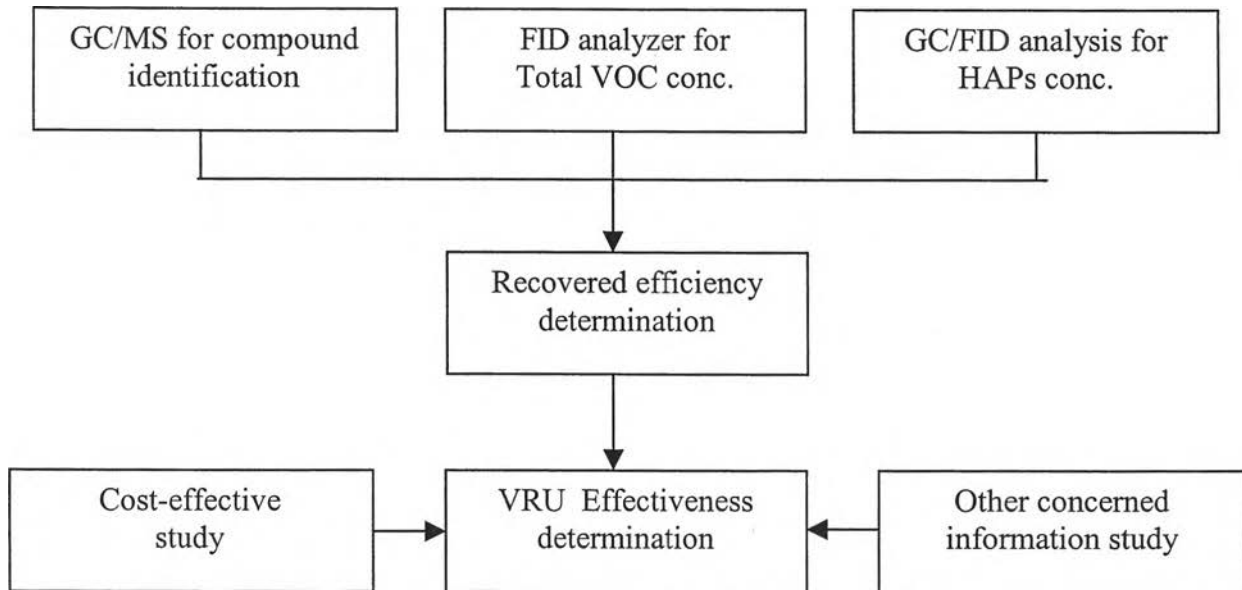




## CHAPTER 3

### EXPERIMENTAL TECHNIQUE AND METHODOLOGY

The procedure for this study is presented graphically in Figure 3.1



**Figure 3.1 Procedure for study**

The vapor recovery unit studied is carbon adsorption. The unit is from Cool Sorption (Thailand) Limited's know how.

#### **3.1 Characteristic of Vapor Recovery Unit in the studying : Carbon Vacuum Adsorbent (CVA)**

In this study, units of vapor recovery have been placed at Fuel Pipeline Transportation Limited (FPT) and The Shell Thailand. The type of units is Carbon Vacuum Adsorbent (CVA), and the work procedure is as follows.

Vapor from the loading point pass through the vapor header to the recovery unit. Prior to the vapor entering the CVA it will pass through a knock-out vessel to ensure that no gasoline enters the carbon bed.

The CVA consists of 2 activated carbon beds, one being connected to the vapor line “adsorption mode”- while the other undergoes regeneration by means of vacuum. Activated carbon has an extremely high surface area in relation to volume and the hydrocarbons are adsorbed in a very thin layer in the surface of the carbon. The carbon can only adsorb a given amount before it approaches saturation. If this occurs throughout the bed, then the vapor will pass through untreated. Consequently, the carbon will be regenerated in order to restore its capacity, so that it can effectively adsorb hydrocarbons in the following cycle.

The regeneration takes place in two stages. First the bed is evacuated until the pressure reaches the level at which the hydrocarbons begin to desorb from the carbon. The bulk of the hydrocarbons are removed in this stage. In order to remove the remainder, it is necessary to introduce a small amount of purge air, to complete the regeneration. From the separator, the vapor which is now very rich in hydrocarbons, passes into the absorber column where the bulk of the hydrocarbon is absorbed in a counter flow of gasoline. The small amount of air present, particularly during the purge stage, passes out of the top of the absorber column and result in a small carry over of hydrocarbons, and is returned to the carbon bed which is in adsorption mode.

