CHAPTER 1
INTRODUCTION

1.1 BTEX Compounds

BTEX compounds are a group of monocyclic aromatic hydrocarbon, consisting of benzene, toluene, ethylbenzene and the three isomers of xylene (o-, m- and p-), and are an important group of volatile organic hazardous pollutants [1,2]. They are present in aviation fuel and petrol (gasoline) and are widely used industrial solvents and raw materials [3].

1.1.1 Benzene

Benzene is a stable colourless liquid at room temperature and normal atmospheric pressure. Its chemical structure is shown in Figure 1.1. It has a characteristic aromatic odour, a relatively low boiling (80.1 °C) and a high vapour. The principal identity, physical and chemical properties of benzene are given in the Appendix (Table A1-A2).

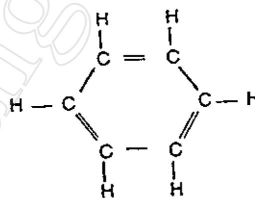

Figure 1.1 Chemical structure of benzene [4].

Major anthropogenic sources of benzene include automobile exhaust, automobile-refuelling operations and industrial emissions. Automobile exhaust probably accounts for the largest anthropogenic source in the general environment. Cigarette smoke, off-gassing from building material and structure files all exposed to benzene mainly through the inhalation of contaminated air, particularly in areas of heavy automobile traffic and around gasoline (petrol) stations and other facilities for

storage and distribution of petrol, and through tobacco smoke from both active and passive smoking. Other sources of exposure have been reported to include industrial emissions and consumer product. However, certain individuals may be exposed to potentially high concentrations of benzene in drinking-water as a result of seepage from underground petroleum storage tanks, landfills, waste streams, or natural gas deposits. Individuals employed in industries that procedure or use benzene or benzene-containing products are probably exposed to much higher levels than the general population. Industrial discharge, landfill leachate, and disposal of benzene-containing waste are also anthropogenic sources.

1.1.2 Toluene

Toluene is a common name for the chemical formed when one hydrogen atom of the benzene molecule is replaced with a methyl group. Its chemical structure is shown in Figure 1.2. Toluene is a clear, volatile liquid at ambient temperature that is flammable and explosive and has a benzene-like odour. The identity, some physical and chemical properties of toluene under standard conditions are presented in the Appendix (Table A3-A4).

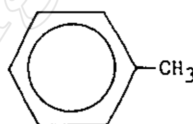

Figure 1.2 Chemical structure of toluene [5].

The Three primary man-made sources of toluene released into the environment :

(a) production sources; toluene can be released into the environment during its production as process losses, fugitive emission, and storage losses (approximately 2%);

(b) Toluene when used as a solvent; toluene is released into the ambient air, as a result of evaporation (approximately 34%);

(c) inadvertent sources; the emission of toluene through its in gasoline can occur from three distinct sources including: evaporative losses from automobile service stations; evaporation from marketing activities (handing and transfer of bulk quantities); and emission from motor vehicles and aircraft (approximately 65%).

Other inadvertent sources of toluene emission into the environment include other manufacturing processes, by-product formation, and cigarette smoke. These is substantial contamination of the environment from seepage in the oceans, on hand, and from the weathering of exposed coal strata.

1.1.3 Ethylbenzene

Ethylbenzene is an aromatic hydrocarbon manufactured by alkylation from benzene and ethylene. Its chemical structure is shown in Figure 1.3. At room temperature ethylbenzene is a colourless liquid with a sweet, gasoline-like adour. The identity, some physical and chemical properties of ethylbenzene are given in the Appendix (Table A5-A6).

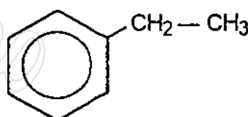

Figure 1.3 Chemical structure of ethylbenzene [6].

Ethylbenzene is present in refined products. It is produced by incomplete combustion of natural material, making it a component of forest files and cigarette smoke.

1.1.4 Xylenes

Xylene exists in the three isomeric forms, ortho- , meta- and para-xylene. Their chemical structures are shown in Figure 1.4. The commercial product is a mixture of all three isomers with m-xylene predominating , usually 60-70%. The technical

product "mixed xylenes" , contains approximately 40% m-xylene and 20% each of ethylbenzene o-xylene and p-xylene. Small quantities of toluene and C_9 aromatic fractions may also be present.

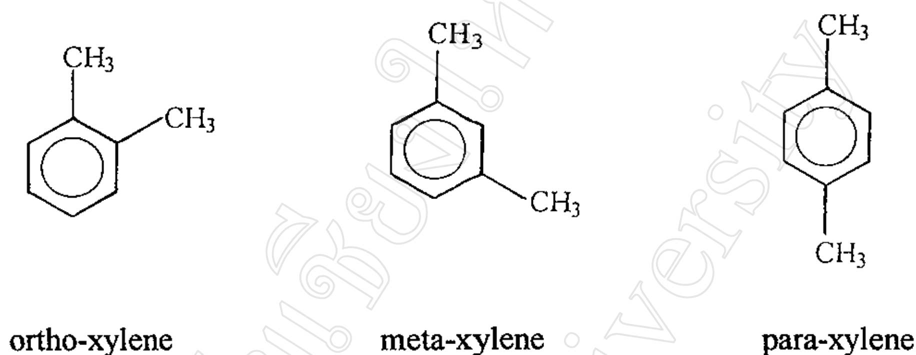

Figure 1.4 Chemical structures of xylene isomers [7].

All three isomers of xylene are soluble in organic solvent. At room temperature the xylenes are colourless liquids with an aromatic odour. The identity, some physical and chemical properties are given in Appendix (Table A7-A8).

Before 1940 virtually all of the aromatic solvent, including xylene, were produced from coal. Most mixed xylene is currently produced by catalysis gasoline as a by product of olefin manufacture during the cracking of hydrocarbons. Small amounts of mixed xylenes are also obtained from coal-derived coke-oven light oil and from disproportionation of toluene.

There are some differences in the composition of commercial xylenes produced from petroleum and from coal-tar. The general composition of xylenes from petroleum is 44% m-xylene, 20% o-xylene, 20% p-xylene and 15% ethylbenzene. The xylenes from coal-tar consists of 45-70% m-xylene, 23% p-xylene, 10-12% o-xylene and 6-10% ethylbenzene. Commercial xylene may also contain small amounts of toluene, trimethylbenzene, phenol, thiophene, pyridine and non-aromatic hydrocarbons and has frequently been contaminated with benzene.

1.2 Uses of BTEX compounds

1.2.1 Benzene

Benzene has large number of industrial, commercial and scientific uses. Approximately, 10% of total use of benzene is in gasoline. However it is still used as a solvent in scientific laboratories, industrial paints, rubber cements, adhesives, paint removers, degreasing agents, production of artificial leather and of rubber goods, and in the shoe industry. For many solvent uses, benzene has been replaced by other nontoxic organic solvents. However, in the past significant human expose occurred when benzene was used as a paint stripper, a carburettor cleaner, in the production of denatured alcohol and rubber cements, and in arts and crafts supplies. It has been reported that benzene vapours cloud be detected from such products as carpet glue, textured carpet, liquid detergent and furniture wax.

1.2.2 Toluene

Toluene is of great importance as a chemical intermediate. Up to 95% of the annually-produced toluene in the USA is blended directly into the gasoline pool as a component to increase the pyrolysis of gasoline (to increase the octane number).

Isolated toluene is much more important as a solvent than either benzene or xylene. Approximately two-thirds of its use as a solvent is in paints, inks, thinners, coatings, adhesives, degreasers, and other formulated products requiring a solvent carrier. Furthermore, toluene is used as a raw material in the organic synthesis of a large number of chemicals such as toluene diisocyanate, benzoic acid, benzaldehyde, xylene, toluene-sulfonylchloride, other derivatives of toluene used as dye intermediates, resin modifiers, germicides, etc. lastly toluene is used as a denaturant in specially-denatured alcohol.

1.2.3 Ethylbenzene

About 95% of ethylbenzene produced is employed for the production of styrene. Ethylbenzene is a constituent (15-20%) of commercial xylene ("mixed xylenes"), and hence used as a component of solvents as a diluter in paints and lacquers , and as a solvent in the rubber and chemical manufacturing industries. Ethylbenzene ("mixed xylenes") can also be added to motor fuels. A typical ethylbenzene content of a reformate is about 4% (by volume).

1.2.4 Xylenes

Approximately 92% of the mixed xylenes produced is blended into gasoline. The remainder is used in a variety of solvent applications as well as to produce the individual isomers of xylene. Xylenes are used as solvents, particularly in the paint and printing ink industries. The single largest end-use of mixed xylenes is in the production of the p-isomer. The major derivatives produced from p-xylene are dimethylterephthalate and terephthalic acid used in the production of polyester fiber, film and fabricated items. The o-xylene is almost exclusively used to produce phathalic anhydride for phthalate plasticizers, and m-xylene is used for the production of isophathalic acid, an intermediate in the manufacture of polyester resins.

