UNIVERSITI PUTRA MALAYSIA

METHOD DEVELOPMENT, SPECIATED MEASUREMENTS AND CALCULATED REACTIVITIES OF BENZENE, TOLUENE, ETHYLBENZENE AND XYLENES FROM VEIDCLE EXHAUST

NORASALWA ZAKARIA

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By

NORASALWA ZAKARIA

**Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Science and Environmental Studies
Universiti Putra Malaysia**

December 2001

For my lovely little girl;

Qistina Saffwah Mohd. Qayyum

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

METHOD DEVELOPMENT, SPECIATED MEASUREMENTS AND CALCULATED REACTIVITIES OF BENZENE, TOLUENE, ETHYLBENZENE AND XYLENES FROM VEHICLE EXHAUST

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Chairperson: **Dr. Puziah Abd. Latif**

Faculty: **Science and Environmental Studies**

Mathematical modeling of ambient air photochemistry requires comprehensive speciation of hydrocarbons from mobile source emission. The objective of this study is to develop a simple and reliable method for analyzing tailpipe emission focusing on benzene, toluene, ethylbenzene and xylenes (BTEX). The method consists of sampling, qualitative analysis and quantitative analysis. The samples were collected in Tedlar bags at cold start and hot start conditions and were injected manually using a gas-tight syringe into Gas Chromatograph-Mass Spectrometer (GC-MS) operated on Electron Impact Ionization (EI) mode.

The method developed has demonstrated ability to produce rapid and reliable separations of exhaust hydrocarbons. An approximate of 50 hydrocarbon compounds were identified in the exhaust ranging from C_4 to C_{12}. It was found difficult to analyze

C_1 to some of the C_4 hydrocarbons without the required accessories for volatile organic gases analysis.

The emission rate of BTEX was emphasized because of its potential carcinogenicity and toxicity. High concentration of BTEX was observed during cold start and hot start. The mean concentrations of BTEX at cold start were as follows: benzene (55.4 ppm), toluene (184.7 ppm), ethylbenzene (50.2 ppm), m-xylene (143.9 ppm), p-xylene (59.0 ppm) and o-xylene (65.4 ppm). The mean concentrations of BTEX at hot start were as follows: benzene (82.4 ppm), toluene (198.3 ppm), ethylbenzene (40.0 ppm), m-xylene (184.0 ppm), p-xylene (62.1 ppm) and o-xylene (50.3 ppm).

The concentrations of BTEX in weighted percentages for all cars were fairly constant. The weighted percentages concentration was used to estimate the photochemical ozone reactivity by applying the Maximum Incremental Reactivity (MIR) factors to the concentrations. The ozone forming potential as a result of BTEX emission from vehicle exhaust were estimated as follows: 3.07 g O_3/ g benzene, 74.64 g O_3/ g toluene, 13.0 g O_3/ g ethylbenzene, 145.8 g O_3/ g m- and p-xylene, and 50.97 g O_3/ g o-xylene. The results suggested that BTEX emitted from the vehicle exhaust increases the formation of photochemical ozone in the atmosphere significantly.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PEMBENTUKAN KAEDAH, PENILAIAN SPESIS DAN PENGUKURAN KEREAKTIFAN BENZENA, TOLUENA, ETILBENZENA DAN XILENA DARI EKZOS KENDERAAN

Oleh

NORASALWA ZAKARIA

Disember 2001

Pengerusi: **Dr. Puziah Abd. Latif**

Fakulti: **Sains Dan Pengajian Alam Sekitar**

Pembentukan model matematik untuk fotokimia udara memerlukan penilaian yang komprehensif terhadap spesis hidrokarbon dari sumber yang bergerak. Tujuan kajian ini adalah untuk membentuk satu kaedah yang ringkas dan berkesan untuk menjalankan analisis ke atas hidrokarbon dari ekzos kenderaan terutamanya benzena, toluena, etilbenzena dan xilena (BTEX). Kaedah ini terdiri daripada teknik peyampelan, analisis kualitatif dan analisis kuantitatif. Semua sampel ekzos diperangkap di dalam beg Tedlar dan disuntik secara manual menggunakan jarum kedap udara ke dalam Gas Kromatografi-Spektrometer Jisim (GC-MS) yang beroperasi pada mod Pengionan Impak Elektron.

Kaedah yang dibentuk telah berjaya mengasingkan konponen-komponen hidrokarbon di dalam ekzos. Secara kasar, 50 spesis hidrokarbon telah dikesan iaitu dari

C_4 hingga C_{12}. Komponen hidrokarbon dari C_1 hingga sebahagian dari C_4 tidak berjaya dikesan oleh alat GC-MS yang digunakan kerana ia memerlukan aksesori tambahan untuk tujuan tersebut.

