CHAPTER 2
EXPERIMENTAL

2

Experimental

2.1 SAMPLING SITES

The location map of the sampling sites in Kuala Lumpur is shown in Figure 2.1. Photographs of the sampling sites are shown in Appendix B.

Kuala Lumpur (latitude 3°08′N; longitude 101°44′E) is situated in the Klang valley region (major center of industry, commerce, administration, and residence in Malaysia), which is a basin located in the southwestern part of the Malaysian peninsula, surrounded by mountains exceeding 1500 m elevation in the east and the straits of Malacca in the west (Figure 2.2) (Abas and Simoneit, 1996).

The dispersive capability of the atmosphere in the Klang valley is very restricted. For example the pattern of airflow over the valley; at night the wind blows from Kuala Lumpur-Petaling Jaya towards Shah Alam, Kelang, and Port Klang. During the day, the flow pattern is reversed; the wind blows from the sea inland. Such pattern causes much of the pollutants produced from within the valley to remain very much where they are (Sani, 1987).

The meteorological factors that have an influence on air pollution levels in this area are: (a) wind speed and direction and their change with height, (b) the temperature structure through the lowest air layers, (c) radiation, (d) sunshine, (e) relative humidity, and (f) rainfall (Sani, 1987).

Kuala Lumpur has a population of 2.2 million (1999). The traffic is a mixture of buses (diesel), cars (gasoline), and motorcycles. The average traffic volume for city roads is about 30,000 vehicles per day, whilst the road-intersections is about 100,000 vehicles per day.

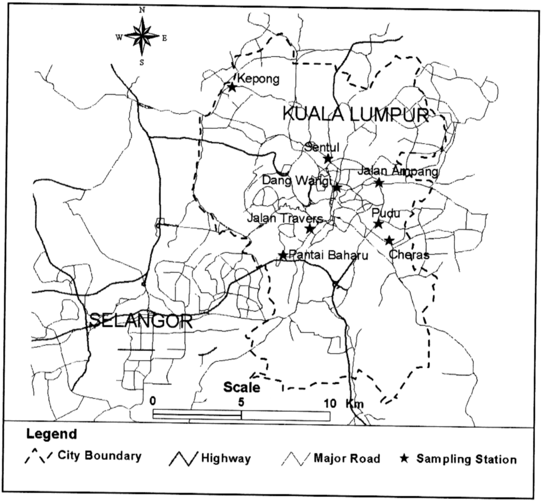

Figure 2.1: Location map of the sampling sites in Kuala Lumpur.

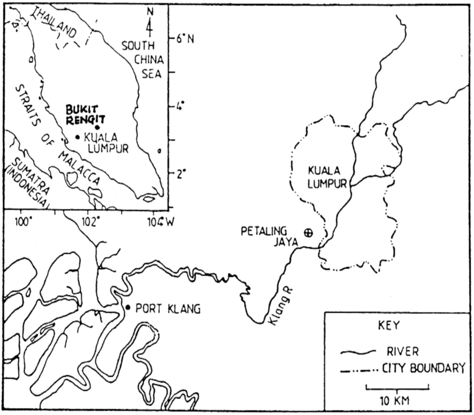

Figure 2.2: Kuala Lumpur and the Klang valley region.

During sampling, the ambient temperatures were typically tropical (23° to 33°C). All samples were collected during the period from 19th November 1998 to 27th January 1999 except those of forest samples, which were collected in the period of 15th to 24th May 2000. In all urban sampling sites, the hi-vol air sampler was set up in police stations so that both safety and power supply are available. Vehicle speeds near these stations are low because of the heavy traffic. Sampling sites were chosen to nearly cover both an inner and an outer circles that represent urban Kuala Lumpur and whose center is the city center.

Site No. 1: Pantai Baharu

The air sampler was set up at ~ 5 m away from a major busy road, which leads to the federal highway that is ~ 50 m behind the site. This highway links the city of Kuala Lumpur to the other major cities of the Klang valley region (e.g., Petaling Jaya, Shah Alam, etc.). Roadside soil particles were collected from different spots around the air sampler, near the main road, and from a car park inside the police station.

Site No. 2: Jalan Travers

The equipment was set up in the station just a few meters (~ 10 m) from the major road (in the third sampling, the instrument was placed adjacent to the road). This road links the suburb of Kuala Lumpur to the city center. Roadside soil particles were taken from the road.