Mixed xylenes are also used in the manufacture of perfumes, pesticide formulations, pharmaceuticals and adhesives, and in the painting, printing, plastics and leather industries.

1.3 Effects of BTEX compounds on Humans

BTEX have many chemical applications and are widely used in the manufacture of paints, synthesis rubber, agricultural chemicals and chemical intermediates [8]. They are also natural components of crude oil and refined petroleum. So, they are increasingly ubiquitous contaminants in soil, sediments, groundwater and surface water, entering the aqueous environment as industrial effluents, municipal waste discharges, atmospheric fallout, and accidental and intentional spills [9]. The contamination of BTEX is a serious environmental problem owing to their potential human toxicity [10].

The following are some of toxic effects of BTEX in human.

1.3.1 Benzene

It is known that benzene produces a number of adverse health effects. The most frequently reported health effect of benzene is bone marrow depression leading to aplastic anaemia. At high levels of exposure a high incidence of these of diseases is probable [4].

Benzene is a well-established human carcinogen. Epidemiological studies of benzene-exposed workers have demonstrated a causal relationship between

benzene exposure and the production of myelogenous leukaemia. A relationship between benzene exposure and the production of lymphoma and multiple myeloma remains to be clarified. The task Group was of the opinion that the epidemiological evidence is not capable of distinguishing a) a small increase in mortality from leukaemia in worker exposed to low levels of benzene, and b) a non-risk situation.

1.3.2 Toluene

The primary effect of toluene is on the central nervous system (CNS). The effect may bedepressant or excitatory, with euphoria in the induction phase followed by disorientation, dysarthria, ataxia, convulsions, and coma [5].

Acute controlled and occupational exposure to toluene in the range of 750 - 5625 mg/m^3 (200 - 1500 ppm) caused dose-related CNS effects. Acute exposure to high levels of toluene (e.g., 37500 mg/m^3 or higher for a few min) during industrial accidents was characterized by initial CNS excitative effects (e.g., exhilaration, euphoria, hallucinations) followed by progressive impairment of consciousness, eventually resulting in seizures and coma.

Single, short-term exposure to toluene (750 mg/m^3 for 8 h) have reportedly caused transient eye and respiratory tract irritation with lachrymation at 1500 mg/m^3.

Irreversible neurological sequelae, such as encephalopathy, optic atrophy and equilibrium disorders have been described in adult chronic toluene abusers. Toluene inhalation was reported to be an important cause of encephalopathy in children (aged 8- 14 years) and may lead to permanent neurological damage.

Transient abnormalities of hepatic enzyme activities have been in abusers of toluene mixtures, but significant permanent hepatic damage dose not occur. Occasional reports of renal damage in glue-sniffers have appered, characterized by a from of distal tubular acidosis. There is no evidence that toluene damages the haematopoietic tissues or the heart.

1.3.3 Ethylbenzene

Human exposure to ethylbenzene occurs mainly by inhalation ; 40-60% of inhaled ethylbenzene is retained in the lung. Ethylbenzene is extensively

metabolized, mainly to mandelic and phenylglyoxylic acids. These urinary netabolites can be used to monitor human exposure [6].

Ethylbenzene has low acute and chronic toxicity for both animals and humans. It is toxic to the central nervous system and is an irritant of mucous membranes and the eyes. The threshold for these effects in humans after short single exposure was estimated to be about 430-860 mg/m^3 (100-200 ppm).

1.3.4 Xylenes

After inhalation exposure the retention in the lungs is about 60% of the inhaled dose. Xylenes are efficiently metabolized. More than 90% is biotransfromed to methylhippuric acid, which is excreted in urine. Xylenes do not accumulate significantly in the human body [7].

Acute exposure to high concentration of xylenes can result in CNS effects and irritation in humans. However, there have been no long-term controlled human studies or epidemiological studies. The chronic toxicity appears to be relatively low in laboratory animals. There is suggestive evidence, however, that chronic CNS effects may occur in animals at moderate concentrations of xylenes. Xylenes appear not to be a mutagen or a carcinogen.

1.4 Regulations Concerning BTEX compounds

BTEX are hazardous carcinogenic and neurotoxic compounds, and are classified as priority pollutants by the US Environmental Protection Agency (EPA), specially benzene, which is a leukaemic agent in humans and has a very low tolerance standard in drinking water of 5 µg/L [3,8]. The National Primary Drinking Water Regulations promulgated by EPA has insituted a maximum contaminant level (MCL) of BTEX in drinking water are shown in Table 1.1 [11]. For the action levels for BTEX are listed in the Dutch Government quality standards for assessment of land contamination [3].

Table 1.1 Standards and regulations for BTEX in drinking water by USEPA [11].

Compound	Maximum contaminant level (MCL)[a]
Benzene	0.005 mg/L (5 ppb)
Toluene	1.0 mg/L (1000 ppb)
Ethylbenzene	0.7 mg/L (700 ppb)
Total xylenes	10.0 mg/L (10000 ppb)

[a] MCL (maximum contaminant level) = highest concentration of a contaminant allowed in public drinking water supplies.

Recently, the BTEX have required great relevance as ubiquitous pollutants of the out door and indoor human environment, as two relevant sources of these compounds are vehicular traffic and tobacco smoking [12]. Since people spend on overage about 90% of the day indoors, attention is mainly paid to indoor air instead of outdoor air pollutant [13]. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a threshold limit value (TLV), refer to airbone concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. These limits are intended for use in the practice of industrial hygiene as guidelines or recommendation in the control of potential health hazards and for no other use [14]. The occupational safety standard for the environmental monitoring has been established by the time-weight average (TWA) limit, and the workplace air standard mandated include an 8-hour time-weight average (TWA) of BTEX as shown in Table 1.2.

Table 1.2 Standards and regulations for BTEX in air-workplace by ACGIH [14-16].

Compound	TWA[a]	
	ppm	mg/m^3
Benzene	10	32
Toluene	100	372
Ethylbenzene	100	434
Xylene (o- ,m- ,p- isomers)	100	434

[a] TWA (time-weight average) = concentration averaged a for a normal 8-hour workday workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

1.5 Analytical Methods for BTEX compounds

The analytical methods used for the determination of BTEX compounds depend upon the media sampled and the level of sensitivity required. In all cases proper sampling procedures, sample storage and preparations are essential prerequistes, particularly as microgram and nanogram quantities are often found in environmental samples.

Gas chromatography offers the greatest specificity and sensitivity of the numerous methods of analysis. Photoionization detectors provide better selectivity and sensitivity of BTEX measurements than flame ionization detectors. Nevertheless, the flame ionization detector is the most common detector used in volatile hydrocarbon analyses; the use of gas chromatography interfaced with computerized mass spectrometry has been developed for samples containing BTEX compounds.

Some of the commonly used method for the determination of BTEX in various media are summarized in Table 1.3-1.6.

Table 1.3 Analytical method for the determination of benzene

Sample	Preparation	Analytical method	Detection limit	Reference
Air	Tenax GC trap, thermal desorption	GC/FID/MS	0.01 μg/m^3	4
Air	direct analysis	UV Spect.	800 μg/m^3	4
Air (ambient)	charcoal trap (badge or tube), desorb with CS_2	GC/FID	0.96 μg/m^3	4
Air (occupational)	porous polymeric sorbent, thermal desorption	GC/FID	0.83 μg/m^3	4
Air	SPME	GC/MS	at the ppt level	17
Air (ambient and exhaled air)	graphitized charcoal trap tube, thermally desorbed by microwave	GC/MS	1.6 μg/L	18
Air (indoor)	charcoal trap, extracted with CS_2-methanol, headspace SPME	HRGC/FID	0.36 μg/m^3	13
Water (surface or effluents)	helium purge, Tenax GC trap, thermal desorption	GC/MS	0.1 μg/L	4

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Table 1.3 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Water	purge with inert gas, Tenax trap, thermal desorption to on-column cryogenic trap	HRGC/MS	0.1 µg/L	4
Water	SPME	GC/MS	15 pg/ml	19
Groundwater	SPME	GC/FID	5 µg/L	20
Water	SPME	GC/FID	0.4 ng/ml	2
Water	headspace SPME	GC/MS	273.9 ng/L	21
Water	direct analysis	Raman	8.2 ppm	9
Water	In-tube SPME	GC/FID	NR	22
Groundwater	headspace extraction	GC/MS	NR	23
Water	headspace SPME	GC/FID	0.6 ng/ml	8
Soil	nitrogen purge, Tenax trap, thermal desorption	GC/FID	1 ng/kg	4
Soil	extracted with methanol-water, SPE	GC/MS	NR	3