Kadar pelepasan BTEX perlu dititikberatkan kerana ia bersifat karsinogen dan toksik. Hasil kajian menunjukkan kepekatan BTEX yang tinggi semasa kenderaan dihidupkan pada permulaan sejuk dan pada permulaan panas. Kepekatan min BTEX pada keadaan permulaan sejuk adalah seperti berikut: benzena (55.4 ppm), toluena (184.7 ppm), etilbenzena (50.2 ppm), m-xilena (143.9 ppm), p-xilena (59.0 ppm) and o-xilena (65.4 ppm). Kepekatan min BTEX pada keadaan permulaan panas adalah seperti berikut: benzena (82.4 ppm), toluena (198.3 ppm), etilbenzena (40.0 ppm), m-xilena (184.0 ppm), p-xilena (62.1 ppm) and o-xilena (50.3 ppm).

Kesan BTEX terhadap pembentukan ozon fotokimia dianggar menggunakan faktor 'Peningkatan Reaktiviti Maksimum' (MIR). Potensi pembentukan ozon akibat pelepasan BTEX dari ekzos kenderaan adalah dianggarkan seperti berikut: 3.07 g O_3/ g benzena, 74.64 g O_3/ g toluena, 13.0 g O_3/ g etilbenzena, 145.8 g O_3/ g m- and p-xilena, dan 50.97 g O_3/ g o-xilena. Ini menunjukkan bahawa kandungan BTEX di dalam ekzos kenderaan mempunyai kesan yang ketara terhadap pembentukan ozon fotokimia di atmosfera.

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Finally, to my lovely husband and parents, thank you for the immense understanding and support.

I certify that an Examination Committee met on 8th December 2001 to conduct the final examination of Norasalwa Zakaria on her Master of Science thesis entitled "Method Development, Speciated Measurements and Calculated Reactivities of Benzene, Toluene, Ethylbenzene and Xylenes from Vehicle Exhaust" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Anuar Kassim, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Puziah Abd. Latif, Ph.D.
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Azman Zainal Abidin, M.Sc.
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Azizi Hj. Muda, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D
Professor/ Dean of Graduate School
Universiti Putra Malaysia

Date: 2 JAN 2002

The thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

AINI IDERIS, Ph.D.
Professor/
Dean of Graduate School
Universiti Putra Malaysia

Date: 14 MAR 2002

DECLARATION

I hereby declare that the thesis is based on my original work except quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

NORASALWA ZAKARIA

Date: 2/1/2002

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LIST OF ABBREVIATIONS

amu	atomic mass unit
BTEX	benzene, toluene, ethylbenzene and xylenes
CS	cold start
EI	Positive Electron Ionization
eV	electroVolt
FID	Flame Ionization Detector
FTP	Federal Test Procedure
GC	Gas Chromatograph
GC-MS	Gas Chromatograph-Mass Spectrometer
HPLC	High Performance Liquid Chromatograph
HS	Hot Start
ID	Internal Diameter
K	Kelvin
min	minute
MIR	Maximum Incremental Reactivity
MS	Mass Spectrometer
m/z	mass to charge ratio
NMHC	Non-Methane Hydrocarbon
ppm	part per million
ppb	part per billion
RI	Relative Intensities
rpm	rotation per minute

r.t	retention time
r.r.t	relative retention time
T	Temperature
TIC	Total Ion Chromatogram
V	Volt

CHAPTER 1

INTRODUCTION

1.1 Introduction

Motor vehicles are recognized as a major contributor of hydrocarbons to the atmosphere in urban area and have been associated with serious environmental problems such as photochemical smog, photochemical ozone and acid rain in addition to adverse effects on human health. Although emissions from individual vehicle are generally low, the combined emissions from the total number of vehicle and the increasing mileage traveled, proved them to be the principal source of anthropogenic pollutant. In Malaysia, an increase in the number of vehicles on the road was reported from 8,510976 in 1997, to 9,141,357 at the end of 1998 (JPJ, 2000).

Traditionally, measurements of auto-vehicle emission were limited to total hydrocarbon (THC), carbon monoxide (CO) and oxides of nitrogen. Other primary pollutants in the exhaust such as hydrocarbons were not emphasized. Hydrocarbons in the exhaust like benzene, toluene, ethylbenzene and xylenes (BTEX) should be emphasized since they react with hydroxyl radicals in the atmosphere to form secondary pollutants that propagate the formation of photochemical ozone. Hence, detailed composition and characterization of vehicular emission is required simply because the individual hydrocarbons has different inherent toxicities and ozone-forming reactivity.

Vehicle exhaust comprises of many hydrocarbons ranging from C_1-C_{12}. The identification of the full spectrum of the compounds present in vehicle exhaust and air is only possible using chromatographic techniques. However, due to instrumentation limitation and costing, the study was limited to C_5 to C_{12} hydrocarbons with particular interest on light aromatic hydrocarbons like benzene, toluene, ethylbenzene and xylene (BTEX). BTEX was chosen because it constitutes a significant fraction of the organic compounds in the exhaust and fuel as well as in the troposphere. Furthermore, benzene is known as carcinogen and others are considered as air toxicants. Table 1.1 shows the comparison between the Recommended Malaysian Guideline and the United States National Ambient Air Quality Standards (NAAQS) of common air pollutants.

