CHAPTER III

EXPERIMENTAL

Apparatus, Chemicals and Materials

Apparatus

1. Gas Chromatograph-Mass Spectrometer

   The apparatus model 8000 series, Mass Spectrometer model MD 800 and AS 800. Autosampler from Fison Instrument.
2. High vacuum Pump

   Gast model 0523-V103-G21DX
3. Soxhlet
4. Rotary Evaporator

   Eyela Rotary Vacuum Evaporator, Tokyo Rikakikai CO., Ltd.
5. Water Vacuum Pump

   Eyela, Aspirator A-3S, Tokyo Rikakikai Co.,Ltd.
6. Water Bath

   Thermolyne, Lybron Corporation, Subsidiary of Sybron Corporation Dubuque, Iowa, USA.

Chemicals and Materials

1. Cyclohexane

   Analysis grade
2. Standard Polycyclic Aromatic Hydrocarbons

   PAHs from EPA 610 with content of : Napthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indene(1,2,3-cd)pyrene, Dibenz(a,h) anthracene and Benzo(g,h,i)perylene.
3. Isoamyl Alcohol
4. Glass-Microfibre Filters.

   Whatman model GF/F, 90 mm diameter
5. Polyurethane Foams

   0.6 g/cm^3 density

Test Engine

The test engine used in this study was a ISUZU 4-cylinder, 2400 cc. The specifications of the engine are shown in Table 3.1

Table 3.1 Characteristics of ISUZU engine.

Model	4FG1
Bore	89.3 mm
Stroke	95 mm
Displacement	2380 liters
Compression ratio	21.5:1
Number of Cylinders	4
Injection	Direct Injection
Power output (Kw, (PS)/rpm)	58(78)/4,300
Torque (N-m, Kg-m)/rpm	153(15.6)/2500
Low Idle Speed	800 rpm

Test Fuel

The test fuels used in this study were base diesel fuel , delivered from Petroleum Authority of Thailand (PTT), and base diesel fuel blended with the oxygenated compound (isoamyl alcohol). The test fuel diesel is summarized below:

Table 3.2 Fuel preparation.

Test fuel	Fuel code
Base diesel fuel	B0I
Base diesel fuel blended with isoamyl alcohol 4 % volume	B4I
Base diesel fuel blended with isoamyl alcohol 6 % volume	B6I
Base diesel fuel blended with isoamyl alcohol 8 % volume	B8I
Base diesel fuel blended with isoamyl alcohol 10 % volume	B10I

B: Base diesel fuel

I: Isoamyl alcohol

Engine Operation

The engine were preconditioned for half hour at the start of each test and then held for 20 minutes at each test condition to establish equilibrium before the particulate gases were sampled. Engine conditions was fixed at no load and speed of 800,1600 and 2400 rpm respectively.

Exhaust Sampling System

1. Collection of Sample

The methods of collection of a particulate sample from light duty diesel are specified. These samples are collected from a modified dilution tunnel shown in Figure 3.1

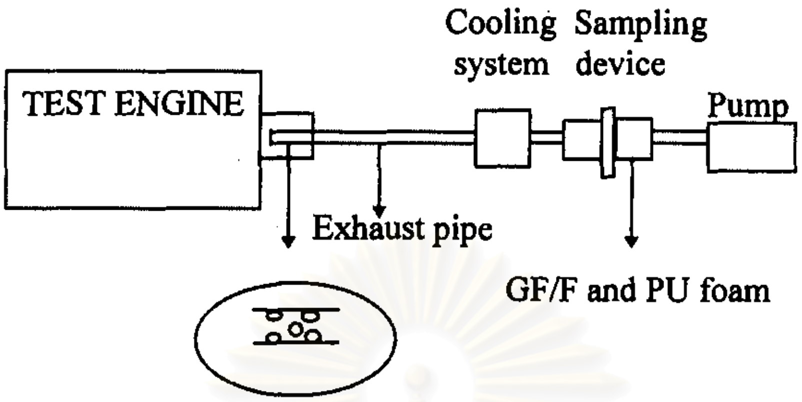

Figure 3.1 Sampling system

Samples of exhaust particulate were taken from the exhaust pipe. The engine utilised an externally air cooled exhaust system to simulate practical engine operating conditions. The exhaust particulates were sampled at the end of the exhaust pipe via a 5/8 -in i.d. stainless-steel probe inserted into the exhaust pipe 10 cm from the exhaust manifold. The exhaust emission were passed to the cooling system and then passed to a Whatman glass fibre GF/F grade filter as recommended by Williams et.al.[8] and to a polyurethane foam by suction with high volume vacuum pump. Exhaust particulates and semi-volatile exhaust samples from the test engine was trapped on the glass-microfibre filter and polyurethane foam and were kept in the dark and stored in a refrigerator until extraction.