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Table 1.3 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Clay	internally cooled SPME device	GC/MS	0.46 pg/g	24
Sediment	purge and trap with methanolic extraction	GC/FID	3.8 mg/kg	25
Mainstream cigarette smoke	filter smoke and direct to GC/MS; for passive smoke collect air in cryogenic, methanol-filled impingers	HRGC/MS	NR	4
Blood	nitrogen purge, Tenax GC-silica-gel trap	GC/MS	0.5 µg/L	4
Blood	extract with toluene, centrifuge; analyse toluene layer	GC/FID	100 µg/L	4
Blood	purge and trap	GC/MS	0.15 µg/L	26
Urine	purge and trap	GC/MS	0.20 µg/L	26
Milk	purge and trap	GC/MS	0.12 µg/L	26
Urine	headspace SPME	GC/MS	25 ng/L	12

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Table 1.3 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Breath	collect on Tenax GC, thermal desorption	HRGC/MS	9.8 ng/m^3	4
Breath	collect on Tenax GC, thermal desorption into on-column cryogenic trap	GC/FID	5.2 $\mu g/m^3$	4
Tissue	add butyl hydroxy toluene to buffered homogenate, centrifuge, analyse supernatant	RID-HPLC/UV	20 pg/g	4

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Table 1.4 Analytical method for the determination of toluene

Sample	Preparation	Analytical method	Detection limit	Reference
Air (ambient)	solid sorbent trap, CS_2 desorption	GC/FID/MS	NR	5
Air	SPME	GC/MS	at the ppt level	17
Air (ambient and exhaled air)	graphitized charcoal trap tube, thermally desorbed by microwave	GC/MS	3.0 $\mu g/m^3$	18
Air (indoor)	charcoal trap, extracted with CS_2-methanol, headspace SPME	HRGC/FID	0.77 $\mu g/m^3$	13
Water	dichloromethane extraction	GC/FID	NR	5
Water	purge and trap	GC/MS	1 µg/L	5
Water	headspace gas analysis	GC/MS	0.1-10 µg/L	5
Water	SPME	GC/MS	5 pg/ml	19
Groundwater	SPME	GC/FID	2 µg/L	20
Water	SPME	GC/FID	0.4 ng/ml	2

Table 1.4 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Water	headspace SPME	GC/MS	47.5 ng/L	21
Water	direct analysis	Raman	30.2 ppm	9
Water	In-tube SPME	GC/FID	NR	22
Groundwater	headspace extraction	GC/MS	NR	23
Water	headspace SPME	GC/FID	0.2 ng/ml	8
Soil	extracted with methanol-water (50+50), SPE	GC/FID	NR	3
Soil	headspace SPME	GC/MS	0.23 ng/g	27
Clay	Internally Cooled SPME device	GC/MS	0.6 pg/g	24
Sediment	purge and trap with methanolic extraction	GC/FID	3.0 mg/kg	25
Blood	headspace analysis	GC/FID/MS	10 µg/L	5
Whole blood	direct injection	GC/FID	NR	5
Blood	purge and trap	GC/MS	7.5 µg/L	5

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Table 1.4 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Blood	purge and trap	GC/MS	0.63 µg/L	26
Urine	purge and trap	GC/MS	0.64 µg/L	26
Milk	purge and trap	GC/MS	0.58 µg/L	26
Urine	headspace SPME	GC/MS	34 ng/L	12
Human breast milk	purge and trap	GC/MS	0.5 µg/L	5
Plastic container	headspace analysis	GC/MS	µg/kg range	5

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Table 1.5 Analytical method for the determination of ethylbenzene

Sample	Preparation	Analytical method	Detection limit	Reference
Air	charcoal trap, CS_2 desorption	GC/FID	0.1 mg/m^3	6
Air	cryogenic trap, thermal desorption	GC/FID	at the ppt level	6
Air	SPME	GC/MS	at the ppt level	17
Air (ambient and exhaled air)	graphitized charcoal trap tube, thermally desorbed by microwave	GC/MS	0.2 $\mu g/m^3$	18
Air (indoor)	charcoal trap, extracted with CS_2-methanol, headspace SPME	HRGC/FID	0.36 $\mu g/m^3$	13
Water	headspace analysis	GC/MS/IR	NR	6
Water	purge and trap	GC/FID	20 µg/L	6
Water	headspace SPME	GC/FID	at the ng/L level	6
Water	SPME	GC/MS	2 pg/ml	19
Groundwater	SPME	GC/FID	1 µg/L	20
Water	SPME	GC/FID	0.05 ng/ml	2

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Table 1.5 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Water	headspace SPME	GC/MS	10.7 ng/L	21
Water	direct analysis	Raman	37.4 ppm	9
Water	In-tube SPME	GC/FID	NR	22
Groundwater	headspace extraction	GC/MS	NR	23
Water	headspace SPME	GC/FID	0.08 ng/ml	8
Soil	extracted with methanol-water (50+50), SPE	GC/FID	NR	3
Soil	headspace SPME	GC/MS	0.08 ng/g	27
Clay	Internally Cooled SPME device	GC/MS	0.24 pg/g	24
Sediment	purge and trap with methanolic extraction	GC/FID	5.0 mg/kg	25
Blood	headspace analysis	GC/ MS	0.01 mg/L	6
Blood	purge and trap	GC/MS	at the ng/L level	6
Urinary	diethyl ether extraction	ITP	0.04 mmol/L	6

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Table 1.5 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Urinary	diethyl ether extraction	HPLC	0.01 mmol/L	6
Blood	purge and trap	GC/MS	0.30 µg/L	26
Urine	purge and trap	GC/MS	0.23 µg/L	26
Milk	purge and trap	GC/MS	0.02 µg/L	26
Urine	headspace SPME	GC/MS	12 ng/L	12
Fish muscle	dichloromethane extraction and clean up on a florisil column	GC/FID	5 µg/g	6
Fish	vacuum extraction	GC/MS	at the ng/g level	6

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Table 1.6 Analytical method for the determination of xylenes

Sample	Preparation	Analytical method	Detection limit	Reference
Air	charcoal trap, CS_2 desorption	GC/FID	1-1000 mg/m^3 (xylene)	7
Air	SPME	GC/MS	at the ppt level	17
Air (ambient and exhaled air)	graphitized charcoal trap tube, thermally desorbed by microwave	GC/MS	1.4 µg/m^3 (m,p-xylene) 0.4 µg/m^3 (o-xylene)	18
Air (indoor)	charcoal trap, extracted with CS_2-methanol, headspace SPME	HRGC/FID	2.2 µg/m^3 (m,p-xylene) 0.37 µg/m^3 (o-xylene)	13
Water	headspace analysis	GC/MS	at the ppb level	6
Water	hexane extraction	GC/FID	1 µg/L (xylenes)	6
Water	SPME	GC/MS	1 pg/ml (m,p-xylene) 1.5 pg/ml (o-xylene)	19
Groundwater	SPME	GC/FID	1 µg/L (m,p-xylene) 1 µg/L (o-xylene)	20

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Table 1.6 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Water	SPME	GC/FID	0.2 ng/ml (p-xylene) 0.2 ng/ml (m-xylene) 0.1 ng/ml (o-xylene)	2
Water	headspace SPME	GC/MS	13.9 ng/L (p-xylene)	21
Water	direct analysis	Raman	48.3 ppm (xylenes)	9
Water	In-tube SPME	GC/FID	NR	22
Groundwater	headspace extraction	GC/MS	NR	23
Water	headspace SPME	GC/FID	0.08 ng/ml (m,p-xylene) 0.08 ng/ml (o-xylene)	8
Soil	extracted with methanol-water (50+50), SPE	GC/FID	NR	3
Soil	headspace SPME	GC/FID	0.05 ng/g (m,p-xylene) 0.07 ng/g (o-xylene)	27
Clay	Internally Cooled SPME device	GC/MS	0.35 pg/g (m,p-xylene) 0.63 pg/g (o-xylene)	24

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Table 1.6 (continued)

Sample	Preparation	Analytical method	Detection limit	Reference
Sediment	purge and trap with methanolic extraction	GC/FID	5.6 mg/kg (m-xylene) 5.1 mg/kg (o-xylene)	25
Blood	headspace analysis	GC/FID	53 µg/L (xylenes)	7
Human milk	purge and trap	GC/MS	NR	7
Blood	purge and trap	GC/MS	1.28 µg/L (m,p-xylene) 0.20 µg/L (o-xylene)	26
Urine	purge and trap	GC/MS	0.88 µg/L (m,p-xylene) 0.13 µg/L (o-xylene)	26
Milk	purge and trap	GC/MS	0.79 µg/L (m,p-xylene) 0.05 µg/L (o-xylene)	26
Urine	headspace SPME	GC/MS	23 ng/L (m,p-xylene) 15 ng/L (o-xylene)	12

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1.6 Solid Phase Microextraction (SPME)

1.6.1 Introduction to solid-phase microextraction [28-32]

Analytical process typically consists of several discrete steps (e.g., separation, quantitation, and data analysis), each of which is critical for obtaining accurate and reproducible results. A sample preparation step is often necessary to isolate the components of interest from a sample matrix, as well as to purify and concentrate the analytes. Despite advances in instrumentation and microcomputer, however, many sample preparation practices are based on nineteenth-century technologies.

