

CHARACTERIZATION OF SOLVENT-EXTRACTABLE
HYDROCARBONS FROM AIRBORNE PARTICULATES
AND STREET DUST OF KUALA LUMPUR

By

NASR YOUSEF M.J. OMAR
DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA

DISSERTATION PRESENTED FOR THE DEGREE OF
MASTER OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR
2001



A510304986

Perpustakaan Universiti Malaya

ABSTRACT

The solvent-extractable hydrocarbons were identified in PM₁₀ airborne particles and roadside soil particles collected at eight locations in the city center and the suburb of Kuala Lumpur, Malaysia during the period from November 1998 to January 1999. Airborne particles were collected using high-volume PM₁₀ sampler on glass fiber filters over 24 h average sampling period. After ultrasonic agitation with dichloromethane, the extracts were concentrated and fractionated on an alumina-silica column into three major fractions (aliphatics, aromatics and polar compounds). The aliphatics and aromatics fractions were then subjected to gas chromatography-mass spectrometric (GCMS) analysis. The major hydrocarbons identified in these fractions were n-alkanes in the range of C₁₁ to C₃₄, polycyclic aromatic hydrocarbons (PAHs) ranging from phenanthrene (3 rings) to coronene (7 rings), and petroleum molecular markers including n-alkylcyclohexanes, pristane, phytane, hopanes, and steranes.

The atmospheric concentrations of n-alkanes in urban Kuala Lumpur vary from 56.34 ± 9.84 to 178.90 ± 41.05 ng/m³, whereas the concentrations in roadside soil particles range from 6.10 ± 4.97 to 13.88 ± 10.07 µg/g. In atmospheric samples, the lower CPI values (CPI ~ 1) and the shift of C_{max} to lower molecular weight (e.g., C₂₅) indicated that vehicular emissions (petrogenic) are the major source of these compounds in airborne particles. However, in roadside soil particles, the biogenic input of n-alkanes was more apparent. This can be illustrated by the higher CPI values and the high molecular weight C_{max} (e.g., C₃₁).

Total PAHs concentrations in the atmospheric particles and roadside soil particles were found to be in the range of 1.84 ± 1.01 to 11.29 ± 4.99 ng/m³ and 0.19 ± 0.10 to 0.26 ± 0.17 µg/g, respectively. Benzo[g,h,i]perylene and coronene, which are indicative of gasoline vehicle emissions were found to be the most abundant PAHs in

airborne particles at all locations. The most abundant PAHs in the roadside soil particles were phenanthrene, fluoranthene, and pyrene. These compounds are indicative of diesel vehicle emissions. Thus, vehicular emissions are the primary contributor to PAHs concentration in Kuala Lumpur.

For both airborne particles and roadside soil particles, the presence of petroleum molecular markers, coupled with the unresolved complex mixture (UCM) reflected the contamination by petroleum residues of vehicular emissions.

The results of this study indicate that the solvent-extractable hydrocarbons in Kuala Lumpur's atmospheric and roadside soil particles are of mixed petrogenic and biogenic sources.

ABSTRAK

Hidrokarbon-hidrokarbon yang boleh diekstrakkan telah dikenalpasti dalam zarahhan terampai PM_{10} dan tanah tepi jalan. Sampel-sampel dikumpul di lapang lokasi di pusat bandar Kuala Lumpur dan persekitarannya untuk tempoh dari November 1998 sehingga Januari 1999. Zarahhan terampai dikumpul di atas kertas turas gentian kaca untuk tempoh kira-kira 24 jam dengan menggunakan pensampel ipadu-tinggi PM_{10} . Selepas diekstrak dengan diklorometana melalui kaedah getaran ultrasonik, ekstrak dipekatkan, dan dilalukan melalui turus alumina-silika bagi mendapatkan tiga pecahan utama, iaitu, alifatik, aromatik dan sebatian-sebatian yang berkutub. Pecahan alifatik dan aromatik seterusnya dianalisis dengan kaedah kromatografi gas-spektrometri jisim (KGSJ). Hidrokarbon-hidrokarbon utama yang dikenalpasti di dalam pecahan-pecahan ini ialah, n-alkana, dari C_{11} ke C_{34} , hidrokarbon aromatik polisiklik (HAP), dari fenantrena (3 gelang) ke koronena (7 gelang), dan penanda molekul petroleum seperti n-alkilsikloheksana, pristana, fitana, hopana dan sterana.

