

CHAPTER III

EXPERIMENTAL

Instruments

Analysis

1. Gas Chromatograph-Mass Spectrometer (GC-MS).

The apparatus model GC 8000 series , AS 800 Autosampler and Mass Spectrometer Model MD 800 from Fison Instrument.

2. GC-MS Condition

Column : DB-1HT capillary column length 30 m.,
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⁺ 70eV)

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

Extraction and Concentration.

1. Soxhlet : 200 mL

2. Heating Mantal

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

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

5. Filters 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. Rotary Pump : GAST, model 0523-V4-G21DX, 1/4 HP
2. Filter Holder : Diameter 3 inch, length 12 inch, Made of Zinc.
3. Probe : Diameter 1 cm, Made of steel.

Exhaust Emission Source

1. Diesel Engine : Type 4JA1, ISUZU 2500 Di
 Numbers of cylinders 4
 Cylinder capacity 2500 cc.
 Max. horse power 87 PS at 4000 rpm.
 Compression ratio 18.4 : 1
2. Eddy current dynamometer : NSDK Nishishiba Electric Co., Ltd. Japan

Chemical and Material

1. Standard PAHs from 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. Sovent : Cyclohexane, CARLO ERBA, Reagent, montetini group. PRE Acs-For analysis Code no.436903

3. Filter :

3.1 Glass Fiber Filters, Type TFAGF41, Diameter 4 inch(10.16 cm) Good efficiency for particulate matter size 10 microns and under to submicron to 0.1 micron

3.2 Polyurethane foam , density 0.022 g/cm^3

4. Cleaning Solution : Sulfuric Acid
Potassium dichromate

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

6. Cetane Number Improver :

6.1 2-Ethylhexyl nitrate, CI0801, the Associated Octel Company limited, 23 Berkeley Square London W1X6DT, United Kingdom

6.2 Di-t-Butyl Peroxide, ARCO Chemical Company, 3801 West Chester, Pike Newtown Square, PA 19073-3287

Fuel Preparation

Cetane number improver were added to base fuel of cetane number 50 with a distillation boiling point (T90 °C) of 338 °C and 357 °C (Table 3.1) . Physical and chemical properties of the diesel fuel were measured before used for engine operation. Physical and chemical properties are cetane number, cetane index, API gravity, specific gravity, viscosity, pour point, sulphur content, copper corrosion, carbon residue, water & sediment, ash, flash point, boiling piont, color, and aromatic content.

Table 3.1 Fuel Preparation

DIESEL FUEL	CODE	T90 °C	CETANE No.
CN50/357 = A	DTH50X	357	50
CN53/357	DTH53X	357	53
CN56/357	DTH56X	357	56
CN50/338 = B	DTL50X	338	50
CN53/338	DTL53X	338	53
CN56/338	DTL56X	338	56
A + N 0.05% vol	DTH53N	357	53
A + N 0.14% vol	DTH56N	357	56
A + N 0.30% vol	DTH59N	357	59
B + N 0.05% vol	DTL53N	338	53
B + N 0.14% vol	DTL56N	338	56
B + N 0.30% vol	DTL59N	338	59
A + P 0.05% vol	DTH53P	357	53
A + P 0.14% vol	DTH56P	357	56
A + P 0.30% vol	DTH59P	357	59

A = Base diesel fuel of cetane number 50 and T90 = 357 °C

B = Base diesel fuel of cetane number 50 and T90 = 338 °C

N = 2-ethylhexyl nitrate

P = Di-t-butyl peroxide

Engine Operation

Before sampling exhaust emissions, the engine was preconditioned for 30 min at 2500 rpm to attain a constant temperature. To obtain an extensive data set at comparable engine power settings, sampling was undertaken with the speed of 2500 rpm and at 0, 50 and 80 % of full load. Samples were collected at speeds of 1500 and 3500 rpm at 80% of full load. Exhaust temperature and air:fuel ratio were measured during sampling exhaust.

