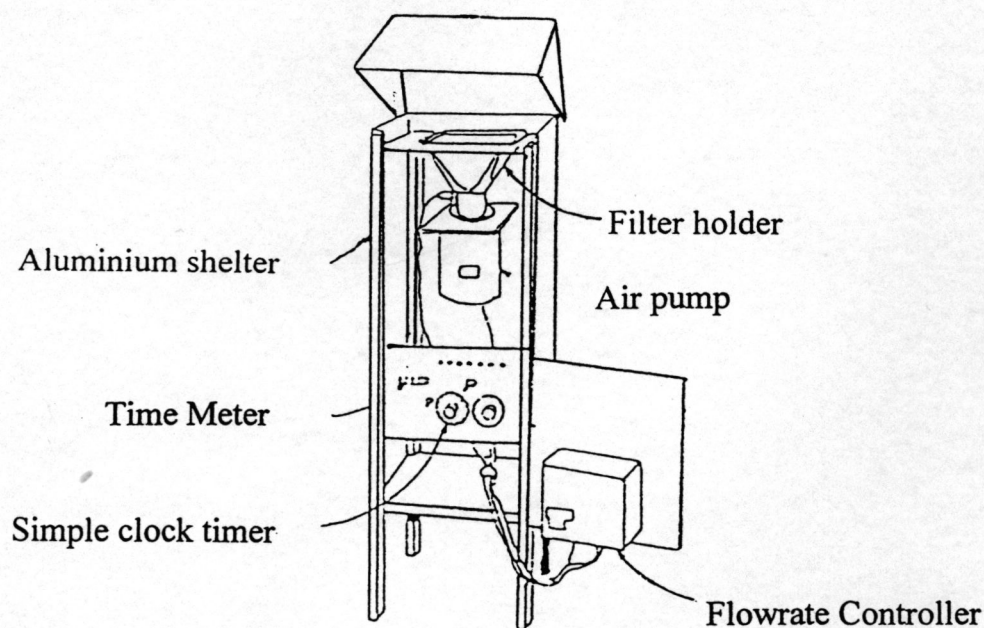


Figure 3-1 High Volume Air Sampler

### 3.2 Chemicals and Materials

1. Solution of standard PNA mixture of 16 components ( $\mu\text{g/mL}$ ) in methanol:methylene chloride (1:1), Sigma-Aldrich for EPA 610 containing:

Napthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene and Benzo[ghi]perylene

2.Solvent : Cyclohexane, CARLO ERBA, Reagent, montetini group.  
PRE Acs-For analysis Code No. 436903

3.Filter : Glass Fibre Filters, GRASEBY GMW,  
AIR MONITORING MEDIA, P/N - G810,  
8 inch X 10 inch (20.3 cm X 25.4 cm.)

4.Cleaning Solution : Sulfuric Acid ; MERK  
Potassium dichromate; MERK

5.Grease : Silicone grease Bayer, high vacuum, Tube with 35 gr.,  
Fluka Chemie AG, CH-9470 Budu

### 3.3 Sample Collection

Roadside and off-road air samples were collected from the roofs of National Ambient Air Quality Standards monitoring stations operated by the Pollution Control Department of Thailand (P.C.D.) by the Hi-Volume Air Sampler with Glass fibre filter for 24 hr.

At all sampling sites, the air inlet was located 3 m above ground level. Roadside samples were collected at BangYeeKhan, Pratunam, Yaowaraj and

National Statistical Office (Nat.Stat.Off.). Off-road samples were collected at the Rajabhat Institute, Bansomdej.

BangYeeKhan air samples were sampled at BangYeeKhan Electrical Substation, Charan Sanitwong Road, BangYeeKhan. Sampling periods were between Feb 2 - Feb 20, 1996. There is a traffic isle in the center of a divided six-lane street. There are high buildings (4-floor) standing along the roadside. It was a commercial area.

Pratunam area is located on Ratcha Parop Road, Phyatai between Ratchaprasong and Sriyuthaya Crossroads. Sampling periods were between Feb 21 - Mar 9, 1996. It is a residential and commercial area and has six-lanes. There are high buildings standing along the bothsides of road. This area has a very high intensity of traffic volume and has problems about heavily traffic jam and high TSP concentration.

Yaowaraj area is located on Yaowaraj road, It is a part of China town, and a commercial and residential area similar to Pratunam area. It is a five-lane and has high buildings along with both sides.

The National Statistical Office (Nat.Stat.Off.) is located on LanLaung Road, Ratchadamnern. It has five lanes and a one way system. There are high buildings standing on both sides of the road. This area is an official and commercial area and has less traffic volume than other roadside sampling areas.

The sampling at Bansomdej area was collected at Rajabhat Institute, Bansomdej permanent ambient station. It is more than 50 m away from

Itsaraphab Road and has less traffic volume than other sampling areas. The map of sampling areas is shown in Figure 3-2.