Kepekatan n-alkana di atmosfera Kuala Lumpur berada di antara 56.34 ± 9.84 dan $178.90 \pm 41.05 \text{ ng/m}^3$, sementara kepekatan dalam zarahhan tanah tepi jalan berada di antara 6.10 ± 4.97 dan $13.88 \pm 10.07 \text{ } \mu\text{g/g}$. Nilai CPI yang rendah (~ 1) dan anjakan C_{maks} ke rantai karbon yang lebih pendek (contohnya, C_{25}) menunjukkan bahawa pemancaran daripada kenderaan (petrogenik) merupakan sumber utama hidrokarbon dalam zarahhan terampai. Walau bagaimanapun, input n-alkana daripada sumber biogenik lebih ketara dalam zarahhan tanah tepi jalan. Hal ini ditunjukkan oleh nilai CPI yang lebih tinggi dan C_{maks} pada rantai karbon yang lebih panjang (contohnya, C_{31}).

Jumlah kepekatan HAP di dalam zarahhan terampai dan zarahhan tanah tepi jalan didapati masing-masing berada dalam julat di antara 1.84 ± 1.01 dan $11.29 \pm 4.99 \text{ ng/m}^3$, dan 0.19 ± 0.10 dan $0.26 \pm 0.17 \text{ } \mu\text{g/g}$. Benzo[ghi]perilena dan koronena, yang

merupakan penunjuk bagi pemancaran kenderaan berpetrol, merupakan HAP paling dominan dalam zarah terampai di semua lokasi. HAP paling banyak di dalam zarah tanah tepi jalan ialah fenantrena, fluorantena dan pirena. Sebatian-sebatian ini berasal daripada pemancaran kenderaan diesel. Adalah jelas bahawa pemancaran kenderaan merupakan penyumbang kepekatan HAP primer di Kuala Lumpur.

Bagi kedua-dua zarah terampai dan zarah tanah tepi jalan, kehadiran petanda molekul petroleum beserta campuran kompleks tak teresolusi (CKTR) mencerminkan kontaminasi oleh baki petroleum daripada pemancaran kenderaan.

Keputusan daripada kajian ini menunjukkan bahawa pemancaran kenderaan merupakan satu-satunya sumber penting bagi hidrokarbon terekstrak dalam zarah atmosfera dan zarah tanah tepi jalan.

ACKNOWLEDGEMENTS

First and foremost, my most sincere and profound appreciation to my supervisor, Associate Professor Dr. Mhd. Radzi bin Abas and co-supervisor, Associate Professor Dr. Kamal A. Ketuly for their instrumental role in assisting me to complete this dissertation. Their valuable guidances were essential in the progress of my work.

A special word of thanks to Associate Professor Dr. Noorhayati bte Mohd. Tahir for her valuable assistance. My sincere thanks also go to Mr. Din Mohd. Nor and Mr. Siew Yau Foo for their help in sampling and instrumental analysis.

My gratitude also goes out to the Malaysian government for the valuable financial aid provided which greatly contributed towards the successful completion of my dissertation. A note of thanks to the Chief of Police of Kuala Lumpur for being cooperative and providing a place to set up the air sampler.

My heartfelt thanks also goes out to my parents, brother, sister-in-law, and sisters who have been instrumental in providing moral encouragements for my success. I wish to take this opportunity to express my most heartfelt gratitude to them for all that they have done for me.

I would also like to take this opportunity to thank my fellow friends Abdulbaki, Ahmed, Akram, Avian, Mahmood, and Sufian who had, in more ways than one, pitched in to assist me in my endeavor to complete this work.

To my colleagues Ismat, Kang Ying, Marni, Norzalida, Samir, and William, I take great pleasure in extending my profound gratitude for all their assistance and encouragements.

Last but certainly not least, my thanks to the Department of Chemistry staff for being helpful and friendly.

CONTENTS

	Page
ABSTRACT.....	ii
ABSTRAK.....	iv
ACKNOWLEDGEMENTS.....	vi
LIST OF FIGURES.....	xii
LIST OF TABLES.....	xiv
ABBREVIATIONS.....	xvi
1 INTRODUCTION.....	1
1.1 AIR POLLUTION.....	1
1.2 ORGANIC AIR POLLUTANTS.....	3
1.3 PARTICLES IN THE ATMOSPHERE.....	3
1.4 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND ALKANES.....	4
1.4.1 Definitions, Sources, and Presence in the Atmosphere and Street Dusts.....	4
1.4.2 Transport Behavior in the Atmosphere.....	7
1.4.3 Seasonal, Temporal, and Spatial Variations.....	9
1.4.4 Atmospheric Reactions.....	10
1.4.5 Biodegradation and Toxicology.....	12
1.5 SAMPLING AND SAMPLE PRETREATMENT.....	13
1.5.1 Sampling and Sampling Artifacts.....	13
1.5.2 Sample Pretreatment (Extraction and Separation).....	18
1.5.3 Quantification and Identification.....	26
1.5.4 Storage Conditions of Particulate Samples.....	30