An ideal sample preparation technique should be solvent-free, simple inexpensive, efficient, selective, and compatible with a wide range of separation methods and applications. It should be able to be used to simultaneously separate and concentrate the components and should allow on-site extraction and analysis.

Solid-phase microextraction (SPME) is a new extraction technique which has been developed and commercialized since the beginning of the 1990 by Pawliszyn [32]. SPME requires no solvent or complicated apparatus and can be used to concentrate volatile or nonvolatile components in both liquid and gaseous samples. Analytes are adsorbed from a liquid, through immersion or headspace extraction, onto a phase-coated fused silica fiber. By choosing the sampling approach and the type of fiber, we can selectively remove analytes from interferences and concentrate only the desired analytes being measured. A portable field sampler can concentrate and store organics from the field, and perform through direct exposure to a heated GC injection port or through an SPME/HPLC interface.

Some typical applications for SPME are:

- Industrial applications such as surfactants
- Environmental analysis of water samples
- Flavor analysis of arson samples
- Toxicology analysis of blood alcohol and drugs in urine/serum

- Headspace analysis of the trace impurities of polymers and solid samples

Some offers some important advantages:

- Fast - reduces sample preparation time by 70% ;
  conduct screening analysis for volatile in less than 6 minutes
- Solvent reduction - minimizes the use of solvents and their disposal
- Economical and reusable - more than 50 extractions per fiber on average
- Versatile - adapts to any GC or HPLC system, can be automated with Varian autosamplers

1.6.2 Operating Principle and Construction of SPME devices

1.6.2.1 Basic principles of SPME [28,31,32]

Solid-phase microextraction consists of two processes: partitioning of analytes between the polymeric film coating on the sample and desorption of concentrated analytes into an analytical instrument. In the first process, the coated fiber is expose to the sample and the target analytes are extracted from the sample matrix into the coating. The fiber with concentrated analytes is then transferred to an instrument for desorption, followed by separation and quantitation.

The SPME operating step are as follows :

Sample extraction:

- Pass the needle with the retracted fiber through the sample vial septum.
- Depress the plunger to express the fiber to the sample.
  The fiber can either be immersed in the liquid sample or place in the headspace above the sample. The analytes are adsorbed to the phase on the fiber in 2 to 30 minutes

GC analysis:

- Retract the fiber into the GC injection port.
- Depress the plunger, exposing the fiber in the heated zone of the injector to desorb the analytes onto the column.

- Analyze the sample.

HPLC analysis:

- Insert the needle into the SPME/HPLC interface desorption chamber, with the injection valve in "load" position.
- Expose the fiber and close the sealing camp.
- Switch the injection valve to "inject." Mobile phase will flow through the chamber, desorb analytes and carry them to the column.
- Switch the injection valve to "load," retract the fiber, and remove the needle.

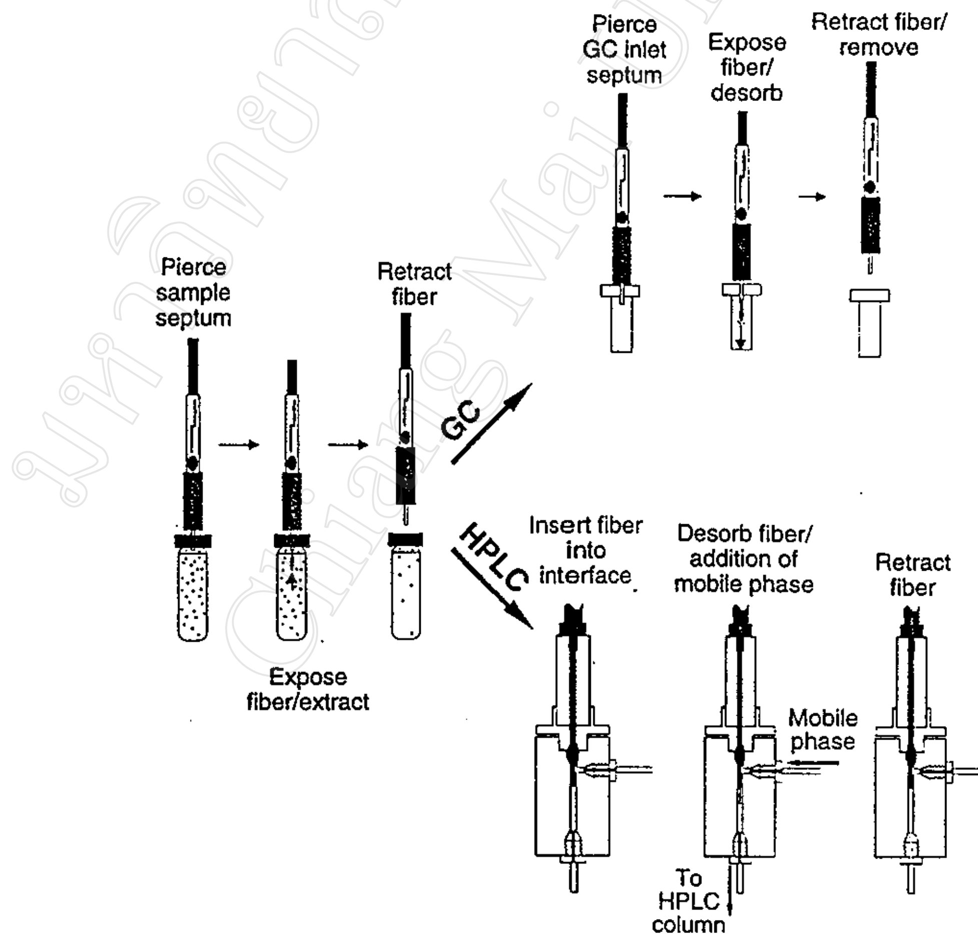

Figure 1.5 The SPME process [31]

In this research, the SPME technique and the performance of SPME fiber coated with poly(dimethylsiloxane) were investigated for the determination of BTEX compounds and desorption of the analytes from the polymeric layer into the carrier gas stream of the heated GC injector.

1.6.2.2 SPME device for GC application [28,31-33]

The first commercial version of the laboratory SPME device was introduced by Supelco in 1993. Figure 1.6 shows an example of the SPME device base on the Hamilton™ 7000 series microsyringe. A commercial SPME device consists of a SPME holder are available in both manual and autosampling modes, and a liquid phase-coated fused silica fiber assembly.

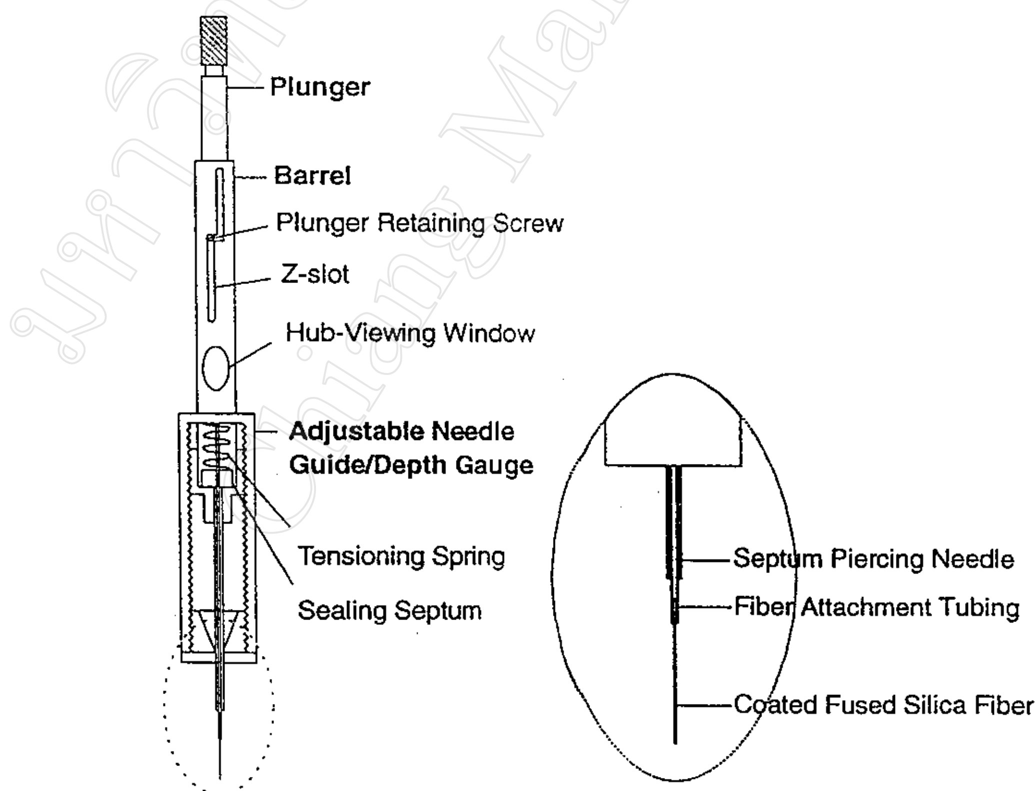

Figure 1.6 SPME device for manual sorption and injection [33]

SPME can be performed manually or by an autosampler. Because the SPME device is basically a syringe, anyone who can use a syringe properly can carry out SPME. The only difference between a normal autosampler and a SPME autosampler is that the plunger movement and timing must be carefully controlled to perform absorption and desorption correctly.

