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BENZENE TOLUENE AND XYLENE
IN EXHAUST FROM MOTORCYCLES

Miss Thitima Rungratanaubon



สถาบันวิทยบริการ
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By Miss Thitima Rungratanaubon
Inter-department Environmental Science
Thesis Advisor Associate Professor Noppaporn Panich, D.Eng
Thesis Co-Advisor Associate Professor Amorn Petsom, Ph.D

Accepted by the Graduate School, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree

.....Dean of Graduate School
(Professor Suchada Kiranandana, Ph.D)

Thesis Committee

.....Chairman
(Assistant Professor Pipat Patanaponpaiboon, Ph.D)

.....Thesis Advisor
(Associate Professor Noppaporn Panich, D.Eng)

.....Thesis Co-Advisor
(Associate Professor Amorn Petsom, Ph.D)

.....Member
(Associate Professor Premchit Tansathit)

.....Member
(Associate Professor Wongpun Limpaseni)

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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....ลายมือชื่อนิสิต.....
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AIR POLLUTION

THITIMA RUNGRATANAUBON : BENZENE TOLUENE AND XYLENE IN
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NOPPAPORN PANICH, D.Eng THESIS COADVISOR : ASSOC. PROF.
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In this study, Benzene, Toluene and Xylene concentrations from gasoline and exhaust emission were measured from 44 in-use motorcycles. The motorcycle samples were considered both engine type (2 and 4-stroke) and engine age (old, moderate and new). The ages of engine were determined as follow: New motorcycles were less than 5 years old, Moderate age motorcycles were in range of 5-10 years old and Old motorcycles were more than 10 years old. Tedlar bag was used to collect the sample of exhaust emission at idle condition. The samples were analyzed using gas chromatography with flame ionization detection (GC/FID). The study revealed that the 2-stroke motorcycle emitted hydrocarbon (Benzene, Toluene and Xylene) about 3-4 times larger than that of 4-stroke motorcycle. The average concentrations of Benzene, Toluene and Xylene from the old 2-stroke motorcycle were found to be 116.15, 261.73 and 39.21 ppm, respectively. While new 4-stroke motorcycle were found to be 11.74, 29.00 and 7.59 ppm, respectively. These result also indicated that there were a significant increase in air pollutant emissions with engine age at significant level (α) 0.05.

Department..... Student's signature.....

Field of study..... Advisor's signature.....

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CHAPTER 1

INTRODUCTION



1.1 General background

Air pollution is one of the most obvious and important environmental problems in many cities of the world especially the Bangkok Metropolitan Area. Urbanization and rapid development of Bangkok have resulted in a great demand for an effective transportation system and traffic. However, an inadequate road infrastructure and the lack of a mass transit system have intensified this problem.

The lack of potential road infrastructure and well-serviced mass transit system encourages people to travel by their own private vehicles. In 1998, the total number of vehicles registered in the Bangkok Metropolitan Area was more than 3.8 million while the road space as a share of total area in Bangkok is only 11%, which is substantial lower than international standard of between 20% to 25%. (Rammont, 1999) The number of vehicles has exceeded the road capacity for years. Then, the more transport increases, the more fuel is burned, and it leads to a higher level of exhaust emission released into the atmosphere. Thus, a major air pollution source is the rapidly increasing number of vehicles travelling on the streets, which are too limited to facilitate them all.

In addition to their possible deleterious effects on human health, motor vehicles emissions have been associated with serious environmental problems such as photochemical smog. Motor vehicle especially motorcycle emit

various types of air pollutants such as carbon monoxide, hydrocarbons, nitrogen oxides, sulfur dioxide and particulate matter. Traditionally, the measurements of mobile source emission were limited to total hydrocarbons (THC), carbon monoxide (CO), and oxides of nitrogen (NO_x).

At present, the Government of Thailand has banned leaded gasoline and substituted unleaded. Unleaded gasoline uses aromatic compounds to increase the octane number. These aromatic compounds mainly comprised benzene, toluene, xylene and ethyl benzene. These pollutants worsen the air in Bangkok and adversely affect human health.(Lervisansak,1996)

In Bangkok, motorcycles are a major source of air pollution because of where traffic is congested, this type of vehicle is extensively used due to its low cost and very convenience. There were approximately 6,190,310 motorcycles in Thailand at the end of 1992, of which 1,048,654 (17 %) are used in Bangkok. (Apinhapath, 1994)

There are several factors which affect the concentration of exhaust emissions such as type of vehicle, state of the motor, the quality of the fuel and lubricating oil, the load of the vehicle, the number of kilometers driven per year per vehicle, and speed of travel. However, air pollution from traffic emissions in any community depends principally on the character of the traffic, street configuration and orientation, land use activities, and the ability of the atmosphere to disperse the pollutant. The effect of car emission in various traffic situations to ambient air leads to air quality management related to emission from passenger vehicles.

1.2 Objectives

The specific objectives of this study are as follows :

1. To determine the concentration of Benzene Toluene and Xylene (as Total Xylene) in motorcycle emissions and in gasoline that motorcycle used.
2. To compare the concentration of Benzene Toluene and Xylene (as Total Xylene) in motorcycle emissions in different age of engine.
3. To compare the concentration of Benzene Toluene and Xylene (as Total Xylene) in motorcycle emissions in 2 different types of engine (2 stroke and 4-stroke engine)

1.3 Scope of the study

In this study focuses on 2 and 4-stroke engines motorcycles emissions and only the major pollutants of Benzene, Toluene, and Xylene (as Total Xylene) were evaluated. The motorcycles sample were classified into 3 categories new, moderate and old motorcycles based on the age of engine each are considered as below :

New age engine of motorcycles are less than 5 years old. (< 5 years)

Moderate age engine of motorcycles are in range of 5 to 10 years old.
(5 – 10 years)

Old age engine of motorcycles are more than 10 years old. (> 10 years)

And all emission samples were collected at idle mode condition only.

CHAPTER 2

LITERATURE REVIEW

2.1 General Information about motorcycles in Thailand

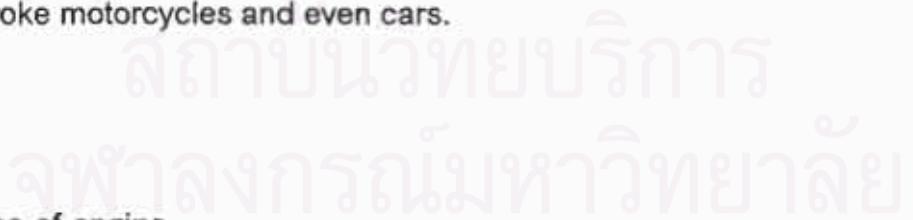
The number of vehicles registered in Bangkok Metropolitan Area (BMA) had more than 3.8 million in 1998. There are many types of vehicle such as passenger car, motorcycles, truck, buses, taxis and three-wheelers (tuk-tuk). These different vehicle groups cause different air pollution problems. While gasoline vehicles produce carbon monoxide, diesel vehicle produce black smoke and oxides of nitrogen, and two stroke engines (motorcycles) produce white smoke and hydrocarbons (Boontharawara et al., 1994). Lead is emitted from vehicles using leaded gasoline but unleaded gasoline vehicles emitted Volatile Organic Compounds (VOCs) instead of lead. (Lertvisansak, 1996; Siriroughudomporn, 1997; Rammnot, 1999)

Observations of high ambient air lead concentrations in Bangkok during 1989 to 1991 triggered The Royal Thai Government to start phasing out lead in gasoline. An aggressive lead phase-out program was then planned and introduced in 1989 with the initial reduction of lead content in the gasoline from 0.45 gm/liter at the end of 1989 and plan for further reduction to 0.15 gm/liter by September 1993. Finally, lead was completely eliminated from regular gasoline in the middle of 1994 and from premium gasoline on January 1 of 1996. (Wangwongwattana, 1998)

The levels of traffic exceed the capacity of the road system in Bangkok city with have only 112 main road with total length of 524 km and 4,280 smaller

roads. It is estimated that the road occupies just only 9% of the city area with very low compared to 22% in London and 24% in New York. As a consequence, major traffic arteries are normally congested. The cars travel at average speed of less than 7 km/h in the business area in Bangkok, and travel at an average speed of less than 20 km/h in other areas. Slow speed, frequency stops, deceleration and acceleration result in greater incidence of incomplete combustion that cause higher emission of carbon monoxide, hydrocarbon, and particulate matter (Apinhapath, 1994).

The number of motorcycles in Bangkok increase sharply as a result of traffic congestion whereby people switch to motorcycles in order to go around the city faster. Motorcycles are currently being used as public taxis for carrying passengers in and delivering messages. The density of motorcycles in Bangkok is not only higher than other areas on the world, it generally is much greater than the 4-wheel vehicle population. Many of these vehicles are powered by very design two-stroke motorcycles (which have been largely phased out in most other areas on the world) which emitted as much as 10 times more hydrocarbons and smoke emission per kilometer driven than do four-stroke motorcycles and even cars.



2.2 Type of engine

Reciprocating internal combustion engines operate on either the 4 stroke or the 2-stroke cycle. The 4-stroke cycle engine is the most commonly used for automotive purposes especially in road vehicles. The 2-stroke engine is sometimes used in small passenger cars, motorcycles, and as outboard marine engines. In the 4-stroke cycle engine as well as the 2-stroke cycle

engine the following 4 processes take place during the cycle of operation (Patterson, cited in Midpanon, 1995) :

1. Charging the cylinder with a fresh charge. This charge is composed of a mixture of fuel and air in the gasoline engine and air only in the diesel engine.
2. Compressing of this charge to a temperature suitable for the proper combustion process which usually starts before the maximum compression pressure is reached. In the gasoline engine the combustion process start by ignition from a spark plug. The pressure of combustion results in a substantial increase into the gas temperature and pressure.
3. Expansion of the high pressure gas.
4. Discharging the exhaust gas.

2.2.1 Four stroke cycle engine

The principle of the 4 stroke cycle engine is illustrated in figure 2.1.

In order to simplify the cycle of operations the valves will be considered in opening and closing of the top or bottom of the piston stroke, although in practice there is a deviation from this assumption

1. Induction stroke.

As the piston starts to move downwards from the top dead center (t.d.c), the inlet valve opens and the displacing piston causes a partial vacuum hence, drawing in a mixture of air and petrol through the inlet port into the cylinder.

2. Compression stroke.

At the bottom dead center (b.d.c), the inlet valve closes and sealing the cylinder, as the piston start to rise thus, compresses the mixture by the predetermined amount.

3. Power stroke.

When the piston is near the t.d.c position, with both valves being closed, the compressed gas is ignited by bridging the spark plug electrodes. This ignites the charge with causes a rise in temperature and subsequent rise in pressure. The piston is being force down the cylinder by burning expanding gas.

4. Exhaust stroke.

At b.d.c., the exhaust gas opens and as the piston rises, the exhaust gas escape through the open valve until at t.d.c. This valve closes and the piston once again commences a new induction stroke. The engine is being carried over its idle stroke by the energy stored in the flywheel (Warapetcharayut, 1994 and Phong, 1999)

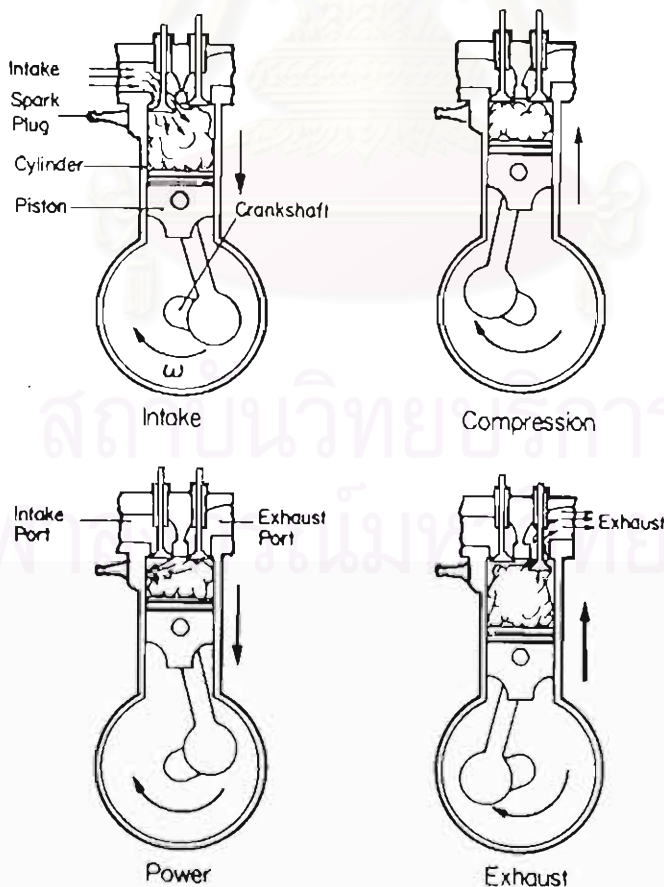


Figure 2.1 The 4 stroke cycle engine (Source : Ferguson, 1986)

2.2.2 Two stroke cycle engine

The principle of the 2 stroke cycle engine is illustrated in figure 2.2

Upward stroke, The piston rises near to top dead center (t.d.c) compresses gas in the combustion chamber. At the same time the inlet from carburetor will flow through the port and reed valve (thin plate, made of mix metal, one end is fixed and another end open only one pass) into the inlet port under the cylinder like the induction stroke combined with compression stroke of four-stroke.

Downward stroke, The sparking plug ignites the charge which cause a rise in temperature and consequential rise in pressure followed by downward movement of piston. During this stroke, the reed valve is sealed off and the confined rises to the top of the cylinder and pushed out most of the exhaust gases at the same time filling the cylinder with a new charge. This stroke is similar to the combined power stroke and exhaust stroke. It can be noted that the crankcase of two-stroke which should be intended for lubricant oil in four-stroke must become the keep inlet. Then, the lubricant of two-stroke becomes different from four-stroke (Warapetcharayut, 1994 and Phong, 1999)

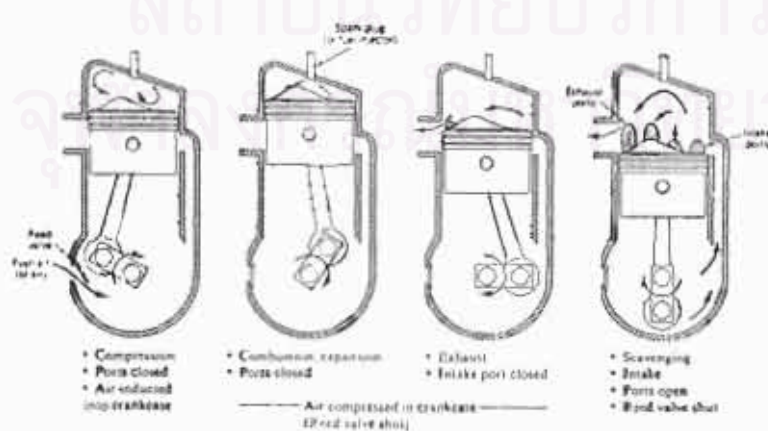


Figure 2.2 The 2 stroke cycle engine (Source Ferguson, 1986)

2.3. Comparison of Two and Four-Stroke Cycles

The two-stroke engine is simpler in construction than four-stroke, therefore cheaper to manufacture than the four-stroke design. Its lubrication system is more simple and able to develop a smoother torque. This is due to the fact that it has one power stroke per revolution whereas the four-stroke has one power-stroke for every two revolutions of the crankshaft thus the power stroke must carry the piston through the other three stroke. In the two-stroke cycle, however, the exhaust gases are not fully scavenged from the cylinders and these spent gas will not burn but occupy part of the combustion space. This leaves less space for the incoming charge and lowers the volumetric efficiency. The volumetric efficiency being the ratio of the weight of the induced charge and the theoretical charge is needed to completely fill the swept volume at atmospheric pressure and normal temperature. Also due to the method of scavenging, some of the new charges escape with the exhaust gases. The two-stroke engine which requires decarbonizing more frequently than the four-stroke has a tendency to overheat. A four-stroke engine gives a greater economy. It is more quiet in running, develops more power, runs better at lower revolutions per minute, and has a wider speed range than the two-stroke engine. By fitting a flywheel of specific size and weight to the crankshaft and arranging the cylinders to fire in a definite order, the torque fluctuations can be smoothed out (Dolan, cited in Phong, 1999).

2.4 Air pollutions from motorcycle

The air pollution emission from motorcycles can be divided into the following three sources:

- 1) Exhaust gases (CO, HC, NO_x, Pb and smoke).
- 2) Fuel evaporative gas (HC).
- 3) Blow-by gas.

Table 2.1 Rate of Air Pollution Generation (%) (Source: Phong 1999)

Sources	4-stroke			2-stroke		
	CO	HC	NO _x	CO	HC	NO _x
Exhaust gas	100	55	100	100	80	100
Fuel evaporative Gas	-	25	-	-	-	-
Blow-by gas	-	20	-	-	20	-

2.4.1 Exhaust Gases

Components of exhaust gas are CO, HC and NO_x. The generation ratio of which varies remarkably with the vehicle running conditions and the fuel used.

Carbon monoxide (CO)

1. The CO emission is generated from the combustion chamber due to the fact that the theoretical complete combustion is not available. The CO generation is effected by the air-fuel ratio (A/F).

2. The CO generation characteristics are the same for 4-stroke and 2-stroke engines (Japan automobile manufacturers association Inc., cited in Warapetcharayut, 1994).

Nitrogen oxides (NO₂)

1. Nitric oxide (NO) is formed by oxidation of nitrogen (N₂) in the atmosphere during high temperature combustion in the combustion chamber and its emitted outside. The emitted NO change to nitrogen dioxide (NO₂) in reaction with O₂ from the air.

2. The presence of oxides of nitrogen, NO_x (i.e. a mixture of NO₂ and NO), in town air is very largely from internal combustion engines. The major component of the oxides of nitrogen formed in the combustion zone is nitric oxide, NO. The quantities of the oxides of nitrogen formed are complicated function of temperature, pressure, time of action, and the quantity of the reactants present. When released into the atmosphere, nitric oxide oxidizes to nitrogen dioxide. But at concentration less than 50 ppm, this oxidation take place slowly so that NO_x present in the polluted air is mainly nitric oxide. In sunlight, especially in presence of organic material (hydrocarbons), this conversion is greatly accelerated (Impens, cited in Phong 1999).

3. The NO_x generation from 2 stroke engines, in contrary to HC emission is less than one fourth of that from 4 stroke engines when compared exhaust mass emission between 2 stroke, and 4 stroke engine in CEC mode test. The reason is report that the scavenging efficiency is poor for 2 stroke engines, and as a result, the intake mixtures are diluted with the remaining burnt gas

with makes the combustion hard (Thai motorcycle manufacturers group, cited in Warapetcharayut, 1994)

Hydrocarbon (HC)

1. Unburned fuel and decomposed fuel (HC) are discharged due to the blow-through of the intake mixture which is caused by the overlap of the intake and exhaust valves (especially great for small, high power engines), incomplete combustion chamber wall (quenching), and mis-firing caused by defective ignitor plug.

2. The unique mechanism of The two-stroke engines which used fresh mixtures to scavenge the burnt mixtures, emit hydrocarbons six to eight times large than those of the four-stroke engines. The generation mechanism is as follows :

As the fresh mixture are for scavenging, its result much burnt gases to remain in the cylinder and unstable combustion can be caused especially at idling and low load running.

Since scavenged by the fresh mixture gases as the road increases, the amount of the fresh mixture becomes larger which blows through. HC generation is higher at low and high load conditions and lower at medium load condition. However, even at medium load the HC generation is five to six time higher than that of 4-stroke engines (Japan automobile manufacturers association, Inc., cited in Phong 1999)

In theory, the suitable air-fuel ratio (A/F) which is the best economically fuel consumption is 14.6 and the highest engine power ratio is approximately 12.5

The A/F ratio has relative component of exhaust gases as follow:

1. The rich A/F ratio will cause less NO_x but lean air will cause incomplete combustion, so there is the increase CO, HC.
2. The lean A/F ratio (A/F to 16) will cause less CO, HC but increase in NO_x
3. The very lean of A/F ratio will cause less NO_x , and CO but increase HC.

If A/F ratio of less than 16 will cause bad driving from pounding engine etc., then it is not suitable in real driving. (Thai motorcycle manufacturers group, cited in Warapetcharayut, 1994)

2.4.2 Blow by gases

The burnt of gases which leaked from between the pistons of cylinder enter into the crankcase and is emitted into the air through the breather port (Japan automobile manufacturers association, Inc., cited in Phong 1999)

2.4.3 Evaporative gases

The evaporative gases are emitted into the air from a fuel system such as the breather of fuel tank or the carburetors. (Japan automobile manufacturers association, Inc., cited in Phong 1999)

2.5 Gasoline as Motorcycle fuel

2.5.1 Fuels

Stone (1985) defined the meaning of fuel as follow fuels are often mixtures of hydrocarbons, with bonds between carbon atoms, and between hydrogen and carbon atoms. During combustion these bonds are broken, and new bonds are formed with oxygen atoms, accompanied by a release of chemical energy. The principal products are carbon dioxide and water.

As combustion does not pass through a succession of equilibrium states it is irreversible, and the equilibrium position will be such that entropy is a maximum. The different compounds in fuels are classified according to the number of carbon atoms in the molecules. The size and geometry of the molecule have a profound effect on the chemical properties. Each carbon atom requires four bonds; these can be single bonds or combinations of single, double and triple bonds. Hydrogen atoms require a single bond.

An important family of compounds in petroleum (that is, petrol (gasoline) or diesel fuel) are the alkanes, formerly called the paraffins. Table 2.2 lists some of the alkanes; the different prefixes indicate the number of carbon atoms. The alkanes have a general formula C_nH_{2n+2} , where n is the number of carbon atoms. Inspection shows that all the carbon bonds are single bonds, so the alkanes are termed “saturated” For example, propane has the structural formula

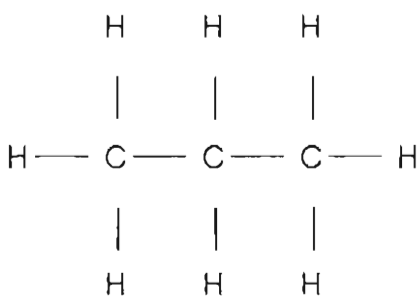


Table 2.2 Alkane family of compounds (Source : Stone, 1985)

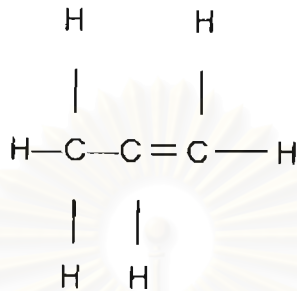


Formula	Name	Comments
CH ₄	methane	'Natural gas'
C ₂ H ₆	ethane	
C ₃ H ₈	propane	'Bottled gas'
C ₄ H ₁₀	butane	
C ₅ H ₁₂	pentane	Liquids at room temperature
C ₆ H ₁₄	hexane	
C ₇ H ₁₆	heptane	
C ₈ H ₁₈	octane	
·	·	
C ₁₆ H ₃₄	cetane	
·	·	
·	·	
etc.		

When four or more carbon atoms are in a chain molecule it is possible to form isomers. Isomers have the same chemical formula but different structures, which often leads to very different chemical, properties. Iso-octane is of particular significance for spark ignition engines; although it should be called 2,2,4-trimethyl-pentane, the isomer implied in petroleum technology is

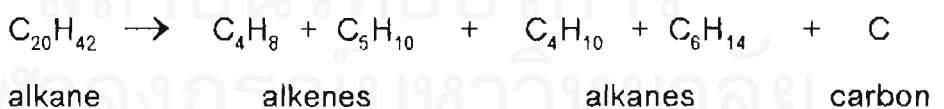


Compounds that have straight chains with a single double bond are termed alkenes (formerly defines); the general formula is C_nH_{2n} . An example is propylene, C_3H_6 :



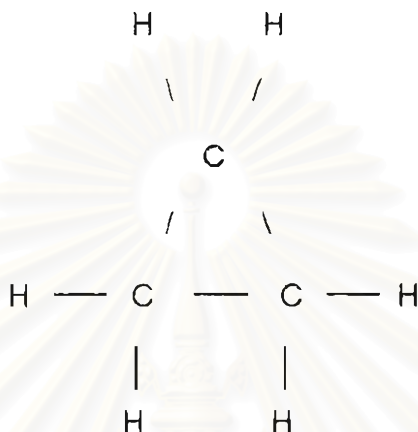
Such compounds are termed “unsaturated” as the double bond can be split and extra hydrogen atoms added, a process termed “hydrogenation”.

Most of the alkene content in fuels comes from catalytic cracking. In this process the less volatile alkanes are passed under pressure through catalysts such as silica or alumina at about 500°C . The large molecule are decomposed, or cracked, to form smaller more volatile molecules. A hypothetical example might be

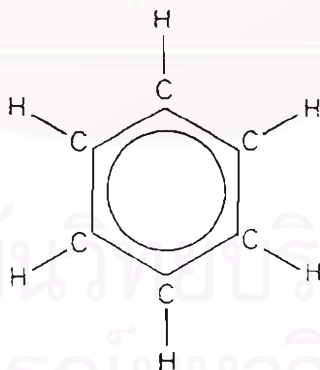


A disadvantage of alkenes is that they can oxidise when the fuel is stored in contact with air. The oxidation products reduce the quality of the fuel and leave gum deposits in the engine. Oxidation can be inhibited by the addition of alkyl phenol, typically 100 ppm (parts per million by weight).

Hydrocarbons can also form ring structures, which can be saturated or unsaturated. Cyclo-alkanes are saturated and have a general formula C_nH_{2n} in petroleum technology they are called naphthenes. An example is cyclopropane.



Aromatic compounds are unsaturated and based on the benzene molecule, C_6H_6 . This has an unsaturated ring best represented as



The inner circle signifies two groups of three electrons, which form molecular bonds each side of the carbon atom plane. The structure accounts for the distinct properties of the aromatic compounds. Benzene and its derivatives occur in many crude oils but in particular they come from the distillation of coal.

The final class of fuels that have significance for internal combustion engines are the alcohols, in particular methanol(CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$):



2.5.2 Characteristics of gasoline

The properties of gasoline (petrol) are discussed by Stone (1985) as follows : The two most important characteristics of petrol are its volatility and octane number (its resistance to self-ignition). Volatility is expressed in terms of the volume percentage that is distilled at or below fixed temperatures. If a petrol is too volatile, when it is used at high ambient temperatures the petrol is liable to vaporise in the fuel lines and form vapour locks. This problem is most pronounced in vehicles that are being restarted, since under these conditions the engine compartment is hottest. If the fuel is not sufficiently volatile the engine will be difficult to start, especially at low ambient temperatures.

The volatility also influences the cold start fuel economy. Spark ignition engines are started on very rich mixtures, and continue to operate on rich mixtures until they reach their normal operating temperature; this is to ensure adequate vaporisation of fuel. Increasing the volatility of the petrol at low temperatures will evidently improve the fuel economy during and after starting. Blackmore and Thomas cited in Stone (1985) point out that in the USA as

much as 50 per cent of all petrol is consumed on trips of 10 miles or less. Short journeys have a profound effect on vehicle fuel economy, yet fuel consumption figures are invariably quoted for steady state conditions.

Fuel volatility is specified in British Standard 4040: 1978, and these data are compared with typical fuel specifications from Blackmore and Thomas cited in Stone (1985) in table 2.3. This is plotted with further data in figure 2.3.