Site No. 3: Dang Wangi

The air sampler was set adjacent to the road. This site is situated in the center of Kuala Lumpur with major roads linking to the other parts of the city. Roadside soil particles were sampled from an open car park that is close to the main roads.

Site No. 4: Jalan Ampang

This road is considered one of the busiest roads in Kuala Lumpur. The air sampler was set up at ~ 10 m away from the road. Roadside soil particles were collected from the road.

Site No. 5: Cheras

The instrument was set up adjacent to the main road. This road links the city center to Cheras area. Roadside soil particles were sampled from the roadside and from a motorcycle parking area inside the police station.

Site No. 6: Pudu

This site is close to site No.5. The air sampler was located ~ 15 m from the main road. Roadside soil particles were taken from the road.

Site No. 7: Sentul

The air sampler was set up inside the police station ~ 2 m from the main road. Roadside soil particles were collected from the roadside and near a petrol station.

Site No. 8: Kepong

The instrument was placed in a small garden ~ 10 m from the major road. Roadside soil particles were taken from the road.

Site No. 9: Bukit Rengit

The location is a forest Research/Training Station belonging to the Wildlife Department of Malaysia. The station is located about 17 km from major highway, which links two major cities (Kuala Lumpur and Kuantan) approximately 60 km from Kuala Lumpur and surrounded by hills. Roadside soil particles were taken from the station car park.

2.2 REAGENTS, GLASSWARE AND APPARATUS

All solvents used were of HPLC grade. Dichloromethane and hexane were obtained from J.T.Baker (USA) and methanol was obtained from Mallinckrodt (USA). Water for deactivation of silica and alumina was prepared by deionizing distilled water (Maxima Ultra-Pure water, Elgastat Maxima, ELGA, England).

All glassware used in the analytical work was soaked in 2-3% (v/v) Decon 90 (UK) overnight, rinsed with water, dried in the oven at 150°C, wrapped with aluminum foil, and rinsed with methanol and dichloromethane before use.

Sieves used for sieving roadside soil particles were cleaned by sonication for 15-30 min, and then were soaked in 2-3% (v/v) Decon 90, rinsed with water and air-dried.

A Branson 1200 (USA) ultrasonic cleaner was used for samples extraction and a Büchi rotary-evaporator system (Switzerland) was used for the concentration steps.

2.3 PREPARATION OF STANDARDS

2.3.1 Internal standards

Tetracosane-d_{50} (98% purity) was obtained from Isotec (USA). Tetracosane-d_{50} stock solution (109.76 μg/mL) was prepared by accurately weighing 5.60 mg of solid tetracosane-d_{50}, dissolved in n-hexane and quantitatively transferred to 50 mL volumetric flask and made up to the mark with n-hexane.

Anthracene-d_{10} and perylene-d_{12} (99% purity) were obtained from Supelco (USA). Stock solutions, 79.20 μg/mL for anthracene-d_{10} and 79.24 μg/mL for perylene-d_{12}, were prepared by quantitatively transferring 1 mL of 1980.00 μg/mL anthracene-d_{10} and 1980.99 μg/mL perylene-d_{12} solutions into a 25 mL volumetric flask and made up to the mark with dichloromethane.

2.3.2 External standards

Two alkanes standards (Tables 2.1a and b) and three PAHs standards (Tables 2.2a-c) were used throughout the analytical work. They were obtained from PolyScience (USA) and prepared by weighing exact amount of each individual compound, dissolved in either n-hexane or dichloromethane, quantitatively transferred to 250 mL volumetric flask, and made up to the mark with n-hexane or dichloromethane (the final alkane solution was in n-hexane, while PAH solution was in 60:40 hexane-dichloromethane).

Tables 2.1a and b: Alkanes standards.