SPME Holder Assembly

The holder protects the phase-coated fiber, and controls exposure of the sample for adsorption and correct placement in the heat zone of a GC injection port to desorption. The holder is reusable indefinitely and accepts any of the replaceable fiber assemblies shown below.

SPME Fiber Assembly

SPME fiber assemblies can be reused for up to 100 analyses, or more, depending on the particular application and the care that they are given. For reuse, simply condition heat before and after every analysis. Choose the assembly that is appropriate for the SPME holder, manual or automated.

Because different groups of analytes can be extracted by difference types of coating materials for SPME fibers, a variety of coating materials have been used for SPME. For organic compounds, the basic principle of "like dissolves like" applies. Polar coatings such as polyacrylate and carbowax extract polar compounds such as phenols and carboxylic acid very effectively, whereas nonpolar coatings such as poly(dimethylsiloxane) retain hydrocarbons very well. SPME can be used to analyze a wide range of compounds in various matrices through proper optimization or modification of SPME procedures. The different types of commercially available fibers are commonly used fibers for more selective determination of different compound classes, which are summarized in Table 1.7. The reduction of the film thickness from 100 to 7 μm produces a bound phase which is more stable at higher temperatures and allows the analysis of compounds with higher boiling points. Thus, the desorption process is much faster since the diffusion out of the 7 μm coating is much easier than desorption out of the 100 μm coating.

Table 1.7 Commonly used SPME fibers [30,34].

Fiber	Property
100μm Polydimethylsiloxane	High sample capacity Max. exposure temperature[a] 200 °C For volatile, low-, mean-boiling (< 200 °C) and polar compounds (e.g. VOCs) tolerates concentrations of organics up to 1%
30 μm Polydimethylsiloxane	Characteristics between the 100 μm and the 7 μm fiber Max. exposure temperture[a] 280 °C recommened desorption temperature 220-270 °C
7 μm Polydimethylsiloxane	Bound phase for higher desorption temperatures Max. exposure temperature[a] 340 °C recommended desorption temperature 220-320°C For semivolatile, high-boiling point (> 200 °C) and apolar compounds e.g., PAHs)
85 μm Polyacrylate	High capacity Max. exposure temperature[a] 310 °C recommended desorption temperature 220-300°C For both polar and non-polar compounds (e.g. hydrophilic pesticide and phenol) tolerates concentrations of organics up to 10%

[a] Max. temperature recommended by the manufacture

1.6.2.3 Extraction modes of SPME [32]

Three basic types of extractions can be preformed using SPME : direct extraction, headspace configuration, and a membrane protection approach. Figure 1.7 the differences among three modes.

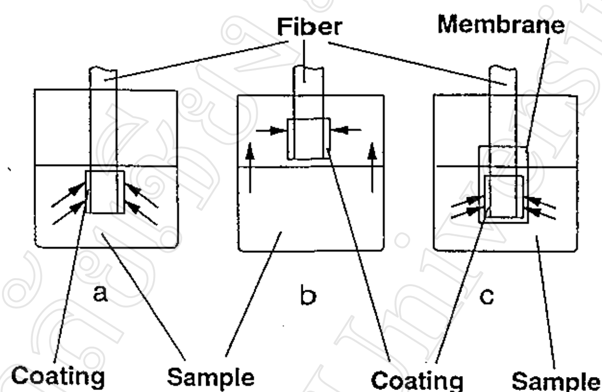

Figure 1.7 Modes of SPME operation : (a) direct extraction, (b) headspace SPME (c) membrane-protected SPME [32].

In the direct extraction mode (Figure 1.7 a), the coated fiber is inserted directly into the sample and the analytes are transported directly from the sample matrix to the extracting phase. To facilitate rapid extraction, some level of agitation is required to transport analytes from the bulk of the solution to the vicinity of the fiber. For gaseous samples, natural convection of air is sufficient to facilitate rapid equilibration. For aqueous matrices, more efficient agitation techniques, such as fast sample flow, rapid fiber or vial movement, stirring or sonication are required.

In the headspace mode, the analytes need to be transported through the barrier of air before they can reach the coating. This modification serves primarily to protect fiber coating from damage by high molecular weight and other nonvolatile interferences present in the sample matrix.

Figure 1.7 C shows the principle of indirect SPME extraction through a membrane. The main purpose of the membrane barrier is to protect the fiber against damage, similar to the use of headspace SPME when very dirty samples are analyzes.

Table 1.8 Sampling mode selection criteria [32,35]

Sampling mode	Analyte properties	Matrices
direct	medium to low volatility	gaseous samples, liquid (preferably simple)
headspace	high to medium volatility	liquid (including complex), solids
membrane protection	low volatility	complex sample

1.6.3 Theoretical aspects of SPME

The principle behind SPME is the partitioning of analytes between the sample matrix and the extraction medium. The amount of analyte adsorbed by the coating at equilibrium is directly related to its concentrations in the sample both the direct and the headspace extraction as shown in Figure 1.8.

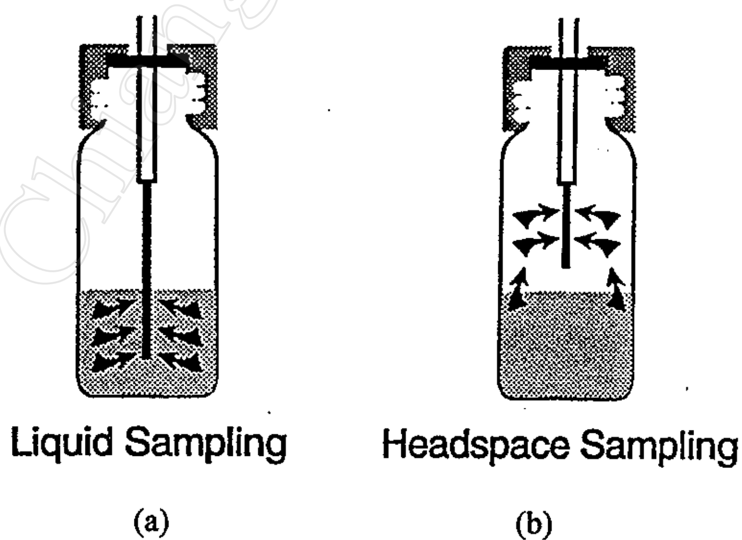

Figure 1.8 Mode of SPME operation : (a) direct extraction mode (b) headspace extraction [36]

1.6.3.1 Amount extracted in two-phase systems : direct extraction

Let us first examine the direct extraction of the analytes from a homogeneous water from into a fiber's liquid polymer phase coating. Figure 1.9. shows the geometry of the two-phase system investigated, where b-a is the coating thickness.

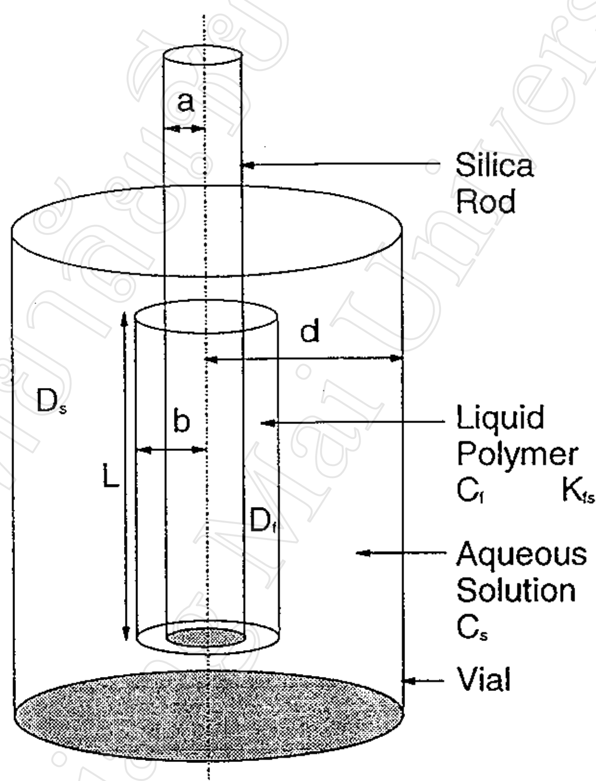

Figure 1.9 Graphic representations of the SPME/sample system configuration, with dimensions and parameters labeled as follows: *a*, fiber coating inner radius; *b*, fiber coating outer radius; *L*, fiber coating length; *d*, vial inner radius; C_f, analyte concentration in the fiber coating; D_f, analyte diffusion coefficient in the fiber coating; C_s, analyte concentration in the sample; D_s, analyte diffusion coefficient in the sample; K_{fs}, analyte distribution coefficient between fiber coating and sample; $K_{fs} = C_f/C_s$ [37].