The unit is provided with an automatic energy saving function if loading has stopped, all functions are set on stand by, once both carbon beds have been thoroughly regenerated. When on stand by, the carbon beds are kept clean and active by means of occasional regeneration in long intervals. When normal load resumes, the plant will automatically restart.

#### Specification of the activated carbon used in VRU

Palletized thermal activated mineral coal based

Density (Vibrated)	: 380-420 kg/m <sup>3</sup>
Specific surface	: >1500 m <sup>2</sup> /gram
Ash content	: <8%
Grain size	: 95% > 3.15 mm
Hardness	: >96
Water content	: < 8%

Auto ignition temperature : > 450 C

Pore size distribution :

Microspores  $r < 1$  mm : 0.38 ml of pores per gram activated carbon equal to 16% of carbon volume

Mesopore  $r = 1-25$  mm: 0.26 ml of pores per gram activated carbon equal to 11% of carbon volume

Macropore  $r > 25$  mm : 0.36 ml of pores per gram activated carbon equal to 15% of carbon volume

Summarized the pore volume is 42% of activated carbon volume.

### 3.2 Schedule of sampling

At gasoline terminal of The Shell Thailand, the samples were taken at night on Monday through Friday and during the day on Saturday and Sunday. The samples were taken only day-time FPT gasoline terminal. Samples were taken at two periods, peak loading period and normal loading period, approximately.

### 3.3 Sampling Procedure

Apparatus used in sample collection

1. The 40 Liter Tedlar bag (SKC,USA) was encased in another bag of black polythene to prevent any photochemical reaction occurring in the sample. The bags were washed by zero air and then checked for residues before re-used.
2. Portable air sampling pump : Escort Elf® Sampling Pump, MSA,USA
3. Low flow adjustable : Gemini Twin-Port Sampler, MSA,USA
4. Rigid box
5. The sampling inlet (probe) made of Teflon® tube length depending on the work.
6. Adsorbent tube (Charcoal tubes : SKC No. 226-09: 8 mm OD x 110 mm length) packed with two sections of activated carbon (400/200mg), SKC,USA
7. Temperature detector
8. Zero air used for bag cleaning
9. Bubble Flow Calibrator, Gilian®, USA

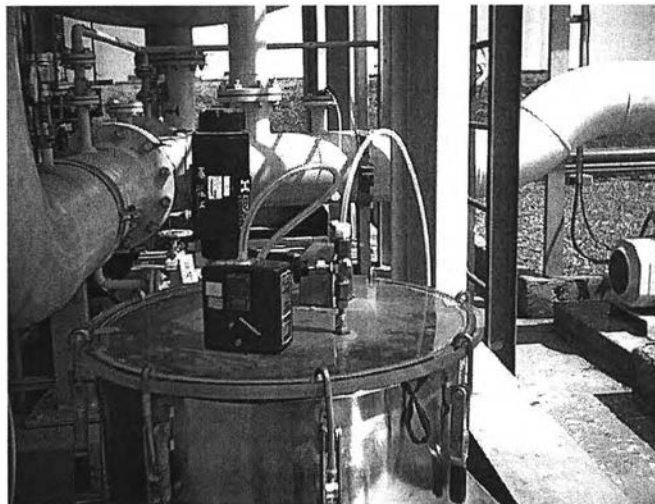
#### 10. Glass wool

The samples were taken during all oil loading operated by simultaneously inlet and outlet samples. The samples were taken for 2 periods, normal period and peak loading period with 1 hour on each period.

Due to the fact that the outlet sampling point limited the area to place all sampling equipment, a stainless pipe was connected from the vent point down to earth. The outlet sampling line and inlet sampling point are shown as figure 3.2 and 3.3 respectively.



**Figure 3.2 Outlet Sampling Line**



**Figure 3.3 Inlet Sampling Point**

The vapor samples collection of Tedlar bag were operated as follows:

Assemble the sample train as shown in Figure 3.3, leak check both the bag and the container. Then, connect the vacuum line from the needle valve to the Teflon sample line and place the end of the Teflon probe at the centroid of the sampling point and start the personnel pump to obtain a flow 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag. When the pump was operating, a vacuum is created in the box. Then, the gas flowed into the bag immediately by the vacuum force. The sampling rate was maintained at 0.5 liter per minute for one hour. At the end of the sampling period, shut off the pump and disconnect the vacuum line from the bag container. Record the temperature, ambient temperature and initial and final sampling time.