	(a)		(b)	
No.	Compound	Conc. (μg/mL)	Compound	Conc. (μg/mL)
1	Decane	14.90	Undecane	36.64
2	Dodecane	15.57	Dodecane	37.06
3	Tetradecane	15.00	Tridecane	37.44
4	Hexadecane	15.00	Tetradecane	28.29
5	Heptadecane	15.10	Pentadecane	28.34
6	Pristane	15.08	Hexadecane	20.89
7	Octadecane	15.01	Heptadecane	19.82
8	Phytane	15.28	Pristane	9.90
9	Eicosane	15.16	Octadecane	20.08
10	Heneicosane	15.00	Phytane	9.90
11	Docosane	14.95	Nonadecane	20.37
12	Tetracosane	15.07	Eicosane	20.04
13	Hexacosane	15.05	Heneicosane	19.94
14	Squalane	20.60	Docosane	20.83
15	Octacosane	15.05	Tricosane	19.86
16	Triacontane	15.00	Tetracosane	20.61
17	Dotriacontane	30.00	Pentacosane	19.98
18	Tetratriacontane	6.74	Hexacosane	20.89
19			Octacosane	19.68
20			Triacontane	41.94
21			Dotriacontane	42.61
22			Hexatriacontane	44.27

Tables 2.2a and b: PAHs standards.

(a) (b)

No.	Compound	Conc. (µg/mL)	Compound	Conc. (µg/mL)
1	Naphthalene	31.61	Naphthalene	7.94
2	1-methylnaphthalene	19.02	Acenaphthylene	7.89
3	1-ethylnaphthalene	16.71	Acenaphthene	19.86
4	Acenaphthylene	34.05	Fluorene	7.98
5	Acenaphthene	24.52	Dibenzothiophene	19.88
6	2,3,6-trimethylnaphthalene	17.38	Phenanthrene	19.82
7	Fluorene	38.00	Anthracene	19.82
8	Phenanthrene	36.67	4,5-methylenephenanthrene	19.72
9	Anthracene	33.34	Fluoranthene	19.64
10	2-methylphenanthrene	11.38	Pyrene	19.66
11	1-methylphenanthrene	2.59	1,2-benzanthracene	39.80
12	3,6-dimethylphenanthrene	16.76	Chrysene	19.98
13	Fluoranthene	20.86	Benzo(b)fluoranthene	8.02
14	Pyrene	30.35	Benzo(k)fluoranthene	8.03
15	1-methylpyrene	12.86	Benzo(e)pyrene	20.00
16	Chrysene	28.04	Benzo(a)pyrene	19.62
17	Perylene	17.90	Perylene	20.00
18			Indeno(1,2,3-cd)pyrene	7.93
19			Dibenz(a,h)anthracene	7.98
20			Benzo(g,h,i)perylene	40.00
21			Anthanthrene	20.00
22			Coronene	20.00

Table 2.2c : PAHs standard.

No.	Compound	Conc. (µg/mL)
1	Naphthalene	31.36
2	Acenaphthylene	21.78
3	Acenaphthene	26.14
4	Fluorene	30.97
5	Phenanthrene	29.52
6	Fluoranthene	32.54
7	Pyrene	31.68
8	Chrysene	19.80
9	Benzo(e)pyrene	25.74
10	Dibenz(a,h)anthracene	6.34

2.4 SAMPLING AND SAMPLE PREPARATION

2.4.1 Airborne particles

Airborne particulate samples were acquired with a PM_{10} high-volume air sampler (Ecotech 2000 hi-vol sampler and 10 micron size selective inlet, Australia) fitted with annealed (300°C for 8 h) glass fiber filters (20.3 × 25.4 cm^2 surface, Whatman EPM 2000, England), and operated at a flow rate of ~ 1.12 m^3/min, sampling period was 24 h (starting at 11:00 am) for all samples.

Prior to sampling the glass fiber filters were wrapped with aluminum foil, equilibrated in a desiccator (< 50% relative humidity) for at least 24 h, and weighed.

Reweighing of the exposed filters was done at similar conditions of temperature and humidity as the initial weighing. Exposed filters were then folded, stored in a 500 mL glass jar to which ~ 5 mL of dichloromethane was added to inhibit microbial activity, and kept refrigerated until the day of analysis.

Airborne particulate samples were collected from eight different sites around the city of Kuala Lumpur, Malaysia (Section 2.1). The sampling was carried out three times at each sampling site. Details of the sites, dates of sampling and conditions at the time of sampling are given in Tables 2.3a-c.

Table 2.3a: First sampling of airborne particulate samples.