The samples were collected for 24 hr at each sampling site following this schedule :

- BangYeeKhan Area : Feb 2 - Feb 20, 1996.
- Pratunam Area : Feb 21 - Mar 9, 1996.
- Yaowaraj Area : Mar 12 - April 8, 1996.
- Nat.Stat.Off. : April 11 - April 28, 1996. and
- Bansomdej samples were collected over the entire study period (Feb 2 - April 28, 1996).

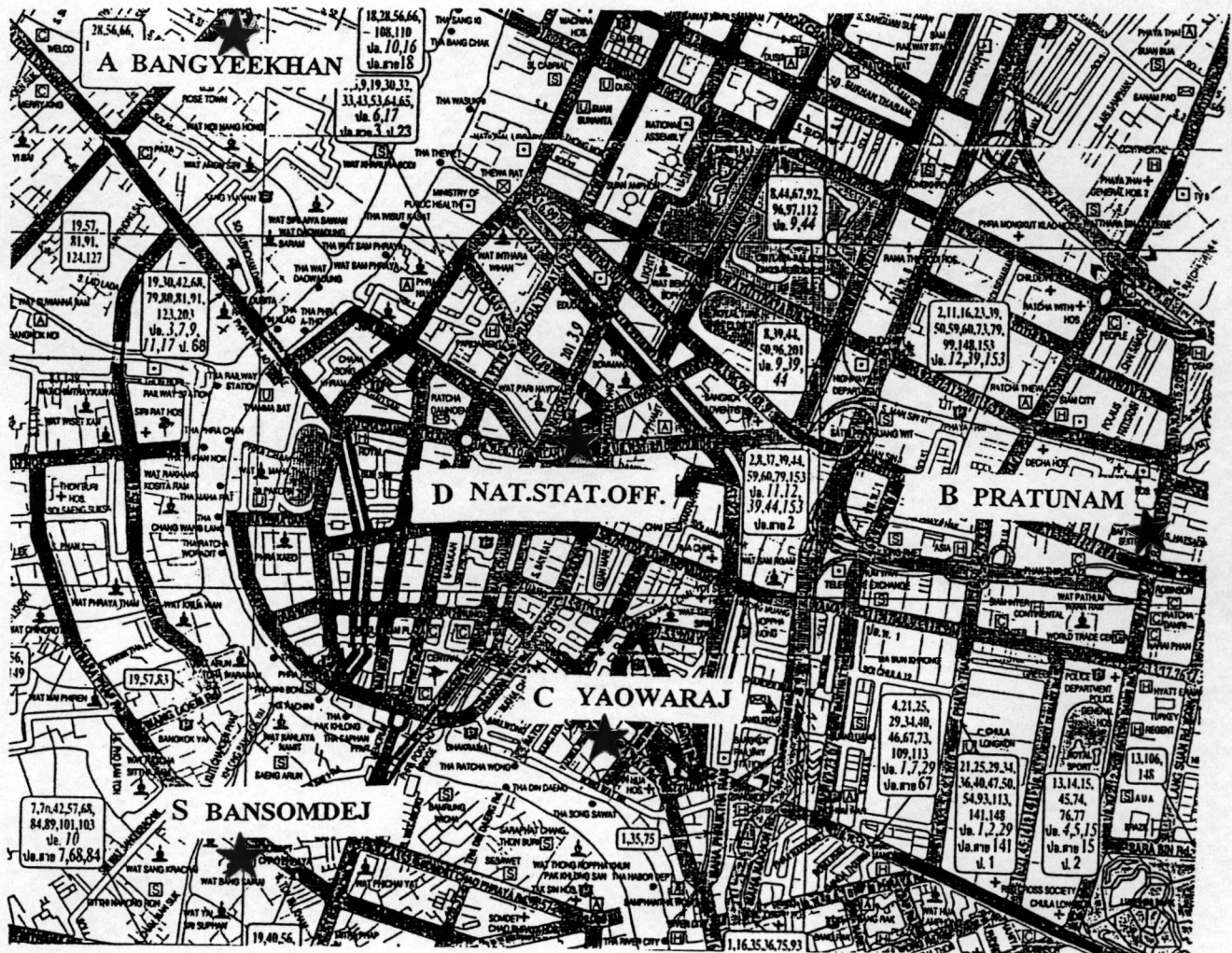


Figure 3-2 Map of Sampling Areas

### 3.4 Filter Extraction

A half of a filter loaded with total suspended particulates (TSP) was cut into pieces and placed into the extraction apparatus. Cyclohexane(350 ml) was added, and one or two clean boiling chips were added . Then it was extract for 12 hours.

After extraction, the extract was poored into the evaporating flask. The round bottomed flask and soxhlet apparatus were rinsed with 20 to 30 mL of cyclohexane to complete the quantitative transferring. .