2.Analysis of Samples

2.1 Extraction

The glass fibre filter and the polyurethane foams exposed to the exhaust were extracted with 300 mL cyclohexane for 12 hours by soxhlet extraction. The cyclohexane Soxhlet extracts were allowed to evaporate by rotary evaporator until the volume was less than 10 mL and then tranferred to a 10 mL volumetric flask. The remaining extract was rinsed with a small amount of cyclohexane and this solution was added to the volumetric flask. These aliqouts were refrigerated until subjected to GC-MS analysis.

2.2 Gas Chromatography - Mass Spectrometry

PAHs were identified and quantified by GC-MS. The GC-MS conditions to analyze the PAH samples are listed below:

Column:	DB-1HT capillary column length 30m, ID 0.25 mm, film thickness 0.1 μm
Carrier Gas:	Helium
Oven:	60 °C (1min) to 150 °C rate 20 °C/min 150 °C (3min) to 200 °C rate 8 °C/min 200 °C (3min) to 310 (8min) rate 8 °C/min
Injection temperature:	250 °C
Detector:	MS (EI^+ 70 eV)

Before a sample was injected, the GC-MS was preconditioned for a hour at an oven temperature of 250 °C, to flush contaminants from the column. An injection volumn of 1.0 μl was injected by autosampler.

At least two duplicate GC-MS injections was made for each sample. PAHs were identified by comparing peak retention times and mass spectra of reference standards.

Quantitative estimations were carried out by comparing the integrated peak area of molecular ion of samples to the corresponding standard calibration curve.

Blank samples were analyzed for the quantity of contaminants from materials and equipment used for the sample collection and analysis of the samples. The PAH found in the blanks was only napthalene and the quantity of this compound in the blank samples was generally less than 10 % of the amount in each samples.

Data Evaluation

Polynuclear aromatic hydrocarbon mixture for EPA 610 was used as the standard for establishing the calibration curve. The standards were prepared by diluting a stock dilution of the polynuclear aromatic hydrocarbon mixture for EPA 610 or the more concentrated one with cyclohexane solvent. A minimum of three concentrations of standard solutions were prepared. One of the external standards had a concentration near, but above, the minimal detection limit (MDL) of the detector and the others corresponded to the expected concentration ranges of samples. All standard solutions were kept in the refrigerator at -4 °C until the analysis was performed.

The standard were analyzed by GC-MS using the same condition employed for all samples. Retention time and response peak area of each component were recorded and the standard calibration curves were established by plotting the response peak area against the concentration of standard PAHs. All the calibration curves and their linear equations are shown in Appendix C.

Linear equation of standard calibration:

Standard substances	Linear equations
Naphtahene	$Y = 316966X - 58620$
Acenaphthylene	$Y = 574{,}053X - 123{,}187$
Acenaphthene	$Y = 704{,}818X - 151{,}459$
Fluorene	$Y = 733{,}809X - 191{,}459$
Phenanthrene	$Y = 570{,}450X - 111{,}287$
Anthracene	$Y = 339{,}762X - 69{,}536$
Fluoranthene	$Y = 654{,}756X - 142{,}477$
Pyrene	$Y = 539{,}170X - 113{,}867$

Where

Y = Peak Area of Chromatogram
X = Concentration (ppm)

The quantity of each PAH found in the diesel exhaust can be evaluated by the following method.

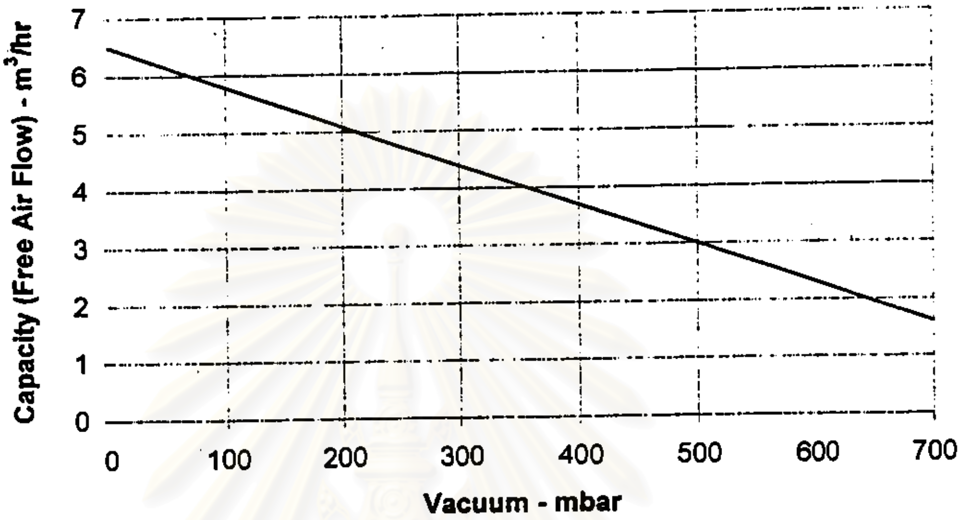

Figure 3.2 Pressure performance curve for measure volume of exhaust emission

The linear equation of this curve is:

$$F = (-6.97\times10^{-3}\times P) + 6.49$$

where

F = Flow rate of exhaust (m^3/h)