Site no.	Sample		Date sampled	Elevation above street (m)/weather description	Volume sampled (m^3)
	First round				
	Name	Site name			
1	PBA1	Pantai Baharu	19/11/98	Street level/sunny	1620.0
2	JTA1	Jalan Travers	21/11/98	~2m/sunny	1620.0
3	DWA1	Dang Wangi	23/11/98	Street level/raining afternoon	1617.6
4	JAA1	Jalan Ampang	25/11/98	Street level/rainy	1616.4
5	CHA1	Cheras	27/11/98	Street level/sunny	1614.0
6	PUA1	Pudu	30/11/98	~3m/raining at night	1611.6
7	SEA1	Sentul	2/12/98	Street level/raining at night	1611.6
8	KEA1	Kepong	4/12/98	Street level/raining afternoon and night	1607.4

Table 2.3b: Second sampling of airborne particulate samples.

Site no.	Sample		Date sampled	Elevation above street (m)/ weather description	Volume sampled (m^3)
	Second round				
	Name	Site name			
1	PBA2	Pantai Baharu	9/12/98	Street level/sunny	1610.4
2	JTA2	Jalan Travers	11/12/98	~2m/drizzling at night	1608.0
3	DWA2	Dang Wangi	14/12/98	Street level/drizzling in morning	1609.8
4	JAA2	Jalan Ampang	16/12/98	Street level/sunny	1603.2
5	CHA2	Cheras	18/12/98	Street level/sunny	1606.8
6	PUA2	Pudu	21/12/98	~3m/sunny	1607.4
7	SEA2	Sentul	23/12/98	Street level/drizzling	1607.4
8	KEA2	Kepong	25/12/98	Street level/raining	1603.8

Table 2.3c: Third sampling of airborne particulate samples.

Site no.	Sample		Date sampled	Elevation above street (m)/ weather decription	Volume sampled (m^3)
	Third round				
	Name	Site name			
1	PBA3	Pantai Baharu	4/1/99	Street level/cloudy	1612.2
2	JTA3	Jalan Travers	6/1/99	Street level/raining afternoon	1609.8
3	DWA3	Dang Wangi	27/1/99	Street level/sunny	1610.4
4	JAA3	Jalan Ampang	8/1/99	Street level/drizzling	1609.8
5	CHA3	Cheras	10/1/99	Street level/sunny	1609.2
6	PUA3	Pudu	12/1/99	~3m/raining at night	1606.8
7	SEA3	Sentul	14/1/99	Street level/raining at night	1610.4
8	KEA3	Kepong	16/1/99	street level/drizzling	1605.0

2.4.2 Roadside soil particles

Roadside soil particles were collected using a small brush and a trowel, air dried for four to nine days, stored in a 500 mL glass jar, and sieved through a series of different size sieves into different fractions (a, b, c, d, e, f, and g), where a > 2 mm, 600 μm < b < 2 mm, 300 μm < c < 600 μm, 150 μm < d < 300 μm, 106 μm < e < 150 μm, 53 μm < f < 106 μm, and g < 53 μm. Each fraction was then weighed and fractions c, d, e, f, and g were combined, stored in a 500 mL glass jar, homogenized by shaking the glass jar by hand several times, and kept in this manner or frozen whenever possible until the day of analysis. Tables 2.4a-c describe the details of roadside soil particles, while Tables 2.4d-f show relative mass distributions (%) of these samples.

Table 2.4a: First sampling of roadside soil particles.

Site No.	Sample		Date sampled	Weight extracted (g)
	First round			
	Name	Site name		
1	PBD1	Pantai Baharu	19/11/98	4.01
2	JTD1	Jalan Travers	21/11/98	4.01
3	DWD1	Dang Wangi	23/11/98	4.01
4	JAD1	Jalan Ampang	25/11/98	4.01
5	CHD1	Cheras	27/11/98	4.01
6	PUD1	Pudu	30/11/98	4.01
7	SED1	Sentul	2/12/98	4.01
8	KED1	Kepong	4/12/98	4.01

Table 2.4b: Second sampling of roadside soil particles.

Site No.	Sample		Date sampled	Weight extracted (g)
	Second round			
	Name	Site name		
1	PBD2	Pantai Baharu	9/12/98	4.01
2	JTD2	Jalan Travers	11/12/98	4.01
3	DWD2	Dang Wangi	14/12/98	4.01
4	JAD2	Jalan Ampang	16/12/98	4.00
5	CHD2	Cheras	18/12/98	4.01
6	PUD2	Pudu	21/12/98	4.01
7	SED2	Sentul	23/12/98	4.01
8	KED2	Kepong	25/12/98	4.01

Table 2.4c: Third sampling of roadside soil particles.