Table 2.3 Volatility of different petrol blends (source : Stone, 1985)

	BS4040		Less volatile	Volatile	North-west Europe		Central Africa
	Min.	Max.			Summer	Winter	
Distillate evaporated at 70°C (per cent V/V)	10	45	10	42	23	35	10
Distillate evaporated at 100°C (per cent V/V)	36	70	38	70	45	50	38
Distillate evaporated at 160°C (per cent V/V)			80	98	80	95	80
Distillate evaporated at 180°C (per cent V/V)	90						
Final boiling point °C	-	220					
Residue (per cent V/V)		2					
Symbol used in figure 2.3	⊗	⊙	-	-	⊠	⊡	-

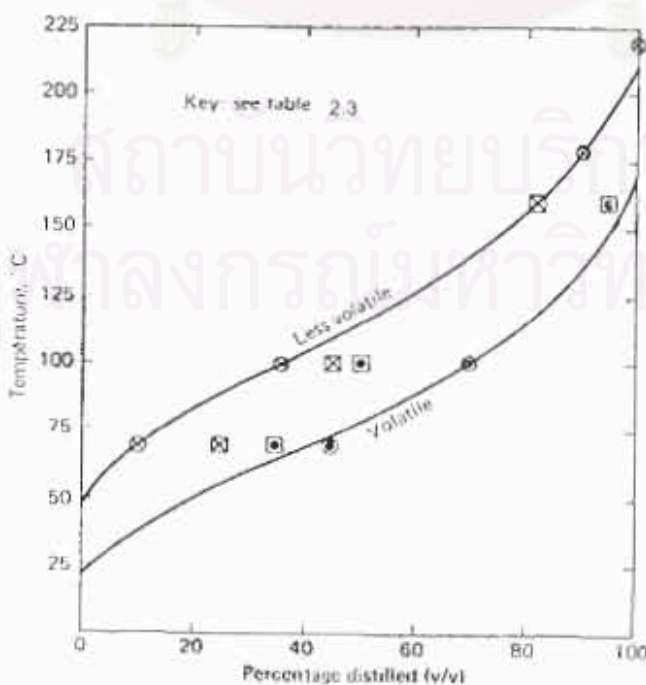


Figure 2.3 Distillation curves for petrol (Source : Stone, 1985)

Table 2.3 shows how the specification of petrol varies to suit climatic conditions. Petrol stored for a long time in vented tanks is said to go stale; this refers to the loss of the more volatile components that are necessary for easy engine starting.

The octane number of a fuel is a measure of its anti-knock performance. A scale of 0-100 is devised by assigning a value of 0 to n-heptane (a fuel prone to knock), and a value of 100 to iso-octane (a fuel resistant to knock). A 95 octane fuel has the performance equivalent to that of a mixture of 95 percent iso-octane and 5 percent n-heptane by volume. The octane requirement of an engine varies with compression ratio, geometrical and mechanical considerations, and also its operating conditions. There are two commonly used octane scales, research octane number (RON) and motor octane number (MON), covered by British Standards 2637: 1978 and 2638: 1978 respectively. Both standards refer to the Annual Book of ASTM (American Society for Testing and Materials) Standards Part 4 7 - Test Methods for Rating Motor, Diesel and Aviation fuels.

The tests for determining octane number are performed using the ASTM-CFR (Cooperative Fuel Research) engine; this is a variable compression ratio engine similar to the Ricardo E6 engine. In a test the compression ratio of the engine is varied to obtain standard knock intensity. With the same compression ratio two reference fuel blends are found whose knock intensities bracket that of the sample. The octane rating of the sample can then be found by interpolation. The different test conditions for RON and MON are quoted in ASTM Standards Part 47, and are summarised in table

Table 2.4 Summary of RON and MON test conditions (source : Stone, 1985)

Test conditions	Research octane number	Motor octane number
Engine speed, rpm	600 ± 6	900 ± 9
Crankcase oil, SAE grade	30	30
Oil pressure at operating temperature, psi	25-30	25-30
Crankcase oil temperature	135 ± 15°F (57 ± 8.5°C)	135 ± 15°F (57 ± 8.5°C)
Coolant temperature		
Range	212 ± 3°F (100 ± 1.5°C)	212 ± 3°F (100 ± 1.5°C)
Constant within	± 1°F (0.5°C)	± 1°F (0.5°C)
Intake air humidity, grains of water per lb. of dry air	25-50	25-50
Intake air temperature	See <i>ASTM Standard Part 47</i>	100 ± 5°F (38 ± 2.8°C)
Mixture temperature		300 ± 2°F (149 ± 1.1°C)
Spark advance, deg. btdc	13	14-26 depending on compression ratio
Spark plug gap, in.	0.020 ± 0.005	0.020 ± 0.005
Breaker point, gap, in.	0.020	0.020
Valve clearances, in.		
Intake	0.008	0.008
Exhaust	0.008	0.008
Fuel/air ratio	Adjusted for maximum knock	

Table 2.4 shows that the motor octane number has more severe test conditions since the mixture temperature is greater and the ignition occurs earlier. There is not necessarily any correlation between MON and RON as the way fuel components of different volatility contribute to the octane rating will vary. Furthermore, when a carburetted engine has a transient increase in load, excess fuel is supplied. Under these conditions it is the octane rating of the more volatile components that determines whether or not knock occurs. The minimum octane requirements for different grades of petrol are given by BS4040, see table 2.5.

Table 2.5 Octane number requirements for different fuel grades
(source : Stone, 1985)

Grade designation	RON	MON
5 star	100.0	86.0
4 star	97.0	86.0
3 star	94.0	82.0
2 star	90.0	80.0

The attraction of high octane fuels is that they enable high compression ratios to be used. Higher compression ratios give increased power output and improved economy. The octane number requirements for a given compression ratio vary widely, but typically a compression ratio of 7.5 requires 85 octane fuel, while a compression ratio of 10.0 would require 100 octane fuel. There are even wide variations in octane number requirements between supposedly identical engines.

Of the various fuel additives, those that increase octane numbers have greatest significance. In 1922 Midgely and Boyd discovered that lead-based compounds improved the octane rating of fuels. By adding 0.5 grams of lead per litre, the octane rating of the fuel is increased by about 5 units. The lead additives take the form of lead alkyls, either tetramethyl lead $(\text{CH}_3)_4\text{Pb}$, or tetraethyl lead $(\text{C}_2\text{H}_5)_4\text{Pb}$. (Stone, 1985). Present, most countries have restrictions on the use of lead in fuels for environmental reasons.

When gasoline lead content is either reduced or eliminated then, if octane quality is to be maintained, refineries have to resort to the increased use of certain components. Traditionally refineries have used aromatic components, which comprise mainly benzene, toluene, xylenes and ethyl benzene, from reforming processes to provide octane quality. These aromatic components or sometimes call volatile organic compounds (VOCs) are emitted in significant quantities from vehicles. Using of aromatics in unleaded gasoline is producing health and environmental dangers greater than that from lead itself when this fuel is used in cars not fitted with a catalyst. VOCs are precursors of photochemical smog and tropospheric ozone. Exposure to VOCs and other air toxics has been linked to adverse health effects. Specific VOCs, for instance, benzene may also lead to increases in diseases such as lung cancer and leukaemia. (Lertvisansak, 1996)

2.5.3 Gasoline in worldwide

Perry and Gee (1993) reported that the widespread introduction of unleaded and low lead fuels has naturally resulted in significant changes in fuel compositions as refineries attempt to maintain the octane quality of fuels. Different countries, due to variation in resources have different refinery capabilities which significantly affect their flexibility in approaching fuel reformulation.

The most common means to replace the octane numbers lost as lead is removed is to increase the severity of the reforming process, as this is common to almost all refineries and does not require significant additional investment. However, this leads to an increase in the level of aromatic compounds in the fuel. Alkylation, isomerisation and polymerisation processes

have been used in developed countries to overcome this. Australia for example has invested in isomerisation plants and as a result has limited rises in the aromatic content of unleaded fuels. In Western Europe despite the use of upgraded facilities at many refineries the main means to maintain the octane quality of unleaded fuels has been to increase the use of reformat. In developing countries in the Far East and South America, where resources are limited this is also the most practical means to achieve suitable octane numbers. As a result fuel aromatic levels in these countries have increased as lead is reduced. Aromatic levels of 40-50 % by volume are now common both in Europe and countries from the Far East and South America.

2.6 The aromatic hydrocarbons

Fawell and Hunt (1988) studied about the aromatic hydrocarbons and they explained that; the structure of several of the aromatic hydrocarbon reviewed are shown in Figure 2.4. These compound are used in industry in very large quantities.

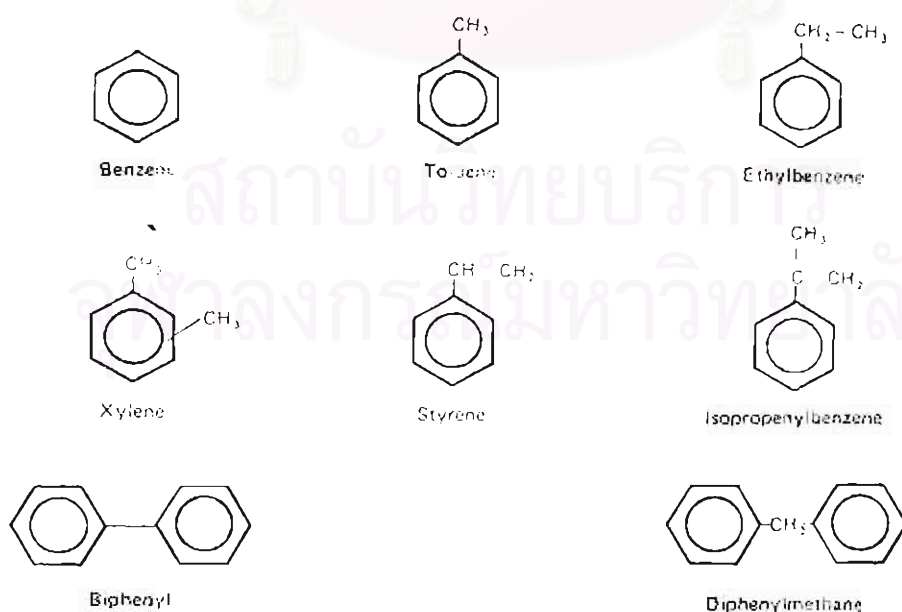


Figure 2.4 The structure of some of the aromatic hydrocarbons widely used in industry. (Source : Adapted from Fawell and Hunt, 1988)

The most important source of environmental exposure are air and food. Water is only a minor source, except where specific pollution incidents have occurred. In the WRC survey, benzene, toluene and xylene were the most frequently detected compound, occurring 13/14, 14/14, 14/14 samples respectively.

Toxicological information on the aromatic hydrocarbons varies markedly. Benzene, toluene, styrene and biphenyl are the most comprehensively studied, but there is relatively little or no information available on the other compounds.

Fawell and hunt (1988) reviewed many studies about Aromatic hydrocarbons that included Benzene, Toluene and Xylene. Their book, "Environmental toxicology : organic pollutants" explained both toxic of each substance and toxicity on human health as follow:

2.6.1 Benzene

2.6.1.1 Introduction

Benzene has been the most extensively studied of all the aromatic hydrocarbons, and the literature has been reviewed by several groups. Benzene is principally produced by fractional distillation of crude oil, catalytic dehydrogenation, and solvent extraction. Estimated annual world-wide production is over 15 million tonnes. Benzene is used as a solvent and a fuel additive, but primarily as a raw material in the manufacture of ethylbenzene, styrene, cyclohexane, nylon, dyes, pesticides, resins and detergents.

CASRegNo :	71-43-2
Molecular weight :	78.1
Boiling point :	80.1 °C
Solubility :	1780 mg/l at 20 °C
Evaporative half-life in water of depth 1 m :	4.81 hours at 25 °C
Threshold odour concentration in water :	2-31 mg/l

2.6.1.2 Exposure

1. Air

The major source of atmospheric benzene is vehicle exhausts . Most data suggest that average benzene levels are in the low ppb range, although much higher levels have been reported in the vicinity of benzene-associated industries and in the ambient air of petrol . An analysis of atmospheric benzene in the UK has reported higher levels than those found else-where. In a relatively rural area a level of 61 ppb was found, while near the M1 at Luton benzene was measured at 155 ppb.

2. Food

Benzene is found in many foodstuffs and beverages at significant levels, and the NCI have estimated that an individual could ingest as much as 250 µg/day of benzene from this source .

3. Water

Exposure data for water are rather limited, though both American and Canadian studies have suggested average drinking water concentrations in the nanogram per litre range . The US EPA study reported the highest level of benzene found in a finished water as 10 µg/l. The survey by the WRc identified benzene in 13 out of 14 treated water samples examined.

4. Relative exposure

In an assessment of the relative exposure of an individual to benzene by the US EPA, water was suggested to contribute 1.4%, food 17.7% and ambient air 80.9% to an overall daily intake of 1.1 mg of benzene. This calculation was based on perhaps a rather low ambient air benzene level of 1 ppb, a rather high water level of 10 $\mu\text{g/l}$ and an intake from food of 250 $\mu\text{g/day}$. The Canadians, however, have calculated an average yearly intake of 125 mg of benzene, of which 91 mg is derived from food, 33 mg from air, 0.007 mg from water and 1 mg from other sources. The more realistic assumptions included in this calculation are a drinking water concentration of 10 ng/l, an intake from food of 250 $\mu\text{g/day}$, and an ambient air level of 2.5 ppb, of which 50% is retained by the body. These estimates indicate that exposure to waterborne benzene at current levels is almost insignificant in comparison to exposure from other sources.

2.6.1.3 Toxicokinetics

1. Absorption

No information appears to be available with regard to the gastrointestinal absorption of benzene, though a value of around 40-50% has been reported in several studies for respiratory absorption in humans. Percutaneous absorption has been demonstrated to occur slowly in man and rhesus monkey.

2. Distribution

Autoradiographic and pharmacokinetic studies have shown that benzene has an affinity for nervous and adipose tissue, with high levels also found in the bone marrow, liver, spleen and blood.

3. Metabolism

Benzene is metabolised primarily in the liver to phenol, catechol, quinol and hydroxyquinol, and subsequently to conjugates of ester sulphates and glucuronides. In bone marrow, phenol appears to be the major metabolite shortly after exposure, though catechol and hydroquinone predominate subsequently . It is thought that secondary metabolites of the latter two compounds are probably responsible for the toxic effects of benzene in the bone marrow .

4. Excretion

The elimination of benzene by the lungs has been reported to be around 12% of the retained dose in humans but up to 70% in experimental animals. Excretion in the urine as free or conjugated phenols accounts for 50-87% of retained benzene in humans, but only 23% is eliminated in this way by rodents

2.6.2 Toluene

2.6.2.1 Introduction

Toluene (toluol, phenylmethane, methylbenzene, methacide) is a volatile and flammable aromatic hydrocarbon commercially produced by the petrochemicals industry. Most is converted to benzene but some is used directly in the manufacture of dyes, saccharin, perfumes, caprolactam, pharmaceuticals, detergents and TNT. It is also used as a gasoline additive and solvent.

CAS Reg No:	108-88-3
Molecular weight:	92.13
Boiling point:	110.6 °C
Solubility:	515 mg/l at 20 °C
Evaporative half life in water of depth 1 m:	5.18 hours at 25 °C
Threshold odour concentration in water:	1 mg/l

2.6.2.2 Exposure

1. Air

Atmospheric contamination by toluene has been linked with automobile exhaust emissions on several occasions . One study of Toronto air samples reported a correlation between traffic density and atmospheric toluene , while a British study found a rural toluene level of 29 ppb at Freshwater (LOW) and an urban toluene concentration of 72 ppb near the MI at Luton .

2. Food

Very little information is available with regard to the levels of toluene in foodstuffs, although it has been detected in fish .

3. Water

Toluene has been identified in several surveys of raw and treated water in the US at average concentrations of less than 1 µg/l. The highest level recorded was 11 µg/l in New Orleans finished water .Toluene was found to be present in all 14 drinking water samples in the WRc survey. Levels in surface waters were generally less than 1 µg/l, but up to 5 µg/l was found in some groundwaters .

2.6.2.3 Toxicokinetics

1. Absorption

The pulmonary retention of toluene, which is dependent on the atmospheric concentration, ventilation rate and body weight, was estimated, to be about 50% of the inhaled dose in volunteers after 5. Although gastrointestinal absorption is slower than respiratory absorption, it is likely that most of an oral dose of toluene would be retained. Toluene can be absorbed through the skin, but the process is far slower than through either the lungs or the gastrointestinal tract.

2. Distribution

Due to the high affinity of toluene for fat, its distribution is dependent primarily on the lipid content of individual tissues. Body fat provides a large reservoir for toluene, as illustrated in a mouse study in which tissue saturation was not reached after a 3-hour exposure to 4000 ppm of toluene vapour

3. Metabolism

The metabolism of toluene by the liver has been well characterised. Toluene is metabolised rapidly through its methyl side-chain, via benzyl alcohol and benzaldehyde, to benzoic acid. Benzoic acid is conjugated with glycine, and excreted in the urine as hippuric acid. Some conjugation of side-chain metabolites with glutathione has been reported in rats. There is also evidence that a small amount of ring oxidation can occur during toluene metabolism. Ortho-, meta- and para-cresols have been detected in the urine of workers exposed to toluene.

3.3.4 Excretion

The major mode of excretion for toluene is via the urine, largely as hippuric acid. However, variation of urinary hippuric acid concentrations due to dietary factors makes this parameter a poor index of exposure, especially at low levels. Some unchanged toluene can be eliminated in the expired air.

2.6.3 Xylene

2.6.3.1 Introduction

Xylene (dimethylbenzene) is produced by the chemical industry and from the distillation of petroleum, coal tar and coal gas. It is used as a solvent in resins, lacquers, enamels and rubber cements, in aviation fuel, and in the manufacture of polyester, pharmaceuticals, dyes, insecticides, asphalt and naphtha. The three isomeric forms of xylene (ortho-, meta- and para-) all possess similar physicochemical properties.

CAS Reg No (mixed):	1330-20-7
Molecular weight:	106.17
Boiling point:	138 °C
Solubility:	180 mg/l at 20 °C
Evaporative half-life in water of depth 1 m:	5.61 hours at 25 °C
Threshold odour concentration in water:	1-2 mg/l

2.6.3.2 Exposure

1. Air

Thorburn and Colenutt cited in Fawell and Hunt (1988) detected a xylene concentration of around 16 ppb in the rural atmosphere of Freshwater

(IOW) and a level of 49 ppb near the MI at Luton. Data by Holzer et al cited in Fawell and Hunt, 1988) also suggest higher levels of xylene in urban air compared to rural air in the US.

2. Food

No data appear to be available with regard to the presence of xylene in food.

3. Water

The xylenes were identified in all 14 treated water samples of the WRc survey (Water Research Centre 1981 cited in Fawell and Hunt, 1988). A Japanese study detected xylene in both filtered river water and in tap water . The US EPA have reported a xylene concentration of 4.1 μ g/l in the treated water supply to New Orleans .

2.6.3.3 Toxicokinetics

1. Absorption

In man, about 60% of inhaled xylene is retained by the lungs. Percutaneous absorption also occurs . Although there are no data on gastrointestinal absorption, xylene would be expected to be readily absorbed in view of its lipophilic nature.

2. Distribution

The distribution of xylene in the body is dependent on the fat content of individual tissues. The highest levels of xylene are found in lipid-rich tissues such as the adipose tissue, subcutaneous fat, adrenal glands, brain and liver.

3. Metabolism

The metabolic pathways differ for each xylene isomer. The meta- and para-isomers are 80-90% metabolised to the corresponding toluic acids and glycine conjugates. Only 60% of ortho-xylene is transformed to ortho-toluic acid, and of this roughly half remains free, about half is conjugated with glucuronide, and only 0.3% is conjugated with glycine. Aromatic ring oxidation to hydroxyxylenes (xylenols) has also been reported for each isomer, but this appears to be only a very minor route. Methylbenzylmercapturic acids have also been identified as metabolites of xylenes, though only transformation of ortho-xylene in this manner appears to be of any quantitative significance.

4. Excretion

Xylene is excreted in the urine as methylhippuric acids, free toluic acids, toluoglucuronic acids, dimethylphenols and methylbenzylmercapturic acids. A small amount of unchanged xylene can be exhaled from the lungs.

2.7 Health effects of VOCs on human health

Volatile organic compounds or VOCs, a wide range of hydrocarbon compounds with boiling point between approximately 50 °C and 250 °C and which at the room temperature, produce vapours (Harrison, 1997). Many of VOCs play an important role in atmospheric chemistry. This is especially true for substituted aromatic VOCs such as benzene, toluene and xylene which have a high risk potential effect on environment and human health. Only short exposure to high level of some VOCs can cause temporary dizziness; lengthy or repeated exposure can irritate the eyes and lungs and may effect the

nervous system. Some VOCs, such as benzene, are cancer causing agents. Many of researches studied about the toxic effect of these VOCs on human. One of the popular books that collected a lot of data about the toxicology of VOCs on environment and human health is “Environmental toxicology : Organic pollutants” by J.K Fawell and S.Hunt (1988). They investigated many incidents of harmful effect of VOCs on human and they collected many information from many studied of this in their book as follow ;

2.7.1 Benzene

2.7.1.1 Acute and subacute toxicity

Severe human exposure to benzene can cause convulsions, coma, paralysis and death from respiratory or cardiac failure. At sublethal doses, CNS excitation followed by depression, giddiness, headaches, nausea and unconsciousness is often found. Pathological effects include petechial haemorrhages of several tissues, cerebral edema, hypo- and hyperplasia of the bone marrow, and congestion of the kidney.

2.7.1.2 Chronic toxicity

The most commonly observed effects of chronic benzene toxicity in experimental studies are associated with the depression of bone marrow function, and normally take the form of pancytopenia, a reduction in the numbers of many kinds of blood cells. Much recent work has been involved in the study of these effects and the ultimate reactive species responsible.

2.7.1.3 Genotoxicity

Although there is strong evidence for benzene-related genetic damage in mammalian systems, mutagenicity of benzene has yet to be demonstrated in bacterial assays.

Lyon cited in Fawell and Hunt (1988) reported negative findings for benzene mutagenicity in a host mediated assay and in bacterial plate assays with *Salmonella typhimurium* TA98 and TA100, but found chromosomal aberrations in bone marrow cells of rats given 0.5 ml/kg of benzene by intraperitoneal injection. This compound has given positive results in one forward gene mutation assay: resistance to 6-thioguanine at the HGPRT locus in a metabolically competent human lymphoblastoid cell line .

2.7.1.4 Carcinogenicity

With the exception of leukaemias, the only other tumors which have been associated with exposure to benzene are zymbal gland carcinomas and mammary carcinomas reported in a single study by Maltoni and Scarnato cited in Fawell and Hunt (1988). In this study, Sprague-Dawley rats dosed orally with 250 mg/kg of benzene for 52 weeks developed 4/33 leukaemias in males, 8/32 zymbal gland carcinomas and 7/32 mammary carcinomas in females. Control values were 3/30 mammary carcinomas, 1/30 leukaemias and 0/30 zymbal gland carcinomas in females, and 0/30 for both leukaemias and zymbal gland carcinomas in males. It was also noted that the latency period for mammary tumors was reduced from 110 weeks to 88 weeks.

Gavage cited in Fawell and Hunt (1988) studies of benzene in corn oil at doses of 0-200 mg/kg in male rats and 0-100 mg/kg in female rats and male and female mice gave rise to an increase in tumors at multiple sites.

2.7.1.5 Reproductive toxicity

Transplacental transfer of benzene is a poorly studied subject, though one report has found similar levels of benzene in both maternal and cord-blood under low-level exposure conditions.

Some evidence for teratogenicity has been reported in CF-1 mice given 3 ml/kg of benzene by subcutaneous injection on the thirteenth day of gestation. This study is difficult to interpret, however, due to the absence of control data. No teratogenic effects were seen in the susceptible chick embryo system.

In general, the evidence would not indicate a teratogenic potential for benzene. Retardation of foetal development, the most common reproductive effect, is characterized by decreased foetal weight and ossification. This effect appears to occur only at doses which also cause a decrease in maternal weight gain. The retardation foetal development may therefore be due to the toxicity of benzene in the mother.

2.7.2 Toluene

There are several comprehensive reviews of the health effects of toluene. Much of the information has arisen from occupational exposure and from the abuse of solvents and glues which contain toluene.

2.7.2.1 Acute and subacute toxicity

Acute exposure to toluene results in CNS depression and membrane irritation, though sudden deaths due to cardiac arrhythmias have been reported in some cases of toluene abuse. There is little evidence to indicate that toluene is acutely toxic to any organ system other than the CNS even at very high doses. The oral LD50 for rats is about 7.0 g/kg. Two subacute studies in rats have noted slight increases in hepatic cytochrome P-450 levels (Elovaara et al 1979, Chand and Clausen 1982 cited in Fawell and Hunt, 1988).

2.7.2.2 Chronic toxicity

Studies in experimental animals have on the whole failed to show significant organ damage, even after exposure to very high doses of toluene. Rodents exposed to 12 000 ppm of toluene vapour in 3-hour cycles, 5 times/week for 8 weeks, exhibited inebriation but no lung, liver or kidney damage. In another inhalation study where rats, guinea pigs, monkeys and dogs were exposed continuously (107 ppm for 90-127 days) or intermittently (1085 ppm, 8 hours/day, 5 days/week for 6 weeks) to toluene, no changes in body weight gain, haematological parameters or the morphology of several organ systems were reported in any species. Both male and female rats exposed to 30, 100, 300, or 1000 ppm of toluene for 13 weeks also failed to show any significant effects, even at the highest dose level. No changes in clinical chemistry, urinalysis, haematology, histopathology or ophthalmology were found in groups of 120 male and 120 female F-344 rats exposed by inhalation to 0, 30, 100 or 300 ppm, 6 hours/day, 5 days/week for up to 2 years. This very low toxicity of toluene has also been found in other studies (Wolf et al 1956, Carpenter et al 1976 cited in Fawell and Hunt, 1988). Toxic effects,

similar to those found with benzene, reported in early experiments on toluene are likely to be attributable to benzene contamination rather than to the toxicity of toluene itself .

Apart from several studies where visual signs of nervous distress were evident following exposure to high doses, relatively few studies have been carried out to assess the effects of toluene on the nervous system of experimental animals . However, changes in EEG patterns have been reported in rats and cats. Several studies of occupationally exposed subjects have suggested health effects of toluene, most of which are associated with the nervous system.

2.7.2.3 Genotoxicity

Toluene has given negative results in the Ames test with *Salmonella typhimurium* TA100, TA1535, TA1537, TA1538 and TA98, both in the presence and absence of rat liver S-9 or hamster liver S-9, at doses ranging from 10 to 2000 $\mu\text{g}/\text{plate}$.

Bos et al cited in Fawell and Hunt (1988) reported that toluene was negative for unscheduled DNA synthesis in primary rat hepatocytes, but no experimental details were given. In vivo clastogenic effects of toluene have been documented in the bone marrow of rats injected with 1 g/kg daily for 12 days and in another study where rats were exposed by inhalation to 112 ppm, 4 hours daily, for 4 months. In the latter study it was estimated that 0.8 g/kg/day of toluene induced the same frequency of chromosomal damage as 0.2 g/kg/day of benzene. Donner et al cited in Fawell and Hunt (1988) were unable to show an increased incidence of chromosomal aberrations in the

bone marrow cells of Wistar rats exposed to 300 ppm, for 6 hours/day, 5 days/week, for 15 weeks. However, there was a significant increase in sister chromatid exchanges at 11 and 13 weeks, but not at 15 weeks. Toluene was not found to induce recessive lethal mutations in *Drosophila melanogaster*. Chromosomal studies of toluene-exposed workers have also produced equivocal results for clastogenic activity. Forni et al cited in Fawell and Hunt (1988) did not detect a significant increase in lymphocyte chromosomal aberrations in workers exposed to the compound for up to 15 years.