In two-phase systems (gaseous sample-coating or liquid sample-coating) at equilibrium, the initial amount of the analyte present in the sample is distributed between the sample and the SPME fiber coating. The mass balance in such system can be described in the following way:

$$C_o V_s = C_s V_s + C_f V_f \qquad (1.1)$$

where C_o is the initial concentration of the analyte in the sample.

V_s is the sample volume.

C_s is the concentration of the analyte in the sample at equilibrium.

C_f is the concentration of the analyte in the fiber coating at equilibrium.

V_f is the volume of the coating.

Partitioning between the sample and fiber coating is governed by the partition coefficient, K_{fs} also called the distribution constant :

$$K_{fs} = \frac{C_f}{C_s} \qquad (1.2)$$

Combination of eqns. (1.1) and (1.2) and a few simple rearrangement yield the final expression describing the amount extracted by the SPME fiber at equilibrium, n :

$$n = \frac{K_{fs}\, C_o\, V_s\, V_f}{V_s + K_{fs}\, V_f} \qquad (1.3)$$

1.6.3.2 Amount extracted in three-phase systems : headspace SPME [28,32,38,39]

In most cases, liquid samples are placed in vials with some headspace remaining inside. At equilibrium, by definition the chemical potentials of the analyte in all three phase (liquid sample-headspace-fiber coating) must be the same. The geometry of SPME headspace extraction is illustrated in Figure 1.10.

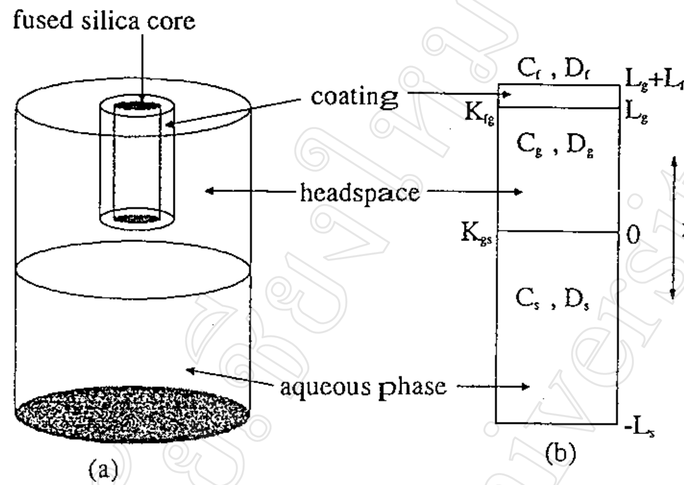

Figure 1.10 (a) Geometry for SPME headspace sampling. (b) One-dimensional model of the three-phase system: K_{fg} and K_{gs} are the coating/headspace and headspace/water partition coefficients; D_f, D_g and D_s are the diffusion coefficients of the analyte in the coating, headspace, and water; C_f, C_h and C_s are the concentrations in the coating, headspace, and water; L_f , L_g and L_s are the thickness of coating, headspace, and aqueous phase [39].

The amount of analytes adsorbed by the liquid polymeric coating is related to the several equilibriums of analytes in the three-phase system. Since the total amount of an analyte the total amount of an analyte should be the same during the extraction, we have

$$C_o V_s = C_f V_f + C_s V_s + C_h V_h \quad (1.4)$$

where C_o is the initial concentration of the analyte in the aqueous solution.

C_f, C_s, and C_h are the equilibrium concentrations of the analyte in the coating, the aqueous solution, and the headspace, respectively

Vf, Vs, and Vh are the volume of the coating, the aqueous solution, and the headspace, respectively

If we define coating/gas partition coefficient as;

$$K_{fg} = \frac{C_f}{C_g} \qquad (1.5)$$

and gas/water partition coefficient as;

$$K_{gs} = \frac{C_g}{C_s} \qquad (1.6)$$

The amount of the analyte adsorbed by the coating, $n = C_f V_f$, can be expressed as;

$$n = \frac{C_o V_f V_s K_{fg} K_{gs}}{K_{fg} K_{gs} V_f + K_{gs} V_h + V_s} \qquad (1.7)$$

1.6.4 SPME method development [28,31,32,34,40]

The basic method development using SPME is very similar to other types of chromatographic method development .The generic procedure is as follows :

(1) To choose the appropriate fiber for the analysis

As commercial development of SPME proceeds, a number of fiber types will become available. The choice of fiber will depend on the sample to be analyzed. The fiber paramrters to be considered in making this choice are:

- Phase polarity

The greater the polarity of the fiber coating, the higher its affinity for polar molecules, such as amines and alcohols. With this in mind, a fiber can be chosen that will selectively adsorb certain classes of molecules.

- Phase thickness

Phase volume is proportional to the square of the phase thickness, and is directly proportional to the partition ratio. In other words, the thicker the phase, the greater the amount of solute adsorbed. On the other hand, thicker phases will lead to slower desorption of solutes in the GC injector, particularly for higher boiling point solutes. In general, higher molecular weight solutes require thinner fiber phases.

- Phase upper temperature limit

Each of the fiber coatings has a characteristic upper temperature limit. Just as with a GC column, exceeding this limit can lead to breakdown of the phase and excessive bleeding. Since this bleed occurs at the head of column, the bleed

components will elute as distinct peaks, causing interference to the analysis. Adsorbed solutes with boiling point above the phase upper temperature limit will desorb slowly. If the desorption time is not long enough, desorption of such high boilers will not be quantitative and carryover occur. Thus, a phase should be chosen with a sufficiently high upper temperature limit for the solutes of interest, as well as possible contaminants. Figure 1.11 illustrates the general guidelines which can be used to determine the choice of coating for a given application.

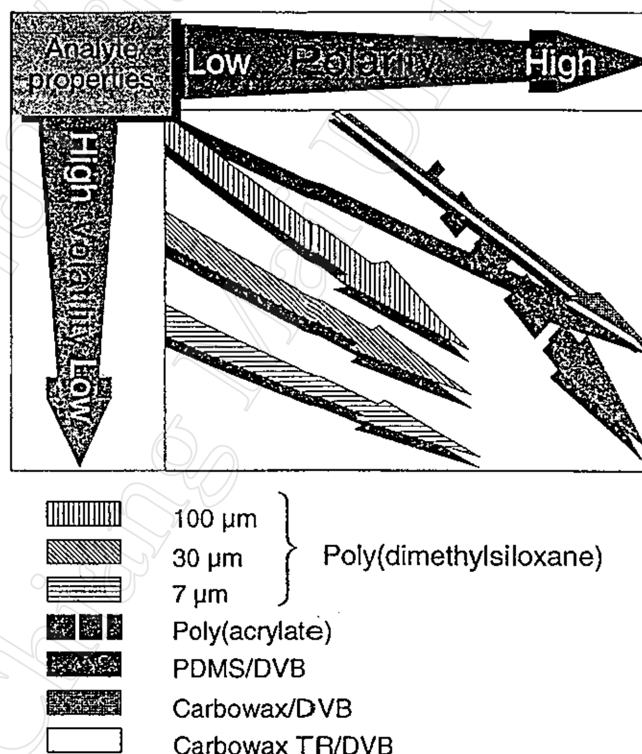

Figure 1.11 coating selection guide [32].

(2) To condition the fiber :

All type of fibers will adsorb contaminants while exposed to air during storage. Thus, the fiber should always be conditioned before the first analysis by inserting it for a period of time into a hot GC injector that inert carrier gas flowing

through it. If the injector is connected a column and detector, the progress of the conditioning can be monitored by observing the detector baseline with the column at its maximum analysis temperature, so that any desorbed components will be minimally retained. Conditioning of the fiber should be done at its temperature limit. New fiber may take as much as an hour to condition, but this time is expected to improve as fiber technology develop.

(3) To determine initial GC conditions for the analysis :

Generally, a temperature program from ambient to 50 °C above the desorption temperature will be a good starting point. If standards are available and can be injected with a microliter syringe, the column separation conditions can be worked out in advance of the SPME conditions.

(4) To determine adsorption and desorption times :

Start with adsorption times of 2, 5, and 10 min for three separate runs. The relative peak responses will point toward the optimum adsorption time. In some cases, adsorption times up to 30 min will be necessary. Desorption times of 1 to 2 min are usually adequate, but adequacy of desorption time should be tested by following a desorption of standards with a blank run. In the other words, only a desorption cycle should be performed with the same fiber, to see if there is any carryover of the higher boiling components. If late eluting peaks are observed that correspond to sample components, then a longer desorption time or a higher desorption temperature is required. The fiber upper temperature limit should not be exceeded. If liquid sampling of volatiles leads to contamination from high boiling impurities, headspace sampling with the fiber should be attempted and the extraction mode selection guideline as recommended in Table 1.8.

1.6.5 Applications of the SPME on Environmental Analysis

The following Table 1.9 are listed some application of SPME with different type of analytes and samples.

Table 1.9 Some application of SPME on environmental analysis.