Then, all tedlar bag gas samples were drawn on-site into adsorbent tube as follows:

Both the inlet and outlet sample bags were drawn through coconut based charcoal tube using a portable air-sampling pump with adjustable low flow holder. The sampling rate was maintained at 0.05 liter per minute for inlet sample for 2 minutes. The sampling rate was maintained at 0.1 liter per minute for outlet for 10 minutes. Then the charcoal tubes were sealed by m-parafilm, recorded number and date of sampling and then kept at temperature under - 4 °C before going to analysis.

#### *Data Recording*

At the time of sampling, the necessary information to be recorded were

- Type and volume of product loaded
- Date and time
- Ambient temperature, inlet and outlet temperature

### **3.4 Analytical procedures**

#### **3.4.1 Total VOCs analysis**

### Apparatus

1. a flame ionization detector (FID) of PIERBURG, FID PM-2000 Standard, Germany (Figure 3.3)
2. Stainless three way, Sweeklog, USA
3. Teflon tube
4. Purified Nitrogen gas (99.99%) , Thai Industrial Gas (TIG) Thailand
5. Propane ( $C_3H_8$  + Air) as standard gas with range between 10-16,500 ppm $C_3$  , Thai Industrial Gas (TIG) Thailand

The amount of total VOCs of both inlet and outlet samples were determined by a flame ionization detector (FID) of PIERBURG, FID PM-2000 Standard.



**Figure 3.4 : Flame Ionization Detector (FID) of PIERBURG, FID PM-2000**

**Standard.**

The measuring principle of FID is detailed below;

Inside the FID detector a hydrogen-helium flame is maintained by supplying it with hydrocarbon-free Burner air fed with sample gas

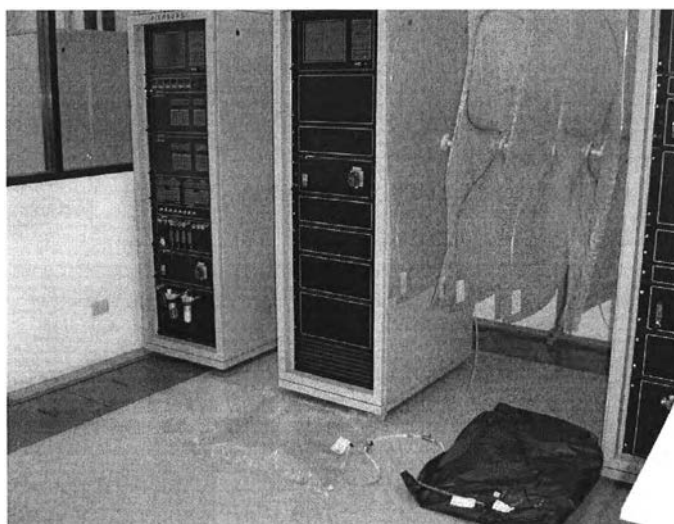
Inside the flame the carbon atoms are ionized. The ionized sample gas permits a small quantity of current to flow between two electrodes with a potential difference, installed inside the detector. This measuring current, approximately proportional to the number of carbon atoms, is amplified and displayed.

This measuring method is a relative measurement, i.e. the measuring value is created from a comparison between the physical effects of the gases to be measured and a gas of known concentration. The entry of the span gas concentration and the subsequent adjustment define the reference basis of the measuring equipment.

Since the detector is sensitive only to carbon atoms, a real concentration measurement (displayed in part per million (ppm)) can only be carried out if the gas composition is known; for identical volume concentration levels of methane and propane the detector shows almost three times the concentration for propane. As a result this method is particularly suited to determining the mass of carbons in a gas per volume unit that is bound in hydrocarbons.

The use of propane or methane as a comparison gas leads to a display of the measuring values in the unit ppm C<sub>3</sub>. (Pierburg Operating Manual Analyzer FID PM-2000, 1997)

In the case of an exceedingly high concentration of inlet samples to measure by FID analyzer, purified Nitrogen gas (99.99%) was adopted with dynamic dilution technique to dilute the samples. Stainless three ways was assembled with teflon line. One was connected to Nitrogen gas bag while the another was connected to sample bag as shown in figure 3.4. The dilution ratio of sample to N<sub>2</sub> gas is 1:53 approximately.