Table 1.1: Comparison Between Recommended Malaysian Guideline (RMG) And National Ambient Air Quality Standards (NAAQS)

Pollutant	**Averaging Time**	**RMG** (ppm)	($\mu g/m^3$)	**NAAQS** ($\mu g/m^3$)
Ozone	1 hr	0.10	200	235
	8 hr	0.11	120	
CO*	1 hr	30	35×10^3	10×10^3
	8 hr	9	10×10^3	
NO_2	1 hr	0.17	320	
	24 hr		113	
SO_2	10 min	0.19	500	
	1 hr	0.13	350	
	24 hr	0.04	105	365
Particle	24 hr		260	
TSP	1 yr		90	260
PM10	24 hr		150	150
	1 yr		50	

* measurement in mg/m^3

Source: Azman, 2000

1.2 Statement of the Problems

The analysis of BTEX emitted from motor vehicle exhaust is required for two reasons. Firstly, under the Clean Air Act (CAA) of the United States, promulgated in 1990, benzene, toluene, and the xylenes have been listed as air toxicants. Furthermore, benzene is carcinogenic. Secondly, benzene and its derivatives have been associated with serious environmental problems such as photochemical ozone and photochemical smog. Each of the compounds has a different ozone reactivity or ozone forming potential. Therefore, the concentration of benzene, toluene, ethylbenzene and xylenes from the motor vehicles should be determined accurately and must be monitored continuously since the main anthropogenic source of benzene and its derivatives comes from motor vehicles. For these to be accomplished, the analytical method for BTEX analysis, using the available instrument, must be developed.

Accurate measurements and the information acquired from the analysis is beneficial as the baseline for considering the requirement for regulating benzene released from the motor vehicles as well as in the fuel. In addition, the ozone forming potential, as a result of BTEX emission from the vehicle exhaust, can also be estimated.

1.3 Objectives of the Study

The objectives of the study are as follows:

1. To develop a rapid and reliable method for trace level analysis for routine monitoring of the volatile organic compounds, originated from motor vehicle exhaust and ambient air;
2. To identify and quantify BTEX in motor vehicle exhaust;
3. To identify and quantify BTEX in fuel formulations and compare them to the emission from various motor vehicles;
4. To estimate photochemical ozone reactivity of BTEX as a result of vehicle exhaust emission.

1.4 Scope and Limitation of The Study

1. The main scope of the study is to develop an analytical method for BTEX analysis using Gas Chromatograph-Mass Spectrometer. The gaseous samples will be introduced manually into the GC, using a gas tight syringe, but the liquid sample will be injected into the GC using an auto-injector. Other accessories required for gaseous analysis like automatic gas sampling valve, cryogenic concentrator and a purge and trap unit are not available at the moment.

2. The exhaust samples collected in this study were limited to the exhaust from the cars only. Other gaseous samples that were collected for instance the ambient air samples and a motorcycle's exhaust, were only used for comparison purposes only.

1.5 Significance of the Study

To the author's best knowledge, no studies have yet been conducted or published in Malaysia involving a detailed speciation of hydrocarbons in vehicle exhaust, although it is recognized as major anthropogenic pollutants. Thus this study will provide information on the strategy to develop an alternative method for analysis of volatile compounds especially BTEX by direct injection of gaseous sample using gas tight syringe into the GC-MS instead of using gas sampling valve or a purge and trap unit.

In environmental context, characterization of vehicle exhaust is needed for several reasons. A complete speciation enable prediction of the quantity of ozone created as a result of vehicle emission. Also, the technique and the method developed can be used to collect data on the amount of BTEX emitted in enclosed area like underground car park or tunnel with no or poor ventilation so that by using these information, proper regulation can be enforced to regulate BTEX emission and proper control measure can be installed where appropriate.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Organic compounds cover a wide range of groups including aliphatic hydrocarbons, aromatics, halogenated hydrocarbons and oxygenated hydrocarbons. Table 2.1 below shows the categoeries for organic compounds, which are based on their boiling point. Light aromatic hydrocarbons like benzene, toluene, ethylbenzene and xylenes or BTEX, which have boiling points ranging from 80°C to 144°C are categorized as volatile organic hydrocarbons (VOC).

Table 2.1: Categories of Organic Compounds

Categories	Boiling Point (°C)
Very Volatile Organic Compound (VVOC)	< 0 to 50-100
Volatile Organic Compound (VOC)	50-100 to 240-260
Semi Volatile Organic Compound (SVOC)	240-260 to 380-400

Source: Rafson, H.J. 1988

Various aspects of BTEX were studied due to its adverse effects towards human and to the environment. To human, benzene is a carcinogen and its derivatives are considered as air toxicants. In air photochemistry, BTEX plays an important role in the formation of photochemical ozone. Physical properties of BTEX are tabulated in Table 2.2.