2.7.2.4 Carcinogenicity

In an inhalation study, groups of 120 male and 120 female F-344 rats were exposed to 0,30,100 or 300 ppm of toluene for 6 hours/day, 5 days/week for up to 2 years. No significant increase in tumour incidence was found. Two skin painting studies in mice, one for lifetime and the other for one year, also found no evidence of carcinogenicity. Lijinsky and Garcia cited in Fawell and Hunt (1988) did report one skin papilloma and one skin carcinoma in a group of 30 mice receiving topically applied toluene (16-20 μ l) twice weekly for 72 weeks. Toluene has not been tested for carcinogenicity by the oral route.

2.7.2.5 Reproductive toxicity

Nawrot and Staples cited in Fawell and Hunt (1988) have provided some evidence for the teratogenicity of toluene. CD-1 mice were given 0.3,0.5 or 1.0 ml/kg body weight of toluene by gavage on days 6-15 of gestation. Increased embryonic mortality was apparent at all doses, decreased foetal weight was noted at 0.5 and 1.0 ml/kg, and a significantly increased incidence of cleft palate was found at the highest dose. There was no evidence for

maternal toxicity at any dose level. Embryotoxicity was observed in mice exposed by inhalation to 133 ppm on days 6-13 of gestation, and in rats exposed to 399 ppm, 8 hours/day on days 1-21 of gestation. Mice were exposed to 0, 200 or 400 ppm toluene by inhalation on days 6-16 of gestation. There was a significant shift in the foetal rib profile at 400 ppm and an increase in dilated renal pelvis at 200 ppm. At 400 ppm neonatal weight was significantly increased at day 1 post partum .

2.7.3 Xylene

Although the toxicology of Xylene has not been comprehensively reviewed, there are several sources available which provide useful information.

2.7.3.1 Acute and subacute toxicity

Acute exposure to very high doses of xylene can cause erythema, dehydration, defatting and blistering of the skin, irritation of mucous membranes, peripheral vasodilation, giddiness, fatigue, 'drunkenness', narcosis and unconsciousness. Studies on experimental animals have shown that xylene has a relatively low order of acute toxic potential. Mixed xylenes have an oral LD50 in the rat of 4.3 g/kg and an inhalation LC50 in the rat of 6700 ppm, while para-xylene has an inhalation LC50 in the same species of 4740 ppm .

The most common effects of acute exposure to lower levels of xylene are CNS related. Gamberale et al cited in Fawell and Hunt(1988)exposed 8 healthy men to 1300 mg/m³ of xylene in inspired air for 70 minutes, 30 minutes

of which was spent on a bicycle ergometer (100 W). The authors reported clear evidence of performance decrement in three out of a battery of behavioural tests. Changes in dopamine and noradrenaline levels in selected areas of the brain have been found in rats exposed by inhalation to 2000 ppm of xylene, 6 hours/day for 3 days.

2.7.3.2 Chronic toxicity

Despite previous indications that xylene may possess the haematotoxic properties of benzene, the evidence from more recent studies would not support this. It is likely that contamination of xylene samples by benzene may have been responsible for the effects seen in earlier studies.

No significant changes in blood parameters were found in rats and rabbits exposed by inhalation to 690 ppm of mixed xylenes, 8 hours/day, 6 days/week for 130 days. Exposure of rabbits to 1150 ppm for 55 days in the same study was found to result in lowered numbers of erythrocytes and leukocytes, and an increase in platelet numbers. A long-term inhalation study of ortho-xylene in several species failed to show significant changes in body weight or haematological parameters after continuous exposure to 78 ppm of xylene vapor for 90 days, or after 30 repeated exposures to 780 ppm of xylene. Similarly, no myelotoxic effects were observed in rabbits given 300 mg/kg/day of xylene by subcutaneous injection for 6 weeks or 700 mg/kg/day of xylene for 9 weeks.

Enhanced activities of hepatic microsomal 7-ethoxycoumarin O-deethylase, 2,5-diphenyloxazole hydroxylase and UDP-lucuronyltransferase have been reported in rats exposed by inhalation to 300 ppm of technical

grade xylene, 6 hours/day, 5 days/week for 18 weeks. Histological examination did not reveal liver damage (Elovaara et al 1980 cited in Fawell and Hunt,1988).

2.7.3.3 Genotoxicity

All three isomers of xylene have given negative results for mutagenicity in the Ames test with *Salmonella typhimurium* TA98, TA100, TA1535, TA1537 and TA1538, both in the presence and absence of either rat liver or hamster liver S-9, and at doses ranging from 1.0 to 500 $\mu\text{g}/\text{plate}$ (Bos et al 1981, Haworth et al 1983 cited in Fawell and Hunt,1988).

Xylenes have been shown not to be mutagenic in the salmonella/microsome assay, bacterial DNA repair, not cause chromosome aberrations or sister chromatid exchanges in mammalian cells in vitro. Equivocal results were obtained in *Drosophila* germ cells but they did not cause chromosome aberrations in rat bone marrow in vivo. Dose levels of 0.0152-1.52 mg/ml of xylene were not found to increase chromosome aberrations or sister chromatid exchanges in human lymphocytes in vitro. Although no experimental data were given, Bos et al cited in Fawell and Hunt (1988) reported that ortho-, meta- and para-xylene had given negative results for unscheduled DNA synthesis in primary cultures of rat hepatocytes. Mohtashamipur et al cited in Fawell and Hunt.(1988) report that ortho, meta- and para-xylenes did not induce micronuclei in the bone marrow polychromatic erythrocytes of mice.

2.7.3.4 Carcinogenicity

Although no evidence for carcinogenicity was found in two 6-month skin painting experiments in mice, these studies were of insufficient duration, and therefore only very limited conclusions can be drawn. Long-term studies of mixed xylenes (60% meta, 14% para and 9% ortho- and 17% ethylbenzene) given by gavage at doses of 250 or 500 mg/kg to rats and 500 or 1000 mg/kg to mice, indicated no evidence of carcinogenicity (US National Toxicology Program 1986/1991 cited in Fawell and Hunt, 1988).

2.7.3.5 Reproductive toxicity

Xylene has been found at higher concentrations in cord blood than in maternal blood. Two studies in mice have reported teratogenic effects of xylene. Nawrot and Staples cited in Fawell and Hunt (1988) dosed CD-1 mice by gavage with 0.3, 0.75 or 1.0 ml/kg/day of pure ortho; meta-, or para-xylene on days 6-15 of gestation. Increased incidences of cleft palate and foetal resorptions were found at the two higher dose levels with the ortho- and para-isomers.

2.8 Review of the emission research

2.8.1 Emission from vehicles in Thailand research

Warapetcharayut (1994) studied the exhaust gas emissions from 2 – stroke motorcycles (over 125 CC.) using different lubricating oil and found that; 15 two - stroke motorcycle from 4 trade names; YAMAHA, KAWASAKI, SUZUKI and HONDA were tested in his research. Both new and old motorcycles having a cylinder capacity size of more than 125 CC. were tested.

This study is an attempt to compare the pollutants level of exhaust gases by using 2 different types of lubricating oil. Five major primary pollutants were considered : CO, HC, NO_x, Pb and white smoke. In this research, the percent of reduction of average exhaust gas concentration at idle conditions from low to high in terms of exhaust gases are NO_x, HC, CO ; in term of trade names are YAMAHA, HONDA, SUZUKI and KAWASAKI when compared both using regular lubricating oil (No Poly isobutylene – PIB) and low smoke lubricating oil (with PIB). The percent reduction of average emission load on chassis dynamometer from low to high are CO, NO_x, and HC when compared both using the regular lubricating oil (No Poly isobutylene – PIB) and the low smoke lubrication oil (with PIB). The white smoke was significantly decreased from average 30.2% to 9.6% or 68.21% reduction when changed from using the regular lubricating oil (No Poly isobutylene – PIB) to low smoke lubrication oil (with PIB). The result from this study are shown in table below :

Brand name	Pollutants	Without PIB	With PIB	% Reduction
YAMAHA	CO (%)	3.74	3.77	-0.8
	HC (ppm)	13116	12050	8.13
	NO _x (ppm)	1.06	0.75	29.25
KAWASAKI	CO (%)	3.63	3.25	10.47
	HC (ppm)	10525	9033	14.17
	NO _x (ppm)	1.29	0.64	50.39
SUZUKI	CO (%)	3.51	3.38	3.70
	HC (ppm)	12276	9987	18.64
	NO _x (ppm)	1.19	0.74	37.82
HONDA	CO (%)	3.51	3.51	0.00
	HC (ppm)	10155	8537	15.93
	NO _x (ppm)	0.92	0.62	32.61

Apinpath (1994) studied the exhaust gas emissions from 2 – stroke motorcycles (of less than 125 CC.) using different lubricating oil. And found that ; The exhaust emission of motorcycles was studied to determine the correlation between the emissions, CO, HC, NO_x, and white smoke, and the types of lubricating oil, regular and low smoke oil.

The motorcycles are selected randomly from the motorcycle taxis of which their cylindrical capacity is less than or equal to 125 cc. The engine and oil tank were cleaned before adding the test autolube oil. The emissions were measured at every 1,000 km of distance driven up to 5,000 km using both the regular and the low smoke oils. By the action of PIB containing in the low smoke oil, visible smoke was reduced to 51.8% in the new motorcycle and 71.8% in old motorcycle. There is no difference on pollutants emission when using the low smoke and the regular oil. Similar results were obtained from emission loading measurement in which the test motorcycles were driven on a chassis dynamometer according to the standard driving pattern.

In addition, CO emission is not depended on the period of service of motorcycle. The relation is unclear on HC emission and period of service of motorcycle. Moreover, there is a possibility that low smoke oil will reduce NO_x emission in some model of motorcycles.

Suksomsankh (1990) investigated the exhaust gas from gasoline engines which registered in Bangkok. The vehicle sample in this study including passenger cars, 2 and 4 stroke motorcycles, taxis and 2 stroke tricycles. Gas sample were collected directly from the exhaust pipes of motor vehicles at 5 different speeds : idling speed which usually found in traffic jam

condition, 10, 18, 28 kms / hour which were averaged travelling speed in Bangkok, and 60 kms / hour which was a city limit of Bangkok.

Concentration of CO, NO_x, Total hydrocarbons and composition of hydrocarbons in gas samples were analyzed. Results from this study showed that the highest concentrations of CO and HC were found in gas samples from 2 and 4 stroke motorcycles. The highest levels of oxides of nitrogen were emitted from passenger cars taxis.

Concentration of HC components in gas samples from 2-stroke engine motorcycles were higher than those from 4-stroke motorcycles. Benzene, Toluene, and Xylene, which are strongly toxic to human health, were major aromatic hydrocarbons found in gas samples from both 2 and 4 stroke engine motorcycles. The results of amount of Benzene, Toluene and Xylene from exhaust gas samples at idle condition are shown on the following table :

Type of vehicles	Type of pollutant and concentration (ppm)							
	Benzene		Toluene		Meta and Para Xylene		Ortho Xylene	
	Mean	range	Mean	range	Mean	range	Mean	range
Passenger cars	53.44	10.29-240.63	175.35	17.06-1359.11	467.91	14.22-2153.58	41.43	4.03-262.09
2-Stroke motorcycles	355.51	93.62-767.89	866.11	225.23-1722.26	621.05	170.21-1399.20	221.82	49.37-428.64
4-Stroke motorcycles	145.48	7.07-777.37	468.80	25.15-2673.43	371.21	25.45-2050.34	117.37	9.35-644.99

Muttamara and Leong (2000) studied on monitoring and assessment of exhaust emission in Bangkok street air. Measurement of the exhaust emission from gasoline-powered motor vehicles in Bangkok were performed on chassis dynamometer.

A fleet of 10 vehicles of different model years and manufacturers were selected to measure the air pollutants in the exhaust effluent. The study revealed that carbon monoxide and hydrocarbon emissions averaged 32.3-64.2 and 1.82-2.98 g/km, respectively, for 1990-1992 cars and decreased to 17.8-40.71 and 0.75-1.88 g/km, respectively, for 1994-1995 cars.

A monitoring program for air pollutant concentrations in ambient air was also conducted to evaluate the air pollution problems in Bangkok arising from vehicle exhaust emission. Four air sampling stations were strategically established to cover the Bangkok Metropolitan Region (BMR). Composite air samples in this study area were collected during the day/night times and weekday/weekend.

The average concentrations of suspended particulate matter, carbomonoxide, and nitrogen dioxide in Bangkok street air were found to be 0.65 mg/m³ (24 hours average), 19.02 mg/m³ (8 hours average) and 0.021 mg/m³ (1 hour average), respectively.

The average concentrations of Benzene and Toluene in ambient air of the study area were found to be 15.07-50.20 and 25.76-130.95 µg/m³, respectively, for 8 hour average. These result indicated that there was a significant increase in air pollutant emission with increasing car mileage and

model year. Subsequent analysis of data showed that there were only 20 % of test vehicles complied to approved emission standard. The finding also revealed that there was a correlation between the average air pollutant concentrations with average traffic speed in each traffic zone of Bangkok metropolitan region (BMR).

Lertvisansak (1996) study on the benzene concentration in vehicle emission using unleaded gasoline and found that benzene in exhaust gas was measured from 12 used cars.

The exhaust gas from car was studied to determine the correlation between benzene concentration versus mileage, and model year. The charcoal tubes were used to collect the sample of exhaust gas. Samples were collected from the car under two conditions, one was collected on chassis dynamometer and the other was collected at idle mode.

There was a modest increase in benzene emission with older model year but there was not found the correlation with the mileage. The maximum benzene emission was found to be 28.68 mg/m^3 from Toyota model year 1990. The lowest level of benzene emission was found in 3 new cars (1 Toyota and 2 Nissan) with installation of catalytic converter. The average benzene concentration of exhaust gas from Toyota, Nissan and Mitsubishi are 0-17.4 , 0-22.02 and 0.76-18.26 mg/m^3 respectively. The concentrations of benzene from old model car (1990-1992) were 4.4-22.02 mg/m^3 while the same for new model car were 0-4.14 mg/m^3 . The results of benzene emission when the car was performed on chassis dynamometer were calculated from total

hydrocarbon (THC) and benzene concentration was estimated to be 3 % of THC.

The result of his study is shown on the following table :

Trade name	Model year	Capacity	Benzene (mg/m ³)	Toluene (mg/m ³)
Toyota	1995	1600	1.81	2.34
	1995	1600	1.32	3.28
	1990	1600	17.44	27.87
	1991	1600	7.64	11.5
	1995	2200	ND	ND
	1990	2000	4.4	12.24
Nissan	1995	1500	ND	ND
	1995	1500	ND	ND
	1990	1600	22.02	31.19
Mitsubishi	1994	1500	4.14	6.26
	1995	1500	0.76	0.89
	1992	1500	18.26	44.75

Phong (1999) studied on the air pollutant levels associated with traffic volume : a case study of motorcycles in Bangkok. This study focused on exhaust gas emission from two-stroke and four-stroke motorcycle engines. Ambient air quality and traffic volume of vehicle in Bangkok was also examined. Testing exhaust gas emission under idle conditions shows that concentration emission from two-stroke is higher than four-strokes. Carbon

monoxide (CO) emission is relatively low in both two and four-stroke engine. Hydrocarbon (HC) emission from two-stroke engines is higher than standard.

Driving cycle test shows that exhaust gas emission from two and four-stroke engine is higher than standard, while HC emitted from four-stroke is lower. The study also shows that benzene in ambient air exceeded the WHO guidelines. The main air pollution problem in Bangkok is suspended particulate matter (SPM) and particulate matter (PM-10). Particulate concentration in Bangkok streets is relatively high and reaches alarming levels due to the poor engine tuning and maintenance, and engine overloading. Carbon monoxide (CO) during the daytime varies from peak to non-peak hours and vehicle emission contributes to the concentration of CO in ambient air. The number of motorcycles takes into account of 25-30 percent of total number of vehicles. Finally, air pollution in Bangkok has reached alarming level, requiring immediate measure to reduce and minimize impact on human health and the environment.

Sirroughudomporn (1997) investigated the benzene and toluene emission from vehicles in Bangkok ambient air. A monitoring program for benzene and toluene concentrations in ambient air in this study was conducted to evaluate the air pollution problems in Bangkok city arising from vehicle exhaust emission. Four air sampling stations were strategically established to cover the Bangkok Metropolitan Area. The ambient air samples were earned out to determine the correlation of different traffic configurations between peak hour and non peak hour, weekday and weekend, finally between day-time and night-time.

The minimum and maximum concentrations of benzene and toluene in ambient air of the study areas were in the range of 12.34-35.82 ($\mu\text{g}/\text{m}^3$) and 17.43-93.55 ($\mu\text{g}/\text{m}^3$) for 8-hour average, respectively.

The highest benzene and toluene concentrations were found at Yaowaraj sampling station while the lowest benzene and toluene concentrations were found at Land Development Division sampling station. From the results, it should be noted that benzene and toluene concentrations for peak hour were unexpected to be lower than non peak hour. On the other hand, benzene and toluene concentrations for weekday and day-time were considerably higher than weekend and night time respectively.

The finding also shown that there was a correlation between the average benzene and toluene concentrations with average traffic speed in each traffic zones. In general, the benzene concentrations were exceeded WHO guidelines while the toluene concentrations were well below this guidelines, in respect to all the traffic zones in Bangkok.

2.8.2 Emission from vehicles in other countries research

Duffy et.al (1998) studied the emissions of Benzene, Toluene, Xylene and 1,3-Butadiene from a representative portion of the Australian car fleet. In this study, the exhaust emissions of the air toxics benzene, toluene, total xylenes and 1,3-butadiene have been measured in the cold transient (CT), cold stabilised (CS) and hot transient (HT) phases of the Australian Design Rule (ADR) 37/00 Drive cycle for 19 pre-1986 non-catalyst-equipped vehicles fuelled with leaded petrol, and 56 post-1985 catalyst-equipped vehicles

fuelled with unleaded petrol. The details of the car samples are shown in table 2.6.

Table 2.6 Distribution by age and manufacture of the 75 vehicles tested for exhaust emissions of benzene, toluene, xylene and 1,3-butadiene using the ADR 37/00 drive cycle (Source: Duffy et. al, 1998)

Year of manufacture	Manufacture					Total by year	No. with oxidative catalysts	No. with 3-way catalysts	Avg. odometer reading
	Ford	Holden	Toyota	Mitsubishi	Nissan				
Pre-1986, non-catalyst-equipped, fuelled with leaded petrol									
1980	1	2	—	1	—	4	—	—	192,852
1981	3	1	2	—	—	6	—	—	157,640
1982	1	—	2	—	1	4	—	—	125,843
1983	1	1	—	—	—	2	—	—	195,413
1984	2	—	—	—	—	2	—	—	196,700
1985	—	—	1	—	—	1	—	—	127,046
Total	8	4	5	1	1	19			
Post-1986, catalyst-equipped, fuelled with unleaded petrol									
1986	3	—	2	1	1	7	4	3	134,049
1987	3	3	—	3	—	9	4	5	123,062
1988	2	—	1	2	1	6	3	3	85,385
1989	3	—	1	4	—	8	5	3	73,428
1990	4	2	2	—	1	9	4	5	86,387
1991	3	5	5	—	4	17	3	14	58,562
Total	18	10	11	10	7	56			

Per vehicle exhaust emissions, averaged over the 3 phases of the ADR 37/00 test, of 1,3-butadiene, benzene, toluene, and total xylenes for the older vehicles were about 19, 139, 240 and 164 mg/km respectively. The corresponding emissions for the better 46 of the 56 post-1985 vehicles tested were 1.7, 28.1, 36.4, and 27.0 mg/km respectively (table 2.7 and 2.8).

Table 2.7 Per vehicle exhaust emission (mg/km) of benzene, toluene, xylene and 1,3-butadiene calculates as aweighted average over the three phases of the ADR 37/00 Drive cycle for 19 pre-1986, nc-lp and 56 post-1985, ce-ulp motor vehicles (Source: Duffy et. al ,1998)

Vehicle group		Benzene Avg. ADR	Toluene Avg. ADR	Xylenes Avg. ADR	1,3-butadiene Avg. ADR
19 Pre-1986, nc-lp	Max	234.3	425.0	292.9	40.3
	Min	59.9	92.0	64.3	5.0
	Ratio Max to Min	3.9	4.6	4.6	8.1
	Average	139.1	240.5	164.0	18.7
	Std	52.3	94.2	60.4	9.9
56 Post-1986, ce-ulp	Max	146.4	281.5	238.5	24.6
	Min	8.8	11.8	8.4	0.4
	Ratio Max to Min	16.6	23.9	28.4	61.5
	Average (all 56)	41.8	61.9	46.5	3.6
	Std	34.7	65.7	50.4	5.2
	Average (better 46)	28.1	36.4	27.0	1.7
	Std	13.5	17.4	13.5	1.2
	Average (worst 10)	104.8	179.5	136.3	12.0
	Std	32.5	78.4	61.1	7.3
	Post-1986/Pre-1986 (%)	30.1	25.7	28.4	19.3
Better 46 Post-1986/Pre-1986 (%)	20.2	15.1	16.5	9.1	

Table 2.8 Comparison of previously reported exhaust emission (mg/km) of benzene, toluene, xylene and 1,3-butadiene with those recorded in the present study (Source : Duffy et.al, 1998)

Place	Vehicle age		Details	Fuel	Emissions (mg km)				Reference
	group	Type of study			Benzene	Toluene	Xylenes	1,3-Butadiene	
USA	1975 1976 1977 1978 1979 1980 1981 1982 Average	FTP	3 cars, year catalysts introduced	Regular grade	77.3	157.4	166.0	—	Sigby et al. (1987)
			4 cars		47.9	101.2	57.2	—	
			4 cars		54.4	108.9	119.3	—	
			5 cars		63.3	169.5	78.2	—	
			5 cars		51.8	125.4	76.3	—	
			7 cars		25.1	39.4	39.4	—	
			12 cars		15.4	20.7	19.3	—	
			6 cars		11.4	11.8	11.4	—	
			Average		36.0	65.3	50.6	—	
			USA	In-use fleet	Roadside Tracer gas technique	site 1	In-use average	54.8	
site 2		81.6				177.2	149.5	—	
site 3		111.7				222.1	198.8	—	
site 4		113.9				235.3	204.9	—	
UK	Late 1980's vehicles Mostly 1986 As received	Mini portable CVS	ECE - cold start, 18.51 km hr ⁻¹	Premium grade	189.8	411.4	501.4	—	Bailey et al. (1990)
			ECE - hot start, 18.53 km hr ⁻¹	Leaded	163.8	356.9	430.4	—	
			On-road urban, 21.38 km hr ⁻¹	97 octane	195.6	453.5	599.6	—	
			On-road suburban, 41.73 km hr ⁻¹		100.5	236.8	296.3	—	
			Cross-country rural, 54.53 km hr ⁻¹		66.1	142.3	174.0	—	
			Motorway 1, 90.72 km hr ⁻¹		46.2	91.6	93.0	—	
			Motorway 2, 111.36 km hr ⁻¹		51.5	89.0	84.1	—	
USA	1989 1989 1983-1985 1983-1989	FTP	20 newer vehicles	Industry average certification fuel	6.8 4.3	— —	— —	0.53 0.44	Gorse et al. (1991)
			14 older vehicles	Industry average certification fuel	10.0 7.8	— —	— —	1.11 0.64	
			With three way catalyst	European 95 RON	12.1	—	—	0.64	
			Without three way catalyst	European 95 RON	67.5	—	—	5.36	
USA	1989 Volvo 1989 Volvo 1990 Rover 1987 VW	FTP	High tech, non-catalyst car	European 95 RON	64.4	—	—	7.00	Jemma et al. (1992)
			Carburettor, non-catalyst	European 95 RON	111.3	—	—	8.90	
			4 cars (1970-1978)	Average premium	97.6	211.5	—	1.85	
USA	Non-catalyst Oxidation catalyst 5-way catalyst Adaptive learning		5 cars (1975-1982)		17.2	31.9	—	0.01	Hoekman (1992)
			5 cars (1983-1990)		12.1	22.9	—	0.04	
			5 cars (1986-1989)		12.4	18.7	—	0.00	
			Fort McHenry Tunnel	In-use average	14.9	28.7	32.8	1.76	
USA	In-use fleet	Tunnel	Tuscarora Tunnel	In-use average	9.2	14.3	14.6	1.26	Sagbiel et al. (1996)
			67 vehicles	In-use average	—	110-790	—	—	
Australia	In-use	US 1975 FTP						Nelson and Quigley, (1994)	
Australia	In-use	FTP (ADR 37)	19, pre-1986 cars	Batch fuel	139.1	240.5	164.0	18.7	This study
			56, post-1986 vehicles	representative of standard grade	41.8	61.9	46.5	3.6	
			10, worst post-1986 cars	Australian petrols	104.8	179.5	136.3	12.0	
			46, best post-1986 cars		28.1	36.4	27.0	1.7	
			7 cars		79.9	136.5	100.1	1.1	
			9 cars		63.5	105.3	84.0	1.3	
			6 cars		41.2	48.8	35.7	2.0	
			8 cars		22.9	30.7	22.1	1.7	
			9 cars		36.6	43.0	39.8	1.2	
			17 cars		26.4	37.7	28.1	1.8	

The remaining 10 high polluting post-1985 vehicles had emission rates comparable to those vehicles not equipped with catalytic converters, suggesting that about 20% of post-1985 vehicles have malfunctioning or poorly operating catalysts. For the non-catalyst-equipped, pre-1986 vehicles, CS and HT emissions were about 60% of the CT emissions. For the better 46 post-1985 vehicles, average emissions during the CS and HT phases were about 20-25%, 12-16%, 11-14%, and 7-13% of the CT emissions for benzene, toluene, the xylenes, and 1,3-butadiene, respectively.

The emissions from a small number (9) of non-catalyst-equipped, pre-1986 vehicles were determined using unleaded and leaded petrol (table 2.9 and 2.10).