SPME fiber coating	Analytes	Samples
95 µm poly(dimethylsiloxane)	volatile chlorinated hydrocarbons	air, water [41]
100 µm poly(dimethylsiloxane)	volatile organic compounds (VOCs)	air [17]
100 µm poly(dimethylsiloxane) 85 µm poly(acrylate)	fatty acids	air, water [42]
65 µm carbowax divinylbenzene 100 µm poly(dimethylsiloxane) 85 µm poly(acrylate)	amines	air, water [43]
100 µm poly(dimethylsiloxane)	chlorobenzenes	soil [44]
85 µm poly(acrylate)	chlorophenols	soil [45]

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Table 1.9 (continued)

SPME fiber coating	Analytes	Samples
15 µm poly(dimethylsiloxane)	polyaromatic hydrocarbons	water [46]
100 µm poly(dimethylsiloxane)	nitropbenzene, isophorone, 2,4-dinitrotoluene and 2,6-dinitrotoluene	water [47]
100 µm poly(dimethylsiloxane)	nitrigen and phosphorus containing pesticide	water [48]
7 µm poly(dimethylsiloxane) 100 µm poly(dimethylsiloxane) 85 µm poly(acrylate)	volatile organic compounds	water [49]
100 µm poly(dimethylsiloxane) 85 µm poly(acrylate)	organophosphorus pesticides	water [50]

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Table 1.9 (continued)

SPME fiber coating	Analytes	Samples
7 µm poly(dimethylsiloxane) 100 µm poly(dimethylsiloxane) 85 µm poly(acrylate)	haloethers	water [51]
65 µm carbowax divinylbenzene	aromatic amines	water [52]
100 µm poly(dimethylsiloxane)	carbonyl compounds	water [53]
100 µm poly(dimethylsiloxane)	organochlorine pesticides	water [54]
65 µm carbowax divinylbenzene	triazine herbicides and their degradation products	water [55]

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1.7 Gas Chromatography

In gas chromatography the compounds to be analyzed are vaporized and eluted with the aid of a gas a mobile phase through the column. The mobile phase is used alone as a carrier gas, so that interactions of the mobile phase with the analyte are of no significance. A solid substance can serve as a stationary phase on which the constituents to be separated can be adsorb. In practice, the used of a liquid as a stationary phase is preponderant for the analysis of organic compounds. It is termed gas-liquid chromatography (GLC) or simply gas chromatography. The predominant separation principle is the partition of substance between the liquid stationary phase and the gaseous mobile phase [56].

1.7.1 Principles of gas chromatography [57-58]

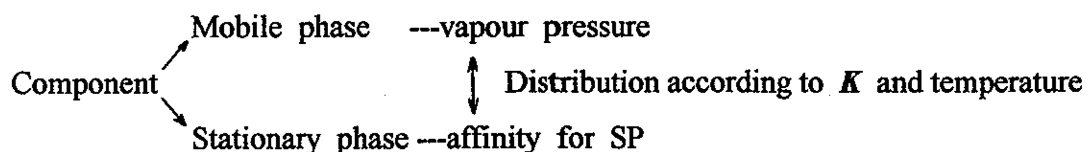
In the case of gas-liquid chromatography (GLC) using a column with the liquid stationary phase coated onto the inert support particles. A gaseous mobile phase transporting components as a vapour over a stationary phase, separation being effected by interaction of the individual components with the stationary phase resulting in retardation according to their distribution ratio (K) :

$$K = \frac{C_{SP}}{C_{MP}} \qquad (1.8)$$

where C_{SP} is the concentration of the component in the a unit volume of stationary phase

C_{MP} is the concentration of the component in a unit volume of mobile phase.

In GC the distribution ratio is dependent on the component vapour pressure, the thermodynamic properties of the bulk component band and affinity for the stationary phase. The equilibrium is temperature dependent and, therefore, the stationary phase column must be precisely and accurately maintained.



1.7.2 Resolution [57-58]

An ideal chromatogram is obtained when all the analytes in a sample mixture are separated with base line resolution in the minimum analysis time. In practice the chromatographic parameters are select to obtain the best practical separation. The most appropriate stationary phase and column system are chosen after considering the polar characteristics of the analytes, their volatility range and selecting the optimum mobile phase velocity and column system temperature programme. Resolution is a function of retention characteristic of the components, column efficiency (band broadening) and the selectivity or separating capabilities of a column. These are reflected by the terms retention factor (capacity factor), k, column efficient, N, and

separation factor, α

$$\text{where } k = \frac{t_R}{t_M} = \frac{t_R - t_M}{t_M} \tag{1.9}$$

$$\alpha = \frac{k_B}{k_A} \tag{1.10}$$

$$N = \frac{l}{H} = 16\left(\frac{t_R}{W_b}\right)^2 = 5.54\left(\frac{t_R}{W_h}\right)^2 \tag{1.11}$$

$$\text{and when } t_M \text{ is significant} \quad N_{eff} = 16\left(\frac{t_R}{W_b}\right)^2 = 5.54\left(\frac{t_R}{W_h}\right)^2 \tag{1.12}$$

where t_M is dead time ; t_R and t_R are retention time and corrected retention time, respectively.

W_b and W_h are base width of a peak and width at half height.

N and N_{eff} are column efficient and effective column efficiency.

k_A and k_B are retention factors for components A and B.

H is HETP, height equivalent to a theoretical plate or equilibrium step height.

l is column length.

For a given column length, optimum column efficiency is obtain when the equilibrium step or plate height is at a minimum, that is, the column band broadening

processes described by the van deemter equation are minimized by selecting the optimum velocity of the mobile phase.

Adjacent peaks are considered resolved if there baseline separation, that is, if the sum of their half widths is less than the separation between the peak maximum. The ratio of peak separation to half widths is a measure of the resolution (Figure 1.12) :

$$R_s = \frac{(t_{RB} - t_{RA})}{\frac{1}{2}(W_{bB} + W_{bA})} = \frac{2\Delta t}{(W_{bB} + W_{bA})} \approx \frac{\Delta t}{W_{bB}} \qquad (1.13)$$

For an acceptable separation without too long an analysis time R_s should be between 1.2 and 1.8. Note that baseline resolution is achieved at R_s~1.5. The resolution can be directly obtained from a chromatogram.

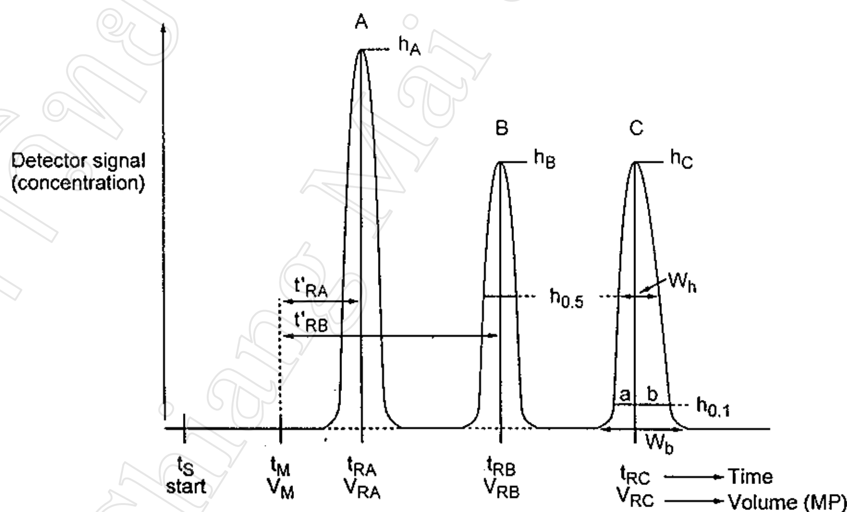


Figure 1.12 Data and symbols on chromatograms of A, B and C [57].

1.7.3 Columns and stationary phase [57]

The key to good GC separations is to use the most appropriate stationary phase and column at the optimum mobile phase velocity and column temperature. The main factors to consider when specifying the system for analysis of a given sample mixture are

- to note the boiling point range and vapour phase characteristics of the components and number of component ;
- to identify the polar and non-polar characteristics of the components in the mixture and their functional groups ;
- selection of a stationary phase/column system and stationary phase film thickness to give the required selectivity and separation factors ;
- optimising the carrier gas velocity for the fastest analysis time and minimum dead time set at the elution temperature of critical pair of the peaks, helium should be used as a carrier gas if at all possible;
- optimising the temperature programme or selecting the best temperature for isothermal analysis ; and
- testing the system using a standard mixture either representative of the sample(s) to be analysed or a mixture which includes compounds of differing polar character and boiling points.

1.7.4 Gas chromatography instrumentation [57-62]

The instrumentation for GC incorporates the features common to all forms of chromatography, namely a mobile phase, sample introduction system, a stationary phase and a detector system. GC has a gaseous mobile phase, the carrier gas a column containing the stationary phase, with sample introduction by syringe injection. The detector generates a minute signal current requiring an amplifier for output to produce the chromatogram. Column temperature, instrument variables and signal processing are controlled by a microprocessor.

In this work, GC/FID and GC/MS were obtained to identify and determine of BTEX compounds in samples.