The evaporating flask was placed in a water bath of a rotavap at 40-50°C. When the apparent volume of liquid reached 10 mL, the evaporating flask was removed and allow it to drain and cool at least 10 minutes. 5 mL of extract is recommended for this operation.

The solution was transfered to a Teflon-sealed screw-cap bottle, protected from light by wrapping with foil and stored it in a freezer at -4 °C before GC/MS analysis.

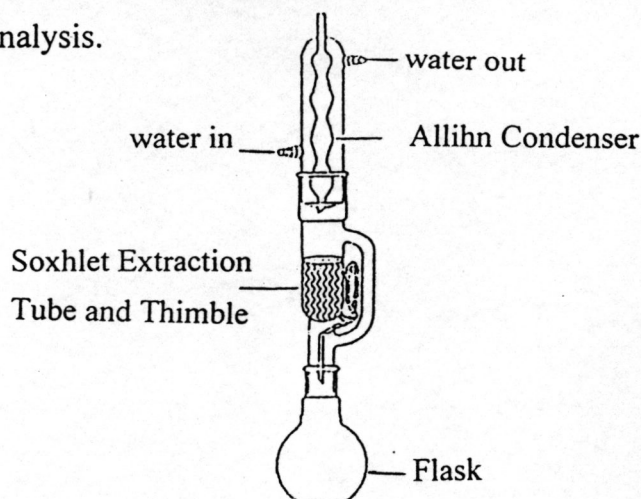


Figure 3-3 Soxhlet Extraction Apparatus

### 3.5 Analysis by GC/MS

Aliquots of 1  $\mu\text{L}$  of sample was injected to GC (0.25 mm. I.D.DB-1 Hitemp. coated ( $d_r = 0.1 \mu\text{m}$ ) fused -silica capillary column.(J&W Scientific, Folsom,CA,USA.).

The carrier gas used was helium with flow rate of 45 cm/sec. The temperature of GC was initiated at 60  $^{\circ}\text{C}$  for 1 min, increased to 150  $^{\circ}\text{C}$  with rate of 20  $^{\circ}\text{C}/\text{min}$  and held for 3 minutes, then increased to 200  $^{\circ}\text{C}$  with rate of 8  $^{\circ}\text{C}/\text{min}$  and held for 3 minutes, and then increased to 310  $^{\circ}\text{C}$  with rate of 8  $^{\circ}\text{C}/\text{min}$  and held for 8 min. The transfer line and ion source were heated at temperature of 250  $^{\circ}\text{C}$ . The mass spectrometer was operated in the  $\text{EI}^+$  mode with electron ionization energy of 70 eV. The mass spectrometer scan type:full scan range of 50-400 amu was scanned at a rate of 400 amu/sec. The injection technique was splitless and the injector temperature was 250  $^{\circ}\text{C}$ .

### 3.6 Calibration

External standard calibration procedure :

1. Calibration standards at the minimum of three concentration levels were for each parameter of interest by adding volume of one or more stock standards to a volumetric flask and then were diluted to volume with cyclohexane. One of the external standards was at a concentration near, but above, the method detection limit (MDL) and the other concentrations were corresponded to the expected ranges of concentrations that are found in real samples or were defined the working of the detector.

2. Each calibration standard were analyzeand peak height or area responses were tabulated against the mass injected. The results were prepared a calibration curve for each compound.

3. The working calibration curve was verified on each working day by the measurement of one or more calibration standards. The response for any parameter was varies from the predicted response by more than  $\pm 10\%$ , the test was repeated by using a fresh calibration standards.

### 3.7 Calculation

A calibration curve was constructed by plotting the peak areas of PNA against the PNA amount in the solution. The PNA levels calculated from the calibration curve were corrected for the 99.99 % purity of the PNA reference.

Concentration of each component was calculated from linear equations of calibration curves as shown in Appendix G.

Linear Equation for:

$$\text{Phenanthrene} \quad Y = 67146X - 4566.5$$

$$\text{Fluoranthene} \quad Y = 79563X - 6874.5$$

$$\text{Pyrene} \quad Y = 43230X - 3848$$

Where :

Y = peak areas ,

X = The amount of PNA (Phenanthrene) in solution, ppm

An example for phenanthrene calibration curve equation

$$Y = 67146X - 4566.5$$



$$X = (Y + 4566.5) / 67146$$

when calculated for PNA concentrations in atmosphere

$$C = \{X \times 10 \text{ mL or } 5 \text{ mL} \times 2^a\} / \text{Air Volume}$$

Where :

X = The PNA concentration in sample, ppm

C = The PNA concentration in atmosphere,  $\mu\text{g}/\text{m}^3$

Y = The peak area from GC/MS analysis

10 mL = the extraction volume of samples, mL

$\times 2^a$  = a half of filter extracted should be multiplied by 2 for full

filter

Air Volume = Total Air Volume from Hi-Volume Air Sampler,  $\text{m}^3$