Table 2.9 Per vehicle exhaust emission (mg/km) of benzene, toluene, xylene and 1,3-butadiene during the cold transient (CT), cold stabilised (CS), and hot transient (HT) phase of the ADR 37/00 Drive Cycle
(Source : Duffy et.al, 1998)

Vehicle group	Benzene					Toluene					Xylenes					1,3-butadiene					
	Emissions			Ratios		Emissions			Ratios		Emissions			Ratios		Emissions			Ratios		
	CT	CS	HT	CS/CT	HT/CT	CT	CS	HT	CS/CT	HT/CT	CT	CS	HT	CS/CT	HT/CT	CT	CS	HT	CS/CT	HT/CT	
Pre-1986	Average	192.9	130.7	115.0	0.67	0.59	357.1	220.7	192.6	0.62	0.54	241.7	153.9	126.7	0.63	0.52	19.2	20.6	14.1	1.07	0.75
	Std	130.1	46.6	36.3			245.3	77.9	61.7			138.3	53.6	40.3			11.4	11.9	8.8		
Post-1986	Average (worse 10)	134.3	102.8	86.3	0.77	0.64	242.1	173.5	143.7	0.72	0.59	190.6	129.8	107.3	0.64	0.56	15.9	10.8	11.5	0.68	0.72
	Std	39.7	34.6	31.0			76.2	91.7	72.3			65.8	70.9	57.7			6.6	8.3	6.5		
Average (all 56)		84.8	30.8	30.2	0.36	0.36	119.0	42.2	41.1	0.3	0.3	107.7	31.0	29.5	0.29	0.27	7.4	2.7	2.7	0.36	0.36
	Std	46.6	18.9	30.9			77.9	73.2	37.1			64.6	55.2	44.2			3.8	5.4	5.1		
Average (better 46)		73.7	13.2	18.0	0.21	0.24	116.6	13.7	18.8	0.12	0.16	89.7	9.5	12.1	0.11	0.14	3.7	0.4	0.7	0.07	0.12
	Std	40.9	14.3	10.5			35.1	14.4	13.5			48.8	8.4	8.0			3.8	0.6	0.7		

Table 2.10 Emission of toluene, xylene and 1,3-butadiene relative to those of benzene determined in the present study compared to those reported in a recent study of the Sydney Harbour Tunnel (Source : Duffy et.al, 1998)

	Ratio to Benzene		
	Toluene	Xylenes	1,3-Butadiene
Pre-1986, nc-lp cars	1.73	1.18	0.13
Worst 10 post-1985, cc-ulp cars	1.71	1.30	0.11
All 56 post-1985, cc-ulp cars	1.48	1.11	0.09
Better 46 post-1985, cc-ulp cars	1.30	0.96	0.06
Sydney Harbour Tunnel study (Duffy and Nelson, 1996)	1.79	1.29	0.21

The emissions of all four target compounds were found to be significantly lower when unleaded petrol was substituted for leaded petrol. The greatest percentage emission reductions were observed for the CT phase, ranging from 25% for 1,3-butadiene to 35% for toluene. Emissions averaged over the 3 phases were reduced by 10% for 1,3-butadiene and by 16-18% for the aromatic compounds. Per vehicle total (heat build and hot soak) evaporative emissions of 1,3-butadiene, benzene, toluene and xylenes from pre-1985 vehicles during the Sealed Housing Evaporative Determination tests were 36, 646, 679 and 260 mg per test, respectively. Corresponding values for the post-1985 vehicles were much lower at 14, 76, 131 and 65 mg per test, respectively. Heat build evaporative emissions of the four air toxics from pre-1986 vehicles were greater than those from the newer vehicles by factors ranging from 2.8 for 1,3-butadiene to 16 for benzene. The corresponding values for hot soak emissions were 1.8 and 5.2 respectively.(table 2.11 and 2.12)

Table 2.11 Per vehicle exhaust emission of benzene, toluene, xylene and 1,3-butadiene from 9 pre-1986 vehicles when fuelled with either lead or unleaded petrol (Source : Duffy et.al, 1998)

	Petrol	Benzene				Toluene				Xylenes				1,3-butadiene			
		CT	CS	HT	AVG ADR	CT	CS	HT	AVG ADR	CT	CS	HT	AVG ADR	CT	CS	HT	AVG ADR
Average	LP	216.7	135.5	116.8	146.6	418.3	234.0	203.5	262.6	279.7	166.8	141.3	182.7	18.9	16.4	11.5	15.5
Std		154.2	33.7	19.0	44.5	295.3	59.8	39.3	87.4	141.0	47.9	31.9	54.3	12.6	7.9	9.3	8.7
Average	ULP	143.7	123.2	106.2	122.8	269.9	210.8	183.6	215.6	193.0	147.6	124.3	150.6	14.1	15.9	10.4	14.0
Std		36.0	37.1	22.7	30.8	73.8	65.2	45.8	58.9	49.8	46.4	34.3	41.0	7.5	7.9	6.7	7.2
% reduction using ULP		34	9	9	16	35	10	10	18	31	12	12	18	25	3	9	10

Table 2.12 Heat build and hot soak evaporative emission (mg/test) of benzene, toluene, xylene, 1,3-butadiene for 4 pre-1986, nc-lp and 8 post-1985, ce-ulp vehicles (Source : Duffy et.al, 1998)

Compound	Heat Build		Hot soak		Total	
	Mean	Std	Mean	Std	Mean	Std
Pre-1986, nc-lp cars						
Benzene	365.2	199.6	280.5	102.3	645.7	188.4
Toluene	334.8	77.6	343.7	127.1	678.5	78.7
Xylenes	96.6	34.6	163.0	75.1	259.6	104.0
1,3-butadiene	26.5	17.1	9.2	4.0	35.6	19.2
Post-1985, ce-ulp cars						
Benzene	22.4	17.1	53.7	43.8	76.0	52.0
Toluene	34.3	24.3	96.2	48.0	130.5	59.1
Xylenes	17.3	11.1	47.8	19.4	65.2	25.3
1,3-butadiene	9.4	7.6	5.0	7.9	14.4	9.9

Nelson and Duffy (1984) investigated the non-methane hydrocarbon (NMHC) compositions of the exhausts from 67 vehicles in "on the road" condition and driven through an urban driving cycle on a chassis dynamometer, on their research in Australia. The major components were ethylene (11.2% w/w of NMHC), toluene (10.2%), acetylene (8.7%), m,p-xylenes (6.5 %), benzene (5.0%), propylene (5.0%) and i-pentane (4.8 %). These compounds have also been reported as significant components in the exhausts from two similar populations of American vehicles. The NMHC compositions were found to be insensitive to the mass emission rates of hydrocarbons from the vehicles, except for the combustion-derived olefins, ethylene and propylene, which were affected by engine modifications introduced to satisfy emission control requirements. A close relationship was found between petrol composition and exhaust composition but this did not correspond simply to emissions of unburnt petrol. The aromatics are enriched relative to the alkanes in exhaust when compared with their proportions in the petrol. The results of their study are shown in table 2.13.



Table 2.13 Average exhaust hydrocarbon compositions (%w/w NMHC) for Sydney vehicles (Source : Nelson and Quigley, 1984)

Hydrocarbon	Composition (each vehicle equally weighted)		Composition (weighted according to vehicle emission rates)
	Average	Standard deviation	
Ethane	1.4	0.5	1.2
Ethylene	11.2	3.2	10.1
Acetylene	8.7	2.7	8.9
Propane	0.1	0.1	0.1
Propylene	5.0	1.6	4.4
Methylacetylene	0.4	0.3	0.4
<i>n</i> -Butane	2.1	0.6	2.2
<i>i</i> -Butane	1.0	0.3	1.1
<i>l</i> -Butene	0.9	0.3	0.8
<i>i</i> -Butene	1.4	0.6	1.2
<i>trans</i> -2-Butene	0.6	0.4	0.6
<i>cis</i> -2-Butene	0.5	0.2	0.4
<i>n</i> -Pentane	3.0	0.7	3.3
<i>i</i> -Pentane	4.8	0.9	5.3
Cyclopentane	0.4	0.1	0.4
1-Pentene	0.2	0.1	0.2
<i>trans</i> -2-Pentene	0.3	0.2	0.3
<i>cis</i> -2-Pentene	0.3	0.2	0.3
2-Methyl-1-butene	0.3	0.2	0.3
2-Methyl-2-butene	0.5	0.2	0.5
<i>n</i> -Hexane	1.9	0.4	2.0
2-Methylpentane	2.3	0.4	2.4
3-Methylpentane	1.6	0.3	1.7
2,2-Dimethylbutane	0.3	0.2	0.4
2,3-Dimethylbutane	0.6	0.1	0.6
Methylcyclopentane	1.0	0.2	1.0
Cyclohexane	0.6	0.2	0.6
C ₆ Olefins	0.7	0.2	0.7
Benzene	5.0	0.7	4.9
<i>n</i> -Heptane	0.8	0.2	0.9
2-Methylhexane	1.5	0.3	1.6
3-Methylhexane	1.2	0.3	1.3
2,4-Dimethylpentane	0.3	0.1	0.3
Methylcyclohexane	0.6	0.2	0.6
Other C ₇ cycloalkanes	0.3	0.2	0.3
Toluene	10.2	0.9	10.2
<i>n</i> -Octane	0.4	0.1	0.4
2,2,4-Trimethylpentane	1.0	0.4	1.0
Other C ₈ alkanes	3.2	0.7	3.2
Ethylbenzene	1.9	0.2	1.9
<i>m,p</i> -Xylenes	6.5	0.9	6.7
<i>o</i> -Xylene	2.5	0.4	2.5
<i>n</i> -Nonane	0.2	0.1	0.2
Other C ₉ alkanes	1.7	0.4	1.7
<i>n</i> -Propylbenzene	0.4	0.1	0.5
<i>i</i> -Propylbenzene	0.2	0.1	0.2
1,2,4-Trimethylbenzene	1.9	0.3	2.1
1,3,5-Trimethylbenzene	0.7	0.1	0.8
<i>m,p</i> -Ethyltoluenes	2.0	0.3	2.1
<i>o</i> -Ethyltoluene	0.6	0.2	0.6
<i>n</i> -Decane	0.4	0.1	0.4
Other C ₁₀ alkanes and aromatics	0.9	0.4	0.9
C ₁₁ and C ₁₂ alkanes and aromatics	3.6	1.1	3.6

Brocco et.al (1997) investigated the types and amounts of aromatic hydrocarbon in urban air of Rome. Aromatic hydrocarbons were measured in Rome during 1992-1993 by means a differential optical absorption spectrometer (DOAS) and an automatic gas chromatograph (VOC analyzer). The mean distribution of aromatic hydrocarbons was: benzene 12.6%, toluene 35.4%, and remaining species 42%. The mean yearly concentrations of toluene (128 and 138 μgm^{-3}) were 2-3 times higher than those of benzene (40 and 47 μgm^{-3}). The highest concentrations of aromatic hydrocarbons were measured during the stagnant winter period. The diurnal behavior of aromatic hydrocarbons suggests that motor exhaust emissions are their dominant source. The different reactivities of benzene and toluene during photochemical smog episodes were discussed. The results of their study are shown in table 2.14. and figure 2.5, 2.6 .

Table 2.14 Comparison of volatile hydrocarbons in Rome
(Source : Brocco et.al, 1997)

Alkanes	μgm^{-3}	Alkenes	μgm^{-3}	Aromatics	μgm^{-3}
Ethane	12.4	Ethene	22.4	Benzene	35.5
Propane	23.8	Propene	18.4	Toluene	99.7
<i>i</i> -Butane	30.9	<i>t</i> -2-Butene	8.6	Ethylbenzene	17.6
<i>n</i> -Butane	35.5	1-Butene	4.1	<i>m</i> -/ <i>p</i> -Xylene	54.6
Cyclopentane	3.5	<i>i</i> -Butene	17.2	<i>o</i> -Xylene	25.1
2-Methyl butane	74.4	<i>c</i> -2-Butene	3.9	1,3,5-Trimethylbenzene	22.6
<i>n</i> -Pentane	23.3	1,3-Butadiene	4.6	1,2,4-Trimethylbenzene	21.0
Methyl-cyclopentane	12.7	3-Methyl-1-butene	2.9	1,2,3-Trimethylbenzene	5.2 33.7%
Cyclohexane	1.1	<i>t</i> -2-Pentene	6.0		
2-Methyl pentane	27.3	2-Methyl-2-butene	11.4		
3-Methyl pentane	19.3	1-Pentene	1.3		
<i>n</i> -Hexane	15.8	2-Methyl-1-butene	1.1		
2,3-Methyl hexane	29.3	<i>c</i> -2-Pentene	3.0 12.6%		
<i>n</i> -Heptane	9.6				
<i>n</i> -Octane	3.2 38.6%				
Acetylene	31.2 3.7%				

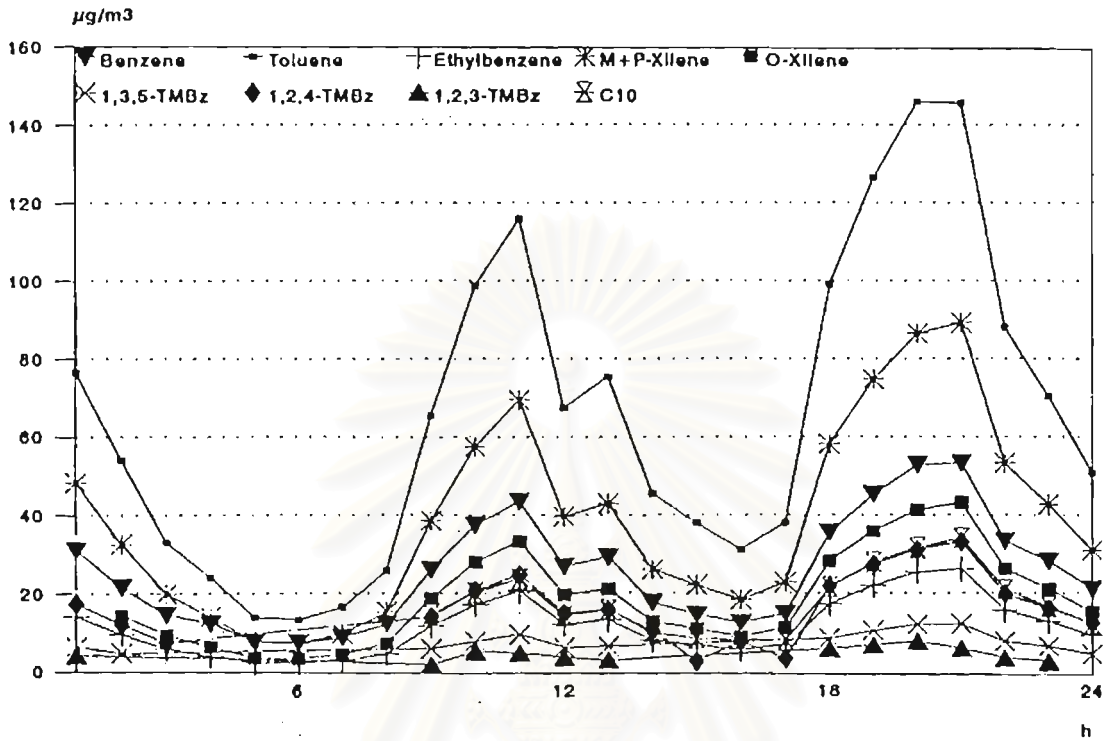


Figure 2.5 Mean diurnal concentration of aromatic hydrocabons In Roam (Source : Brocco et.al, 1997)

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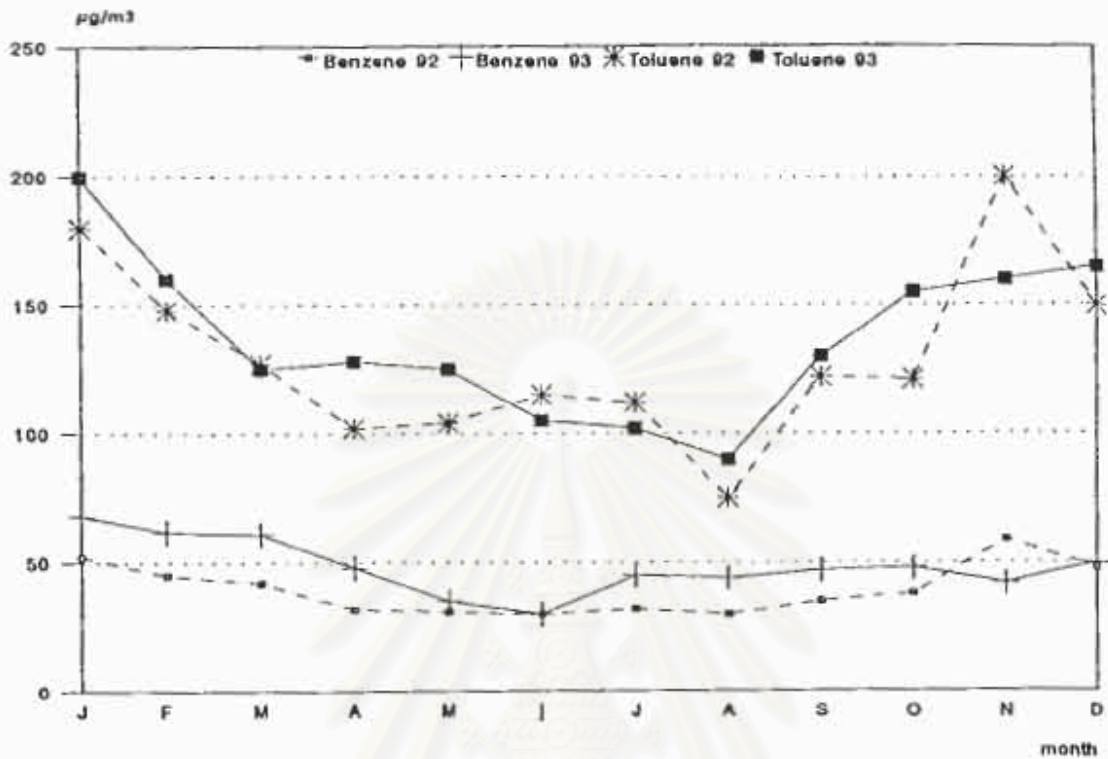


Figure 2.6 Average monthly concentrations of benzene and toluene in Rome during 1992 -1993 (Source : Brocco et.al, 1997)

Candeli et.al (1974) investigated the carcinogenic air pollutants in the exhaust from a European car operating on various fuels. The influence of some fuel variables on polycyclic aromatic hydrocarbons (PAH) emission was studied. The fuel variables taken into consideration were: tetra-ethyl-lead (TEL) content (0 and 0.63 gl^{-1}); fuel aromaticity (0, 6 and 48 per cent) and type of aromatic at constant total level of aromatics (benzene, xylene and hydrocarbons with 9 and 10 carbon atoms). The results are shown in table 2.15 and 2.16.

Table 2.15 Physical constants and fuel composition (Source : Candeli et.al, 1974)

Physical and chemical properties	Fuel A*	Fuel A-TEL*	Fuel B*	Fuel B-TEL*	Fuel C*	Fuel C-TEL*	Fuel D†	Fuel E†	Fuel F†
Real VP kg cm ⁻³ (ASTM D 323)	0.472		0.590		0.492				
Specific gravity 15°C g cm ⁻³ (ASTM D 1298)	0.691		0.701		0.763		0.764	0.759	0.766
NORM‡ (ASTM D 2699)	90.0	102.6	91.8	98.0	92.9	99.5	91.6	90.3	89.0
NOMM§ (ASTM D 2700)	88.4	99.7	78.0	81.4	82.7	91.2	88.3	87.3	84.4
Sensitivity TEL g l ⁻¹	1.6	2.9	13.8	16.6	10.2	8.3	3.3	3.0	4.6
Aromatics (" _v vol.) (ASTM D 1319)	0	0	6	6	47.7	47.7	48	48	48
Olefins (" _v vol.) (ASTM D 1319)	0	0	47	47	0	0	0	0	0
Paraffins (" _v vol.) (ASTM D 1319)	100	100	47	47	52.3	52.3	52	52	52

* Fuels with commercially typical distillation curves.

† Synthetic fuels.

‡ NORM: number octane research method.

§ NOMM: number octane motor method.

|| Sensitivity—Difference between NORM and NOMM.

Table 2.16 Composition of the aromatic component of test fuels (C,D,E and F) at constant total aromatics (Source : Candeli et.al, 1974)

Compounds	C* (% vol.)	D† (% vol.)	E‡ (% vol.)	F‡ (% vol.)
Benzene	3.04	47.91	0.39	0.42
Toluene	12.46	0.09	0.28	0.14
Ethyl-benzene	2.59		9.98	0.08
para-Xylene	3.76		7.47	0.12
meta-Xylene	6.66		19.58	0.36
ortho-Xylene	3.57		9.14	0.55
iso-Propyl-benzene	0.12		0.11	0.12
n-Propyl-benzene	0.65		0.06	1.36
1:3- plus 1:4-methyl-benzene	4.09		0.27	9.14
1:3:5-Trimethyl-benzene	1.53		0.08	3.27
1:2-Methyl-ethyl-benzene	0.84		0.06	2.47
1:2:4-Trimethyl-benzene	4.44		0.24	12.35
1:2:3-Trimethyl-benzene	1.47		0.06	5.31
Aromatics C ₁₀ *	2.47		0.28	12.31

* Fuel with commercially typical distillation curve.

† Synthetic fuels.

‡ Aromatics 48 per cent, paraffin 52 per cent.

Each test consisted of European test cycles on a dynamometer bench, using a European engine of average displacement for European cars (1608 cm³) and without deposits in the combustion chamber.

The results obtained show that it is not possible to generalize about the effect of TEL on PAH emission: in two cases the addition of TEL reduced and in one case it increased the PAH emission. Increasing fuel aromaticity increases PAH emission, but these results apply only to the three leaded tested fuels, and not to the same fuels unleaded. In three synthetic unleaded fuels at constant total aromatics the type of aromatic present strongly affected the PAH emissions: it seems that simple aromatic hydrocarbons, such as benzene or xylene, produce less PAH than C₉ and C₁₀ hydrocarbons.

Moschonas and Glavas (1996) investigated the C_3 - C_{10} hydrocarbons in the atmosphere of Athen, Greece. A fifty-seven C_3 - C_{10} paraffins, olefins and aromatics were identified and quantified in the atmosphere of Athens in samples collected in electropolished canisters in the early morning hours of summer months. Aliquots of air were cryocollected in glass beads and cryofocused prior to separation in a capillary column and analysed by GC-MS. The aromatic fraction predominates with maximum benzene and toluene concentrations of 19 and 39 ppbv, respectively. Through comparison with NMHC emission profiles of other cities, it is inferred that vehicle emissions and paint solvents are the two main sources of the observed NMHC. All results in this study are shown in the table 2.17 and 2.18.



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Table 2.17 NMHC in Athens and other urban centers, unit ppbv

(Source : Moschonas and Glavas, 1996)

Hydrocarbon	Vienna	Hamburg	Sydney	Chicago	Osaka	Athens* average	Athens* range
Ethane	28.3 ^b		7.5	6.4	24.3 ^c	NM	NM
Ethylene		5.5	12.5	3.5	23.3	NM	NM
Acetylene		8.8	10.1	4.1		NM	NM
Propylene	6.3 ^d	2.9	7.4	1.4	6.1	3.9	0.7-12.6
Propane		2.1	5.9	3.2	8.9	1.2	0.4-2.6
Isobutane	1.8	3.8	4.7	1.2	5.1	1.1	0.3-3.1
Isobutene + 1-butene	2.5		2.4		3.6	0.9	0.2-3.0
n-Butane	4.9	7.8	7.5	6.0	11.0	2.1	0.4-6.4
trans-2-Butene	1.8		1.1		1.1	0.4	0.1-0.8
cis-2-Butene	0.9		1.0		0.9	0.3	0.1-0.8
Isopentane	6.9	6.4	9.0	4.1	10.6	11.7	4.6-25.6
1-Pentene			0.4		0.4	0.4	0.1-1.1
n-Pentane	4.5	5.1	5.0	3.8	7.7	4.2	1.0-11.6
1,3-Pentadiene						0.2	0.05-0.5
1,1-Dimethyl-cyclopropane						0.7	0.2-2.5
2-Methyl-1-butene			0.5		0.7	0.4	0.1-1.1
2-Methyl-2-butene			1.3		0.5	1.4	0.4-4.0
2,2-Dimethyl-butane			0.5			0.8	0.3-1.6
Cyclopentene			0.8			0.2	0.05-0.5
1-Ethyl-1-methyl-cyclopropane						0.1	0.1-0.2
2,3-Dimethyl-butane			0.9		0.8	0.6	0.2-1.5
2-Methyl-pentane	3.2		2.6	2.4	3.9	3.3	1.3-6.9
3-Methyl-pentane	1.9		1.6	2.4	3.1	2.3	0.9-4.7
1-Hexene				2.4		0.2	0.1-0.5
n-Hexane	2.2	3.8	2.1	2.0	5.5	1.6	0.6-4.2
2-Methyl-2-pentene						0.3	0.2-0.7
cis or trans-3-Methyl-2-pentene						0.2	0.1-0.3
trans-3-Hexene						0.2	0.1-0.3
cis-3-Methyl-2-pentene						0.3	0.2-0.7
Methyl-cyclo-pentane	1.4		1.2		1.7	0.7	0.3-1.4
Benzene	6.0	3.2	2.6	2.4	5.1	5.0	0.8-18.7
Cyclohexane	0.6		0.9		0.8	0.3	0.1-0.8
2-Methyl-hexane	1.1		1.2		1.5	1.8	0.6-5.7
2,3-Dimethyl-pentane			0.7		0.6	0.3	0.1-0.8
3-Methyl-hexane	1.1		0.8		1.7	3.5	1.0-8.7
n-Heptane	1.4		0.7		2.0	2.4	0.4-7.8
Methyl-cyclohexane	0.5		0.6		0.7	1.8	1.0-3.5
Toluene	10.9	8.2	8.9	3.8	31.1	14.3	3.4-39.0
2-Methyl-heptane					0.6	2.3	0.4-8.2
3-Methyl-heptane	0.5				0.7	0.8	0.4-2.2
n-Octane	0.4		0.4		0.6	0.6	0.4-1.2
Ethyl-benzene	1.8	2.2	1.3	0.6	3.8	2.7	0.6-8.1
m + p-Xylenes	5.7	5.2	3.9	1.5	7.7	12.1	2.6-29.8
3-Methyl octane						1.0	0.5-1.5
o-Xylene	2.3	1.8	1.5	0.4	2.8	3.7	1.4-6.4
Nonane	0.2		0.4		0.7	1.7	0.5-2.7
2,3,7-Trimethyl-octane						0.9	0.8-1.0
Propyl-benzene	0.5		0.4			1.1	0.4-1.6
1-Ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene	2.1		1.1		3.1	9.5	2.5-14.9
1,2,3-Trimethyl-benzene					0.6	3.3	0.9-5.4
3-Methyl-nonane						1.0	0.8-1.1
1-Ethyl-2-methyl-benzene	0.6		0.4		0.7	2.2	0.9-3.2
1,3,5-Trimethyl-benzene	0.7		0.5		1.2	9.2	2.8-14.2
Decane	0.6		0.5		0.9	3.1	0.8-5.0
1,2,4-Trimethyl benzene	2.4		1.3		2.9	3.9	0.9-6.6
1-Ethenyl-2-methyl-benzene						0.9	0.8-1.0
1-Methyl-3-propyl-benzene						1.3	0.3-2.1
2-Diethyl-benzene						2.3	0.7-3.5
1-Methyl-2-propyl-benzene						0.4	0.3-0.4
2-Ethyl-1,4-dimethyl-benzene						1.8	1.6-2.0
Sum of paraffins, ppbC	221.0	133.0	250.1	131.5	353.5	217.2	56.9-670.4
Sum of olefins, ppbC	58.5	36.9	100.4	31.8	143.9	28.2	7.7-74.9
Sum of aromatics, ppbC	247.4	150.2	164.8	61.0	439.2	479.1	63.8-1138.3

Note: Vienna = Lanzerstorfer and Puxbaum (1990), Hamburg = Bruckmann et al. (1988), Sydney = Nelson and Quigley (1982), Chicago = Aronian et al. (1989), Osaka = Tsujino and Kowata (1993)

* This work

^b Sum of C₂ hydrocarbons

^c 10% ethane and 90% acetylene.