- Gas chromatography - Flame ionization detector (GC/FID)

The modules of a gas chromatograph are illustrated in Figure 1.13 the differences in gas chromatographic systems lie in the carrier gas used, in the sample injection system, as well as in the columns and detector used.

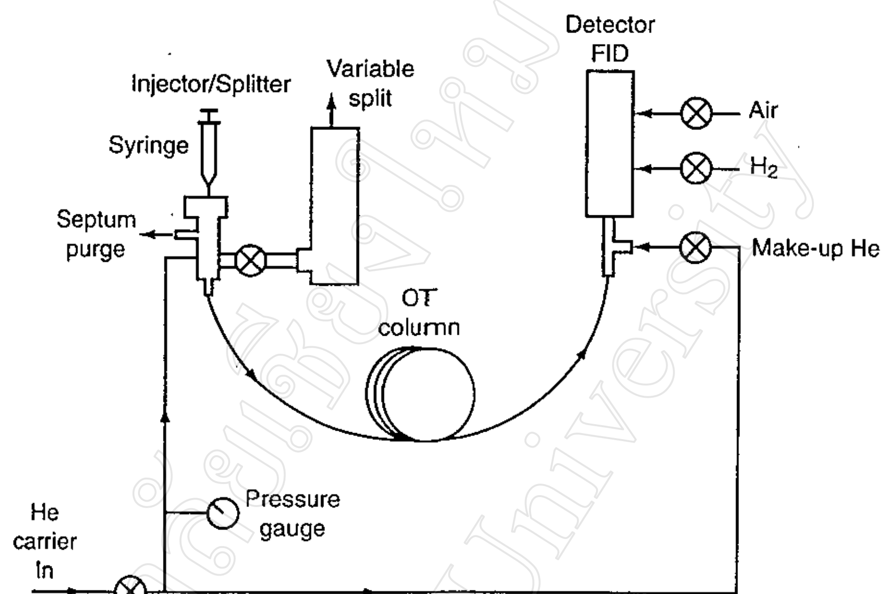
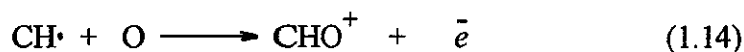


Figure 1.13 Schematic of a typical gas chromatograph [58].

The latter are termed "detectors" and form an independent part of the gas chromatograph. Their use is based on the various physical and chemical properties of the eluted substances or products formed by their reaction inside the detector.

The FID is regarded as the universal GC detector and hence is used for routine and general purpose analyses. The detection principle is based on the change in the electric conductivity of a hydrogen flame in an electric field when feeding organic compounds. The organic compounds. The organic compounds escaping from the separation column are pyrolyzed; that is to say, fragmented. During subsequent oxidation by oxygen which is fed into the flame from outside, ions are formed by the following reaction :



$$CH\cdot + O \longrightarrow CHO^{+} + \bar{e} \qquad (1.14)$$

The flow of ions is recorded as a voltage drop accross a colector electrode (figure 1.14). The FID is sensitive to all compounds which contain C-C or

C-H bondings. It is also insensitive to the nonflammable gases: H_2O, CO_2, SO_2, or No_x. The FID is distinguished by a very low detection limit and a large linear range. However sample constituents are destroyed.

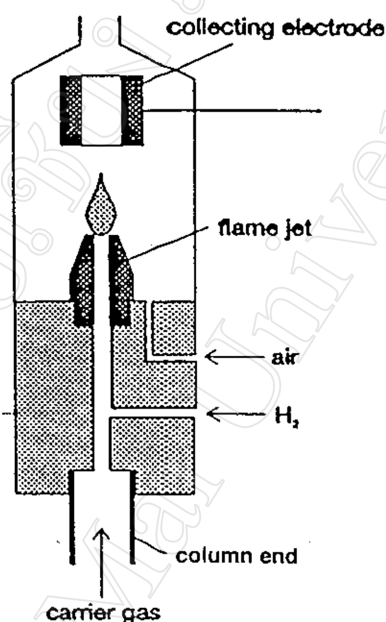


Figure 1.14 Principle structure of a flame ionization detector [56].

- Gas chromatography - Mass spectrometry (GC/MS)

Chromatography combined with various detection techniques is one highest performance and most often used analytical methods. Among these chromatography coupled on-line to mass spectrometry (MS) combines the advanges of chromatography (high selectivity and separation efficiency) and mass spectrometry (structural information and further increase in selectively), while being relatively straightforward to accomplish.

Figure 1.15 shows a block diagram of a typical computerized gas chromatograph/mass spectrometer (GC/MS). This system consists of three separate units that are coupled together physically and /or electronically. A gas chromatograph separates mixtures and introduces sample molecules, then analyzes and detects the

resulting ions ; and a computer system controls the operation of the GC and the MS, as well as providing data manipulation during and after data collection.

The heart of a mass spectrometer is the mass analyzer. It performs the fundamental task of separating the charged fragment based on their m/z, and dictates the mass range, accuracy, and sensitivity. There are five common types of mass analyzers : quadupoles, ion traps, time-of -flight (TOF), magnetic sectors, and

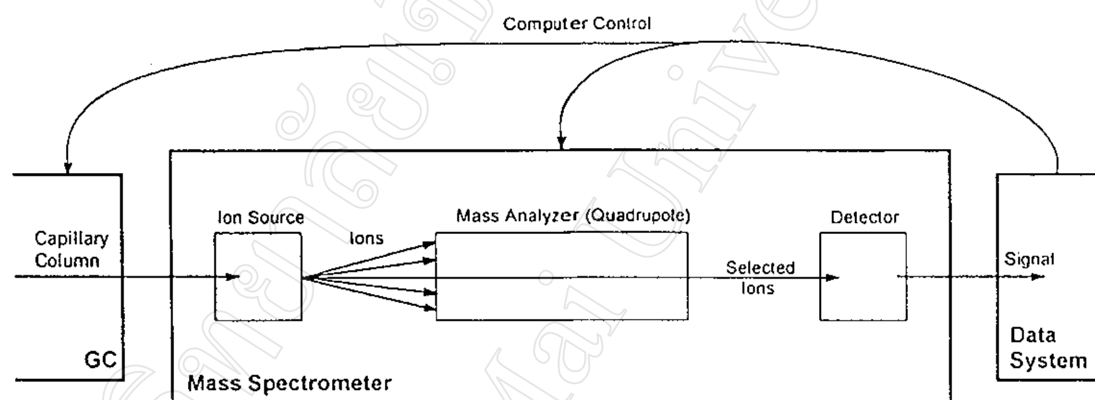


Figure 1.15 Block diagram of a GC/MS/computer system [61].

Fourier-transform-ion cycrons (FT-ICR). Over the years, guadupole-MS has become increasingly popular. Quadupole mass analyzers are based on the ion focusing the Greek electrical engineer Christophilos. The word "quadupole" is derived from the Latin word for four (quaduplus), and "pole," to describe the array of four rods that are used. As is seen in Figure 1.16, the quadupole mass filter cosists of four rods are used to generate equal but out-of-phase electric potentials; one is alternating current (AC) frequency of applied voltage that falls in radiofrequency (RF) range, and one is direct current (DC). The potential difference can be varied to create an oscillating electrical field between two of the opposite rods, resulting in their having equal but opposite charges.

When, for example a positive-charged ion enters the quadupole field it will be instantly attracted toward a rod maintained at a negative potential , and if the

potential of that rod change before the ion impacts, it will be defected, i.e., change direction. Thus every stable ion entering the quadupole region traces a sine-wave-type pattern on its way to the detector. By adjusting the potential on the rods, selected ions, a mass range, releasing them from the influence of the oscillating field, and are pumped away by the vacuum pumps.

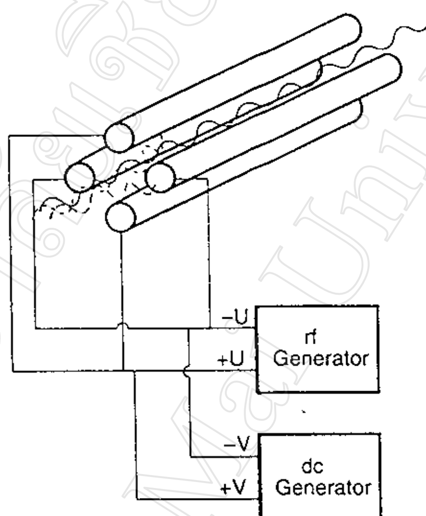


Figure 1.16 Quadupole mass analyzer [61].

1.8 The Aims and Scope of the Research Project

The aims of this research work can be summarized as follows.

1.8.1 To study and obtain the optimum GC conditions for BTEX analysis in water.

1.8.2 To investigate and optimize the extraction conditions for headspace solid-phase microextraction in the GC analysis of real water samples.

1.8.3 To determine BTEX compounds in real water samples using the optimum conditions of GC and SPME.

1.8.4 To confirm the identification of BTEX components in real water samples by GC-MS.