1.6 OBJECTIVES.....	31
2 EXPERIMENTAL.....	32
2.1 SAMPLING SITES.....	32
2.2 REAGENTS, GLASSWARE, AND APPARATUS.....	37
2.3 PREPARATION OF STANDARDS.....	37
2.3.1 Internal Standards.....	37
2.3.2 External Standards.....	38
2.4 SAMPLING AND SAMPLE PREPARATION	40
2.4.1 Airborne Particles.....	40
2.4.2 Roadside Soil Particles.....	41
2.4.3 Miscellaneous Samples (Reference Samples).....	43
2.5 EXTRACTION.....	44
2.5.1 Airborne Particles.....	44
2.5.2 Roadside Soil Particles.....	44
2.6 FRACTIONATION.....	45
2.7 INSTRUMENTAL ANALYSIS.....	46
2.8 IDENTIFICATION AND QUANTIFICATION.....	46
2.9 RECOVERY AND REPRODUCIBILITY.....	48
2.9.1 Fractionation Recovery.....	48
2.9.2 Recovery Studies.....	48
2.9.3 Reproducibility.....	49
2.10 PROCEDURAL BLANKS.....	49
3 RESULTS AND DISCUSSION.....	50
3.1 REFINEMENT OF METHOD.....	50
3.1.1 Optimization of Chromatographic Conditions.....	50
3.1.2 Optimization of Fractionation Procedure.....	51

3.2 GENERAL CHARACTERISTICS OF AIRBORNE PARTICLES AND ROADSIDE SOIL PARTICLES.....	55
3.2.1 Total PM ₁₀ Particles (TPM _{10P}).....	55
3.2.2 Extractable Organic Matter from Airborne Particulate Samples..	56
3.2.3 Extractable Organic Matter from Roadside Soil Particles.....	58
3.2.4 Percentages of Identified Organics in TSEOM.....	60
3.3 SOURCES OF AIRBORNE PARTICULATE MATTER.....	61
3.3.1 Internal Combustion Engines.....	61
3.3.2 Plants.....	62
3.3.3 Street Dust as a Source and Sink.....	63
3.4 n-ALKANES.....	64
3.4.1 Diagnostic Parameters and Calculations.....	64
3.4.1.1 Carbon Preference Index (CPI).....	64
3.4.1.2 Carbon Number Maximum (C _{max}).....	64
3.4.1.3 Plant Wax n-Alkanes.....	64
3.4.2 Sources of n-Alkanes.....	64
3.4.2.1 Petrogenic Sources.....	64
3.4.2.2 Biogenic Sources.....	66
3.4.3 n-Alkanes in Airborne Particles, Roadside Soil Particles, and Lubricating Oils.....	66
3.4.3.1 n-Alkanes in Airborne Particulate Samples.....	66
3.4.3.2 n-Alkanes in Roadside Soil Particles.....	71
3.4.3.3 n-Alkanes in Lubricating Oils.....	74
3.4.3.4 Plant Wax n-Alkanes.....	75
3.4.3.5 Comparison of Airborne Particulate Samples and Roadside Soil Particles.....	76

3.5 UNRESOLVED COMPLEX MIXTURE (UCM).....	77
3.5.1 UCM in Airborne Particulate Samples, Roadside Soil Particles, and Lubricating Oils.....	78
3.6 PETROLEUM MOLECULAR MARKERS.....	83
3.6.1 n-Alkylcyclohexanes.....	83
3.6.2 Isoprenoid Hydrocarbons (Pristane and Phytane).....	85
3.6.2.1 Sources in Crude Petroleum and the Environment.....	85
3.6.2.2 Pristane and Phytane in Airborne Particulate Samples, Roadside Soil Particles, and Lubricating Oils.....	85
3.6.2.3 Pristane to Phytane Ratio (Pr/Ph).....	88
3.6.3 Pentacyclic Triterpanes and Steranes.....	89
3.6.3.1 Sources, Formation, and Occurrence in Fossil Fuels and the Environment.....	89
3.6.3.2 Hopanes and Steranes as Petroleum Molecular Markers.....	91
3.6.3.3 Hopanes and Steranes in Environmental Samples.....	91
3.6.3.4 Geochemical Diagnostic Parameters and Interpretations.....	97
3.6.3.4.1 Ratio A.....	100
3.6.3.4.2 Ratio B.....	101
3.6.3.4.3 Ratio C.....	101
3.6.3.4.4 Ratio D.....	101
3.6.3.4.5 Ratio E.....	102
3.6.3.4.6 Ratio F.....	102
3.6.3.4.7 $\beta\alpha$ -Moretanes.....	103
3.6.3.4.8 Other Parameters.....	103