^d Sum of C₃ hydrocarbons

Table 2.18 Meteorological data and related air pollutant concentrations measured during the hour of hydrocarbon sampling (Source : Moschonas and Glavas, 1996)

Date	CO (ppm)	NO _x (ppb)	Wind speed (m s ⁻¹)	Wind direction	ΣNMHC (ppbC)*
June 9	5.3	144	3.5	S-SW	1128
10	3.1	97	1.8	NE	420
11	3.0	90	1.3	NW	465
12	4.5	256	1.4	S-SW	1310
May 6	4.9	246	2.6	S-SW	1341
7	1.9	78	1.6	W	432
9	3.0	109	1.0	W-SW	283
10	4.1	103	3.5	N-NE	527
July 7	7.2	392	0.7	SW	1884
8	2.6	76	3.6	N-NE	753
9	4.9	253	0.6	W	1272
11	3.5	145	0.3	SW	1177

* ppbC = 10⁻⁹ v/v carbon.

Many articles that published on the internet involved in the sources dispersion and effects of Benzene, Toluene and Xylene on the environment.

The article from <http://www.ubavie.gv.at/publikationen/reports/r124s.htm> by Hanus-Ilmar A., Hrabcik I Wien, concerning about "Ambient air concentrations of benzene, toluene and xylene (btx) (konzentrationen von benzol, toluol und xylolen in umgebungsluft. -Deutsche Zusammenfassung) November 1995. (Reports; UBA-95-124) as :

Ambient air concentrations of benzene, toluene and xylene (btx) –

Summary :

Due to its cancerogenous character benzene, a highly volatile aromatic hydrocarbon, nowadays becomes increasingly important in environmental studies. Compared to benzene, toluene and xylene, the simplest methylated aromatic compounds, are less toxic but however being functionally ozone-precursor substances they can have a harmful effect on the environment.

Benzene emissions are mainly caused by vehicle exhaust. The exhaust gas consists of both benzene as an unburned fuel component as well as benzene being a dealkylation product of substituted aromatic hydrocarbons. Toluene and xylene constitute the highest amounts of hydrocarbons. Therefore the reduction of the content of benzene and other aromatic compounds is under discussion all over Europe.

Measurements of ambient air concentrations of benzene in the urban area of Vienna in 1992/93 showed that the planned limiting value for the ambient air concentration of benzene was exceeded at several measurement points.

Based on these results the Austrian Federal Environmental Agency in co-operation with the Federal State Authorities realised a national measuring programme in order to register the ambient air concentrations of these aromatic hydrocarbons. The programme included 44 sampling locations with different air pollution levels (low polluted, near traffic, petrol stations). At 26 sites sampling took place all over the year as continuous series of two week expositions. This proceeding was necessary to get annual means for the planned limiting value. At most of the sites the measuring height was 1.5 meters above ground. Additionally, at two sampling sites measurements at a

higher exposition level were carried out in order to obtain information about the vertical distribution of btx-concentrations.

The method used in this study was passive sampling. This is an effective and low-cost method for long-term control of ambient air pollution. At each sampling site sorption tubes with activated carbon were exposed during a period of two weeks. Then the tubes were sent to the laboratory of the Austrian Federal Environment Agency for chemical analysis. For gas chromatography the substances that had adsorbed and concentrated on the activated carbon, were desorbed in liquid carbon disulphide. The results of GC-measurements are mean values for the exposition time (14 days each).

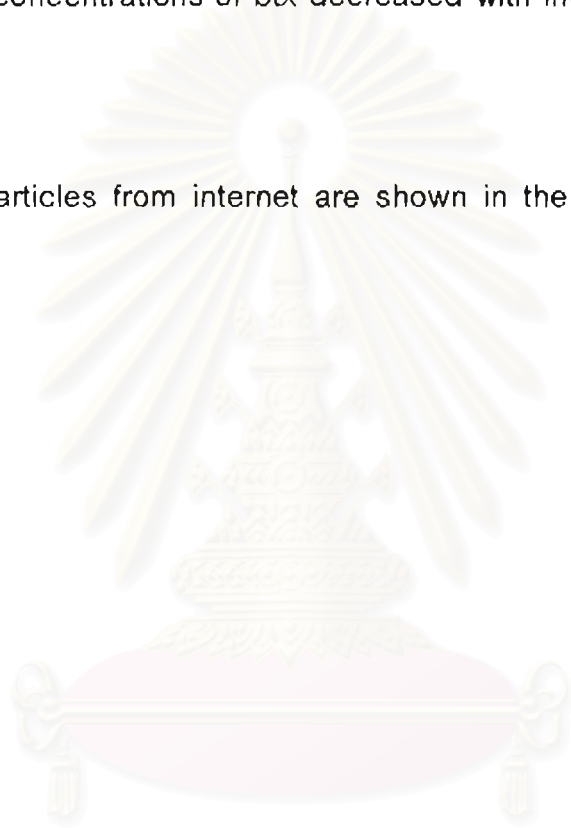
The 14-days means at those sampling sites characterised by heavy traffic, ranged from 5 to 20 $\mu\text{g}/\text{m}^3$, with a maximum value of 28 $\mu\text{g}/\text{m}^3$. At rural sampling locations the 14-days mean values of benzene were about 2 $\mu\text{g}/\text{m}^3$, during the winter month they partially reached 5 $\mu\text{g}/\text{m}^3$. The concentrations of toluene and xylene correlated with those of benzene.

These 14-days mean values were used for calculation of the annual mean value. The results showed, that at five out of 26 sampling sites the planned limiting value of 10 $\mu\text{g}/\text{m}^3$ for ambient air concentrations of benzene. The respective relations of the single aromatic compounds at the sites close to heavy traffic remained constant during the year.

An increase of concentration of aromatic hydrocarbons was observed at many measuring sites during the winter month. The seasonal tendency was distinctly marked at sampling sites near heavy traffic in the urban area of Graz,

whereas in Vienna no increase of btx - concentration was stated during the winter month. The same phenomenon already existed during the measuring period 1992/93. In Vienna the annual mean value did not show any considerable variation compared to 1992/93. Only at one single site an insignificant decrease could be detected. As already indicated in previous investigations the concentrations of btx decreased with increasing measuring height.

And many articles from internet are shown in the appendix A in this research.



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CHAPTER 3

EXPERIMENTAL INVESTIGATIONS

3.1 Materials for sampling collection

1. 20 liter Tedlar bag as sampling bag
2. Black plastic bag
3. Purified nitrogen gas (N_2) (99.999%)
4. Temperature detector
5. Vacuum box
6. Air pump
7. Teflon tube
8. Moisture trap scrubber with Magnesium perchlorate ($Mg(ClO_4)_2$)
9. Three ways valve

The materials pictures in this study are shown in figure 3.1 and 3.2.

3.2 Motorcycle

In this experiment, 44 samples of two and four-stroke motorcycles were studied. All of these motorcycles have displacement size of 100-150 cc. They are classified into three groups. The first group is new motorcycles with less than 5 years old. The second group is moderate age motorcycles with 5 to 10 years old and the last group is old motorcycles with more than 10 years.

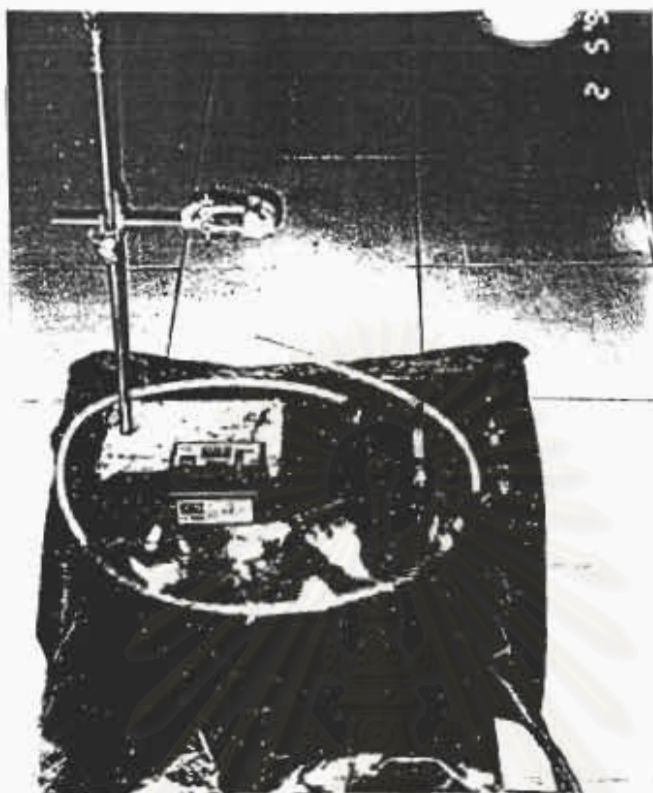


Figure 3.1 Materials for the study : Tedlar bag, black plastic bag, moisture trapped scrubber, temperature detector, syringe, clamp holder and air pump

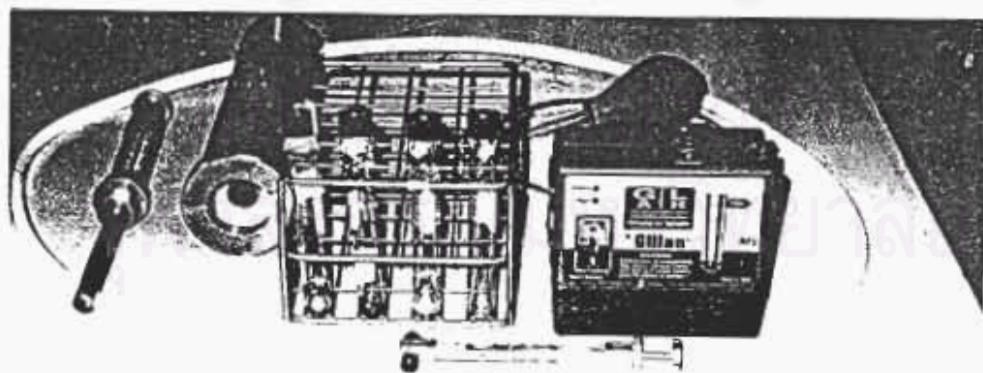


Figure 3.2 Materials for the study and gasoline sample

3.3 Exhaust of motorcycles

For exhaust samples, The exhaust of motorcycle was collected at idle condition only. Three air pollution parameters Benzene, Toluene and Xylene (in form of total Xylene that includes ortho-, meta-, and para- form) were analyzed. All of the concentration of Benzene, Toluene and Xylene were calculated in both Part Per Million (ppm) and Milligram per Cubic Meter (mg/m^3) units.

3.4 Fuel

The fuel used in this study was unleaded gasoline that included the octane number both 91 (regular grade) and 95 (premium grade). The brand name of gasoline was not fixed and depended on each motorcycle used in its fuel tank.

3.5 Sampling method

3.5.1 Exhaust gas sampling

The exhaust sampling was collected at idle condition. Before each sampling and measurement, the motorcycle was warm up for at least 10 minutes and temperature at the end of exhaust pipe not less than 50°C . A vacuum box for exhaust gas sampling is shown in Figure 3.3

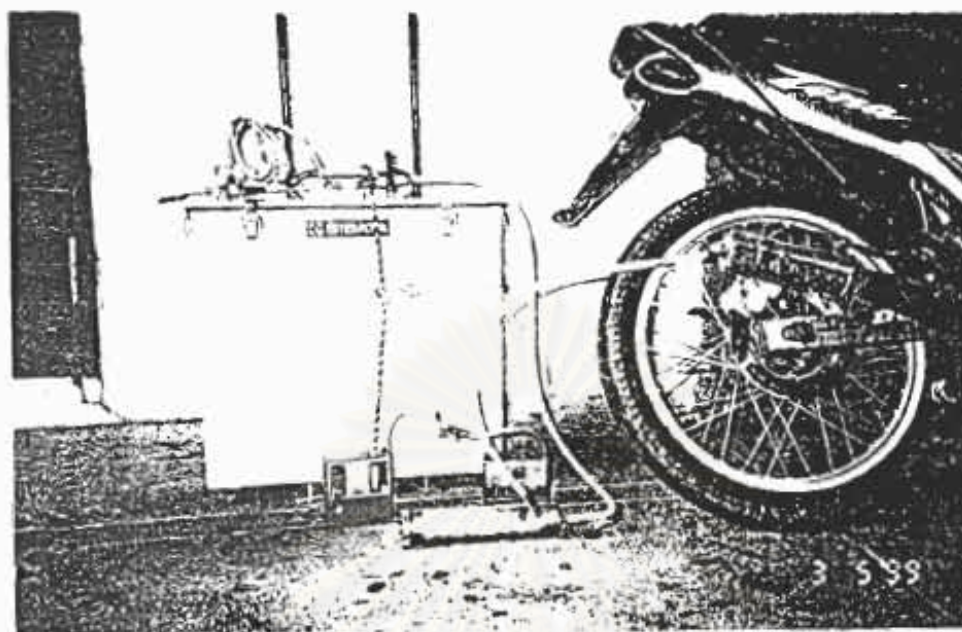


Figure 3.3 Vacuum Box

The Tedlar sampling bag, was washed by purified N_2 (99.999%) at least 3 times before used. The exhaust sample was pumped into 20 liter Tedlar bag that was also covered by a black plastic bag to prevent an occurrence of photo-oxidation reaction. The exhaust gas collection instruments were operated as follows:

1. The end of Teflon tube and temperature detector had to be inserted deeply to the exhaust pipe and the other end of Teflon tube was connected with the moisture scrubber.
2. From the scrubber, the Teflon tube was connected with three ways valve. From one end of the valve, it was connected with sampling

bag in vacuum box, while the other end was separated from the vacuum box.

3. The bottom of the vacuum box was connected with an air pump.

The collection of exhaust gas sample procedure is

Step 1, Stopcock 1 is closed and stopcock 2 is opened while the vacuum pump is operated. The air in the box is evacuated so that a vacuum condition occurs in the box.

Step 2, Stopcock 1 is still closed, while the stopcock 3 is opened to ventilated the exhaust gas from tailpipe until the temperature of exhaust gas from tailpipe is reached 50°C .

Step 3, Stopcock 3 is then closed while stopcock 1 is opened immediately. (The stopcock 2 is remain opened to continue the vacuum condition in the box). Then, the exhaust gas from tailpipe flow into the bag immediately by the vacuum force.

Step 4, After the exhaust gas is collected for approximately 5 minutes or the volume of exhaust gas in the bag is about 10 liter, stopcock 1 and 2 are then closed respectively and then the air pump is off. The bag is taken out for an analysis in the laboratory within 3 hours after collection.

The diagram and picture of exhaust gas sample collection using vacuum box were shown in figure 3.4 and 3.5.

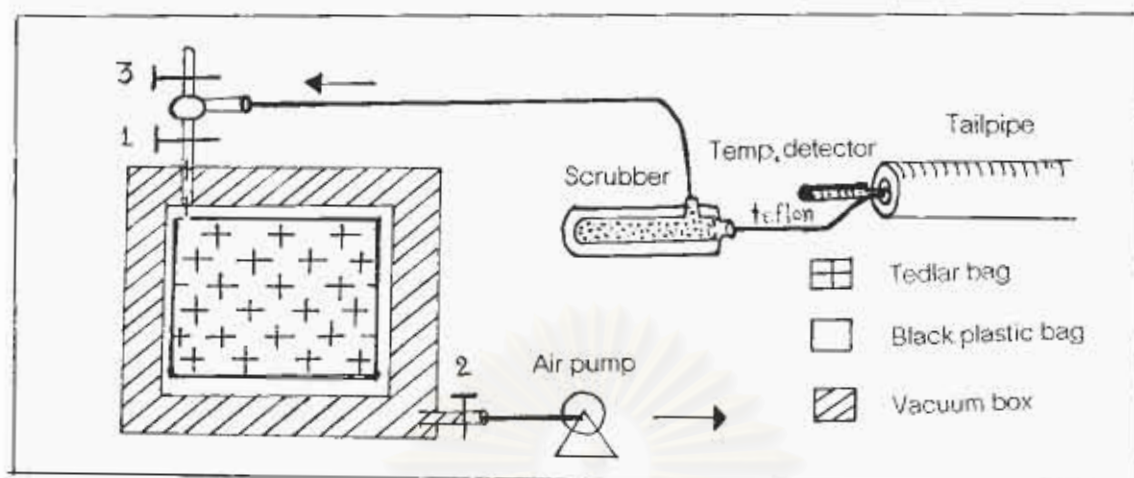


Figure 3.4 Diagram of vacuum box

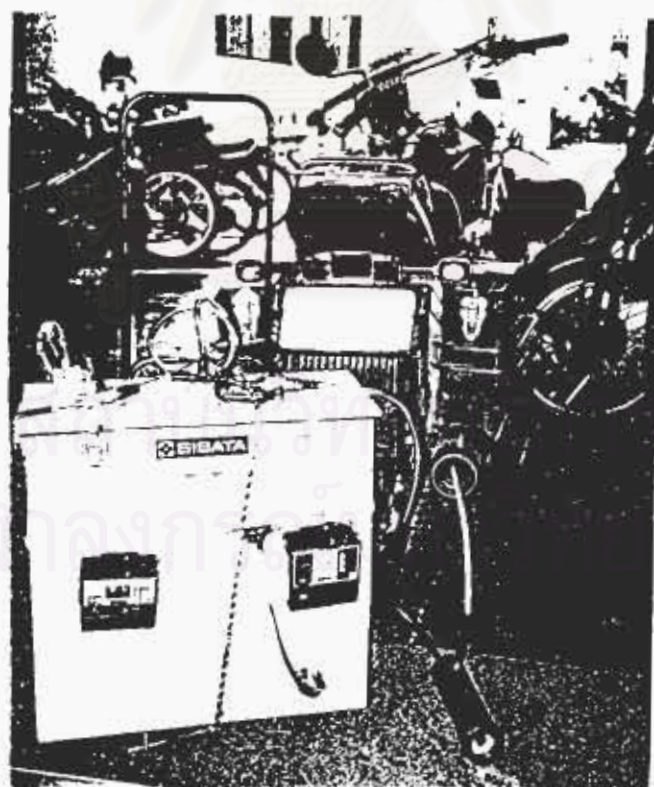


Figure 3.5 Collecting exhaust sample

3.5.2 Gasoline sampling

The gasoline sample was collected by using a plastic tube to withdraw the gasoline from fuel tank directly and approximately 5 ml of sample was collected and then kept in the refrigerator at 20 °C for laboratory analysis later.

After sampling, the exhaust gas sample in the Tedlar bag and the gasoline sample in vial were brought to the laboratory for the analysis of Benzene, Toluene and Xylene concentration by Gas Chromatography with Flame Ionization Detection (GC/ FID). This process took about 10 minutes for each bag and about 25 minutes for each gasoline tube.

3.6 Instrument for sample analysis

Concentrations of Benzene, Toluene and Xylene were analyzed by Gas Chromatography (figure 3.6). The experimental conditions of this study are shown below :

1. Brand of GC	Hewlett – Packard 5890 series II
2. Column	DB-1
3. Carrier gas	Purified N ₂ (99.999%)
4. Temperature program	30 ⁰ C, hold for 2 min. 10 ⁰ C per min.to100 ⁰ C, hold for 1 min.
5. Temperature at injection port	200 ⁰ C
6. Detector	Flame ionization detector (FID) (heat to 300 ⁰ C)

7. Exhaust gas sample used 1 ml.
8. Gasoline sample used 1 μ l.
9. Standard BTX used 1 μ l.



Figure 3.6 Gas Chromatography

3.7 Preparation of standard solution

All reagents that used in this preparation were AR (Analytical reagent) grade. First, the standard solution was prepared by adding 125 μ l Benzene (C_6H_6), 75 μ l Toluene ($C_6H_5CH_3$) and 50 μ l Xylene ($(CH_3)_2C_6H_4$) into the 250 ml Acetone (CH_3COCH_3). Then, it is mixed by hard shaking, and keep it in the refrigerator at 20 $^{\circ}$ C.

3.8 Calculation

The concentrations of Benzene, Toluene, and Xylene in the motorcycle emission samples and gasoline samples were measured with a Flame Ionization Detector (FID) of Gas chromatography (GC). The standard solutions, which contained Acetone 250 ml, Benzene 125 μl , Toluene 75 μl and Xylene 50 μl , had a total volume of 250250 μl . The volume of 1 μl standard solution, 1 μl gasoline sample and 1 ml exhaust gas were used for calculation of each substance concentration.

When the standard solution or samples were injected into the Injection port of Gas Chromatography (GC) at temperature 200 $^{\circ}\text{C}$. All hydrocarbon components were evaporated immediately and moved into the column by the carrier gas (N_2) in the state of gas. After detecting by the Flame Ionization Detector (FID) the peak areas of Benzene, Toluene, and Xylene were appeared (known as the chromatogram). The concentrations of each substance in samples can be calculated by comparing with the known concentration of standard solution. The calculation procedures are shown in the appendix B.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Background information

In this study, 44 samples of 2 and 4-stroke motorcycles have been selected and tested. The motorcycles were classified into 3 groups based on the ages of motorcycles. The motorcycles with aged less than 5 years old is classified as new motorcycles, the ages of motorcycles in ranges of 5-10 years old is moderate age group, and the motorcycles which had ages more than 10 years old is old motorcycles. The motorcycles from the car park around the Chulalongkorn University were selected by interviewing the motorcycle owner. The Tedlar bag in the vacuum box was used to collect the exhaust gas, from motorcycle at stationary idle mode. All exhaust gas samples were taken to the chemical laboratory at STREC (Science and Technology Research Equipment Centre) to analyze the concentration of Benzene, Toluene and Xylene (as Total Xylene) within 3 hours after collecting.

Among the motorcycle used in this study, the moderate age and the old of 4-stroke motorcycles are rarely found. Since of the 4-stroke motorcycles had not been popular to the public. It is difficult to find the old 4-stroke motorcycles. This is the main important problem in this study.

In this research, concentration of the Benzene, Toluene, and Xylene were investigated from the exhaust of different age group motorcycles. The concentrations of Benzene, Toluene and Xylene in gasoline tank from each

motorcycle were also analysed. The emission comparison of 2 and 4-stroke was to examine in this study. In addition, the effect of engine age on exhaust pollutant was studied as well.

4.2 BTX concentration in exhaust emission

Motorcycle engines can be classified into 2-stroke and 4-stroke types. The engine performance in 2-stroke and 4-stroke motorcycle engines is an important factor on emission components, as 2-stroke engine tend to emit much greater amounts of unburned hydrocarbons than 4-stroke engine of similar size and power. 2-stroke engines also display markedly poorer fuel economy than 4-stroke, but tend to have higher power output, quicker acceleration, and lower manufacturing costs. Because of its advantages in performance and manufacturing cost, especially in Thailand, 2-stroke engines are used extensively in motorcycles.

4.2.1 Concentration of Benzene

The results from the study indicated that the higher average emission concentration of Benzene was found in old 2-stroke motorcycle group. It was also found that, the average concentration of Benzene in new 4-stroke motorcycle group is the lowest when compared with others. The average concentration of Benzene from 2 and 4-stroke motorcycles were 116.15 and 11.74 ppm, respectively.

4.2.2 Concentration of Toluene

As the same as Benzene concentration, the maximum average Toluene emission concentration was found to be 261.73 ppm of old 2-stroke motorcycles, the lowest level of Toluene concentration was found in new 4 stroke motorcycle, the average was 29.00 ppm. It was discovered that the older motorcycle emitted Toluene concentration higher than the newer.

4.2.3 Concentration of Xylene

Similar to the Benzene and Toluene concentration, the maximum and minimum concentration of Xylene in exhaust emission were also found in the old 2-stroke and new 4-stroke motorcycle group, respectively. The average concentrations in both groups were 39.21 and 7.59 ppm, respectively.

The detail data of pollutant concentration emitted from motorcycle in this study was presented in table 4.1

Table 4.1 The detail data of BTX concentrations in exhaust emissions

No.	Benzene				Toluene				Xylene			
	2-stroke		4-stroke		2-stroke		4-stroke		2-stroke		4-stroke	
	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm
1	188.99	59.15	70.61	22.10	474.58	125.95	289.36	76.79	82.88	19.08	82.94	19.10
2	248.66	77.83	95.82	29.99	662.77	175.90	352.32	93.50	94.84	21.84	67.99	15.66
3	609.46	190.76	104.77	32.79	1112.18	295.17	368.56	97.81	151.87	34.97	123.89	28.53
4	382.38	119.69	148.67	46.53	946.36	251.16	394.20	104.62	181.14	41.72	97.82	22.53
5	434.89	135.12	X	X	1008.31	267.60	X	X	183.41	42.24	X	X
6	446.36	139.71	X	X	1364.62	362.17	X	X	255.29	58.79	X	X
7	286.89	89.80	X	X	1334.38	354.14	X	X	242.48	55.84	X	X
Mean	371.09	116.15	104.57	32.85	986.17	261.73	351.11	93.18	170.27	39.21	39.16	21.45
SD	142.55	44.62	32.52	10.18	328.82	87.26	44.63	11.84	66.33	15.27	23.83	5.48
SE	53.87	16.86	16.26	5.09	124.28	32.98	22.31	5.92	25.07	5.77	11.91	2.74
Range	420.47	131.61	78.06	24.43	890.03	236.21	104.84	27.82	172.41	39.70	55.89	12.87
Variance	20320.6	1990.91	1056.11	103.67	108122	7615.83	1992.01	140.31	4399.85	233.37	568.02	30.13

Remark X = Nil data

Table 4.1 The detail data of BTX concentrations in exhaust emissions (continued)

	No.	Benzene				Toluene				Xylene			
		2-stroke		4-stroke		2-stroke		4-stroke		2-stroke		4-stroke	
		mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm
MO DER ATE	1	377.44	118.14	54.97	17.20	725.54	192.55	167.40	44.42	33.47	7.710	53.98	12.43
	2	255.19	79.87	18.19	5.69	588.36	156.15	62.09	16.48	74.77	17.22	12.18	2.80
	3	215.46	67.44	93.31	29.20	377.35	100.14	185.73	49.29	84.13	19.37	28.11	6.47
	4	276.78	86.63	82.75	25.90	781.35	207.37	128.02	33.97	172.60	39.75	29.23	6.73
	5	478.30	149.71	173.45	54.29	1113.25	295.45	336.64	89.34	195.62	45.05	51.12	11.77
	6	437.21	136.85	162.90	50.99	1088.28	288.83	150.04	39.82	224.11	51.61	30.33	6.98
	7	298.61	93.46	X	X	756.13	200.67	X	X	114.50	26.37	X	X
	8	403.38	126.26	X	X	988.08	262.23	X	X	145.25	33.45	X	X
	9	286.02	89.52	X	X	784.67	208.25	X	X	116.17	26.75	X	X
	10	439.49	137.56	X	X	1077.10	285.86	X	X	166.67	38.38	X	X
	Mean	346.79	108.55	97.60	30.55	828.01	219.75	171.65	45.55	132.73	30.57	34.16	7.86
	SD	91.14	28.52	60.62	18.97	239.68	63.61	91.44	24.27	59.05	13.60	15.74	3.62
	SE	28.82	9.02	24.75	7.74	75.79	20.11	37.33	9.90	18.67	4.30	6.42	1.48
	Range	262.84	82.27	155.25	48.59	735.90	195.30	274.54	72.86	190.63	43.90	41.80	9.62
Variance	8306.95	813.87	3675.73	360.13	57444.6	4046.37	8362.37	589.01	3487.06	184.96	247.89	13.14	

Remark X = No data

Table 4.1 The detail data of BTX concentrations in exhaust emissions (continued)

No.	Benzene				Toluene				Xylene			
	2-stroke		4-stroke		2-stroke		4-stroke		2-stroke		4-stroke	
	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm
1	252.67	79.09	42.20	13.21	688.05	182.61	149.48	39.67	151.47	34.88	32.09	7.39
2	267.00	83.57	36.34	11.37	983.44	261.00	101.72	26.99	221.50	51.01	32.50	7.48
3	223.64	70.00	41.33	12.93	701.12	186.07	134.92	35.80	195.40	45.00	55.71	12.83
4	279.39	87.45	40.55	12.69	696.32	184.80	86.76	23.02	127.06	29.26	28.32	6.52
5	255.87	80.09	30.97	9.69	722.93	191.86	88.04	23.36	131.34	30.24	41.11	9.46
6	349.23	109.31	56.18	17.58	890.95	236.45	186.50	49.49	139.85	32.20	36.62	8.43
7	286.55	89.69	15.00	4.69	511.91	135.86	17.46	4.63	36.42	8.39	4.58	1.05
8	240.87	75.39	X	X	305.92	81.45	X	X	36.17	8.33	X	X
9	252.34	78.98	X	X	854.48	226.78	X	X	124.42	28.65	X	X
10	251.27	78.65	X	X	909.44	241.36	X	X	134.79	31.04	X	X
Mean	265.88	83.22	37.51	11.74	726.56	192.82	109.27	29.00	129.84	29.90	32.99	7.59
SD	34.38	10.76	12.55	3.92	202.22	53.67	54.28	14.40	58.53	13.48	15.41	3.54
SE	10.87	3.40	4.74	1.48	63.94	16.97	20.51	5.44	18.50	4.26	5.82	1.34
Range	125.59	39.31	41.18	12.89	676.51	179.54	169.03	44.86	185.33	42.68	51.12	11.77
Variance	1182.18	115.82	157.58	15.43	20893.8	2880.43	2947.00	207.57	3425.78	161.71	237.50	12.59

Remark: X = No data

The results in table 4.1 showed that the old 2-stroke motorcycles had average Benzene, Toluene and Xylene emission concentrations of 116.15 ppm, 261.73 ppm, and 39.21 ppm respectively. While the moderate age 2 stroke motorcycles had average Benzene, Toluene and Xylene emission concentrations of 108.55 ppm, 219.75 ppm and 30.57 ppm respectively. The last group of 2-stroke motorcycles, new motorcycles had Benzene 83.22 ppm , Toluene 192.82 ppm and Xylene 29.90 ppm in the exhaust.