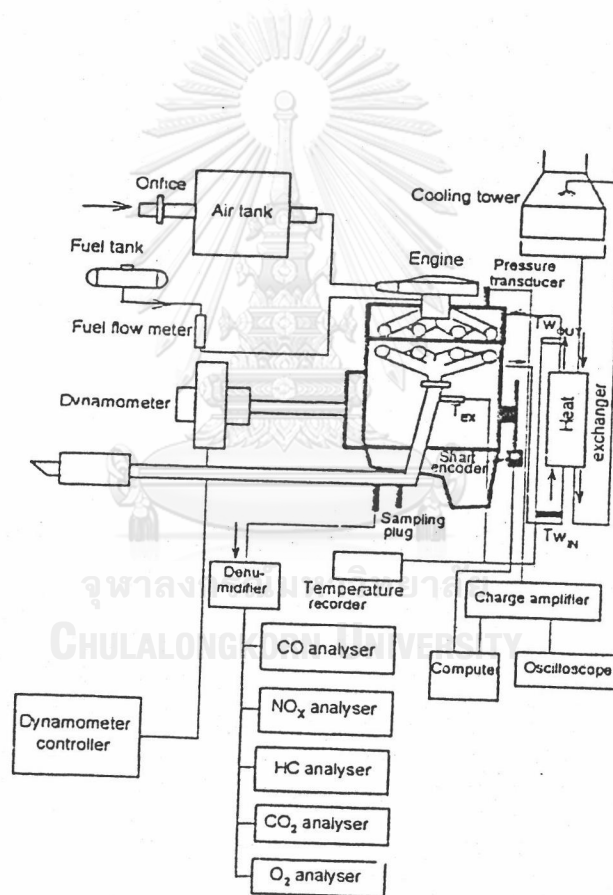


Figure 3.1 Engine Setup in the Laboratory

Sampling Exhaust

The exhaust emission was collected by the sampling system in Figure 3.2. In each sample was collected for 15 min and the pressure was recorded every 5 min.

The sampling system for particulates and gases in exhaust emission was modified from a dilution tunnel. The exhaust emission was cooled by water, to ensure that the vapour phase components of either unburnt fuel or combustion products were condensed out. Condensation of the organic fractions take place largely onto the particulate soot, glass fiber filter and polyurethane foam.

The exhaust emission was sampled at the end of an exhaust pipe via a 1.0 cm diameter probe inserted into the exhaust pipe 30 cm in length. The exhaust emission were passed to the condenser and then passed to the glass fiber filter and polyurethane foam by suction with an air pump. The glass fiber filter and polyurethane foam were kept in the dark and stored in a refrigerator until extraction. The recovery of sampling method was checked by using two pieces of PUF in the sample holder. Then they were analysed separately.

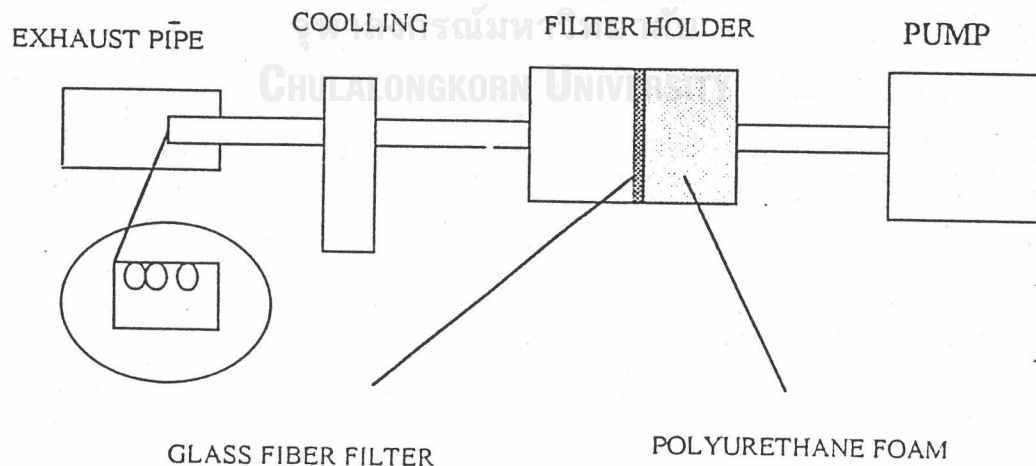


Figure 3.2 Sampling System

Extraction

Both the glass fiber filter and the polyurethane foam containing particulates and gases were extracted with 300 mL of cyclohexane by soxhlet extraction for 12 hours. The extract was concentrated by rotary evaporator until the volume was less than 10 mL. Then it was transferred 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. This sample was stored in a refrigerator until analysis. The extraction efficiency was checked by repeat extraction.