3.7 PYROGENIC MOLECULAR MARKERS (POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)).....	105
3.7.1 Formation and Sources.....	105
3.7.2 Physico-Chemical Modifications of PAHs during Transport and Sampling.....	106
3.7.3 PAHs in Airborne Particulate Samples, Roadside Soil Particles, and Lubricating Oils.....	107
3.7.3.1 PAHs in Airborne Particulate Samples.....	107
3.7.3.2 PAHs in Roadside Soil Particles.....	115
3.7.3.3 PAHs in Lubricating Oils.....	120
3.7.3.4 Comparison of Airborne Particulate Samples and Roadside Soil Particles.....	121
4 CONCLUSION.....	122
REFERENCES.....	126
APPENDICES	
A MASS SPECTRA OF SOME COMMON HYDROCARBONS.....	140
B PHOTOGRAPHS OF THE SAMPLING SITES.....	143
C CHEMICAL STRUCTURES CITED.....	147
D PUBLICATIONS.....	149

LIST OF FIGURES

Figure	Page
1.1 Oxidation of benzo[a]pyrene.....	11
1.2 Quinone formation of benzo[a]pyrene by irradiation.....	11
1.3 Oxidation of benzo[a]pyrene by microorganisms.....	12
1.4 Diagnostic mass spectrometric fragmentations (and their mass to charge ratios) used to monitor some common hydrocarbons.....	29
2.1 Location map of the sampling sites in Kuala Lumpur.....	33
2.2 Kuala Lumpur and the Klang valley region.....	34
3.1 Variations in TPM _{10P} concentrations at different sampling stations.....	56
3.2 Comparison of the mean percentages of organics in urban airborne particles, urban roadside soil particles, forest airborne particles, and forest roadside soil particles.....	61
3.3 Variations in n-alkanes concentrations at different sampling stations for urban airborne particles.....	68
3.4 Distribution diagrams of n-alkanes in airborne particles.....	69
3.5 Typical m/z 85 fragmentograms (for alkanes) for airborne particles and roadside soil particles.....	70
3.6 Variations in n-alkanes concentrations at different sampling stations for urban roadside soil particles.....	71
3.7 Distribution diagrams of n-alkanes in roadside soil particles.....	73
3.8 Distribution diagrams of n-alkanes in lubricating oils.....	75
3.9 Correlation between CPI and % plant wax n-alkanes for airborne particles [urban and forest] and roadside soil particles [urban and forest].....	76
3.10 Typical TIC of the first chromatographic fraction for airborne particles and roadside soil particles.....	79
3.11 Typical m/z 95 fragmentograms (for naphthenes) for airborne particles and roadside soil particles.....	81

3.12	Correlation between CPI and U:R for airborne particles [urban and forest] and roadside soil particles [urban and forest].....	82
3.13	Typical m/z 82 and 83 fragmentograms (for n-alkylcyclohexanes) for airborne particles and roadside soil particles.....	84
3.14	Typical m/z 191 fragmentograms (for hopanes) for airborne particles and roadside soil particles.....	92
3.15	Typical m/z 217 (for $\alpha\alpha\alpha$ -steranes) and 218 (for $\alpha\beta\beta$ -steranes) fragmentograms for airborne particles and roadside soil particles.....	94
3.16	Variations in hopanes and steranes concentrations at different sampling stations for urban airborne particles and roadside soil particles.....	96
3.17	Distribution diagrams of hopanes and steranes for all the samples studied.....	98
3.18	Typical m/z 178, 202, 228, 252, 276, 278, and 300 fragmentograms (for PAHs) for airborne particles.....	108
3.19	Variations in PAHs concentrations at different sampling stations for urban airborne particles.....	109
3.20	Distribution diagrams of PAHs in airborne particles and roadside soil particles.....	112
3.21	Typical m/z 178, 202, 228, 252, 276, 278, and 300 fragmentograms (for PAHs) for roadside soil particles.....	116
3.22	Variations in PAHs concentrations at different sampling stations for urban roadside soil particles.....	119
3.23	Correlation between BgP and total PAHs for airborne particles [urban and forest] and roadside soil particles [urban and forest].....	120