The emission of old 4-stroke motorcycles contains Benzene 32.85 ppm, Toluene 93.18 ppm and Xylene 21.4 ppm . While, the moderate age 4-stroke motorcycles had Benzene 30.55 ppm, Toluene 45.55 ppm and Xylene 7.86 ppm in exhaust. The new 4-stroke motorcycles had concentrations of Benzene, Toluene and Xylene in exhaust which were 11.74 ppm, 29.00 ppm and 7.59 ppm respectively. The average emission concentrations of Benzene, Toluene and Xylene based on age and engine types are shown in table 4.2.

Table 4.2 Averages concentrations of BTX

Ages of motorcycle	Benzene(ppm)		Toluene(ppm)		Xylene(ppm)	
	2-stroke	4-stroke	2-stroke	4-stroke	2-stroke	4-stroke
Old	116.15	32.85	261.73	93.18	39.21	21.45
Moderate	108.55	30.55	219.75	45.55	30.57	7.86
New	83.22	11.74	192.82	29.00	29.90	7.59

4.3 Concentration of BTX in gasoline

The detail data of BTX concentration in gasoline is illustrated in table

Table 4.3 The detail data of BTX concentrations in exhaust and gasoline

No.	Benzene (ppm)				Toluene (ppm)				Xylene (ppm)			
	2-stroke		4-stroke		2-stroke		4-stroke		2-stroke		4-stroke	
	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline
1	59.15	13830.8	22.10	13922.7	125.95	74823.4	76.79	80687.5	19.08	38524.4	19.10	35217.8
2	77.83	8696.02	29.99	11632.8	175.90	17821.7	93.50	74307.9	21.84	42717.5	15.66	42036.3
3	190.76	17239.5	32.79	12989.9	295.17	88915.8	97.81	88171.5	34.97	40710.4	28.53	45319.0
4	119.69	9520.50	46.53	7413.11	251.16	78674.8	104.62	63515.2	41.72	39629.9	22.53	45351.3
5	136.12	13805.2	X	X	267.60	73918.3	X	X	42.24	35707.6	X	X
6	139.71	15876.1	X	X	362.17	85242.9	X	X	58.79	15136.7	X	X
7	89.80	9235.24	X	X	354.14	105146.	X	X	55.84	56854.9	X	X
Mean	116.15	12600.5	32.85	11489.6	261.73	74934.7	93.18	76670.5	39.21	38468.8	21.45	41981.1
SD	44.62	3446.54	10.18	2875.72	87.26	27359.9	11.84	10441.1	15.27	12345.6	5.48	4769.52
SE	16.86	1302.67	5.09	1437.86	32.98	10341.0	5.92	5220.57	5.77	4666.20	2.74	2384.76
Range	131.16	8543.50	24.43	6509.59	236.21	87324.4	27.82	24656.2	39.70	41718.1	12.87	10133.4

Remark: X = No data

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Table 4.3 The detail data of BTX concentrations in exhaust and gasoline (continued)

	No.	Benzene (ppm)				Toluene (ppm)				Xylene (ppm)			
		2-stroke		4-stroke		2-stroke		4-stroke		2-stroke		4-stroke	
		exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline
MO DER ATE	1	118.14	2831.07	17.20	9951.66	192.55	138687	44.42	90469.9	7.71	10856.1	12.43	56515.9
	2	79.87	4169.72	5.69	13844.7	156.15	75214.0	16.48	74370.7	17.22	48046.4	2.80	30855.3
	3	67.44	16507.9	29.20	15308.6	100.14	86167.5	49.29	77648.5	19.37	47876.9	6.47	17316.4
	4	86.63	19793.0	25.90	14359.3	207.37	100663	33.97	80756.1	39.75	17992.0	6.73	26060.7
	5	149.71	18964.6	54.29	4092.27	295.45	118749	89.34	76529.7	45.05	26514.0	11.77	43380.7
	6	136.85	7672.26	50.99	14765.7	288.83	133232	39.82	82147.7	51.61	83706.9	6.98	37410.2
	7	93.46	16437.5	X	X	200.67	96168.3	X	X	26.37	23541.8	X	X
	8	126.26	14009.6	X	X	262.23	98963.5	X	X	33.45	47071.0	X	X
	9	89.52	12357.1	X	X	208.25	70619.8	X	X	26.75	33602.9	X	X
	10	137.56	11758.5	X	X	285.86	60854.0	X	X	38.38	13191.2	X	X
	Mean	108.55	12450.1	30.55	12053.7	219.75	97932.0	45.55	80320.5	30.57	35239.9	7.86	35256.5
	SD	28.52	5921.33	18.97	4342.26	63.61	26092.5	24.27	5717.46	13.60	22127.4	3.62	13772.3
	SE	9.02	1872.49	7.74	1772.72	20.11	8251.18	9.90	2334.14	4.30	6997.30	1.48	5622.52
	Range	82.27	16961.9	48.59	11216.3	195.30	77833.2	72.86	16099.1	43.90	72850.8	9.62	39199.4

Remark: X = No data

Table 4.3 The detail data of BTX concentrations in exhaust and gasoline (continued)

No.	Benzene (ppm)				Toluene (ppm)				Xylene (ppm)			
	2-stroke		4-stroke		2-stroke		4-stroke		2-stroke		4-stroke	
	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline	exhaust	gasoline
1	79.09	17226.8	13.21	15639.0	182.61	110612.	39.67	84486.1	34.88	34643.5	7.39	28912.2
2	83.57	13922.7	11.37	4084.43	261.00	80687.5	26.99	119062.	51.01	35217.8	7.48	53500.4
3	70.00	15519.1	12.93	11559.8	186.07	85304.1	35.80	67103.4	45.00	27932.2	12.83	29994.1
4	87.45	14815.2	12.69	15246.3	184.80	74724.3	23.02	100661.	29.26	22100.5	6.52	39382.9
5	80.09	18711.3	9.69	13764.3	191.86	97054.7	23.36	87602.2	30.24	15507.8	9.46	35703.7
6	109.31	11187.7	17.58	8975.44	236.45	79367.1	49.49	58838.8	32.20	42542.7	8.43	36887.8
7	89.69	13282.7	4.69	10077.3	135.86	74462.0	4.63	58417.6	8.39	25003.9	1.05	37823.8
8	76.39	15275.7	X	X	81.45	78879.4	X	X	8.33	21197.2	X	X
9	76.98	15419.4	X	X	226.78	83288.0	X	X	28.65	19000.6	X	X
10	78.65	16472.0	X	X	241.36	87985.1	X	X	31.04	20197.9	X	X
Mean	83.22	15183.3	11.74	11335.2	192.82	85236.5	29.00	82310.3	29.90	26334.4	7.59	37457.8
SD	10.76	2101.91	3.92	4072.17	53.67	11141.1	14.40	22632.0	13.48	8614.99	3.54	8096.72
SE	3.40	664.684	1.48	1539.13	16.97	3523.15	5.44	8554.09	4.26	2724.30	1.34	3060.27
Range	39.31	7523.60	12.89	11554.6	179.54	36150.7	44.86	60645.0	42.68	27034.9	11.77	24588.2

Remark: X = No data

The ratio of Benzene, Toluene and Xylene in gasoline and exhaust from 2 and 4-stroke motorcycles were shown in table 4.4 and 4.5.

Table 4.4 Ratios of the average gasoline concentrations to the exhaust concentrations of Benzene, Toluene and Xylene for 2-stroke motorcycles.

Age of engine	2-stroke motorcycle								
	Benzene (ppm)			Toluene (ppm)			Xylene (ppm)		
	Gasoline	Exhaust	Ratio in gasoline/exhaust	Gasoline	Exhaust	Ratio in gasoline/exhaust	Gasoline	Exhaust	Ratio in gasoline/exhaust
Old	12600	116	108	74934	261	287	38468	39	986
Moderate	12450	108	115	97932	219	447	35239	30	1174
New	15183	83	183	85236	192	444	26334	29	908

Table 4.5 Ratios of the average gasoline concentrations to the exhaust concentrations of Benzene, Toluene and Xylene for 4-stroke motorcycles.

Age of engine	4-stroke motorcycle								
	Benzene (ppm)			Toluene (ppm)			Xylene (ppm)		
	Gasoline	Exhaust	Ratio in gasoline/exhaust	Gasoline	Exhaust	Ratio in gasoline/exhaust	Gasoline	Exhaust	Ratio in gasoline/exhaust
Old	11489	32	359	76670	93	824	41981	21	1999
Moderate	12053	30	402	80320	45	1785	35256	7	5036
New	11335	11	1030	82310	29	2838	37457	7	5351

The detail from table 4.4 and 4.5 showed that the 4-stroke motorcycle emitted the lower level of hydrocarbons than 2-stroke. For instance, It has to use the benzene in gasoline 1030 ppm to produce 1 ppm of Benzene in exhaust in new 4-stroke motorcycle. While, the 2-stroke motorcycle use only 183 ppm of Benzene in gasoline to produce 1 ppm of Benzene in exhaust. It means that efficiency of pollutant production in 2-stroke motorcycle was greater than the 4-stroke motorcycle. Additionally, The table 4.4 and 4.5 were shown that the old motorcycle in both 2 and 4-stroke motorcycles released the hydrocarbons higher than the new ones.

For example, the 1 ppm Benzene in exhaust of new 2-stroke motorcycle came from 183 ppm in gasoline but Benzene 1 ppm in exhaust of old 2-stroke motorcycle came from 108 ppm in gasoline. As the same way, it is observed that new 4-stroke motorcycle emitted Benzene 1 ppm in exhaust which came from 1030 ppm in gasoline while Benzene 1 ppm in old 4-stroke exhaust which came from 359 ppm in gasoline. This finding showed that the pollutant production of the old engines is much greater than the new motorcycles.

4.4 Engine type and BTX concentration

The Benzene, Toluene and Xylene emission concentrations for all 2-stroke motorcycles were found to be in the ranges of 59.15-190.76, 81.45-362.17 and 7.71-58.79 ppm respectively. Whereas all 4-stroke motorcycles, the Benzene, Toluene and Xylene concentrations were in the ranges of 4.69-54.29, 4.63-104.62, and 1.05-28.53 ppm respectively. The average emissions of Benzene, Toluene and Xylene concentrations from the 2-stroke motorcycle were much higher (approximately 3-4 times) than the emissions from 4-stroke motorcycle due to the different of their combustion process. The lost of part of

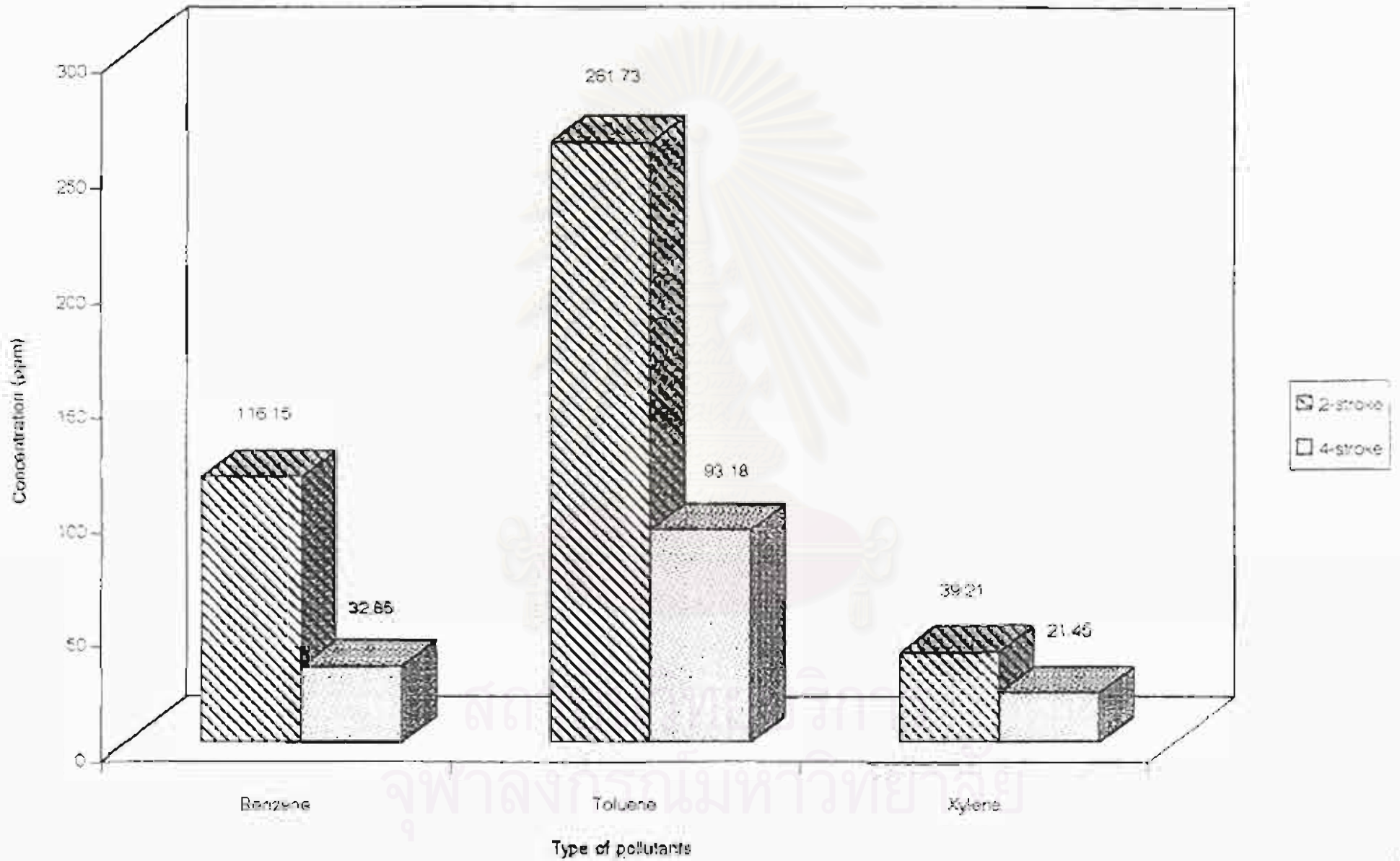
the unburned fuel out the exhaust during scavenging is the major reason for the very high hydrocarbon emissions characteristic of 2-stroke motorcycle engine. The other major reason for high HC emissions from 2-strokes is their tendency to misfire under low load condition.

The lowest concentrations of Benzene, Toluene and Xylene in this study were found in 4-stroke motorcycles of all engine ages (see in figure 4.1,4.2 and 4.3), because they had more completed combustion process than 2-stroke motorcycles.



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Figure 4.1 BTX's concentration of old motorcycles



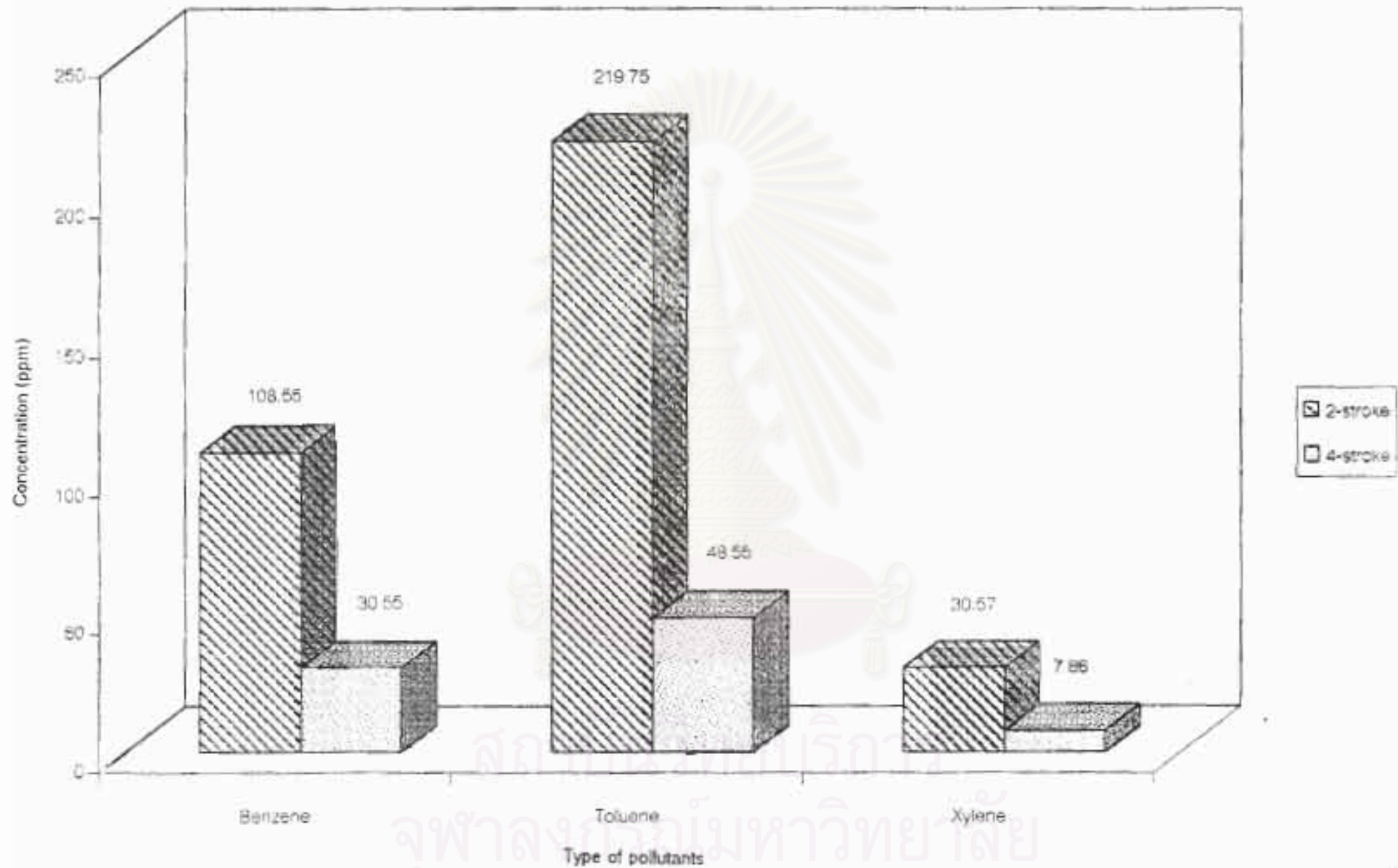
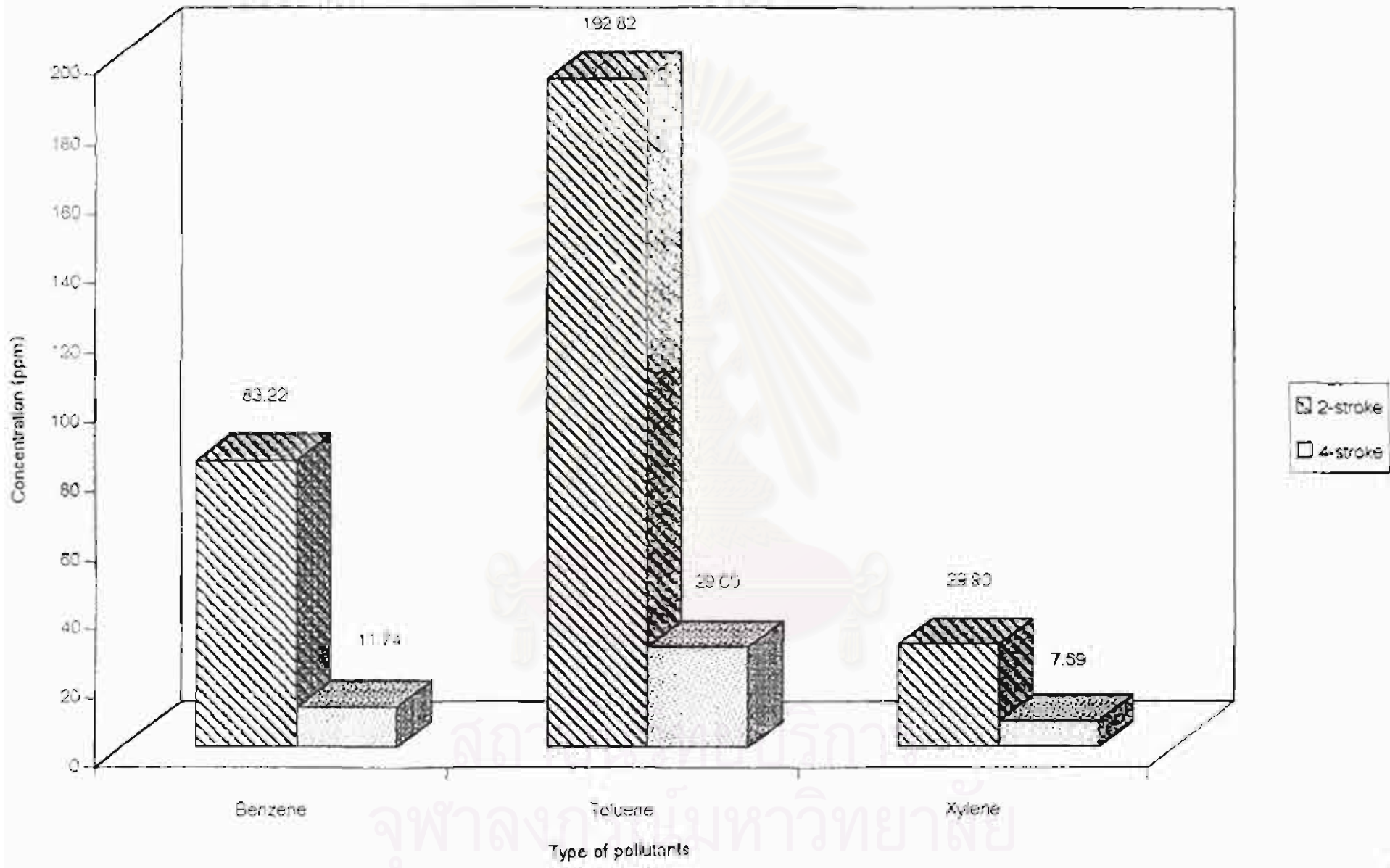


Figure 4.3 BTX's concentration of new motorcycles



4.5 Engine age and BTX concentration

The Benzene, Toluene and Xylene emission concentrations for old motorcycle groups were found to be in the range of 22.10-190.76, 76.79-362.17 and 15.66-58.79 ppm, respectively. The moderate age motorcycle groups were found to be in the range of 5.69-149.71, 164.81-295.45 and 2.80-51.61 ppm, respectively. While the new motorcycle groups were found to be in the range of 4.69-109.31, 4.63-261.00 and 1.05-51.01 ppm, respectively.

Figure 4.4, 4.5 and 4.6 presented that the average Benzene, Toluene and Xylene emission concentrations in the older motorcycle are greater than the newer motorcycles. From the results, it can be noted that the concentration of Benzene, Toluene and Xylene in old motorcycles (more than 10 years old) are the highest and the moderate age motorcycles had Benzene, Toluene and Xylene emission concentration higher than new motorcycle groups. This result showed the possibility of engine's age had effected on pollutant concentrations in motorcycle exhaust.