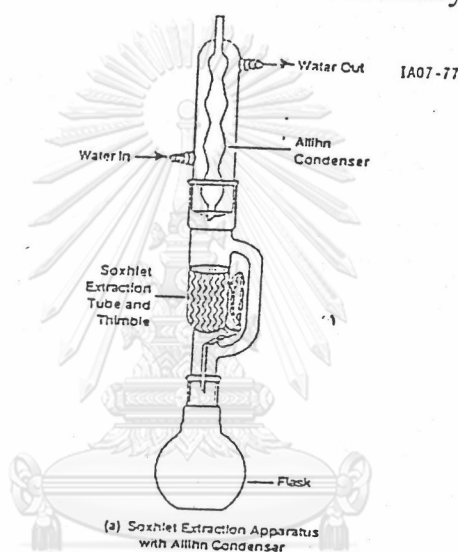


Figure 3.3 Soxhlet Extraction

Sample Analysis

PAHs were identified and quantified by GC-MS. The GC-MS was controlled and the data were collected by MassLab software running on a personal computer. 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 volume of 1.0 μ l was injected by autosampler.

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

Each PAH was quantified by comparing the peak area of each ion chromatogram to the calibration curve.

Blank samples were analyzed for the quantity of contamination from materials and equipment used for the collection and analysis of the samples. The PAHs found in the blanks was only naphthalene and naphthalene derivatives, the amount of these compound in the blank samples was generally less than 10 % of the amount in each sample.

Samples were stored in a refrigerator and analyzed within 120 days of collection. The time between final preparation and completion of the GC-MS injections was less than 4 weeks. In that time however, there was a noticeable decrease in the amount of naphthalene and naphthalene derivative. This probably due to evaporation through the pierced septum of the sample vial. Some samples were reanalyzed after 30 days of further storage. Unlike the original samples, the aged samples did not have quantifiable amounts of PAH with molecular weights from 128 to 156. Therefore naphthalene, naphthalene derivatives and acenaphthene could not be accurately quantified by this method.

Data Evaluation

The amount of PAHs and volume of diesel exhaust were evaluated by the following method.

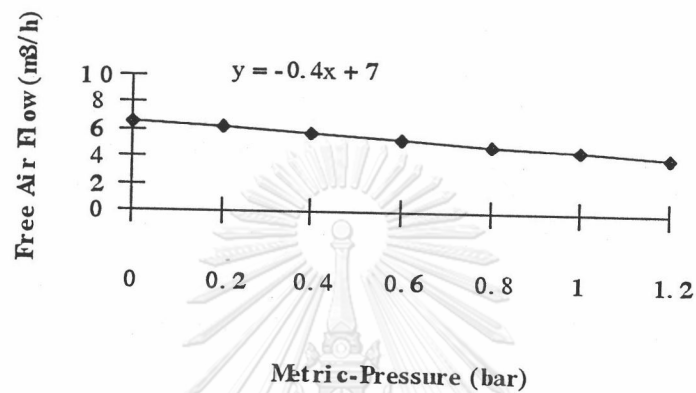


Figure 3.4 Pressure Performance for Measurement of the Volume of Exhaust Emission

Volume of Exhaust Emission

$$V = F \times T$$

$$F = -0.4 \times P + 7$$

Where:

V = Volume of exhaust gas (m³)

F = Pump Flow Rate (m³/h)

P = Pressure (bar)

T = Time of sampling (min)

1 bar = 750.0617 mmHg

This method refers to the specifications of the the air pump.

The concentration of each component was calculated from the linear equations of the calibration curve as shown in Figure C1-C5.