Site No.	Sample		Date sampled	Weight extracted (g)
	Third round			
	Name	Site name		
1	PBD3	Pantai Baharu	4/1/99	4.00
2	JTD3	Jalan Travers	6/1/99	4.01
3	DWD3	Dang Wangi	27/1/99	4.01
4	JAD3	Jalan Ampang	8/1/99	4.00
5	CHD3	Cheras	10/1/99	4.00
6	PUD3	Pudu	12/1/99	4.00
7	SED3	Sentul	14/1/99	4.01
8	KED3	Kepong	16/1/99	4.00

Table 2.4d: Relative mass distributions (%) of first sampling.

Sample		Relative mass distribution (%)				
No.	Name	< 53 μm	53-106 μm	106-150 μm	150-300 μm	300-600 μm
1	PBD1	0.94	9.01	10.04	33.69	46.32
2	JTD1	3.20	18.94	11.12	34.16	32.58
3	DWD1	3.66	24.20	14.03	30.09	28.02
4	JAD1	0.52	16.16	12.55	35.04	35.74
5	CHD1	1.05	17.74	13.14	39.74	28.32
6	PUD1	0.61	14.81	11.21	37.13	36.24
7	SED1	0.38	12.10	10.62	36.20	40.70
8	KED1	0.08	8.19	11.32	44.65	35.76

Table 2.4e: Relative mass distributions (%) of second sampling.

Sample		Relative mass distribution (%)				
No.	Name	< 53 μm	53-106 μm	106-150 μm	150-300 μm	300-600 μm
1	PBD2	0.25	8.02	17.33	35.84	38.57
2	JTD2	0.59	16.17	11.85	32.43	38.96
3	DWD2	2.08	27.20	13.89	31.15	25.69
4	JAD2	0.48	14.65	12.78	39.03	33.06
5	CHD2	2.66	20.56	10.64	34.81	31.34
6	PUD2	1.20	13.09	8.27	42.41	35.03
7	SED2	2.11	14.16	7.86	33.23	42.64
8	KED2	0.80	13.63	8.51	44.87	32.19

Table 2.4f: Relative mass distributions (%) of third sampling.

Sample		Relative mass distribution (%)				
No.	Name	< 53 μm	53-106 μm	106-150 μm	150-300 μm	300-600 μm
1	PBD3	3.21	25.39	13.11	30.58	27.71
2	JTD3	2.05	13.12	10.47	32.89	41.47
3	DWD3	3.82	21.85	12.27	30.84	31.22
4	JAD3	1.90	17.48	11.75	33.97	34.89
5	CHD3	0.96	15.28	12.41	38.18	33.16
6	PUD3	1.23	15.78	10.06	41.77	31.16
7	SED3	0.35	11.01	9.39	36.57	42.67
8	KED3	0.73	13.76	10.50	39.77	35.24

2.4.3 Miscellaneous samples (reference samples)

Forest airborne particulate samples (Table 2.5, BRA1 and BRA2) were collected and treated in the same manner as the airborne particulate samples of Kuala Lumpur except for sampling period (48 h). Forest roadside soil particles (Table 2.5, BRD1 and BRD2) were air dried for two days, sieved through a 250 μm sieve, and stored frozen in a 500 ml glass jar.

Table 2.5: Description of forest airborne particles and roadside soil particles.

No.	Sample		Date sampled	Weather description	Volume sampled (m^3)/ weight extracted (g)
	Name	Site name			
1	BRA1	Bukit Rengit	15/5/00	Drizzling at night	3230.4
2	BRA2	Bukit Rengit	24/5/00	Drizzling in the afternoon	3224.4
3	BRD1	Bukit Rengit	15/5/00	Same as BRA1	8.00
4	BRD2	Bukit Rengit	24/5/00	Same as BRA2	8.00

Fresh lubricating oil (FLO) (0.3 mL) was diluted 20 times with hexane. Used car lubricating oil (ULOC) (0.35 mL), and used motorcycle lubricating oil (ULOM) (0.22 mL) were diluted 20 times with dichloromethane. They were then fractionated as described in Section 2.6. 0.1 mL of the diluted solutions was used for fractionation.

2.5 EXTRACTION

2.5.1 Airborne particles

The filters were extracted three times using ultrasonic agitation for a 15-min period each with 150 mL of dichloromethane. The extractions were carried out within the filter storage jar, and the bath operated at room temperature.