Figure 4.4 Benzene concentration of 2 and 4 stroke motorcycle

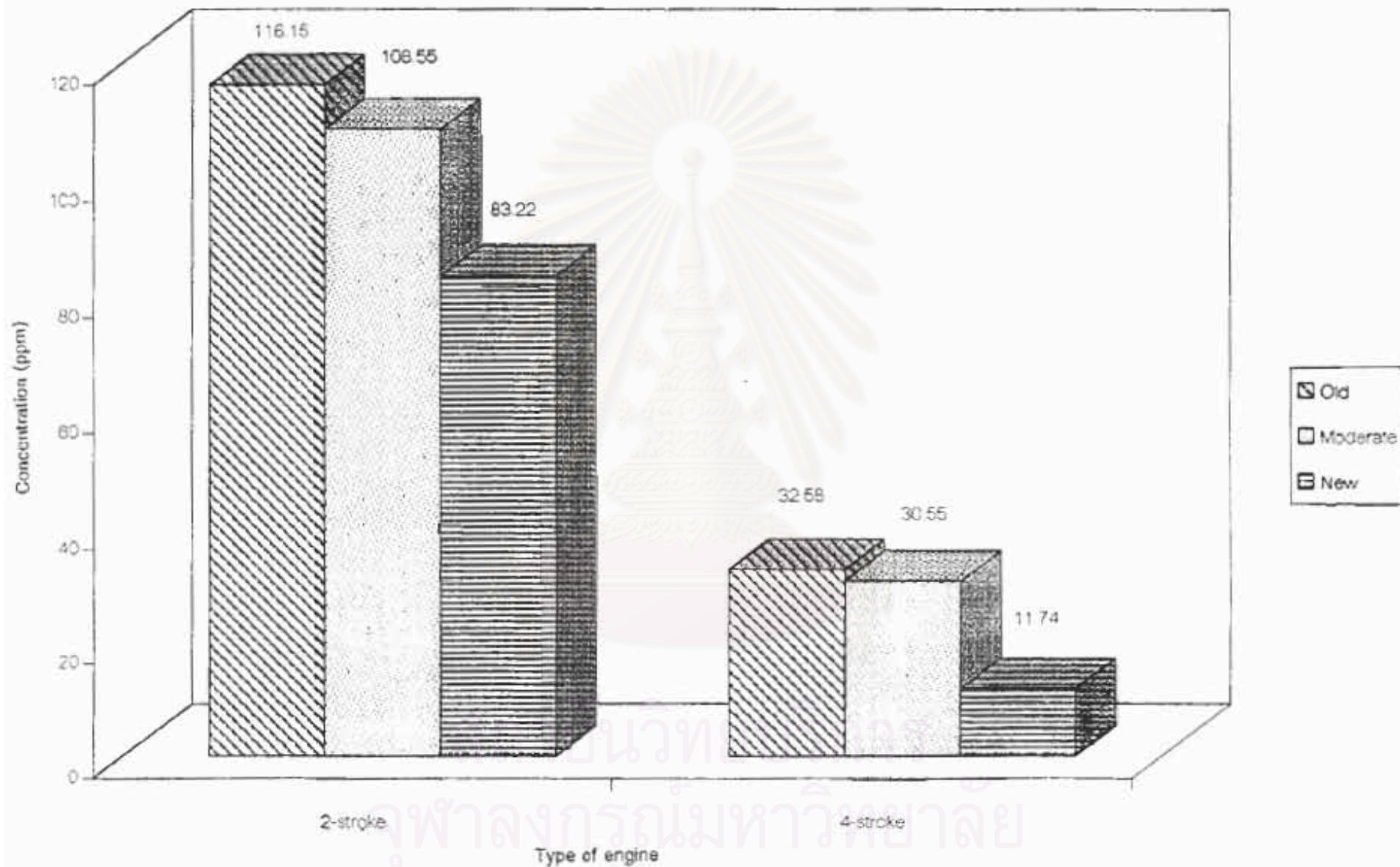
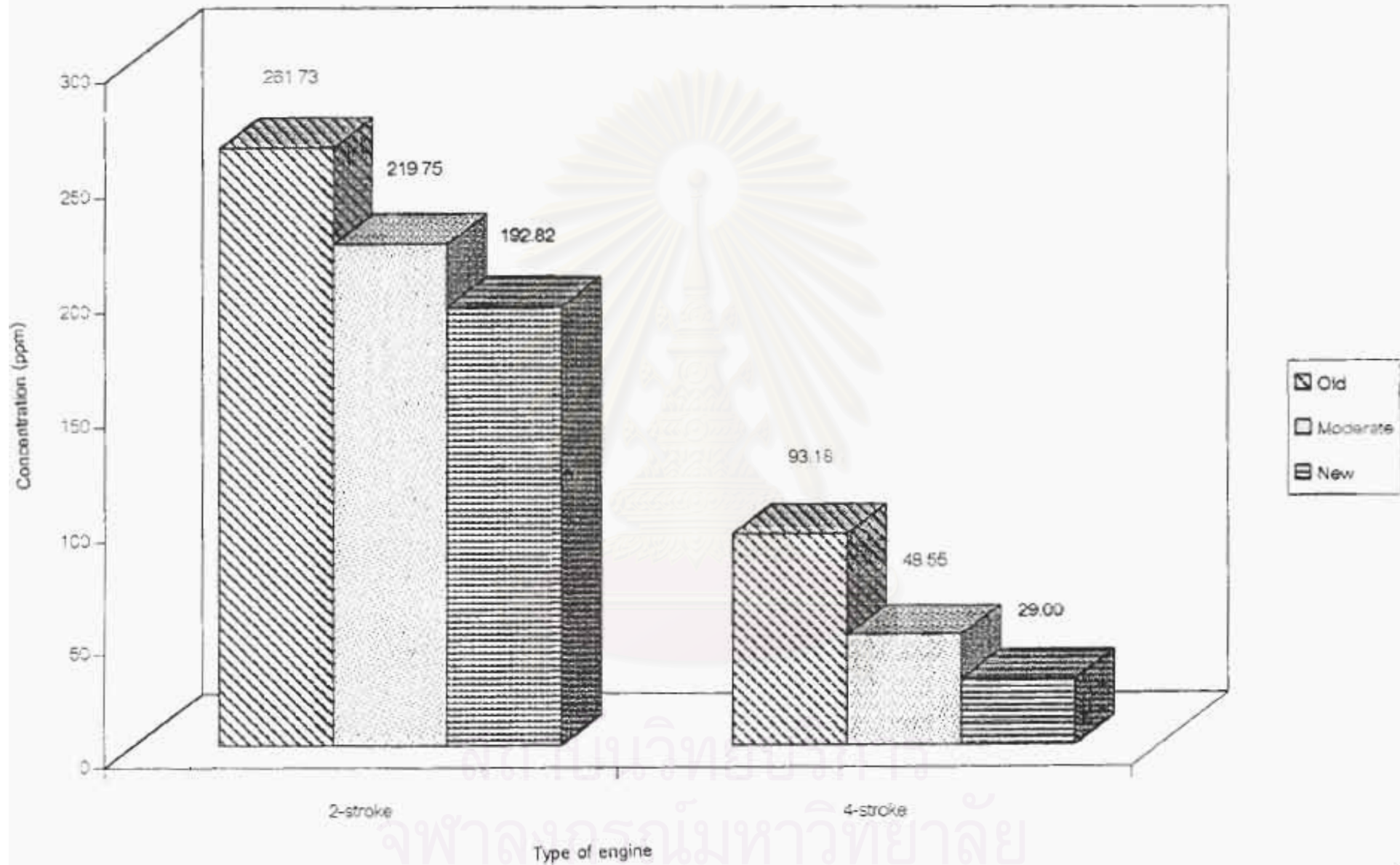
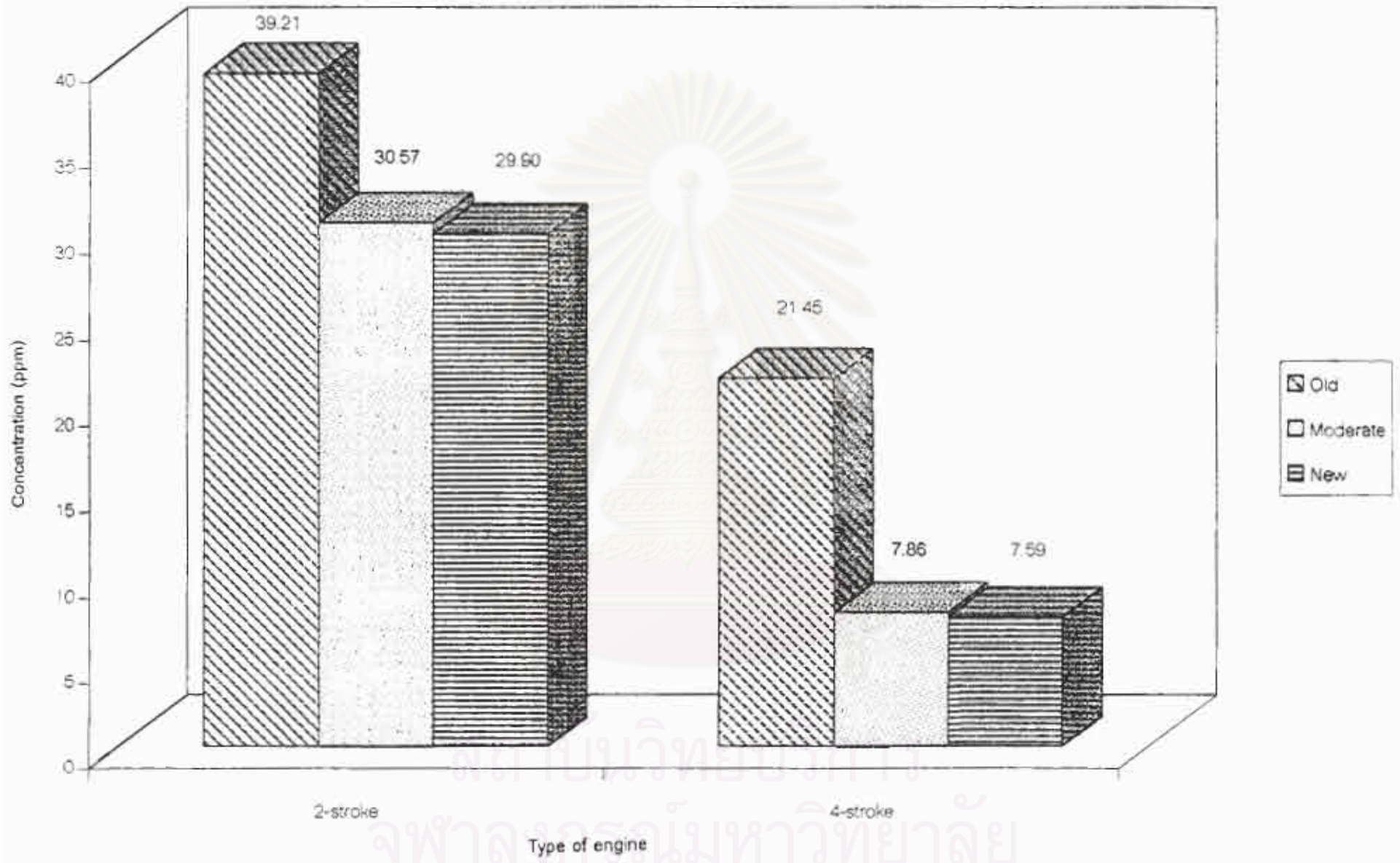


Figure 4.5 Toluene concentration of 2 and 4 stroke motorcycle





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4.6 Effect of engine type and engine age on BTX in exhaust

In this study, The statistical two-way analysis of variance (2-way ANOVA) was used to analyze the influence of engine types (2 and 4-stroke) and age of engine (old, moderate and new) on BTX concentration in motorcycle emission. The statistical programming, SPSS version 6.0 for MS windows, was used to examine the interaction of 2 factors (engine types and engine ages) on the concentration of BTX in emission. The null hypothesis is that

$$H_0 : \mu_{A1} = \mu_{A2} = \mu_{A3}$$

$$H_0 : \mu_{B1} = \mu_{B2}$$

μ_A = Mean concentration of pollutant from factor one (engine ages)

μ_B = Mean concentration of pollutant from factor two (engine types)

and the alternative hypothesis is :

$$H_1 : \text{At least one mean is different}$$

If the results indicate that null hypothesis was fail to reject it means that no interaction between the types of engine (2 and 4-strokes) and ages of engine (old, moderate, new) on BTX concentration in emission. The data for this study is presented in table 4.7

Table 4.7 Influencing of types and ages of engine on emission

	engine	age	benzene	toluene	xylene
1	1	1	59.16	125.96	19.09
2	1	1	77.83	175.90	21.84
3	1	1	190.77	295.17	34.98
4	1	1	119.69	251.17	41.72
5	1	1	136.13	267.61	42.24
6	1	1	139.72	362.17	58.80
7	1	1	89.80	354.15	55.85
8	1	2	118.15	192.56	7.71
9	1	2	79.88	156.15	17.22
10	1	2	67.44	100.15	19.38
11	1	2	86.64	207.37	39.75
12	1	2	149.72	295.46	45.06
13	1	2	136.85	288.83	51.62
14	1	2	93.47	200.68	26.37
15	1	2	126.27	262.24	33.45
16	1	2	89.53	208.25	26.76
17	1	2	137.57	285.86	38.39
18	1	3	79.09	182.61	34.89
19	1	3	83.58	261.01	51.02
20	1	3	70.00	186.08	45.00
21	1	3	87.45	184.81	29.27
22	1	3	80.09	191.87	30.25
23	1	3	109.31	236.46	32.21
24	1	3	89.70	135.86	8.39
25	1	3	75.40	81.46	8.33
26	1	3	78.99	226.78	28.66
27	1	3	78.65	241.37	31.04
28	2	1	22.10	76.80	19.10
29	2	1	29.99	93.51	15.66
30	2	1	32.80	97.82	28.53
31	2	1	46.54	104.62	22.53
32	2	2	17.21	44.43	12.43

	engine	age	benzene	toluene	xylene
33	2	2	5.70	16.48	2.81
34	2	2	29.21	49.30	6.47
35	2	2	25.90	33.98	6.73
36	2	2	54.29	89.35	11.78
37	2	2	50.99	39.82	6.99
38	2	3	13.21	39.67	7.39
39	2	3	11.38	27.00	7.49
40	2	3	12.94	35.81	12.83
41	2	3	12.70	23.03	6.52
42	2	3	9.70	23.37	9.47
43	2	3	17.59	49.50	8.43
44	2	3	4.70	4.64	1.06

Remark : Engine Type 1 = 2-stroke motorcycle

Age 1 = old motorcycle

2 = 4-stroke motorcycle

Age 2 = moderate age motorcycle

Age 3 = new motorcycle

In this study, at the significant level (α) 0.05, the statistical results of the influence of engine type factor and age of engine factor on Benzene, Toluene and Xylene concentration in motorcycle emission from SPSS programming are presented in table 4.8,4.9 and 4.10, respectively.

For the age of engine factor, it is shown that the "Sig. of F" value of the "AGE" if the Sig. of F value is higher than the significant level (α) 0.05. It is mean that the null hypothesis is accepted:

$$H_0 : \mu_{A1} = \mu_{A2} = \mu_{A3}$$

It can be concluded that the mean concentration of pollutant from individual group of factor one has no difference at significant level (α) 0.05.

Table 4.8 Analysis of Variance of Benzene

. SPSS for MS WINDOWS Release 6.0

* * * C E L L M E A N S * * *

BENZENE
by AGE
ENGINE

Total Population

71.09
(44)

AGE

1	2	3
85.87	79.30	53.79
(11)	(16)	(17)

ENGINE

1	2
101.14	23.35
(27)	(17)

ENGINE

	1	2
AGE		
1	116.16	32.86
	(7)	(4)
2	108.55	30.55
	(10)	(6)
3	83.23	11.74
	(10)	(7)

* * * A N A L Y S I S O F V A R I A N C E * * *

BENZENE
by AGE
ENGINE

EXPERIMENTAL sums of squares
Covariates entered FIRST

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	69855.270	3	23285.090	39.296	.000
AGE	6723.247	2	3361.623	5.673	.007
ENGINE	61288.144	1	61288.144	103.430	.000
2-way Interactions	229.241	2	114.620	.193	.825
AGE ENGINE	229.241	2	114.620	.193	.825
Explained	70084.511	5	14016.902	23.655	.000
Residual	22517.070	38	592.554		
Total	92601.581	43	2153.525		

Like the engine age factor, the engine type factor was focused on the "Sig. of F" value of the "ENGINE" if the Sig. of F value is higher than the significant level (α) 0.05. It is mean that the null hypothesis is accepted:

$$H_0 : \mu_{B1} = \mu_{B2}$$

The null hypothesis was illustrated that the concentration of pollutant from factor two had no difference at significant level (α) 0.05.

In this study, the Sig. of F value from factor one (engine ages) in the ANOVA of Benzene (table 4.8) is 0.007. This value lower than the significant level (α) 0.05 means that the null hypothesis is rejected.

Like the factor one, the ANOVA of Benzene (table 4.8) showed the factor two (2 and 4 stroke engine) had the Sig. of F value 0.000 lower than the significant level (α) 0.05 means that the null hypothesis is rejected.



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SPSS for MS WINDOWS Release 6.0

* * * C E L L M E A N S * * *

TOLUENE
by AGE
ENGINE

Total Population

	154.71 (44)		
AGE	1	2	3
	200.44 (11)	154.43 (16)	125.37 (17)
ENGINE	1	2	
	220.67 (27)	49.95 (17)	
	ENGINE		
		1	2
AGE	1	261.73 (7)	93.19 (4)
	2	219.75 (10)	45.56 (6)
	3	192.83 (10)	29.00 (7)

* * * A N A L Y S I S O F V A R I A N C E * * *

TOLUENE
by AGE
ENGINE

EXPERIMENTAL sums of squares
Covariates entered FIRST

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	334046.910	3	111348.970	37.562	.000
AGE	30015.185	2	15007.592	5.063	.011
ENGINE	296406.933	1	296406.933	99.988	.000
2-way Interactions	211.087	2	105.544	.036	.965
AGE ENGINE	211.087	2	105.544	.036	.965
Explained	334257.997	5	66851.599	22.551	.000
Residual	112647.799	38	2964.416		
Total	446905.797	43	10393.158		

Table 4.10 Analysis of Variance of Xylene

SPSS for MS WINDOWS Release 6.0

* * * C E L L M E A N S * * *

XYLENE
by AGE
ENGINE

Total Population

	24.22		
	(44)		
AGE			
	1	2	3
	32.76	22.06	20.72
	(11)	(16)	(17)
ENGINE			
	1	2	
	32.57	10.95	
	(27)	(17)	
		ENGINE	
		1	2
AGE			
	1	39.22	21.46
	(7)	(4)	
	2	30.57	7.87
	(10)	(6)	
	3	29.91	7.60
	(10)	(7)	

* * * A N A L Y S I S O F V A R I A N C E * * *

XYLENE
by AGE
ENGINE

EXPERIMENTAL sums of squares
Covariates entered FIRST

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	5825.890	3	1941.963	14.962	.000
AGE	953.994	2	476.997	3.675	.035
ENGINE	4740.834	1	4740.834	36.527	.000
2-way Interactions	43.425	2	21.712	.167	.847
AGE ENGINE	43.425	2	21.712	.167	.847
Explained	5869.315	5	1173.863	9.044	.000
Residual	4932.024	38	129.790		
Total	10801.339	43	251.194		

It was found that the Sig. of F value from factor one (engine age) in the ANOVA of Toluene (table 4.9) and Xylene (table 4.10) are 0.011 and 0.035, respectively. The Sig. of F value from factor one (engine age) of both Toluene and Xylene are less than the significant level (α) 0.05, it indicated that the null hypothesis is rejected.

Like the factor one, the ANOVA of Toluene (table 4.9) and Xylene (table 4.10) showed that the factor two (2 and 4-stroke engines) both of them had the Sig. of F value 0.000. There are less than the significant level (α) 0.05. It can be interpreted that the null hypothesis is rejected.

This finding showed that the age of engine (old, moderate and new motorcycles) effected on the motorcycle pollutant emission. The older motorcycle emits BTX components in exhaust gas higher than the new one. In addition, the motorcycle pollutant emission is depending on the engine type (2 and 4-stroke engines). The concentrations of BTX components in exhaust gas from 2-stroke engine motorcycles are higher than the 4-stroke engine motorcycles.

The relationship of type and age of motorcycle on the pollutant in exhaust emission are in line with other studies.

Phong (1999), studied on the air pollutant levels associated with traffic volume. The study revealed that concentration emission from 2-stroke is higher than 4-stroke engine vehicle. Thai Motorcycle Manufactures Group (1990) cited in Phong (1999), that the unique mechanism of the 2-stroke engine which

used fresh mixtures to scavenge the burnt mixtures, emit hydrocarbon 6-8 times large than of the 4-stroke engine.

In 1992, the Ministry of Science, Technology and Environment of Malaysia (1992) cited in Weaver (1993) studied on the possibility of banning the use of 2-stroke motorcycles in Malaysia in order to reduce the pollution. But it would be very difficult to implement a ban on two-stroke motorcycle, as they are very popular and widely used by the public, and most users are from low-income groups.

Suksomsankh (1991), studied on the exhaust gas from gasoline engines and found that the concentrations of hydrocarbon components in gas samples from 2-stroke engine motorcycles were higher than the 4-stroke engine motorcycles. Moreover, he also found that Benzene, Toluene and Xylene which are strongly toxic to human health, were major aromatic hydrocarbons found in gas samples from both 2 and 4-stroke engine motorcycle.

Muttamara and Leong (2000) measured the exhaust emission from gasoline-powered motor vehicles in Bangkok. The vehicle samples were performed on chassis dynamometer. A fleet of 10 vehicles of different model years and manufacturers were selected to measure the air pollutants in the exhaust effluent. The study revealed that the hydrocarbon emissions averaged of 1.82-2.98 g/km for 1990-1992 cars decreased to 0.75-1.88 g/km for 1994-1995 cars. This result indicated that there was a significant increase in air pollutant emission with increasing car mileage and model year.

4.7 Comparison with previous study

Table 4.11 showed that the 2-stroke motorcycle emitted exhaust gas pollutant at idle condition higher than 4-stroke. In order to compare the exhaust gas emitted from 2 and 4 stroke motorcycles, the data from previous study were used in this study.

Table 4.11 Exhaust emission compares with the previous study

Concentration (ppm)	Results from this study		Results from previous study*	
	2 stroke	4 stroke	2 stroke	4 stroke
Benzene	307.93	75.15	355.51	145.48
Toluene	674.32	170.75	866.11	468.80
Xylene	99.69	36.92	842.87	488.58

* Study by Suksomsankh (1991)

This table provides the comparison of exhaust gas emission at idle condition. The comparison between this study and Suksomsankh study (1991) showed that there was a fall of 13% - 92% in the exhaust concentrations of Benzene, Toluene and Xylene in 2 and 4-stroke motorcycle.

The low hydrocarbon concentration in exhaust emission may be the cause by the reformulated gasoline have introduced to the public by the new Thai Industrial Standard since 1994, and the new standard of motorcycle emission control level 4 came to force in the year 1998.

4.8 Effect of motorcycle emission on concentration of BTX in ambient air

Duffy et.al (1998) mentioned that motor vehicles are recognized as a major contributor to the atmospheric burden of hydrocarbon in urban areas, and as such have been associated with serious environmental problems such as photochemical smog in addition to deleterious effect on health. Several of studies concerned about the hydrocarbon ambient air pollution that came from motor vehicles.

For instance, Moschonas (1996) investigated C_3 - C_{10} hydrocarbons in the atmosphere of Athens, Greece. In this study found that the aromatic fraction predominates with maximum Benzene and toluene concentrations of 19 and 39 ppbv, respectively. Through comparison with NMHC emission profiles of other cities, it is inferred that vehicle emission was the main sources of the observed NMHC. Otherwise, the study of Siriroughudomporn (1997) reviewed that the highest benzene and toluene concentration were found at Yaowaraj sampling station, Bangkok Thailand that have heavily congested traffic. And also found that benzene and toluene concentrations for weekday and daytime were considerably higher than weekend and nighttime respectively.

Muttamara and Leong (2000) monitor and assess the exhaust emission in Bangkok street air. They found that the 8-hour average concentrations of Benzene and Toluene in ambient air of the study area were found to be 15.07-50.20 and 25.76-130.95 $\mu\text{g}/\text{m}^3$, respectively. The finding revealed that there was a correlation between the average air pollutant concentrations with average traffic speed in each traffic zone of Bangkok metropolitan region (BMR).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The exhaust gases from 44 samples of 2 and 4-stroke motorcycles are collected by Vacuum box at idle condition. The samples are analyzed for three air pollution parameters (Benzene, Toluene and Xylene). The motorcycles were classified into three groups as follow: old, moderate age and new motorcycles. The conclusions of the study can be summarized as follows:

1. The average concentrations of Benzene, Toluene and Xylene in exhaust emission of 2-stroke motorcycle is about 3-4 times larger than that of the 4-stroke motorcycle.
2. Benzene, Toluene and Xylene concentration in exhaust emission of the older motorcycle is higher than the newer motorcycle.
3. The comparison between this study and Suksomsankh study (1991) showed that there was a fall of 13% - 92% in the exhaust concentrations of Benzene, Toluene and Xylene in 2 and 4-stroke motorcycle.
4. Both type and age of engine have much influenced on Benzene, Toluene and Xylene concentration in motorcycle emission.



5.2 RECOMMENDATIONS FOR FURTHER STUDY

1. To find out the concentration of hydrocarbons in vehicle emission on Chassis Dynamometer for real driving pattern.
2. To examine the effect of other vehicles on roadside ambient air such as diesel vehicles.
3. To find out the concentration of Benzene, Toluene and Xylene in ambient air.
4. To find out the concentrations of Benzene, Toluene and Xylene in indoor air (in house) near by the street.
5. To examine the concentration of total hydrocarbon in exhaust emission
6. To examine the concentrations of Benzene, Toluene and Xylene at different vehicle operating condition.

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APPENDIX A

The interesting web site about exhaust gas and gasoline from internet

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[Http://www.ehpnet1.niehs.nih.gov/docs/1996/suppl-6/bezabeh.html](http://www.ehpnet1.niehs.nih.gov/docs/1996/suppl-6/bezabeh.html)

Does Benzene Cause Multiple Myeloma? An Analysis of the Published Case-Control Literature

Two case series and two epidemiological studies in the 1970s and 1980s suggested that benzene exposure might be a risk factor for multiple myeloma. An analysis has now been conducted of the published population-based and hospital-based case-control studies published through mid-1995 that permit examination of the relationship between multiple myeloma and benzene exposure or surrogates for benzene exposure. No increased association was found between multiple myeloma and benzene exposure or exposure to chemical groups that included benzene. The odds ratios from these analyses approximated 1.0. Exposures to petroleum products and employment in petroleum-related occupations did not appear to be risk factors for multiple myeloma. Cigarette smoking, as a surrogate of benzene exposure, was not found to be associated with multiple myeloma, while some studies of products of combustion described as "engine exhaust" did show a significant association with multiple myeloma. In toto, the population-based and hospital-based case-control literature indicated that benzene exposure was not a likely causal factor for multiple myeloma. - Environ Health Perspect 104(Suppl 6):1393-1398 (1996)

And other interesting web sites

<http://www.ubavie.gv.at/publkationen/reports/r124s.htm>

<http://seasilver.threadnet.com/preventorium/petrol1.htm/petrol1>

<http://enviro.nfesc.nany.ril/esc425/VOL6NO2.txt>

APPENDIX B

Calculation of exhaust and gasoline concentrations

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1 Calculation for gasoline samples

1.1 The concentrations in mg/m^3 unit

The standard solutions, with Acetone 250 ml, Benzene 125 μl , Toluene 75 μl and Xylene 50 μl had a total volume as 250250 μl . The amounts of 1 μl standard solution and 1 μl gasoline sample were used to calculate for the concentration of each substance.

From $\text{Weight of substance (g)} = \text{Volume (cm}^3) \times \text{Density (g/cm}^3)$

Density of Benzene is 0.8787 g/cm^3

Density of Toluene is 0.8660 g/cm^3

Density of Xylene is 0.8647 g/cm^3

Std. Solⁿ 250250 μl has Benzene = 125 μl

Std. Solⁿ 1 μl has Benzene = $\frac{1 \times 125}{250250}$ μl

= 4.9950×10^{-4} μl

= 4.9950×10^{-7} ml

Weight of Benzene in Std. Solⁿ is = $(4.9950 \times 10^{-7}) \times 0.8787$

= 4.3891×10^{-7} g

= 4.3891×10^{-4} mg

On the same way, weight of Toluene and Xylene in standard solution can be found as:

Benzene	=	4.3891×10^{-4}	mg
Toluene	=	2.5954×10^{-4}	mg
Xylene	=	1.7227×10^{-4}	mg

When the standard solution or the gasoline samples, with Benzene, Toluene, and Xylene components were injected into the Injection port of Gas Chromatography (GC) at temperature 200°C . All hydrocarbon components were evaporated immediately and moved into the column by the carrier gas (N_2) in the state of gases. After detected by the Flame Ionization Detector (FID), the peak areas of Benzene, Toluene, and Xylene were shown as the chromatogram

If

1. Standard solution

Peak area of Benzene in standard solution is	=	X
Peak area of Toluene in standard solution is	=	Y
Peak area of Xylene in standard solution is	=	Z

2. The gasoline sample

Peak area of Benzene in the gasoline sample	=	X_1
Peak area of Toluene in the gasoline sample	=	Y_1
Peak area of Xylene in the gasoline sample	=	Z_1

The concentrations of Benzene in the gasoline sample were calculated by comparing with the Benzene in standard solution that know the exact concentration.