**Figure 3.5 : Dynamic dilution with purified Nitrogen gas**

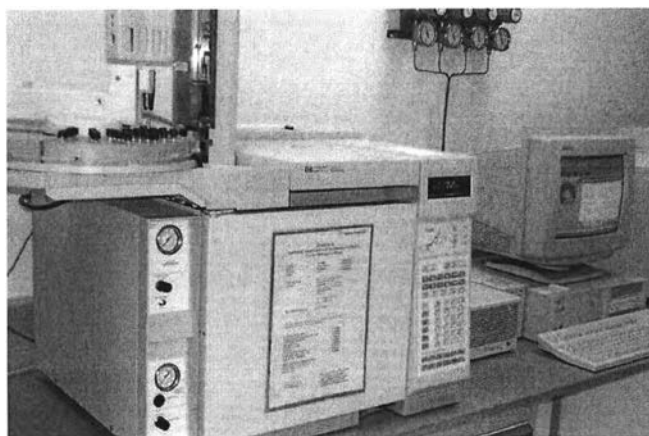
### 3.4.2 Hazardous Air Pollutant (BTEX, MTBE) analysis

After sampling, the charcoal tubes were sent to laboratory and the activated carbon was extracted in 4 ml of carbon disulfide (CS<sub>2</sub>). The extraction was shaken and left to stand for 30 minutes.

The collected BTEX and MTBE were analysed using gas chromatography with flame ionization detector (GC/FID) and a Hewlett Packard HP 6890 series gas chromatograph (Figure 3.6) with condition as below :

- The column used with the GC/FID is an 1% Methyl Siloxane (HP-1) capillary column ( 0.32 mm i.d. x 60 m long , 1.0 µm film thickness).
- Helium carrier gas
- GC Temperatures : injection port
  - : detector 280 °C
  - : oven 40 °C held for 1 minute  
5 °C/min. to 100 °C and held for 1 min.  
10 °C/min. to 180 °C and held for 3 min.

The concentration of all analytes were quantitated using FID measurements and peaks identified on the basis of a comparison of retention times with those in working standard. Five levels calibration were performed utilizing selected in range of about 50 ppmv to 2300 ppmv standards for all compounds. The calculation of regression parameters yielded  $r^2 > 0.999$  as shown in Appendix A.



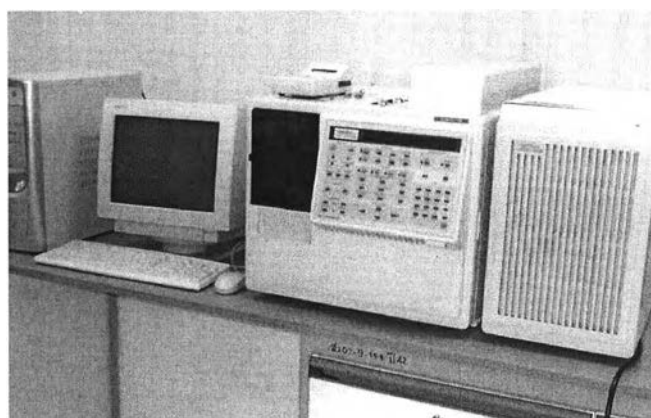
**Figure 3.6 gas chromatography with flame ionization detector (GC/FID)**



### 3.4.3 VOC composition identified

Both bags of inlet and outlet samples were taken to laboratory after 6 hours sampling. Forty milliliter of inlet sample and eighty milliliter of outlet sample were injected to analyse the compounds employing Gas chromatograph mass spectrometry (GC/MS), Varian Saturn 2000, USA (Figure 3.5) with conditions as below :

- The column used with 1% Methyl Siloxane (RTX-1) capillary column (0.53 mm i.d. x 60 m long , 3.0  $\mu$ m film thickness). Restek, USA.
- Helium carrier gas
- GC Temperatures : injection port
  - : detector 250 °C
  - : oven 40 °C held for 2 minute
  - 10 °C/min. to 120 °C and held for 1 min.
  - 10 °C/min. to 220 °C and held for 9 min.



**Figure 3.7 Gas chromatograph mass spectrometry (GC/MS) , Varian Saturn 2000**

A computer search will be done to determine the “best match” between a sample mass spectrum and one in library. A high fit occurs when each sample mass peak is found in the library spectrum, at the same mass and intensity. (B. Kebbekus and S. Mitra, 1998)

### **3.5 Gathering other concerned information**

Other concerned information used to determine the effectiveness of VRU were gathering from existing papers and interviewing concerned people. The information needed in the study such as,

- Investment cost
- Operation cost
- Gasoline recovery volume
- Gasoline price
- Project life
- Income tax rate
- Throughput initial and increasing rate