



CHAPTER 3

RESEARCH METHODOLOGY

3.1 Ambient Air Sampling

3.1.1 Sampling Procedures

3.1.1.1 Sampling Location

Ambient air sampling took place at 4 PCD air monitoring stations (Figure 3.1):

- 1) The Din Daeng station, in central Bangkok with heavy traffic
- 2) Chandrakasem Rajabhat University station, a commercial and residential area north of Bangkok
- 3) Ban Somdej Chao Praya Rajabhat University station, a commercial and residential area south of Bangkok
- 4) Ratburana Post Office station, an industrial area south of Bangkok

3.1.1.2 Sampling Period

Air samples were collected for 4 months during the southwest monsoons; July – October 2003, and 4 months during the northeast monsoons; November 2003 to February 2004. The air samples were collected every 6 days at each station in order to cover each day of a week. These samples were collected in the morning from 8:00 – 12:00 am. in order to get fresh emissions based on Watson, Chow, and Fujita (2001).

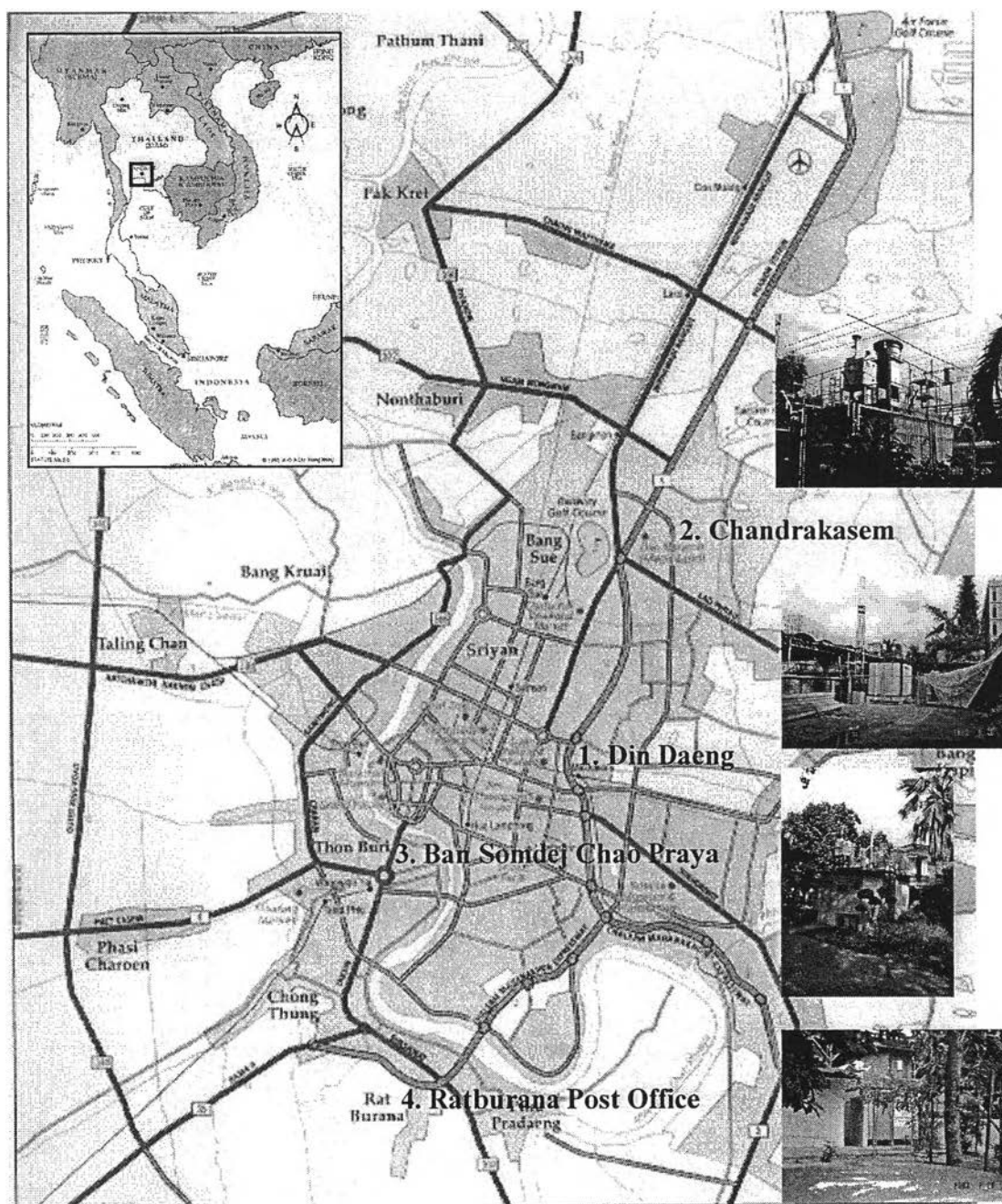


Figure 3.1 Ambient Air Sampling Locations

Prevailing wind direction	
↖	SW monsoon March-October
↗	NE monsoon November - February