Linear Equation for :

Naphthalene $Y = 316966X - 58620$

Acenaphthene $Y = 190805X - 1117$

Phenanthrene $Y = 67146X - 4566$

Fluoranthene $Y = 79563X - 6874$

Pyrene $Y = 43230X - 3848$

Where :

X = Concentration (ppm)

Y = Peak Area of Chromatogram

$$\text{Phenanthrene (ppm)} = (Y + 4566) / 67146$$

$$\text{Phenanthrene}(\mu\text{g}) = \text{Concentration of Phenanthrene (ppm)} \times \text{Volume of Sample (mL)}$$

$$\text{Phenanthrene } (\mu\text{g} / \text{m}^3) = \text{Phenanthrene}(\mu\text{g}) / \text{Volume of exhaust gas (m}^3)$$

Concentrations of other PAHs were calculated in the same way. For alkyl PAHs, the calibration curve of the parent PAH was used.

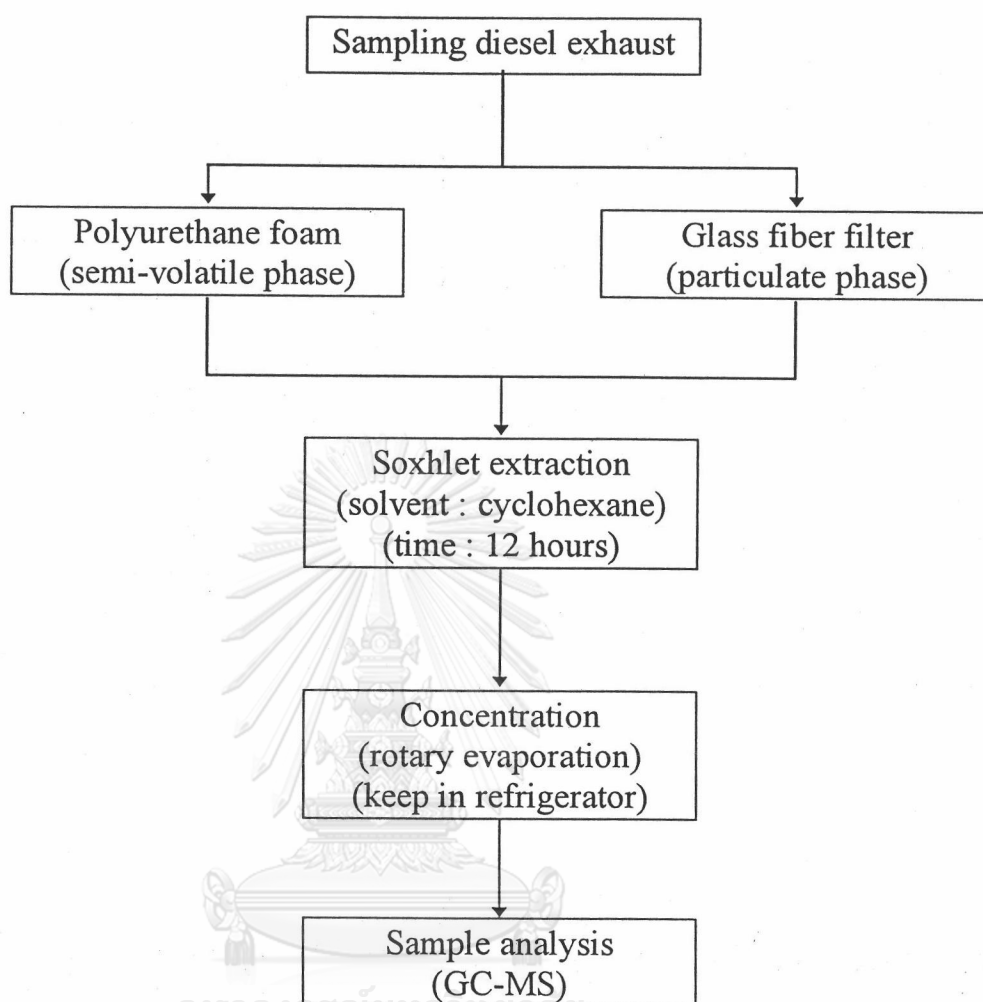


Figure 3.5 Analytical Procedure for PAHs in Diesel Exhaust