P = Pump pressure (mbar)

Volumn of Exhaust Emission:

$$V = F\times T$$

where

V = Volumn of exhaust gas (m^3)

T = Time of sampling (hr)

The concentration of each PAH in 1 μl injected sample was calculated by substitute the response peak area in the corresponding linear equations of the standard calibration curve. The quantity of PAH per cubic metre of exhaust was calculated by the equation

$$Q = \frac{(C \times E)}{V}$$

where

Q = Quantity of PAH per 1 m^3 exhaust ($\mu g/m^3$)

C = Concentration of PAH in μl injected sample (μg/ml)

E = Final volume (ml) of extract sample before GC injection

Example : Calculation of fluoranthene (ppm) in exhaust samples of diesel engine

Pump pressure (P) = 41.960 mbar

Time of sampling (T) = 20 min

Peak area of chromatrgram (A) = 232377

Final volume of extract sample (E) = 10 ml.

$$F = (0.00697 \times 41.960) + 6.49$$
$$= 6.198 \text{ m}^3/\text{h}$$
$$V = 6.198 \times (20/60)$$
$$= 2.07 \text{ m}^3$$

substitute Y = 232377 in the linear equation of fluoranthene calibration curve

$$X = (232377 + 142276.5)/634616.2$$

$$= 0.590 \text{ ppm}$$

$$Q = (0.59 \times 10)/2.07$$

$$= 2.850\ \mu g/m^3$$

PREPARATION SCHEME

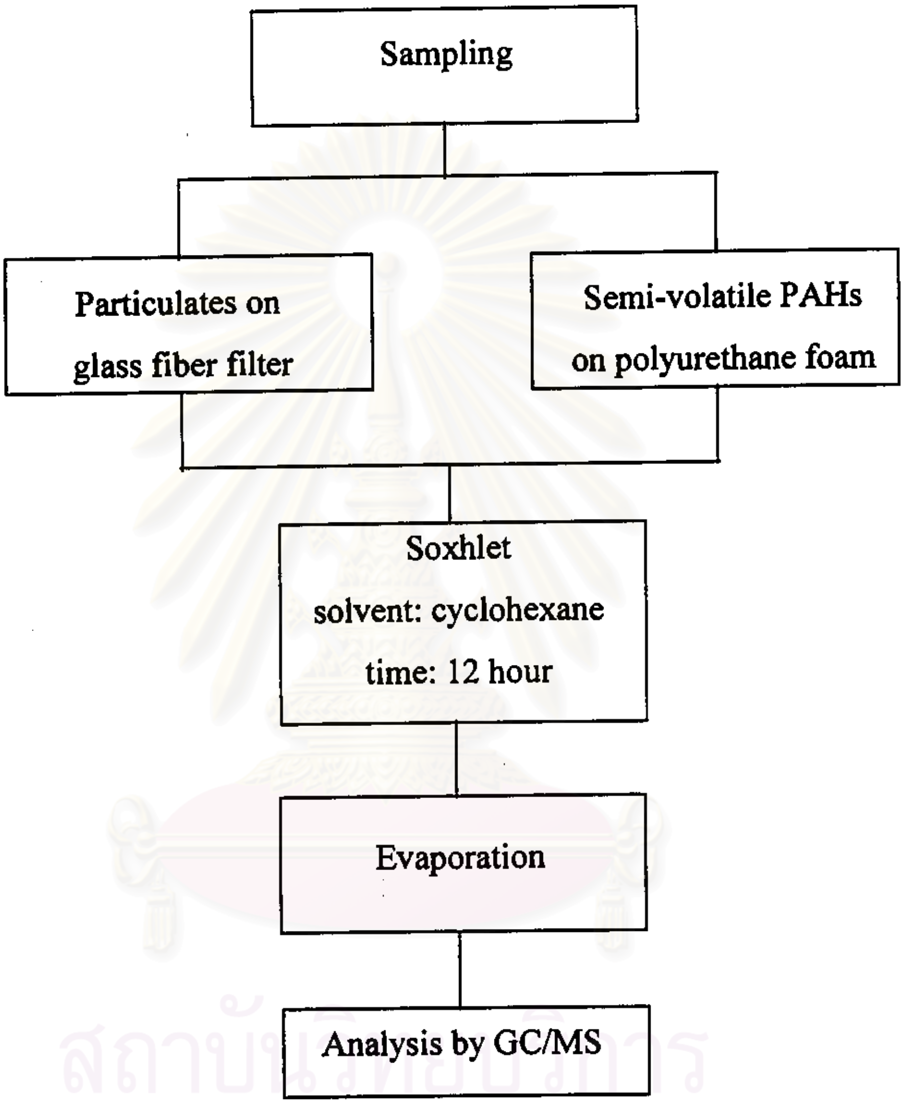

Figure 3.3 Analysis procedure