3.1.1.3 Sampling Method

Procedures of ambient air sampling were as follows;

- a) The ambient air samples were withdrawn by a pump and adsorbed on sorbent tubes, $\frac{1}{4}$ inch O.D., 3.5 inch long packed with chromosorb 106 (Supelco), 250 mg (Figure 3.2 and 3.3).
- b) The recommended sampling flow rate is 10 ml/min (U.S. EPA., 1999). Actual flow rate was 11.0 ± 0.9 ml/min.
- c) The sampling time was 4 hours. When the air sampling ended, that sorbent tube was capped with a brass swagelock, the tube was wrapped with aluminum foil and put in a plastic bag, kept in an ice-box and transported to the laboratory, and kept in a solvent-free refrigerator. The samples were analyzed within one week.
- c) The sorbent tubes for air sampling were cleaned each time before usage at $240\text{ }^{\circ}\text{C}$ for 90 minutes with a tube cleaning device, Dynatherm Analytical Instruments, Inc., Model 60 (Figure 3.4)

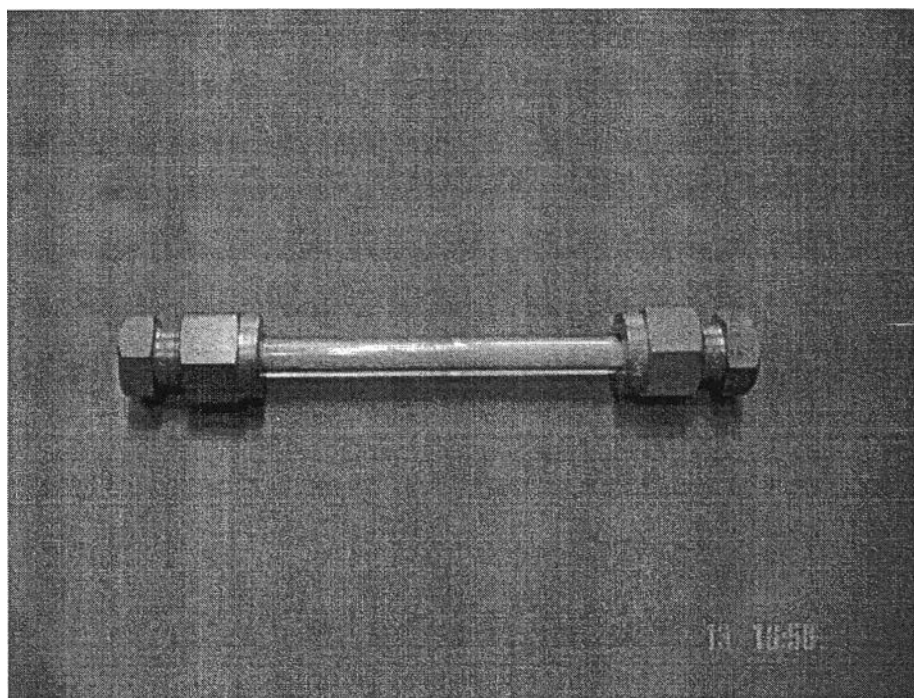


Figure 3.2 Sorbent Tube for Collecting Air Samples



Figure 3.3 Ambient Air Sampling Train



Figure 3.4 Tube Cleaning Device

3.1.2 Analytical Procedures

The air samples were analyzed by a thermal desorption-gas chromatograph/mass spectrometer at the Environmental Research and Training Center, Department of Environmental Quality Promotion, Ministry of Natural Resource and Environment (Figure 3.5). The detail of equipment is as follows,

TDU: Thermal Desorber Unit: Unity, Markes International Limited.

GC/MS: GCMS-QP5000 Shimadzu, Column: Capillary column SPB™ 624, 60 m long, 0.32 mm i.d., thickness 1.8 μm MS: Electron Impact, Quadrupole mass spectrometer

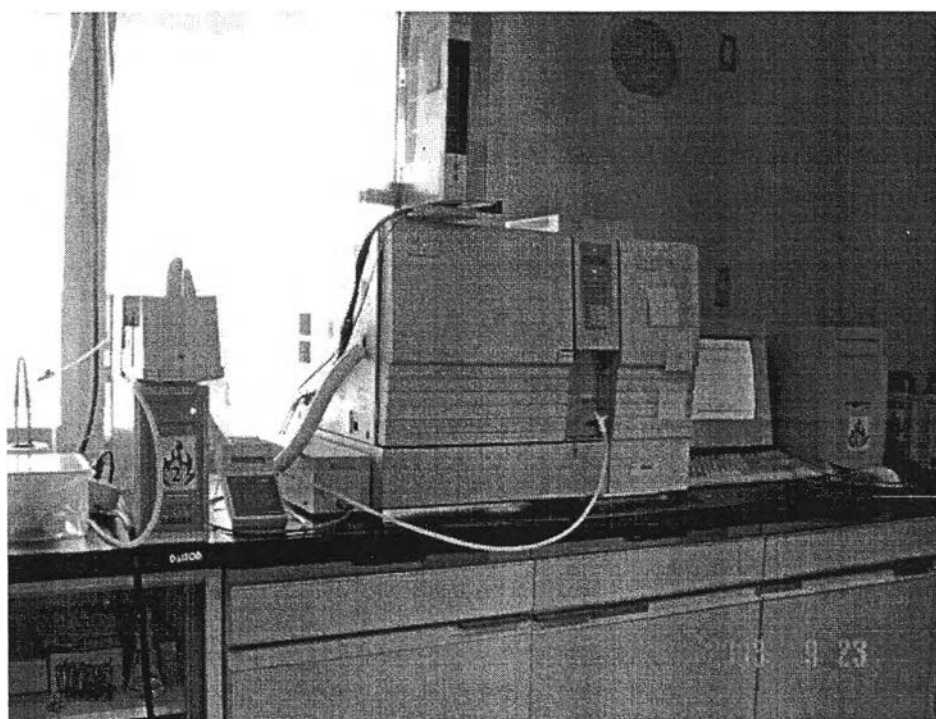


Figure 3.5 GC/MS with Thermal Desorption

Temperature program used was as follows;

TDU Program: Purge 5 minutes, and desorb at 190 °C for 20 minutes

to cold trap –10 °C for 15 minutes then immediately heat to
310 °C to GC column

GC Temperature program: Start at 35 °C. Hold for 5 minutes

Raise at 3 °C/min to 160 °C

Then raise at 20 °C /min to 200 °C. Hold 30 minutes

Solvent cut time 5 minutes

Scan mass from 35 to 200 mass units

As proposed, there were 54 target VOC species (as listed in Appendix A, U.S. EPA, 1998) in ambient air samples to be identified. However, due to limitations of analytical equipment to be explained in paragraph 3.1.2.1, only 18 VOC species in ambient air were quantified.

3.1.2.1 Limitation of Sampling and Analytical Method

1) Chromosorb 106 is suitable to collect ambient air samples in Bangkok where there is high temperature and humidity because it can work in a wide range of temperature; 0-40 °C, and it is hydrophobic. It has a safe sampling volume of 4 liters. These properties are suitable for low level of ambient VOCs (ppb level), although it is not good for C2 to C4 (U.S. EPA. 1999). The VOCs from Ethene to isopentane were excluded from the list of target VOC species.

2) Blank sorbent tubes were cleaned at 240 °C for 90 minutes and analyzed with the same conditions as for the samples. The result showed that there were high artifact of Acetone, Styrene, Benzaldehyde, m-Diethyltoluene, p-Diethyltoluene, and n-Undecane. Acetone and Benzaldehyde are not the target VOC species, therefore having no effect on the results. Styrene, m-Diethylbenzene, p-Diethylbenzene, and n-Undecane were excluded from the list of target VOC species.

3) Due to the high price of mixed standard gases, Cooke, et al. (2001) used GC/MS to qualify VOCs species and used FID to quantify them by using relative response factor of one standard gas; benzene or propane, and this method was recommended by U.S. EPA (1998) as well, but a GC with 2 detectors; MS and FID was not available. This research experimented with 2 sets of the GC/MS and the GC/FID with the same column and the same analytical conditions. The experiment found that retention time of 5 standard gases; benzene, toluene, ethyl benzene, m/p-xylene, and o-xylene, from the MS set and FID set were not comparable as shown in Table 3.1. The results showed that it was not practical to identify VOC species by the GC/MS and use the same retention time to quantify them by the GC/FID, as recommended by Cooke, et al. (2001) and U.S. EPA (1998).

Table 3.1 Retention Times of the 5 Standard Gases from the GC/MS and the GC/FID

VOC species	Retention time, min (MS)				Retention time, min (FID)			
	1	2	3	Average	1	2	3	Average
Benzene	14.174	14.165	14.171	14.170	13.992	13.992	14.013	13.999
Toluene	21.334	21.326	21.329	21.330	20.106	20.106	20.118	20.110
Ethyl benzene	27.825	27.825	27.818	27.823	27.672	27.672	27.673	27.672
m/p Xylene	28.386	28.387	28.375	28.383	30.975	30.975	30.959	30.970
o- Xylene	30.165	30.163	30.149	30.492	31.131	31.131	31.113	31.125

Finally, 41 VOC mixed standard gases were provided by courtesy of Dr. Ian Weeks, Atmospheric Research Division, CSIRO, Australia. These 41 species matched only 18 VOC species target in this study. Table 3.2 showed the proposed target VOCs species and those excluded by previously mentioned limitations.

Table 3.2 VOC Species used in This Study

No.	Target VOC species	41 VOC standards	Excluded by case 1)	Excluded by case 2)	VOCs in this study
1.	Ethylene	Ethylene	X		
2.	Acetylene	Acetylene	X		
3.	Ethane	Ethane	X		
4.	Propylene	Propylene	X		
5.	Propane	Propane	X		
		Propyne			
6.	Isobutane	Isobutane	X		
		Isobutene			
7.	1-Butene	1-Butene	X		
8.	<i>n</i> -Butane	<i>n</i> -Butane	X		
9.	<i>trans</i> -2-Butene	<i>trans</i> -2-Butene	X		
		1-Butyne			
10.	<i>cis</i> -2-Butene	<i>cis</i> -2-Butene	X		
		3-Methyl-1-butene			
11.	Isopentane	Isopentane	X		
12.	1-Pentene	1-Pentene			1
13.	<i>n</i> -Pentane	<i>n</i> -Pentane			2
14.	Isoprene	Isoprene			3
15.	<i>trans</i> -2-Pentene	<i>trans</i> -2-Pentene			4
		2-Methyl-2-butene			
		Cyclopentene			
		4-Methyl-1-butene			
16.	<i>cis</i> -2-Pentene				
17.	2,2-Dimethylbutane				
18.	Cyclopentane	Cyclopentane			5
19.	2,3-Dimethylbutane				
20.	2-Methylpentane	2-Methylpentane			6
21.	3-Methylpentane	3-Methylpentane			7
		1-Hexene			
22.	<i>n</i> -Hexane	<i>n</i> -Hexane			8
		2-Methyl-2-pentene			

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Table 3.2 (Con't)

No.	Target VOC species	41 VOC standards	Excluded by case 1)	Excluded by case 2)	VOCs in this study
23.	Methylcyclopentane				
24.	2,4-Dimethylpentane				
25.	Benzene	Benzene			9
26.	Cyclohexane	Cyclohexane			10
		Cyclohexene			
27.	2-Methylhexane				
28.	2,3-Dimethylpentane				
29.	3-Methylhexane				
30.	2,2,4-Trimethylpentane (isooctane)	2,2,4-Trimethylpentane (isooctane)			11
31.	<i>n</i> -Heptane	<i>n</i> -Heptane			12
32.	Methylcyclohexane				
33.	2,3,4-Trimethylpentane				
34.	Toluene	Toluene			13
		Cycloheptene			
		Cycloheptane			
35.	2-Methylheptane				
36.	3-Methylheptane				
37.	<i>n</i> -Octane	<i>n</i> -Octane			14
38.	Ethylbenzene				
39.	<i>m/p</i> -Xylene	<i>m/p</i> -Xylene			15
40.	Styrene			X	
41.	<i>o</i> -Xylene				
42.	<i>n</i> -Nonane	<i>n</i> -Nonane			16
43.	Isopropylbenzene (cumene)				
44.	<i>n</i> -Propylbenzene				
45.	<i>m</i> -Ethyltoluene				
46.	<i>p</i> -Ethyltoluene				
47.	1,3,5-Trimethylbenzene	1,3,5-Trimethylbenzene			17
48.	<i>o</i> -Ethyltoluene				

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Table 3.2 (Con't)

No.	Target VOC species	41 VOC standards	Excluded by case 1)	Excluded by case 2)	VOCs in this study
49.	1,2,4-Trimethylbenzene				
50.	<i>n</i> -Decane	<i>n</i> -Decane			18
51.	1,2,3-Trimethylbenzene				
52.	<i>m</i> -Diethylbenzene			X	
53.	<i>p</i> -Diethylbenzene			X	
54.	<i>n</i> -Undecane			X	

Standard Gas Analysis

Five cleaned sorbent tubes were sent to Australia, to be adsorbed with VOC mixed standard gases. Three tubes of mixed standard gases were received in Bangkok and used as standard gases. Besides loading standard gases on sorbent tubes, Dr. Ian Weeks did the experiment on the percentage of VOC recovery by thermal desorption. He directly injected the mixed standard gas to the GC/FID and compared the results with the other method by loading standard gases on the sorbent tube and then analyzed these with thermal desorption-GC/FID. A list of VOC species quantified in this study with their GC retention times are shown in Table 3.3.

Table 3.3 Retention Times of 18 VOCs Quantified in This Study

No.	Retention Time, min.			VOC Species
	Mean	SD	%RSD	
1	5.145	0.005	0.098	1-Pentene
2	5.286	0.005	0.097	<i>n</i> -Pentane
3	5.629	0.006	0.099	<i>t</i> -2-Pentene
4	5.845	0.006	0.105	Isoprene
5	7.683	0.006	0.078	2-Methylpentane

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Table 3.3 (Con't)

No.	Retention Time, min.			VOC Species
	Mean	SD	%RSD	
6	7.771	0.006	0.071	Cyclopentane
7	8.351	0.010	0.122	3-Methylpentane
8	9.159	0.008	0.082	<i>n</i> -Hexane
9	12.995	0.010	0.077	Cyclohexane
10	14.055	0.011	0.078	Benzene
11	14.381	0.012	0.083	2,2,4-Trimethylpentane
12	15.122	0.013	0.086	<i>n</i> -Heptane
13	21.195	0.018	0.084	Toluene
14	21.896	0.016	0.072	<i>n</i> -Octane
15	28.249	0.019	0.068	<i>m/p</i> -xylene
16	28.625	0.017	0.058	<i>n</i> -Nonane
17	34.692	0.018	0.053	1,3,5-Trimethylbenzene
18	35.028	0.023	0.064	<i>n</i> -Decane

3.2 Emission Source Profiles

Source profiles are based on data from Bangkok emission inventories, EU countries and source apportionment of VOCs from many big cities and Bangkok. Nine emission source profiles were included in this study.

- 1) The exhaust gas from gasoline vehicles
- 2) The exhaust gas from diesel vehicles
- 3) The vapor of gasolines
- 4) Flue gas from fuel oil boilers
- 5) The vapor of solvent-based paints

- 6) Thinners
- 7) Smoke from biomass burning
- 8) Smoke from food barbequing on charcoal stoves
- 9) Air samples from municipal waste disposal

These emission sources include well-known sources of VOCs in urban air, such as exhaust gases from gasoline and diesel vehicles. The others mentioned are both area and fugitive sources which are difficult to estimate emission loading due to the variation in temperature, quantity of usage and manner of applications.

The vapor of gasolines represent VOCs emitted from fuel tanks and refueling operations. The vapor of solvent-based paints and liquid thinners represent VOCs emitted from solvent usage. Biomass burning emerges as a major source contribution of VOCs in Bangkok (Suwattiga and Limpaseni, 2003). Food barbequing on charcoal stoves is a traditional Thai way of cooking and can be found scattering over Bangkok anytime of the day. Air samples from municipal waste disposal sites represent VOCs emitted from the biological processes.

Although Bangkok has a refinery located in the southern area, the results of the receptor model (Suwattiga and Limpaseni, 2003) did not show significant VOC source contribution from this refinery.

The composition of VOCs from each source was analyzed. The fractions of VOC species were tabulated for each source category. This study used the four existing source profiles which are the exhaust gas from tailpipes of gasoline vehicles, the exhaust gas from tailpipes of diesel vehicles, flue gas from fuel oil boilers, and smoke from burning biomass (Limpaseni, et al., 2003).

The five new emission source profiles were collected and analyzed to include the vapor of gasolines, the vapor of solvent-based paints, liquid thinners, smoke from food barbequing on charcoal stoves, and air samples from municipal waste disposal.

3.2.1 Sampling Procedures

The samples were divided into 2 types, 1) vapor and liquids, and 2) air samples. Vapor and liquid samples: gasoline, and solvent-based paints and thinners were bought from local merchants and analyzed at the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

Air samples: smoke from food barbequing on charcoal stoves and air samples from municipal waste disposal were collected on the sorbent tubes using the same procedure as for the collection of ambient air samples and analyzed at the Environmental Research and Training Center (ERTC), Department of Environmental Quality Promotion, Ministry of Natural Resource and Environment.

Vapor and Liquid

1) Vapor of gasoline

The 5 popular brands of gasoline¹ were purchased from gas stations within Bangkok. The gasoline samples were put in glass bottles with septum screw caps. Vapors of gasoline were withdrawn with a gas-tight syringe and directly injected to the GC/MS.

2) Solvent-based paint

The 5 brands of solvent-based paints² were purchased from hardware stores. These 5 brands had the highest market share of solvent-based paints (Industrial Works Department, 2003). The paint samples were put in glass bottles with septum screw caps. Vapors of solvent-based paints were withdrawn with a gas-tight syringe and directly injected to the GC/MS.

¹ 5 brands of gasoline were Bangchak, Caltex, ESSO, PTT, and Shell.

² 5 brands of paints are Jotun, Nippon Paint, ICI, Thai Kansai Paint, and TOA.

3) Thinner

Five brands of thinner³ from auto-body repair shops were obtained and analyzed for the composition of VOC species. The thinner samples were analyzed by direct injection to the GC/MS.

Air Samples

1) Smoke from food barbequing on charcoal stoves

Air samples from 3 vendors barbequing at three locations along roadsides (1) in front of Chulalongkorn University, (2) on Sri Ayutthaya road, and (3) on Sukumvit 68 road were collected on sorbent tubes (Figure 3.6) and analyzed by the thermal desorption-GC/MS.

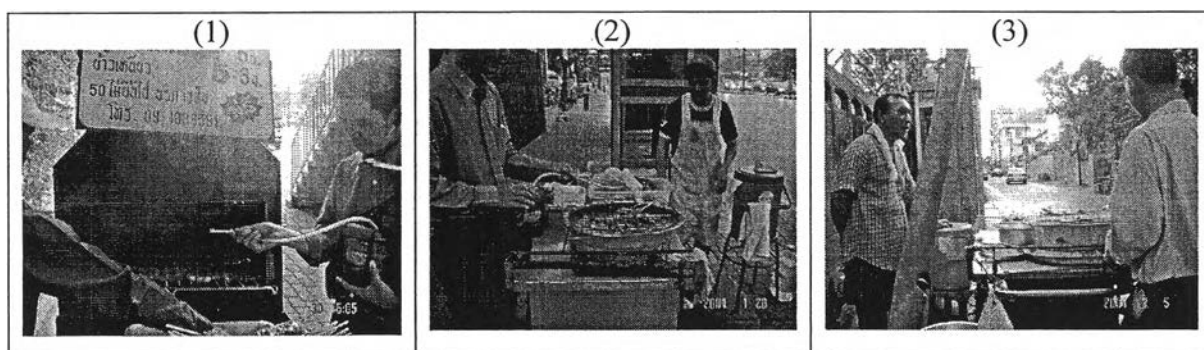


Figure 3.6 Air Sampling of Food Barbequing on Charcoal Stoves

2) Air samples from the municipal waste disposal site

Three air samples were collected at On-Nuch municipal disposal site (Figure 3.7). The air samples were collected on sorbent tubes and analyzed by the thermal desorption-GC/MS.

³ 5 brands of thinner are B.Bank, COCO, Mustang, Pla Lai Nam, and Welco.

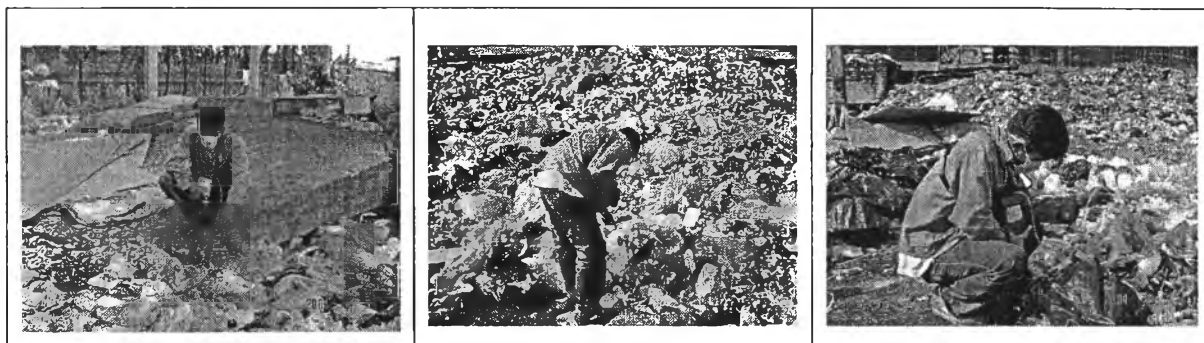


Figure 3.7 Air Sampling at On-Nuch Municipal Waste Disposal Site

3.2.2 Analytical Procedures

The samples of vapors of gasoline and solvent-based paints and thinners were analyzed by the GC/MS, Shimazu QP 5050A, GC Column: CP-sil PONA CB fused Silica WCOT, 100 m long, 0.25 mm i.d., 0.5 μm , MS: Electron Impactor, Mass spectrometer.

Vapor Samples

The analytical procedure used the modified cold trap-GC/MS. The procedure was that an initial section of the GC column was frozen with liquid nitrogen for 10 minutes cold trap. The vapor sample was injected and frozen at the cold trap for 15 minutes before starting the gas chromatograph separation (Figure 3.8).

Temperature program used in identification was as follows;