The extracts were then filtered through a sintered glass funnel for the removal of insoluble particles. The filtrate volume was concentrated to approximately 5 mL by using a rotary-evaporator system followed by using a stream of dry nitrogen gas. The volume was then adjusted to 5 mL exactly by addition of dichloromethane. 1 mL of the filtrate was transferred to a preweighed vial, evaporated to dryness using a stream of dry nitrogen gas, and quantified by weighing the dry aliquot on an analytical balance (Table 3.5, TSEOM).

2.5.2 Roadside soil particles

Approximately 4 g (8 g for forest samples) (Tables 2.4a-c and 2.5) of roadside soil particles (≤ 600 μm for urban samples and ≤ 250 μm for forest samples) were extracted three times using ultrasonic agitation for a 15-min period each with 20 mL of dichloromethane. The extractions were carried out in centrifuge tubes, and the bath operated at 7-9°C starting temperature.

The extracts were then filtered and concentrated to a volume of 10 mL (5 mL for forest samples) as described for airborne particulate samples (Section 2.5.1). 1 mL of the extract was used for quantitation (Table 3.6, TSEOM).

2.6 FRACTIONATION

Fractionation was carried out by using alumina-silica columns. Before use alumina and silica were cleaned as follows: (a) 30 min sonication with methanol, (b) drying the residual of methanol, (c) 30 min sonication with n-hexane, and (d) further cleaning with dichloromethane-methanol (9:1) using three 15 min sonication. Glass wool and sodium sulfate anhydrous were cleaned three times by sonication for a 15-min period each with methanol and the cleaning repeated with dichloromethane.

1 mL of the extract (concentrated to < 0.2 mL by using a stream of dry nitrogen gas) was applied to the top of a glass column (1.0 cm I.D.) containing 2.5 g of neutral alumina (dry packed) (top) (Merck, 70-230 mesh, activity I, activated at 200°C for 4 h) and 1.5 g of silica (slurry packed with n-hexane) (bottom) (Fluka, 230-400 mesh, activated at 200°C for 4 h), the adsorbents was capped with 1.0 g of sodium sulfate anhydrous (activated at 300°C for 4 h), and supported by a small plug of precleaned glass wool inserted at the narrow end of the column, the flow rate was ~ 1.0 mL/min.

The alkanes were obtained in the first fraction (8 mL of n-hexane), the PAHs were collected in the second fraction (8 mL of 1:1 n-hexane-dichloromethane), and the polar compounds eluted in the third fraction (9 mL of 10% methanol in dichloromethane). The first and second fractions were concentrated to approximately 100 μL under reduced pressure at 40°C using a rotary-evaporator system. The volume was then adjusted to 100 μL exactly by addition of n-hexane (alkanes fraction) and n-hexane-dichloromethane (1:1) (PAHs fraction). Fractions were kept frozen in a 2 mL Teflon-lined vial until further analysis.

2.7 INSTRUMENTAL ANALYSIS

Samples were analyzed by gas chromatography-mass spectrometry (GCMS). These analyses were carried out on a Hewlett-Packard Model 6890 gas chromatograph equipped with a Hewlett-Packard Model 6890 mass selective detector provided with a HP ChemStation data acquisition system. Chromatographic conditions are described in Table 2.6.

Table 2.6: Description of GCMS chromatographic conditions.

No.	Parameter	Description
1	Mode	Full-scan GCMS
2	Column	HP-5MS 5% diphenyldimethylpolysiloxane (30 m long, 0.25 mm I.D., 0.25 μm film thickness).
3	Carrier gas	Helium (purity 99.999%).
4	Initial flow	1.2 mL/min.
5	Nominal initial pressure	10.4 psi.
6	Average velocity	40 cm/sec.
7	Injection mode	Splitless (1 min) (1.0-1.4 μL; hot needle technique).
8	Temperature of injector	290°C.
9	Temperature of oven	60°C (held for 2 min), then up to 280°C at 6°C/min, then held at 280°C for 20 min.
10	Temperature of transfer line	300°C.
11	Data for qualitative analysis	Acquired in the electron impact (EI) mode (70 eV), scanning from 50-550 mass units at 1.5 sec/scan.
12	Solvent delay	4 min

2.8 IDENTIFICATION AND QUANTIFICATION

Compound identification was based on the GCMS data (i.e. key fragment ions, Table 2.7, retention times compared to that of external standards, and/or mass spectra).