LIST OF TABLES

Table	Page
1.1 Sampling characteristics of selected methods for gaseous and particulate PAH.....	15
2.1a Alkanes standards.....	38
2.1b Alkanes standards.....	38
2.2a PAHs standards.....	39
2.2b PAHs standards.....	39
2.2c PAHs standards.....	39
2.3a First sampling of airborne particulate samples.....	40
2.3b Second sampling of airborne particulate samples.....	41
2.3c Third sampling of airborne particulate samples.....	41
2.4a First sampling of roadside soil particles.....	42
2.4b Second sampling of roadside soil particles.....	42
2.4c Third sampling of roadside soil particles.....	42
2.4d Relative mass distributions (%) of first sampling.....	43
2.4e Relative mass distributions (%) of second sampling.....	43
2.4f Relative mass distributions (%) of third sampling.....	43
2.5 Description of forest airborne particles and roadside soil particles.....	44
2.6 Description of GCMS chromatographic conditions.....	46
2.7 Key fragment ions for mass spectrometric characterization of hydrocarbons.....	47
3.1 Mean recovery $\pm$ R.S.D. (%) ($n = 3$) for fractionation step.....	52
3.2 Mean recovery $\pm$ R.S.D. (%) ($n = 3$) of C ₂₄ D ₅₀ and PAHs from spiked blank glass fiber filters and roadside soil particles.....	53
3.3 Percentage R.S.D. of reproducibility ($n = 3$).....	54

3.4 Major contaminants observed in procedural blanks and their amount.....	55
3.5 General characteristics of airborne particulate samples.....	57
3.6 General characteristics of roadside soil particles.....	59
3.7 n-Alkanes and UCM in airborne particles.....	67
3.8 n-Alkanes and UCM in roadside soil particles.....	72
3.9 n-Alkanes and UCM in lubricating oils.....	74
3.10 Petroleum molecular markers in airborne particles.....	86
3.11 Petroleum molecular markers in roadside soil particles.....	87
3.12 Petroleum molecular markers in lubricating oils.....	88
3.13 PAHs in airborne particles.....	110
3.14 Diagnostic ratios of PAHs from different sources.....	114
3.15 PAHs in roadside soil particles.....	117
3.16 PAHs in lubricating oils.....	121

ABBREVIATIONS

ANTH	Anthracene
ANTN	Anthanthrene
BaA	Benz[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BeP	Benzo[e]pyrene
BgP	Benzo[g,h,i]perylene
BkF	Benzo[b]fluoranthene
BR	Bukit Rengit
CH	Cheras
CHR	Chrysene
C _{max}	Carbon number maximum
COR	Coronene
CPI	Carbon preference index
dBahA	Dibenz[a,h]Anthracene
DW	Dang Wangi
FLO	Fresh lubricating oil
FLT	Fluoranthene
g	Gram
GC	Gas chromatography
GC-FID	Gas chromatography-flame ionization detector
GCMS	Gas chromatography-mass spectrometry
GCMSMS	Gas chromatography-mass spectrometry-mass spectrometry
h	Hour
hi-vol	High-volume
HPLC	High performance liquid chromatography
I.D.	Internal Diameter
IP	Indeno[1,2,3-cd]pyrene
JA	Jalan Ampang
JT	Jalan Travers
KE	Kepong

LC	Liquid chromatography
m	meter
min	minute
MPHEN	4,5-Methylenepheneanthrene
n	Number of observations
n.a.	Not available
n.d.	Not detected
PAHs	Polycyclic aromatic hydrocarbons
PB	Pantai Baharu
PER	Perylene
PHEN	Phenanthrene
PM ₁₀	Particulate matter $\leq 10\ \mu\text{m}$
PM _{2.5}	Particulate matter $\leq 2.5\ \mu\text{m}$
ppm	Parts per million
PU	Pudu
PYR	Pyrene
RfC	Reference Concentration
RfD	Reference Dose
RIC	Reconstructed ion chromatogram
SE	Sentul
sec	Second
SIM	Selected ion monitoring
SPE	Solid phase extraction
TIC	Total ion chromatogram
TLC	Thin layer chromatography
TPM _{10P}	Total PM ₁₀ Particles
TSEOM	Total solvent extractable organic matter
TSP	Total suspended particles
UCM	Unresolved complex mixture
ULOC	Used car lubricating oil
ULOM	Used motorbike lubricating oil
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
XAD-2	Styrene and divinylbenzene copolymer
σ	Standard deviation