GC Temperature program: Start at 35 °C, hold for 5 minutes

Raise at 3 °C/min to 200 °C, hold for 10 minutes

Scan mass from 35 to 200 mass units

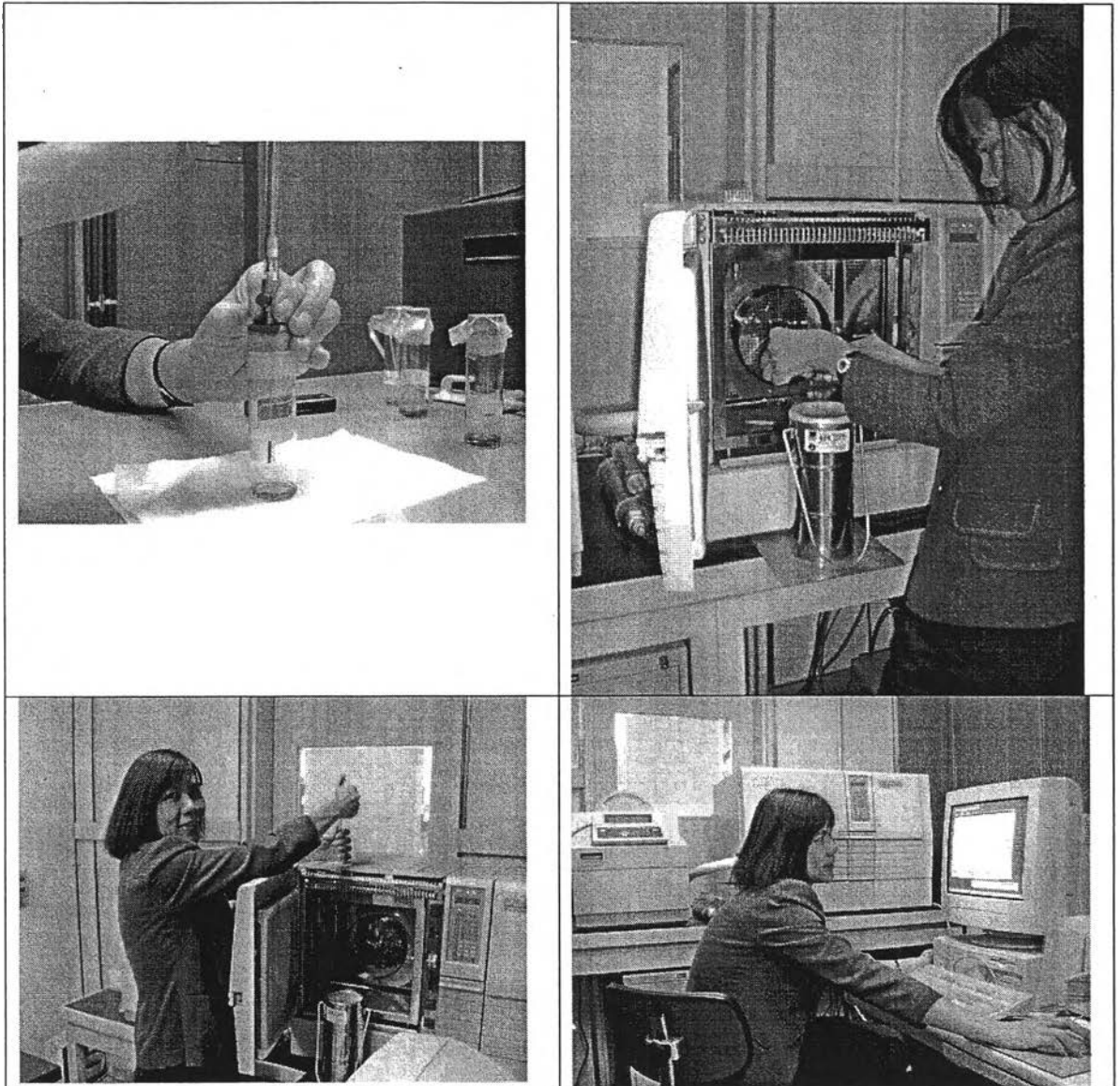


Figure 3.8 Identification of VOCs from Vapors of Gasoline

Liquid Samples

The thinner samples were analyzed by direct injection to the GC/MS.

Temperature program used in identification was the same program as used on the vapor samples.

Air Samples

The analytical procedure for air samples was as follows;

TDU Program: Purge for 5 minutes, and desorb at 190 °C for 20 minutes

to cold trap -10 °C for 15 minutes then immediately heat to
310 °C to GC column

GC Temperature program: Start at 35 °C, hold for 5 minutes

Raise at 3 °C/min to 160 °C

Then raise at 20 °C /min to 200 °C, hold for 30 minutes

Solvent cut time of 5 minutes

Scan mass from 35 to 200 mass units

3.3 CMB Modeling

The chemical mass balance receptor model, U.S. EPA's CMB7, was run by using a set of data from section 3.1 and 3.2. The receptor model is a statistical model used to identify the contribution of sources to receptors. Source contribution is calculated by weighted least-square multiple regression analysis. The equation is shown as follows: (U.S. EPA., 1990)

$$C_i = F_{i1} S_1 + F_{i2} S_2 + \dots + F_{ij} S_j + \dots + F_{iJ} S_J + E \quad i = 1, \dots, I, j = 1, \dots, J$$

Where: C_i = Concentration of VOC species i measured at a receptor site
 F_{ij} = Fraction of VOC species i in emissions from source j
 S_j = Estimation of the contribution of source j
 I = 18 VOC species ($I \geq J$)
 J = 9 source types
 E = Uncertainty

Mukund, Kelly and Spicer (1996) suggested to use a 10% uncertainty on the concentration of ambient air samples and a 20% uncertainty on the fraction of source profiles.

S_j is calculated by the model. After that the model used S_j to calculate the concentration of the VOC fitting species and compare these calculated values to the measured values and to also calculate the parameters: R^2 , TSTAT, chi-square, and percent mass, which show the goodness of fit of the modeling calculation.

The process of modeling is trial and error. During the first step, all sources and VOC fitting species were put into the model. The results from the model calculations showed some sources with a TSTAT value of less than 2 and these are withdrawn from the model. If a chi-square value is still higher than 4 and there is colinearity among the source profiles, some VOC fitting species will be examined pulling out and in until all parameters show the goodness of fit meet the criteria (Table 3.4).

Table 3.4 Summary of the Goodness of Fit Criteria

Parameters	Description	Criteria
R^2	A linear regression of measured and model-calculated values for the VOC fitting species. The closer R^2 is to one, the better the source contribution estimates explain the measured concentration.	0-1
TSTAT	The ratio of the source contribution estimate to the standard error.	>2
Chi-square	The weighted sum of the square of the differences between the calculated and measured VOC fitting species concentration.	0 is very good <1 is good 1-2 is acceptable >4 is not accepted
Percent mass	The percent ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration.	80-120