Quantification was performed from the GC profiles using the external standard method. External standards used for alkanes and PAHs are listed in Tables 2.1b and 2.2b, respectively. Average response factors were calculated for each compound in both alkanes and PAHs standards. Response factors for alkanes that are not available in the standard were calculated as follows:

- Heptacosane: average of the response factors for hexacosane and octacosane.
- Nonacosane: average of the response factors for octacosane and triacontane.
- Hentriacontane: average of the response factors for triacontane and dotriacontane.
- Tritriacontane: same response factor as dotriacontane.
- Tetratriacontane: average of the response factors for dotriacontane and hexatriacontane.

All quantifications were based on the compounds area derived from the ion fragmentogram (Table 2.7).

Table 2.7: Key fragment ions for mass spectrometric characterization of hydrocarbons.

No.	Compound	Key fragment ion (m/z)
1	Alkanes	85
2	Tetracosane-d_{50}	98
3	PAHs	M^+
4	Hopanes	191
5	Steranes	217, 218
6	Naphthenes (UCM)	95

Below, is an outline of the calculations followed in order to determine the compounds concentrations in the studied samples.

$\text{Conc} = \text{Amt} / \text{Vol}_{\text{samp}}$ (or G_{ext}) (Eqn. 2.1)

where,

Conc is the concentration of the component of interest,

$\text{Amt} = [\text{RFav} \times \text{Area} \times \text{Vol}_{\text{binj}} / \text{Vol}_{\text{inj}} \times \text{V}_{\text{extr}} / \text{V}_{\text{frc}} - \text{Amt}_{\text{contm}}] /$

Rec % (Eqn. 2.2),

where,

Amt is the blank and recovery corrected amount of the component,

RFav is the average response factor ($RF = Conc_{es} \times Vol_{inj} / Area_{es}$) (Eqn. 2.3).

where,

$Conc_{es}$ is the external standard concentration,

Vol_{inj} is the injection volume,

$Area_{es}$ is the area of the external standard in the fragmentogram.

Area is the peak area of the component in the fragmentogram,

Vol_{binj} is the total volume before injection into GC,

Vol_{inj} is the injection volume,

V_{extr} is the total volume of the extract,

V_{frc} is the volume of the extract used for fractionation,

Amt_{contm} is the amount of contamination ($Amt_{contm} = Conc_{contm} \times V_{extr}$)(Eqn. 2.4).

where,

$Conc_{contm}$ is the contaminant concentration (wt/v),

V_{extr} is the total volume of the extract of the sample to be corrected,

Rec % is the recovery (e.g., 100% = 1),

Vol_{samp} is the volume of air sampled (m^3),

G_{ext} is the weight of roadside soil particles extracted (g).

2.9 RECOVERY AND REPRODUCIBILITY

2.9.1 Fractionation recovery

Recovery experiments were carried out using the same procedure outlined in Section 2.6. The results are listed in Table 3.1.

2.9.2 Recovery studies

Recovery experiments for the multi-step procedure were carried out for both airborne particulate samples and roadside soil particles following the same procedures described in Sections 2.5.1 and 2.5.2 respectively, in addition to the fractionation step outlined in Section 2.6. The results are shown in Table 3.2.

2.9.3 Reproducibility

Reproducibility of the GC analysis was examined by repetitive injection of alkanes and PAHs standards (Tables 2.1b and 2.2b, respectively). The results are shown in Table 3.3.

2.10 PROCEDURAL BLANKS

Procedural blanks for airborne particulate samples and roadside soil particles were analyzed and quantified. Procedural blank analysis for roadside soil particulate sample was carried out by extracting dichloromethane in a clean centrifuge tube followed by fractionation (Section 2.6) and GCMS analysis. The experiment was repeated three times. As for the airborne particulate sample, an annealed clean glass fiber filter paper was mounted in the hi-vol air sampler for about 24 h followed by extraction (Section 2.5.1), fractionation (Section 2.6), and GCMS analysis.

Solvent blanks (450 mL of dichloromethane and 50 mL of n-hexane concentrated to 100 μL) were also analyzed in order to monitor the background.

The amounts of contaminants that have been quantified (Table 3.4) were subtracted from those of real samples (e.g., contaminants observed on Ab1 were subtracted from airborne particulate samples in the first sampling) in order to assess the actual concentration of hydrocarbons.