Thus

$$\text{Area of Std. Sol}^n \text{ X has benzene} = 4.3891 \times 10^{-4} \text{ mg}$$

$$\text{Area of gasoline sample } X_1 \text{ has benzene} = \frac{(4.3891 \times 10^{-4})}{X_1} \text{ mg}$$

X

$$\text{So, weight of Benzene in gasoline sample is} = \frac{(4.3891 \times 10^{-4})}{X_1} \times X_1 \text{ mg}$$

X

On the same way, it is found that :

$$\text{Weight of Benzene in gasoline sample} = \frac{(4.3891 \times 10^{-4})}{X_1} \times X_1 \text{ mg}$$

X

$$\text{Weight of Toluene in gasoline sample is} = \frac{(2.5954 \times 10^{-4})}{Y_1} \times Y_1 \text{ mg}$$

Y

$$\text{Weight of Xylene in gasoline sample is} = \frac{(1.7277 \times 10^{-4})}{Z_1} \times Z_1 \text{ mg}$$

Z

The amount of gasoline sample used is $1 \mu\text{l}$ and $1 \text{ m}^3 = 1 \times 10^9 \mu\text{l}$

That it means :

$$\text{Sample } 1 \mu\text{l, it has benzene} = \frac{(4.3891 \times 10^{-4})}{X_1} \times X_1 \text{ mg}$$

X

Sample 1 m^3 , it has benzene = $\frac{(4.3891 \times 10^{-4}) \times X_1 \times (1 \times 10^9)}{X}$ mg

$$= \frac{(4.3891 \times 10^5) \times X_1}{X} \text{ mg}$$

Concentration of Benzene in gasoline sample is $\frac{(4.3891 \times 10^5) \times X_1}{X} \text{ mg/m}^3$

X

On the same way, it can be defined that

Concentration of Toluene in gasoline sample is $\frac{(2.5954 \times 10^5) \times Y_1}{Y} \text{ mg/m}^3$

Y

Concentration of Xylene in gasoline sample is $\frac{(1.7277 \times 10^5) \times Z_1}{Z} \text{ mg/m}^3$

Z

1.2 Concentrations in ppm unit

The standard solutions, with Acetone 250 ml, Benzene 125 μl , Toluene 75 μl and Xylene 50 μl had a total volume as 250250 μl . The amounts of 1 μl standard solution and 1 μl gasoline sample were used to calculate for the concentration of each substance.

Std. Solⁿ 250250 μl has Benzene = 125 μl

Std. Solⁿ $1 \times 10^6 \mu\text{l}$, it has Benzene = $\frac{(1 \times 10^6)}{250250} \times 125$

μl

250250

$$= 499.50$$

μl

Concentrations of Benzene in standard solution is = 499.50 ppm

On the same way , it can be defined that

Concentrations of Toluene in standard solution is = 299.70 ppm

Concentrations of Xylene in standard solution is = 199.80 ppm

If

1. Standard solution

Peak area of Benzene in standard solution is = X

Peak area of Toluene in standard solution is = Y

Peak area of Xylene in standard solution is = Z

2. The gasoline sample

Peak area of Benzene in the gasoline sample = X_1

Peak area of Toluene in the gasoline sample = Y_1

Peak area of Xylene in the gasoline sample = Z_1

Area of Std. Solⁿ X has benzene = 499.50 ppm

Area of gasoline sample X_1 has benzene = $\frac{(499.50) \times X_1}{X}$ ppm

So,

$$\text{Concentration of Benzene in gasoline sample is} = \frac{(499.50) \times X}{X} \text{ ppm}$$

On the same way, it can be defined that

$$\text{Concentration of Toluene in gasoline sample is} = \frac{(299.70) \times Y}{Y} \text{ ppm}$$

$$\text{Concentration of Xylene in gasoline sample is} = \frac{(199.80) \times Z}{Z} \text{ ppm}$$

2 Calculation for exhaust gas samples

2.1 Concentrations in mg/m^3 unit

The standard solutions, with Acetone 250 ml, Benzene 125 μl , Toluene 75 μl and Xylene 50 μl , had a total volume as 250250 μl . The amounts of 1 μl standard solution and 1 ml exhaust gas sample were used to calculate for the concentration of each substance.

$$\text{From Weight of substance (g) = Volume (cm}^3\text{) } \times \text{ Density (g/cm}^3\text{)}$$

$$\text{Density of Benzene is } 0.8787 \text{ g/cm}^3$$

$$\text{Density of Toluene is } 0.8660 \text{ g/cm}^3$$

$$\text{Density of Xylene is } 0.8647 \text{ g/cm}^3$$

$$\text{Std. Sol}^{\text{D}} \text{ 250250 } \mu\text{l has Benzene} = 125 \mu\text{l}$$

$$\text{Std. Sol}^{\text{D}} \text{ 1 } \mu\text{l has Benzene} = \frac{1 \times 125}{250250} \mu\text{l}$$

$$= 4.9950 \times 10^{-4} \quad \mu\text{l}$$

$$= 4.9950 \times 10^{-7} \quad \text{ml}$$

$$\begin{aligned} \text{Weight of Benzene in Std. Sol}^n \text{ is} &= (4.9950 \times 10^{-7}) \times 0.8787 \\ &= 4.3891 \times 10^{-7} \quad \text{g} \\ &= 4.3891 \times 10^{-4} \quad \text{mg} \end{aligned}$$

On the same way, weight of Toluene and Xylene in standard solution can be found as :

$$\begin{aligned} \text{Benzene} &= 4.3891 \times 10^{-4} \quad \text{mg} \\ \text{Toluene} &= 2.5954 \times 10^{-4} \quad \text{mg} \\ \text{Xylene} &= 1.7227 \times 10^{-4} \quad \text{mg} \end{aligned}$$

When the standard solution or the exhaust gas samples with Benzene, Toluene, and Xylene components , were injected into the Injection port of Gas Chromatography (GC) at temperature 200 °C. All hydrocarbon components were evaporated immediately and moved into the column by the carrier gas (N₂) in the state of gases. After detected by the Flame Ionization Detector (FID), the peak areas of Benzene, Toluene, and Xylene were shown as the chromatogram

If

1. Standard solution

$$\text{Peak area of Benzene in standard solution is} = X$$

$$\text{Peak area of Toluene in standard solution is} = Y$$

Peak area of Xylene in standard solution is = Z

2. The exhaust gas sample

Peak area of Benzene in the exhaust gas samples = X_1

Peak area of Toluene in the exhaust gas samples = Y_1

Peak area of Xylene in the exhaust gas samples = Z_1

The concentrations of Benzene in the exhaust gas sample were calculated by comparing the Benzene in standard solution that we know the exact concentration .

Thus,

Area of Std. Solⁿ X has benzene = 4.3891×10^{-4} mg

Area of exhaust gas sample X_1 has benzene = $\frac{(4.3891 \times 10^{-4}) X_1}{X}$.mg

X

So,

Weight of Benzene in exhaust gas sample is = $\frac{(4.3891 \times 10^{-4}) X_1}{X}$. mg

X

On the same way, it is found that:

Weight of Toluene in exhaust gas sample is = $\frac{(2.5954 \times 10^{-4}) Y_1}{Y}$. mg

Y

$$\text{Weight of Xylene in exhaust gas sample is } = \frac{(1.7277 \times 10^{-4}) \times Z_{1-}}{Z} \text{ mg}$$

The amount of gasoline sample, we used is 1 ml and $1 \text{ m}^3 = 1 \times 10^6 \text{ ml}$

That it means :

$$\text{Sample 1 ml ,it has benzene } = \frac{(4.3891 \times 10^{-4}) \times X_{1-}}{X} \text{ mg}$$

$$\begin{aligned} \text{Sample } 1 \text{ m}^3 \text{ ,it has benzene } &= \frac{(4.3891 \times 10^{-4}) \times X_{1-} \times (1 \times 10^6)}{X} \text{ mg} \\ &= \frac{(438.91) \times X_{1-}}{X} \text{ mg} \end{aligned}$$

$$\text{Concentration of Benzene in exhaust gas is } \frac{(438.91) \times X_{1-}}{X} \text{ mg/m}^3$$

On the same way, it is found

$$\text{Concentration of Toluene in exhaust gas is } \frac{(259.54) \times Y_{1-}}{Y} \text{ mg/m}^3$$

$$\text{Concentration of Xylene in exhaust gas is } \frac{(172.77) \times Z_{1-}}{Z} \text{ mg/m}^3$$

2.2 Concentrations in ppm unit

From the gas's law defined that 1 g - mole of vapor or gas has volume 22.4 liters at 20 °C and 760 mmHg (1 atm).

At the room temperature (25 °C) and, the volume of vapor is 24.45 liters.

(From : gas's law $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$)

Molecular weight of Benzene = 78.11

Molecular weight of Toluene = 92.13

Molecular weight of Xylene = 106.16

At room temperature (25 °C) and atmospheric pressure 760 mmHg.

Benzene 1 g-mol has weight = 78.11 g

Thus, in state of gaseous

Benzene 78.11 g has the volumes = 24.45 liters

Benzene 78110 mg has the volumes = $24.45 \times 10^6 \mu\text{l}$

Then,

Benzene $(4.3891 \times 10^{-4}) \times X_1$ mg has the volumes

X

$$\frac{(4.3891 \times 10^{-4}) \times X_1 \times (24.45 \times 10^6)}{X \times (78110)} \quad \mu\text{l}$$

$$X \times (78110)$$

$$= \frac{0.13739 \times X_1}{X} \quad \mu\text{l}$$

X

1 ml or $1 \times 10^3 \mu\text{l}$ of the exhaust gas sample was used, That it means:

$$1 \times 10^3 \mu\text{l} \text{ of exhaust gas contains Benzene} = \frac{0.13739 \times X_1}{X} \quad \mu\text{l}$$

$$1 \times 10^6 \mu\text{l} \text{ of exhaust gas contains Benzene} = \frac{0.13739 \times X_1 \times (1 \times 10^6)}{X \times (1 \times 10^3)} \quad \mu\text{l}$$

$$= \frac{137.39 \times X_1}{X} \quad \mu\text{l}$$

Concentration of Benzene in exhaust gas is $\frac{(137.39) \times X_1}{X}$ ppm

X

On the same way, it can be defined that

Concentration of Toluene in exhaust gas is $\frac{(68.88) \times Y_1}{Y}$ ppm

Y

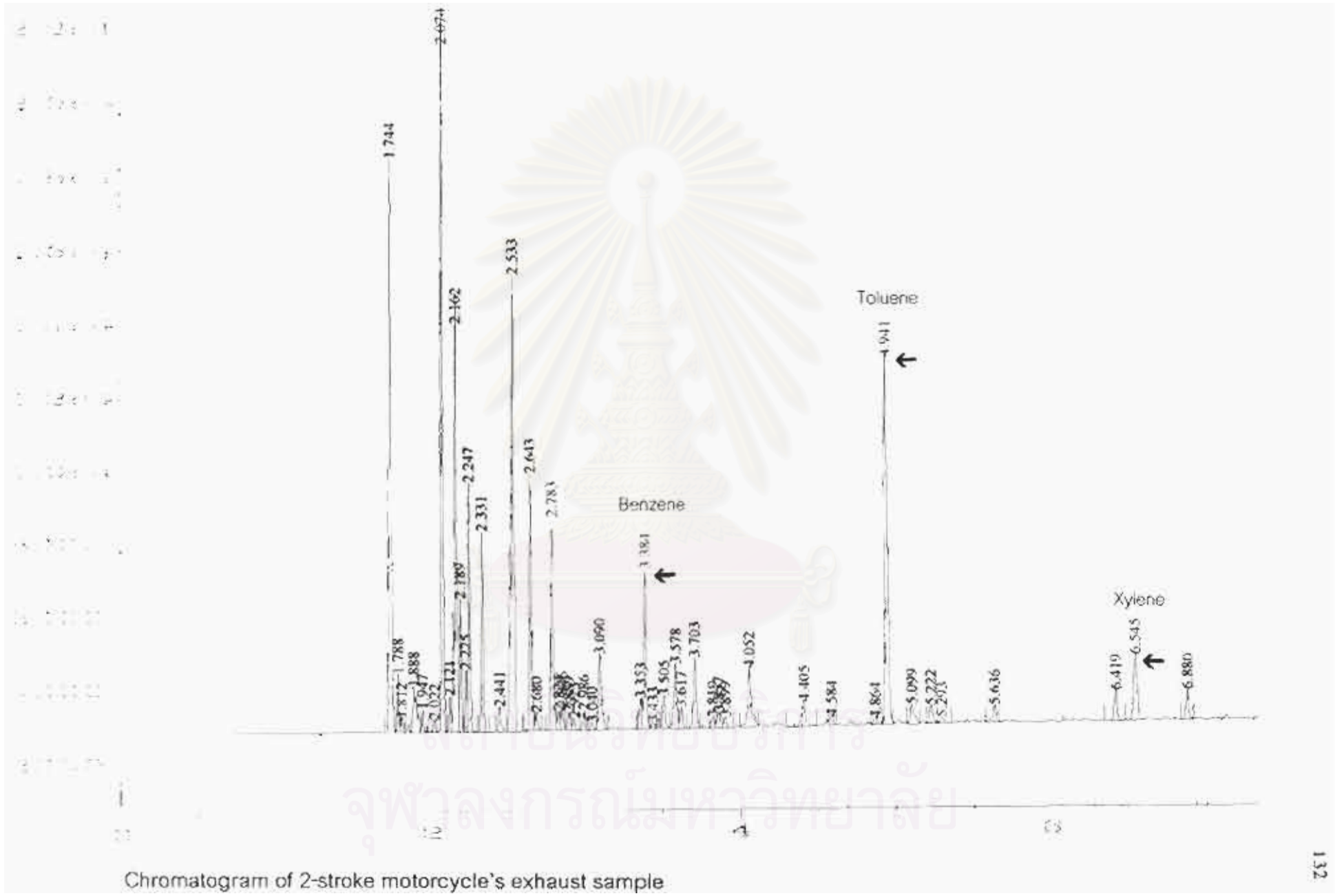
Concentration of Xylene in exhaust gas is $\frac{(39.79) \times Z_1}{Z}$ ppm

Z

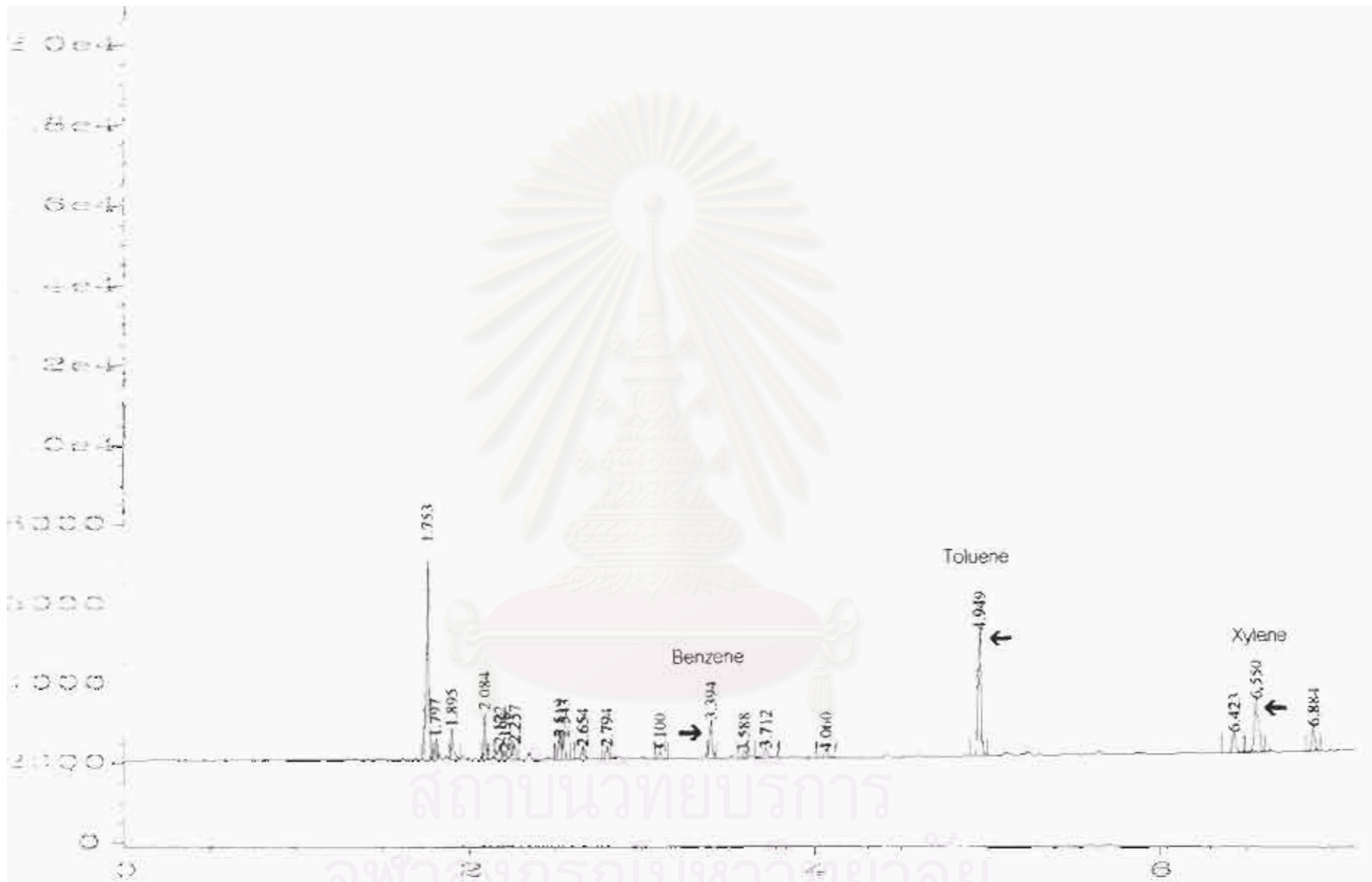
APPENDIX C

Chromatogram of exhaust from 2 and 4 stoke motorcycle
and chromatogram of gasoline

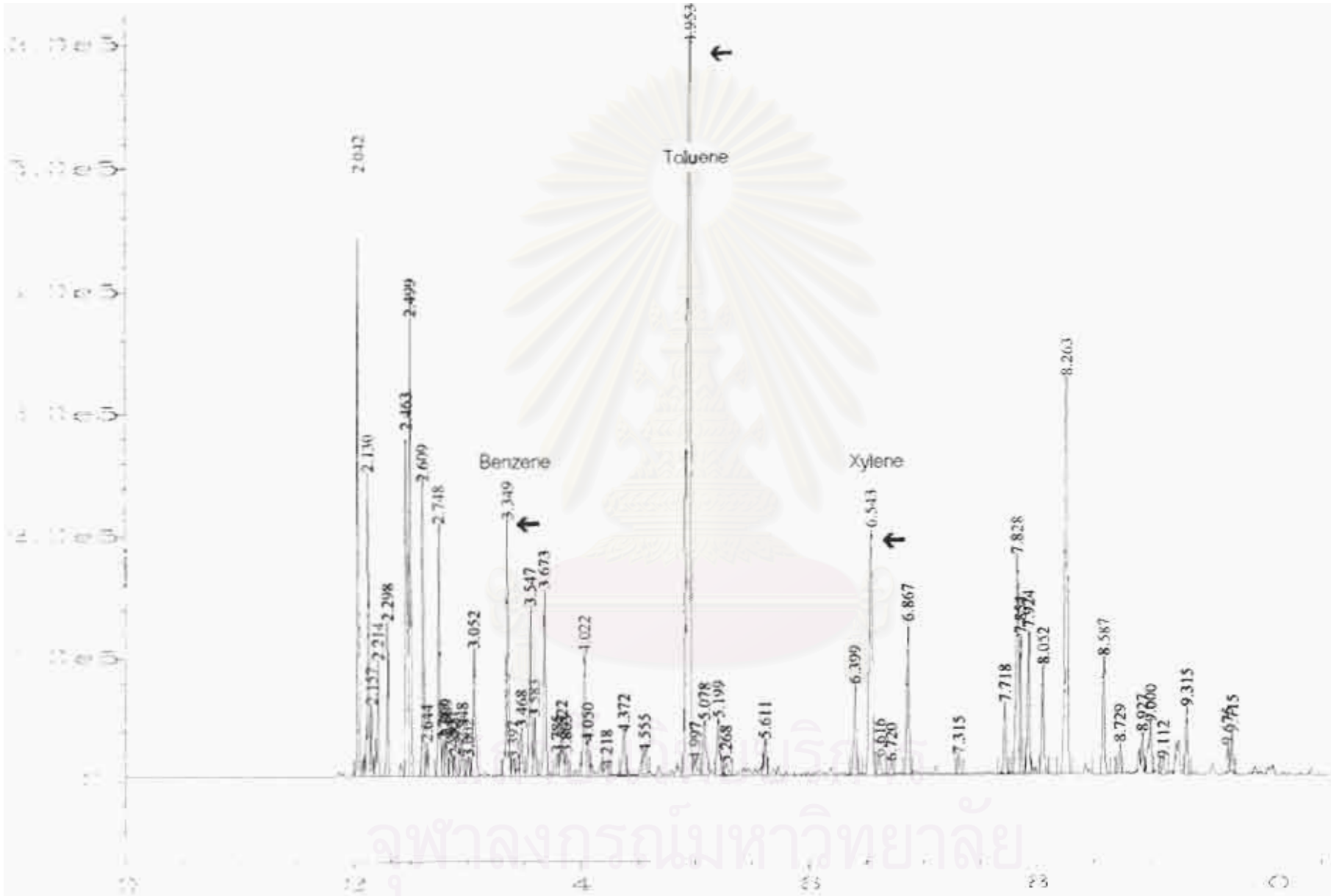
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Chromatogram of 2-stroke motorcycle's exhaust sample



Chromatogram of 4-stroke motorcycle's exhaust sample



Chromatogram of gasoline sample

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APPENDIX D

Questionnaire of used in this study



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Sampling number _____

Type of sample car motorcycle

Name of owner and Telephone No. _____

Date _____ time _____ Pump model Gilian Model 3

General information

1. ยี่ห้อ และรุ่น / Trade mark and model year _____

2. ชนิดของเครื่องยนต์ / Engine type _____

3. จำนวนและความจุของกระบอกสูบ(ซี ซี) / No. of cylinders and capacity _____

4. อายุการใช้งาน (ปี) / Period of use _____

5. เลขไมล์ (ก.ม) / Mileage _____

6. ป้ายทะเบียน / Car plate number _____

7. ชนิดของน้ำมัน (ค่าออกเทน) และยี่ห้อ / Octane type and brand of fuel _____

8. สภาพการใช้งาน

 ใช้งานน้อย / Rarely use (น้อยกว่า 20 ชั่วโมงต่อสัปดาห์ / Less than 20 hr./week) ใช้งานตามปกติ / Moderately use (20-40 ชั่วโมงต่อสัปดาห์ / 20-40 hr./week) ใช้งานมาก / Frequently use (มากกว่า 40 ชั่วโมงต่อสัปดาห์ / More than 40 hr./week)

9. การบำรุงรักษา / Maintenance

 ดี / Good ปานกลาง / Moderate แย่ / Poor

Please specify _____

For car only

10. แคตตาลิติกคอนเวอร์เตอร์ / Catalytic converter มี / Yes ไม่มี / No

ถ้ามีโปรดระบุชนิด / If yes please specify _____

(ถ้าทราบ / If know)

For motorcycle only

11. น้ำมันหล่อลื่นที่ใช้ / Lubricating oil _____

12. ระบบการระบายความร้อนของเครื่องยนต์ / Engine heat exchange _____

Sampling Information

1. ระยะเวลาที่เก็บตัวอย่าง(นาที) / Sampling period _____

2. อุณหภูมิท่อไอเสีย / Tailpipe Temp _____

3. อุณหภูมิบรรยากาศ / Ambient Temp _____

4. สถานที่ ที่เก็บตัวอย่าง / Place of sampling _____

APPENDIX E

Details of motorcycle samples



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2-stroke Motorcycles

	Number	Trade Name	Engine Capacity	Period of use (years)	Octane No. of gasoline	Frequency of use	Main-tenance
Old	1	YAMAHA	125	11	91	1	2
	2	YAMAHA	125	10.5	91	2	2
	3	KAWASAKI	125	18	91	1	2
	4	YAMAHA	125	11	95	3	2
	5	SUZUKI	110	12	95	3	1
	6	YAMAHA	150	10.5	95	1	2
	7	YAMAHA	110	14	95	2	2
Mod-erate	1	KAWASAKI	125	7	91	2	3
	2	YAMAHA	125	5.5	91	2	2
	3	YAMAHA	110	7	95	1	1
	4	KAWASAKI	150	8	95	1	1
	5	KAWASAKI	110	5	95	1	2
	6	YAMAHA	150	6	95	2	2
	7	KAWASAKI	150	7	91	2	1
	8	YAMAHA	125	5	91	1	1
	9	HONDA	150	6	91	3	3
	10	HONDA	150	5	91	1	1
New	1	KAWASAKI	150	1.5	95	2	1
	2	KAWASAKI	110	1	95	2	1
	3	HONDA	150	4	95	1	2
	4	HONDA	110	3	95	3	1
	5	KAWASAKI	125	2	91	2	2
	6	HONDA	110	2	95	1	2
	7	HONDA	125	3	95	2	2
	8	YAMAHA	125	4	95	3	1
	9	KAWASAKI	150	3	91	1	1
	10	HONDA	110	2.5	95	1	2

Explanation: Frequency of use 1 = Rarely use, 2 = Moderately use, 3 = Frequently use

Maintenance 1 = Good, 2 = Moderate, 3 = Poor

4-stroke Motorcycles

	Number	Trade Name	Engine Capacity	Period of use (years)	Octane No. of gasoline	Frequency of use	Maintenance
Old	1	HONDA	100	12	95	1	1
	2	SUZUKI	100	15	95	1	2
	3	HONDA	110	12	95	1	2
	4	SUZUKI	100	15	95	1	2
Mod- erate	1	KAWASAKI	100	8	95	2	2
	2	HONDA	100	9	95	1	1
	3	HONDA	100	5.5	91	2	2
	4	HONDA	100	10	91	1	1
	5	SUZUKI	100	5	91	2	2
	6	HONDA	100	9	95	1	2
New	1	HONDA	110	3 months	95	1	1
	2	SUZUKI	100	3	91	1	2
	3	HONDA	110	1	95	2	2
	4	HONDA	110	10 months	95	2	1
	5	HONDA	100	4	95	2	2
	6	KAWASAKI	110	3 months	95	2	1
	7	HONDA	100	4.5	95	2	1

Explanation: Frequency of use 1 = Rarely use, 2 = Moderately use, 3 = Frequently use

Maintenance 1 = Good, 2 = Moderate, 3 = Poor

BIOGRAPHY

Miss Thitima Rungratanaubon was born on March 20, 1974 in Chantaburi province, Thailand. She has received her Bachelor of Science in General Science from Chulalongkorn University, in 1996. And she has also received her Bachelor of Education in Educational Administration from Sukhothai Thammathirat Open University, in 1999. She was granted a scholarship for her master's degree study at Chulalongkorn University from the academic promoting for young lecturer program, Ministry of University Affairs, Thailand. She was awarded the fellowship from Foreign Commonwealth Office (FCO), U.K for Air Pollution training at Middlesex University, London U.K. At present, she works as a lecturer at the Department of Environmental Science, Faculty of Science Kasetsart University, Thailand.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย