CHAPTER 2

LITERATURE REVIEWS

2.1 Methods for the analysis of VOCs in Air

There are activities both natural and anthropogenic that contribute pollutants to the air. Anthropogenic sources may be divided into two main source, mobile and stationary. The mobile source include automobiles, trains, airplanes, and the major stationary sources are factories, pipeline and storage tanks. Pollutants in air occur at low concentrations since air itself has low density, and the pollutants easily to diffuse and dilute. Volatile compounds are normally present in the vapor form rather than on the particulate phase. The conventional approach to the determination of volatile organic compounds (VOCs) at trace level in ambient air involve several steps: sampling, sample preservation, transportation, storage, sample preparation and analysis. Sampling is a key step in this process. The sampling methods for VOCs include whole air samplers (eg. Canister) or sorbent trap, and followed by analysis by GC or GC-MS. Both have advantages and disadvantages. EPA Method TO-1 and TO-2 employ sorbent trapping to sample air, transport them to the lab, and then thermally desorb to the GC column. On the other hand, EPA method TO-3 uses a cold trap and then desorbs to the column. NIOSH and OSHA use sorbent sampling methods but extract the analytes by solvent, which are then injected to GC for analysis. EPA Method TO-14, TO-15 and TO-18 use the canister samplers to collected the air samples, and which then are brought back to the lab for analysis [6]

2.1.1 Adsorbent trap sampling

Adsorbent trap sampling is a method to trap and concentrate the desired analytes as the air sample passes through, a trap or a cartridge containing an appropriate sorbent. The VOCs are adsorbed on the surface of the packing while other compound pass through. Then the cartridges or traps are returned back to laboratory for analysis. The adsorbed analytes are removed from the catridge either by raising the temperature, or by washing with an appropriate solvent. There are two main parameters that effect the efficiency of this method, breakthrough and analyte recovery. It is important that the trapping material be selected carefully to adsorb the analytes efficiently and selectively, and yet be easily recovered during the desorption step. When air sample pass through a trap, the analytes are retained and eluted at the same time. Figure 2.1a show the progress of the analyte in the trap. Early in sampling, the breakthrough does not occur, but the sample front moves forward. When it reaches the end, it begins to breakthrough which means that the sampling is no longer quantitative. The breakthrough is one of the most important concern so, the configuration of the trap must be designed to be compatible with other parameters. Traps are often designed to have a back up portion for checking the sample breakthrough. In case where multiple analytes of varied volatility are present, a layered trap as shown in Figure 2.1b is used. The trap contains more than one adsorbent packed in series with layers of less retentive adsorbent in the front end and a strong in the back end. The sample is presented into the weak sorbent end which adsorbs difficult-to-desorb compounds while the easy-to-desorb pass along to be adsorbed at the strong sorbent part. Sorbent traps offer several advantages. They are easy to transport since the traps are small. They can be designed to eliminate some interferents, and can reused. There are also some disadvantages, such as, bias against very volatile or very non-volatile compounds,

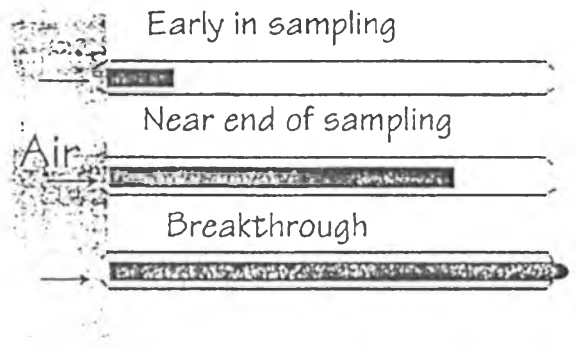


Figure 2.1 a Illustration the contaminate air absorbed in a trap [3].

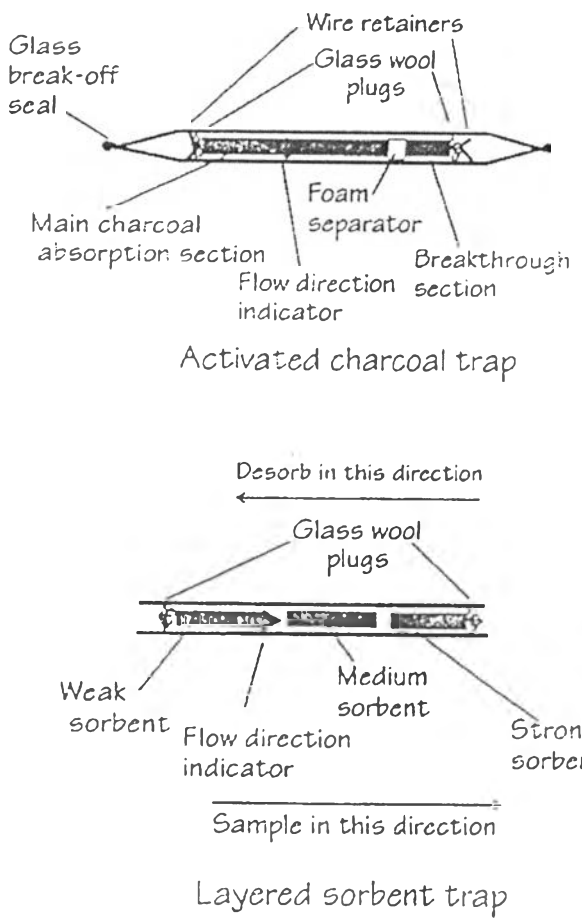


Figure 2.1 b Sorbent trap for sampling VOC_s in air. [3].

can cause contamination of samples with artifacts and may cause errors due to ice plug in trap in when large amount of moisture is present [3].

2.1.1.1 Thermal desorption of VOC samples.

After sorbent sampling step is completed, the traps are brought to the lab for analysis. The adsorbed analytes need to be removed from the sorbent and injected into the GC. The thermal desorption apparatus is shown as in Figure 2.2. It is designed to remove the adsorbed analytes by heating. The carrier gas flushes the recovered analytes to be recollected in a small sorbent trap, which can be rapidly heated to inject a sharp pulse to produce sharp peaks in a chromatogram. Additional traps, such as cryogenic focusing trap may be used to eliminate humidity and serve as a focusing trap for GC.

2.1.1.2 Solvent desorption of VOC samples.

This desorption method is used in case of the adsorbed analytes are strongly adsorbed, or the analytes are unstable and may decompose during desorption process. The analytes from the sorbent trap are removed by a solvent instead of thermal desorption. This method has the advantage of being simpler and less expensive than thermal desorption. The disadvantages are that the sample should have high concentration, and there is always a large solvent peak that interferes in the chromatograms.

2.1.2 Canister sampling

The objective of canister sampling is to collect air sample in containers that must not either add or remove analytes from the sample. The canister are low pressure stainless steel containers, where the internal surface is lined with silica or electrolytically polished to deactivate it. The most commonly used canister of 6-l size is as shown in Figure 2.3a. Air sample is usually filled in cleaned canister by a pump. The canister is brought to laboratory. Whole air samples must be concentrated before being injected into the column. Typical instrumentation for this process is shown in Figure 2.3b. The analytes

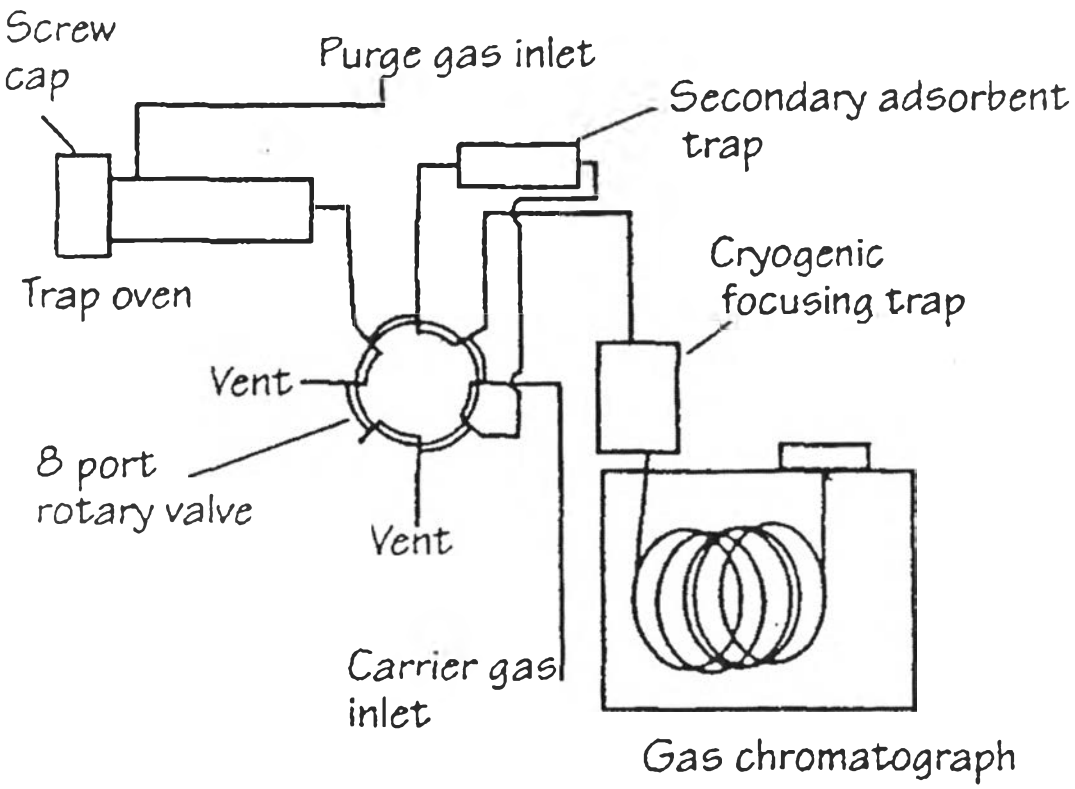


Figure 2.2 Apparatus for desorbing VOCs from an adsorbent trap and connection to GC [3].

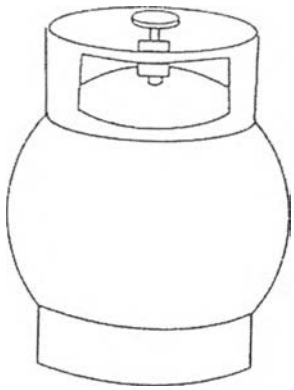


Figure 2.3 a A stainless steel air sampling canister [3].

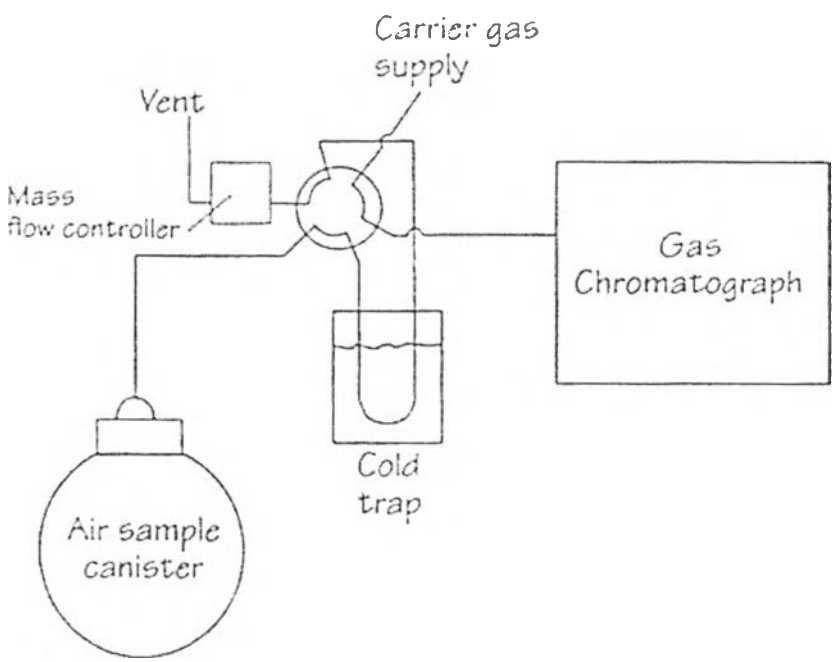


Figure 2.3 b System for determining air volality, sampled in a stainless steel canister. [3].

from the canister are trapped in a cold trap, the trap is heated and the sample is swept into GC column with a stream of carrier gas. The advantages of canister sampling is that there are less chances of contamination or artifact formation since the sample is not heated and the reactive materials are not concentrated while the sample is awaiting analysis. The disvantages are higher cost and inconvenient in handling or transportation and the volatiles can not equilibrate between the sample and the vapor phase (air) at the top of container [3].

2.1.3 Microtrap

Continuous on-line monitoring needs instruments that be amenable to automated operation. Real time or, near real-time analysis is accomplished by the frequency of separating the analytes from matrix and analysis. The higher the frequency, closer it is to near real-time. In general, spectroscopic techniques are used in real-time monitoring because of their speed, such as, FT-IR and MS. However these techniques face seriously challenges with water vapor interference and deconvolution of individual spectra in a complex matrix [7].

GC has been used in continuous monitoring application since 1950, the sample flows through a sorbent trap for a period of time and then thermally desorbed for GC analysis [8]. Usually, a cycle time of hour or several hours. The key component of an on-line sampling system are conditioning, concentratation and injection devices. All these have to be carried out automatically and repeatedly. Typically,sampling valves are used as injectors with the objective of sending the sample intermittently to column. A large volume of sample is injected from sample valve, the generated peaks are broad and the resolution is poor. If a small volume is injected, a small detector response is generated,

leading to low sensitivity. In environmental monitoring where VOCs concentration is usually low, this method is not feasible.

In order to deal effectively with trace monitoring for regulatory compliance, the implemented methods need an automated injection device that can produce high sensitivity and resolution via analyte preconcentration. Recently, a microsorbent trap, referred to as a microtrap, has been developed as an on-line sample preconcentration and injection device for continuous, on-line monitoring of low level organics in vapor phase [7,9-10]. It has been implemented in both air and water monitoring [9-12]. A microtrap is a short, small diameter (0.5 mm to 1.5 mm ID) sorbent trap with low heat capacity; thus it can be heated or cooled very quickly. Fast heating provides narrow injection band, while fast heating-cooling cycle lead to faster operation. The sample flows into the microtrap, which accumulates the VOCs on a sorbent while the background gases pass through. Resistive heating using a pulse of electric current makes an injection for GC separation (or GC-MS) by rapid desorbing the retained organics. Continuous monitoring is achieved by making a series of injections at short intervals generating a series of chromatograms. The amount of accumulated analytes in the microtrap is proportional to sample concentration, and it can be used for quantitative analysis [9]. The microtraps have been used in various modes to serve different analytical needs. They have been used as stand-alone devices or in conjunction with a gas sampling valve which has been referred to as the sequential valve microtrap (SVM) [7,10,13]. Due to its small size, the microtrap can hold a small amount of sorbent. Consequently, the important issue effecting microtrap performance is sample breakthrough. The main factors effecting microtrap performance is the breakthrough volume (BTV) which depends upon the sorbent amount. The sorbent quantity depends upon the diameter and the length of microtrap. The temperature of the microtrap also plays an important role: an increase in temperature

decreases BTV and very low temperatures makes desorption difficult. Pulse time (time for which an electric pulse is applied) also needs to be adequate so that complete desorption is achieved. Several papers discussing these issue have been published [7,9, 13-15]. Such microtrap-based pre-concentration/injection device have shown significant advantages over conventional injectors. They are simple, can be operated automatically in on-line monitoring, yield low detection limits, and can handle relatively large concentration of moisture going into the GC [16-17].

2.1.4 Adsorbents

Adsorption in chromatography was observed since 1960 when Hollis [1,18] started using porous polymer as packing material in GC. Since then, the use of gas-solid chromatography as a tool for the characterization of a sorbent has been greatly improved. This improvement led to the use of sorbents in the field of environmental monitoring. Consider attention has been given to develop adsorbent used in gas-solid chromatography and sample enrichment.

These improvements led to the development of many types of adsorbents which possess one or more functional groups and exists in many molecular sizes and shapes. Kiselev first classified the sorbents by based on the interaction between adsorbent and adsorbate into 3 classes: Class I, Class II and Class III. This is shown in Table 2.1. Class I are adsorbent that possess no ionic charge on the surface, so this class will interact with other molecule by molecular size and shape. The adsorbents in this class are hydrophobic because water has lone-pair as negative charge which will not interact with the adsorbent. Examples of such adsorbents are the graphitized carbon blacks such as Carbopack C, Carbopack B and Carbotrap (supelco Inc). Class II are the adsorbent that possess positive charge, this adsorbent will interact with other molecule by both electrostatic and Van der

Waals interaction. It is hydrophilic adsorbent. Example is Activated silica gel. Class III possess negative charge and have electrostatic interaction with positived charge molecules and Van der Waals interaction with no charge molecule. It is also hydrophobic adsorbent. Examples are Activated charcoal, porous polymers such as Tenax and Carbon molecular sieves.

Kiselev [17,19] also classified adsorbents according to electronic activity, into four groups: n-alkane, aromatic hydrocarbon, organometallics and organic acids, organic bases and aliphatic alcohols [8,17].

Table 2.1 Classification of Adsorbent

Class	Adsorbent	Surface
Class I	Graphitized carbon black	Graphitic carbon (no ion or active groups)
Class II	Activated silica gel	Oxides of silica gel (positive charges)
Class III	Activated charcoal	Oxides of amorphous carbon (negative charges)
	Porous polymers	Organic" plastics" (weak-strong Class III)
	Carbon molecular sieves	Amorphous carbon (weak Class III, can approach Class I)

2.1.5 Breakthrough Volume

The sorbent is filled in microtrap for trapping and concentrating the analytes. The three most significant parameter of a sorbent trap are adsorption capacity, desorption efficiency, and storage stability [17]. A good sorbent should be inert to adsorbed compounds and posses high adsorption capacity. Adsorption capacity or sample capacity is measured by the breakthrough of a constant concentration through the sorbent bed. Normally, breakthrough is defined as the volume in liters required for the outlet concentration to reach 5 % of the (constant) concentration being sampled [17]. Breakthrough in this sense is measured as breakthrough volume (BTV) and can be defined in detail as the calculated volume of carrier gas per grams of adsorbent resin which causes the analyte molecules to migrate from the front of the adsorbent bed to the back of the adsorbent bed [14,20]. So BTV can be measured by multiplying retention time by the flow rate of carrier gas and divide by the weight of the adsorbent resin packed in the trap.

There are several factors that affect BTV such as temperature, humidity, properties of sorbent, properties of gas mixture, flow rate, dimension of trap and linear velocity of carrier gas [17]. BTV can be calculated from the derived Van' t Hoff-type equation by using main effecting parameter: the adsorption temperature and the concentration of the adsorbed compound [1,21-22].

$$D[\log(BTV)]/\, d1/T \quad = \quad -\Delta H_{ad}/\, 2.303R$$

Particularly in a microtrap, BTV is serious issue because it contains a small amount of adsorbent. Detection of the emerging front is somewhat difficult to observe. There are three main accepted methods for determination of BTV. It can be measured based on the variation in response from a microtrap pulse as a function of injection interval. At short injection interval, the amount to be concentrated in microtrap is low,

then generating a low signal in a corresponding chromatogram. Increasing the time interval increases signal intensity until reach at the breakthrough point, and the response does not increase any more eventhough injection interval time is increased. The breakthrough time corresponds to the time at which the maximum response is reached as shown in Figure 2.4 a.

The second method uses the peak shape of the microtrap injection as the sample continuously flow through When the microtrap is heated, a desorption peak occurs and microtrap starts to adsorp analyte from the flowing stream again, thus lower the base line of response signal to a negative peak. As sample begins to breakthrough, the detector response increases to the baseline level again. The horizental line shows region where microtrap pass breakthrough point. No further adsorption takes place. The width of negative peak equals to the breakthrough time as shown in Figure 2.4b.

The third method use the principle of frontal chromatography as shown in Figure 2.4c. At the initially of injection, Microtrap adsorb the analytes, so the begin to increase to a steady state which show breakthrough completely. BTV at this method come from the time require for the concentration front to appear [13].

2.1.6 Application of microtrap

2.1.6.1 Microtrap Gas Chromatography

Continuous, on-line monitoring offers several advantages and challenges over the conventional approach of sampling followed by laboratory analysis. This approach requires automated instruments to perform on-line sampling, sample condition and analysis. It provides near real-time information at lower cost, eliminates contamination and other errors that can be introduced during storage and transportation of the sample and the analytical results can be feed back for process control. GC has been used in

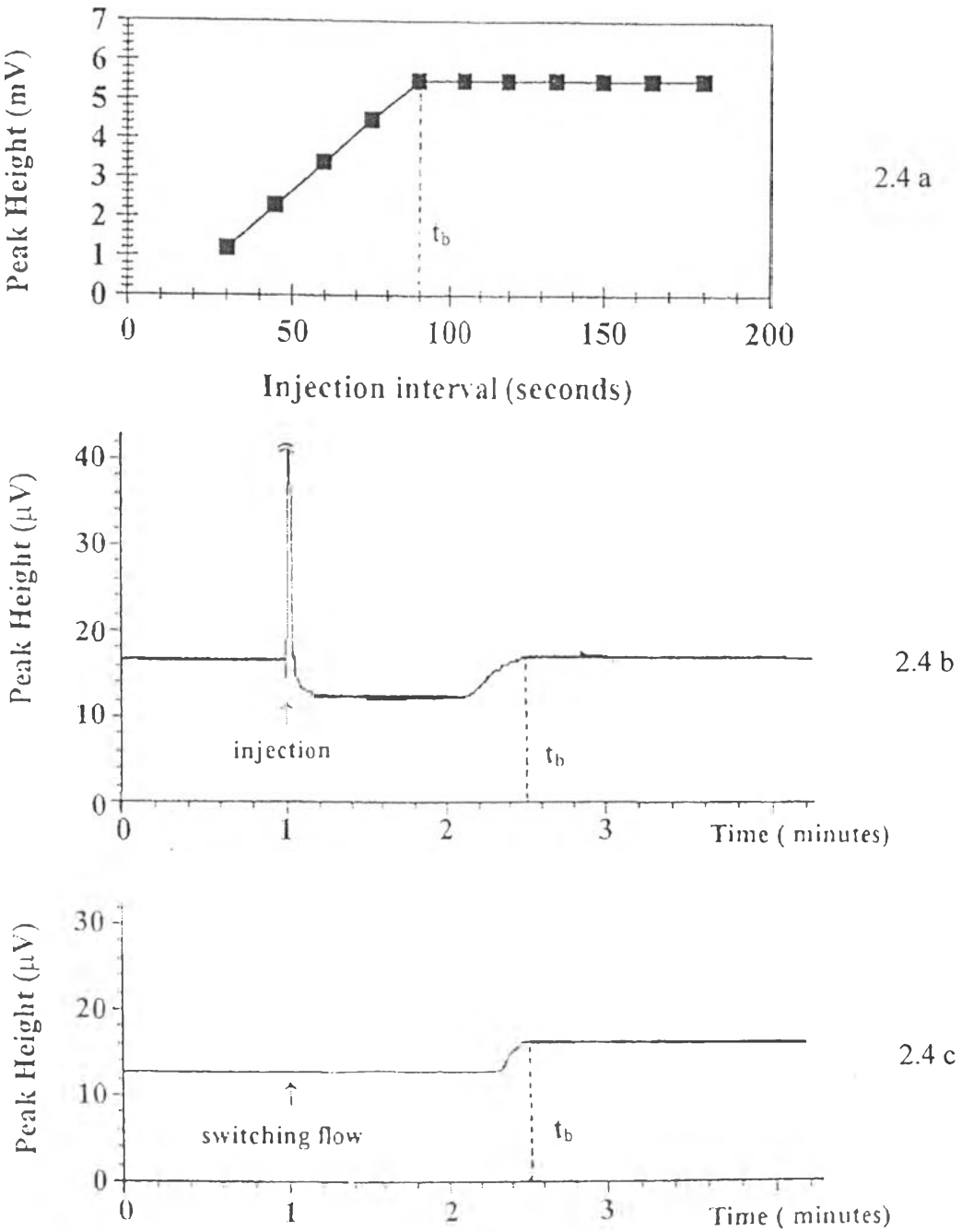


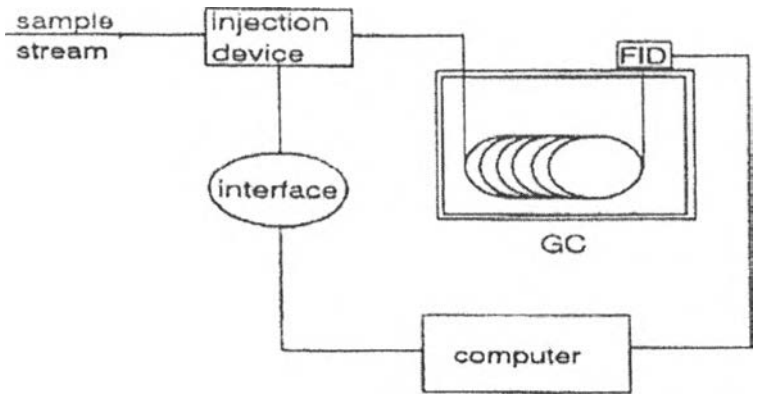
Figure 2.4 Breakthrough time by three different methord. 2.4a : Response of the analytical system as a function of interval between microtrap pulses, 2.4b : Characteristic peak from a microtrap, 2.4c : Chromatogram generated by frontal chromatography [1].

continuous monitoring applications for a long period. Conventionally sample valves have been used to inject a sample into GC. A large injection volume generates broad and low resolution peaks, so the sample valve is not suitable to analyze trace level compound. A sorbent has been used for trapping then transport to laboratory for analysis. This conventional techniques get errors from contamination in transportation process and can not be used in continuous, on-line analysis. The schematic diagram of microtrap- GC is shown in Figure 2.5.

A micro-sorbent trap refer to as microtrap has been used as concentrator and injector in conjunction with GC. Microtrap retain the analytes selectively while the sample is passes through, and then desorbed by an electric current heating. This application of microtrap have several advantages, such as simple instrumentation, low detection limit at sub-ppb level, no interference from moisture, no need of cryogenic trap and can be continuous, on-line monitoring [7,9-10].

2.1.6.2 Microtrap on C-NMOC

There has been a need for a simple, inexpensive method, rugged instrumentation that can perform continuous, on-line monitoring and provide important information. While direct-FIDdetection is inexpensive, rugged and simple, its limitation is that different compound have different response factors in the FID. This performance gives significant uncertainty in the measurement of total organic carbon. The FID also responds to methane. Non-methane organic carbon(NMOC) is a measure of total organic carbon except methane. It is a convenient way of expressing total organic emissions in terms of carbon, and it is a fast and inexpensive method. In NMOC, the measurement is in terms of total carbon irrespective of the specific compounds being emitted. It is designed to produce an equal response for each carbon atom. EPA Standard Method 25 has been used to measure NMOC in air samples, here samples are collected in a canister and then sent to



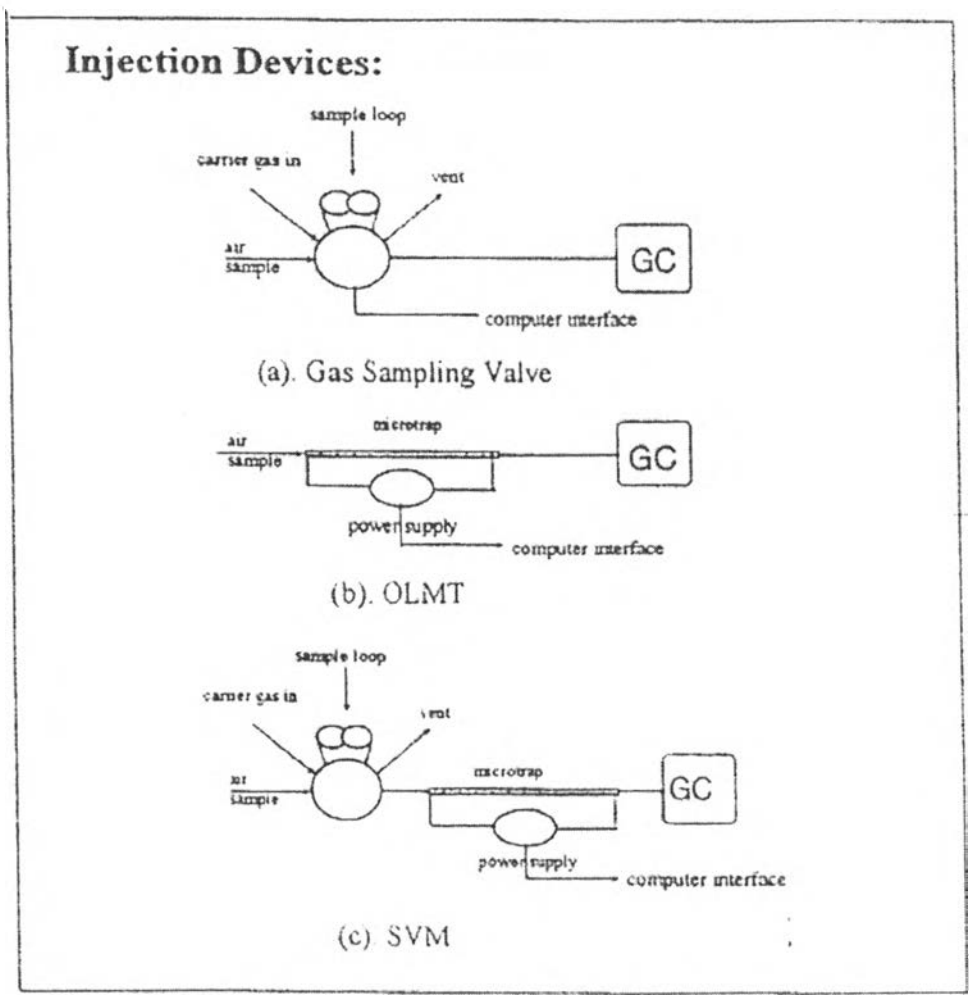


Figure 2.5 Continuous monitoring system showing the different injection systems [1].

laboratory for analysis. The air sample is injected into a GC column for the purpose of separating the organic compounds from carbon dioxide and methane. The organics are then backflushed into NMOC detector. The principle of NMOC detection is to convert all organic compounds into CO_2 by catalytic oxidization, and then to reduce the CO_2 to CH_4 which can be measured by a conventional FID. NMOC is used by EPA standard method 25. However, this method can not handle more than 8 % of CO_2 because the resolution between CO_2 and the organics decrease. So when sample contains large amount of CO_2, the system is not easy to implement. There are also biases due to the moisture content in the sample, and the detection limits are in the ppm range. An important drawback is that, it is not designed for continuous, on-line monitoring.

Microtrap system has been used to solve some of the previous problems, the technique developed is referred to as the continuous-NMOC (C-NMOC) analysis. Microtrap is used to replace GC column and serve as preconcentrator and injector to analysis. A schematic diagram of C-NMOC analyzer is shown in Figure 2.6. The injection system consists of gas sampling valve with a large sample loop. The microtrap is put in series with the gas sampling valve. The detector consists of oxidation unit to convert organics to CO_2 by air, reduction unit to reduce the CO_2 to CH_4 by H_2 and a FID. This method gives low detection limit because a large volume of air is analyzed, There is no interference from moisture since the microtrap allows the moisture through. It can be used for long periods of operation, and can be used as a continuous, on-line monitor [7,9-10,23-24].

2.1.6.3 Microtrap Mass Spectrometry

Mass spectrometry (MS) is a sensitive analytical instrument. It shows both molecular and ionic fragments. The availability of different ionization techniques and MS-MS capabilities of modern iontrap mass spectrometer make MS a powerful analytical

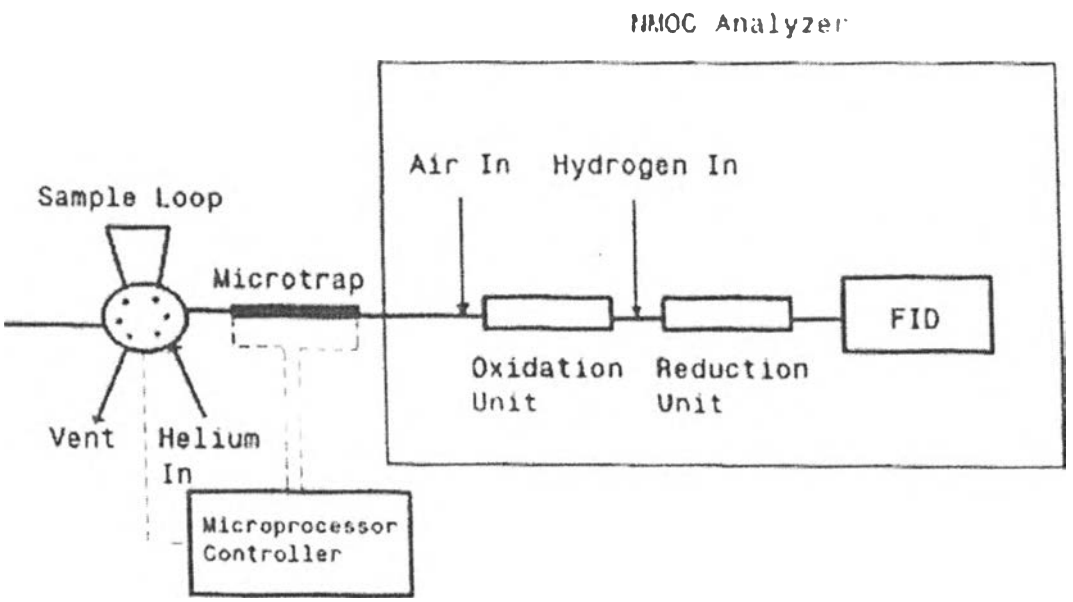


Figure 2.6 Schematic diagram of C-NMOC analyzer [1].

tool. MS have fast response time, high sensitivity and high resolution spectra containing molecular weight and structural information. These characteristics are highly desirable in air monitoring at low concentration level in a complex matrix. One of the challenges in implementing MS as an analytical instrument is that the organics are present in trace concentration but the background gas such as H_2O and CO_2 may be present at higher level. In this condition, MS can be used to determine trace level of compounds but it needs to eliminate the interferences prior to entrance to the ionization chamber of MS, especially moisture which is a source of serious interference to MS. Microtrap has been used as an interface for on-line mass spectrometry for continuous, on-line monitoring. The system is shown in Figure 2.7 The microtrap in the system selectively traps only organics and accumulates it but allows the rest to go through. Thus the microtrap serve as a separator to filtrate interference out before going to MS as well as an on-line preconcentrator. This microtrap mass spectrometry system is also continuous, on-line. The organics are injected into MS by rapid thermal desorption. Corresponding to each desorption, a mass spectrum of the sample components is obtained [25].

2.2 Methods for the analysis of VOCs in water

The measurement of VOCs in water has always been a challenge. VOCs in water exist at low concentrations in ppm to ppb level, the matrices are complex and they are easy to volatilize. The approach to measurement of trace VOCs in water consists of isolating them from water into a vapor phase, and then analysis by either Gas Chromatography Flame Ionization Detector (GC-FID), or Gas Chromatography Mass Spectrometry(GC-MS) [26]. Consequently, the sample preparation is the key step for measurement of trace VOCs in water. The Common sample preparation techniques for VOCs include static head space analysis (HS) [2-3,26-27], dynamic head space extraction

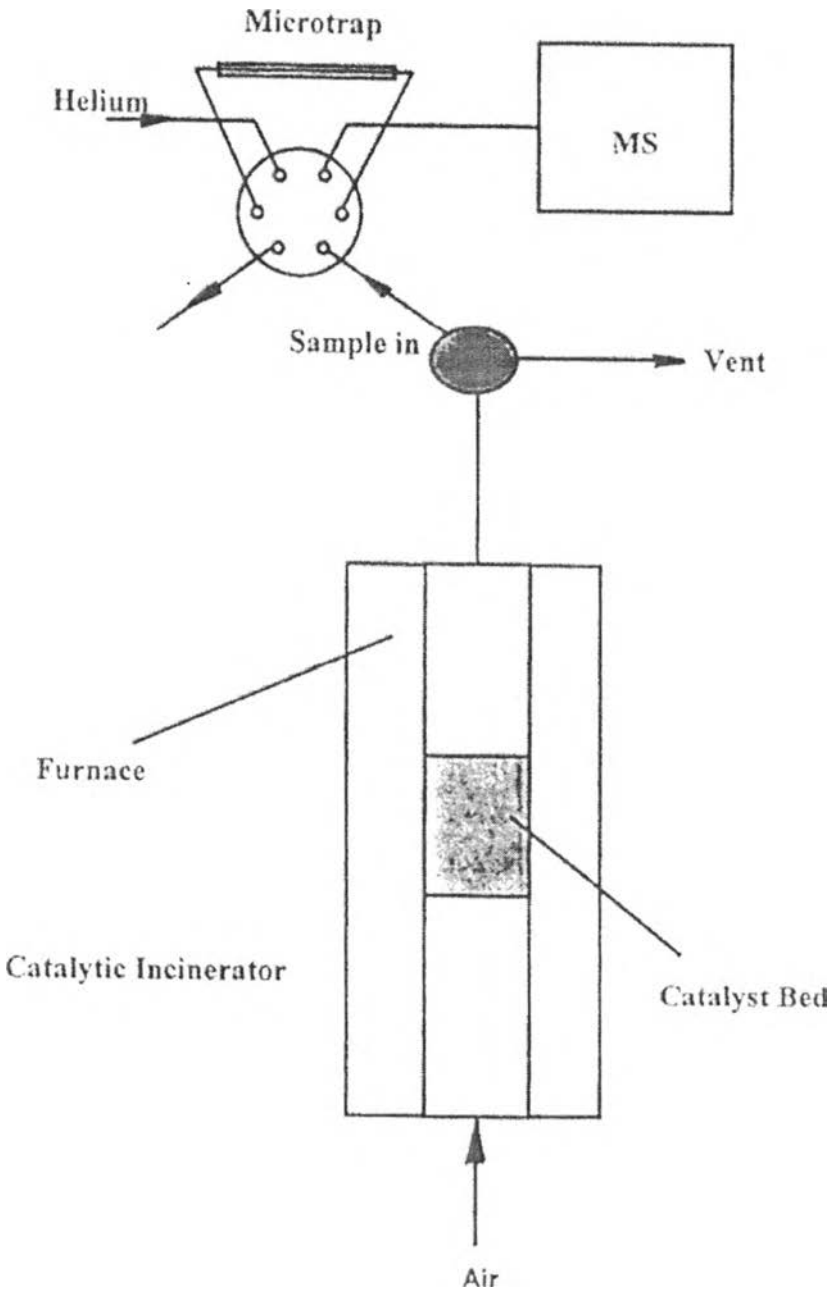


Figure 2.7 Schematic diagram of the Microtrap Mass Spectrometer [1].

(purge and trap) [2-3,28-29], and solid phase micro-extraction (SPME) [2-3,30]. All of these techniques provide excellent analytical results, but are mainly used as laboratory methods. They can not be used for continuous on-line monitoring, which is most important for drinking water, wastewater and groundwater monitoring. Moreover, direct GC analysis not be used in trace monitoring because only a small volume of sample can be injected into the GC column. A large volume causes column overload and leads to an excessive band broadening. Thus preconcentration techniques are needed for trace analysis. Sorbent traps are often used for this purpose. A well-known sorbent trap as preconcentrator approach is cryotrapping, but this is not suitable for samples with high moisture content, which freezes in the traps [7].

2.2.1 Headspace

Static headspace (HS) is one of common sample preparation technique for the qualitative and quantitative analysis of volatile organic compounds from water. It is a method used to study the VOCs present in nonvolatile matrix, without the necessity of carrying out liquid extraction, or forced separation of the volatiles from the matrix. A sample (either liquid or solid), is placed in a headspace vessel or vial(standardized vials made of borosilicate glass, typically 10 or 20 ml). The volatile analytes diffuse migrate to the gas phase (refered to as the headspace) of the vial and establish equilibrium with the concentration in the sample matrix as shown in Figure 2.8 a. The two phases in container are static since while the equilibrium is reached, therefore this technique is also known as static head space analysis.

The relative concentration of volatile in the two phases depend upon the partial pressure of VOCs. The concentration of an analyte in the headspace gas is a function of the concentration in the liquid phase.

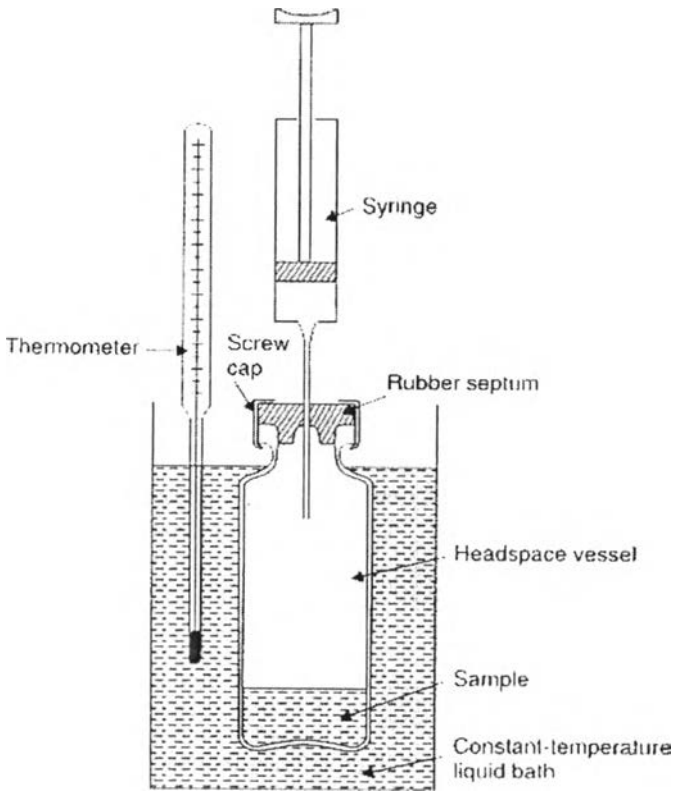


Figure 2.8 a Typical static headspace vial, showing the location of the analytical sample and vial headspace [2].

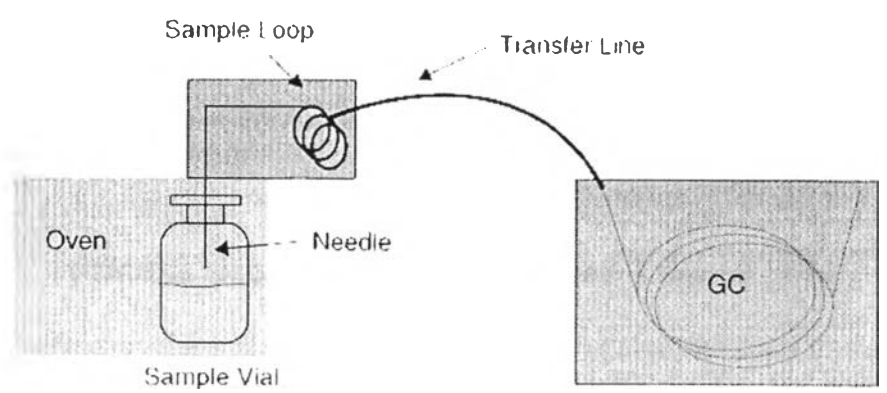


Figure 2.8 b Schematic diagram of headspace extraction autosampler and GC Instrument [2].

$$Conc_{gas} = K \times Conc_{liq}$$

Where K is a constant which is a function of temperature and the matrix [27].

After reaching equilibrium, the gas phase refer to as headspace is swept into a gas chromatography for analysis by manual injection as shown in Figure 2.8 a or autosampler as in Figure 2.8 b [2]. In this way, VOCs can be analyzed without interference by the nonvolatile, or the lesser volatile compounds. The analytes in headspace gas can be analyzed by various methods, but GC is particularly well suited. HS is a mature and reliable method. One of the clear advantages is the ease of initial sample preparation. However, to attain good sensitivity and accuracy, some samples may need a change in the physical state of the matrix. For example, solid samples should be crushed or ground to increase the partition between the solid, and the headspace, and to reduce the times to reach equilibrium. There are several standard methods based on HS-GC from USEPA, ASTM and DIN in Germany.

2.2.2 Solid-phase Extraction

This technique has been studied since 1977, but the term solid-phase extraction was coined in 1982 by employees of the J.T. Baker Chemical Company. This method is the equivalent of liquid-liquid extraction, and uses a tube packed with a few milligrams of sorbents as the stationary solid phase for trapping the analytes. The liquid sample is passed through the SPE packing, and the analytes are selectively retained by the sorbent. To remove some of the unwanted, interfering components originally retained, the packing is washed with solvent. Finally, the analytes on the SPE packing are eluted by passing a few milliliters of suitable solvent through the tube, so the analytes are extracted a small quantity of solvent, which is ready for analysis. The SPE process is as shown in

Figure 2.9. Sometime this method is also known as liquid-solid extraction, or column chromatography

Selectivity of SPE methods depend on three separate mechanism: selective extraction, selective washing of interferents and selective elution of the analytes. To achieve maximum efficiency, it is important to choose the right combination of packing material, washing solvent and elution solvent. SPE has several advantages over liquid-liquid extraction: reduced analysis time, solvent use, cost, and no formation of emulsion. The distinct advantages are higher extraction yield, more selectivity and higher precision than liquid-liquid extraction [3].

2.2.3 Solid Phase Micro-Extraction (SPME)

SPME is a recently developed method for the determination of organic compounds, especially VOCs from aqueous or vapor samples. It was invented by Pawliszyn and coworkers in 1990. The original concept was to develop miniaturized extraction method by using a solid-phase sorbent. It consists of syring-like device with a fused silica fiber, coated with a nonvolatile organic liquid (or a polymer) to serve as the sorbent. The fiber is housed in a syringe needle and can be extended from or retracted into it. During extraction, the needle is inserted into a small vial through the septa. The fiber is extended from the needle and exposed to the sample. The coated fiber is allowed to extract analytes by molecular size and shape on the surface of fiber. Selectivity is adjusted by varying the fiber material, which has different affinity to different types of analytes. Exhaustive extraction of analyte from the sample matrix is not achieved by SPME. By this method, samples are analyzed after equilibrium is reached or at a specified time prior to achieving equilibrium. After extraction, the fiber is retracted into the needle and removed from the vial. and Then the needle is inserted into an analytical instrument,

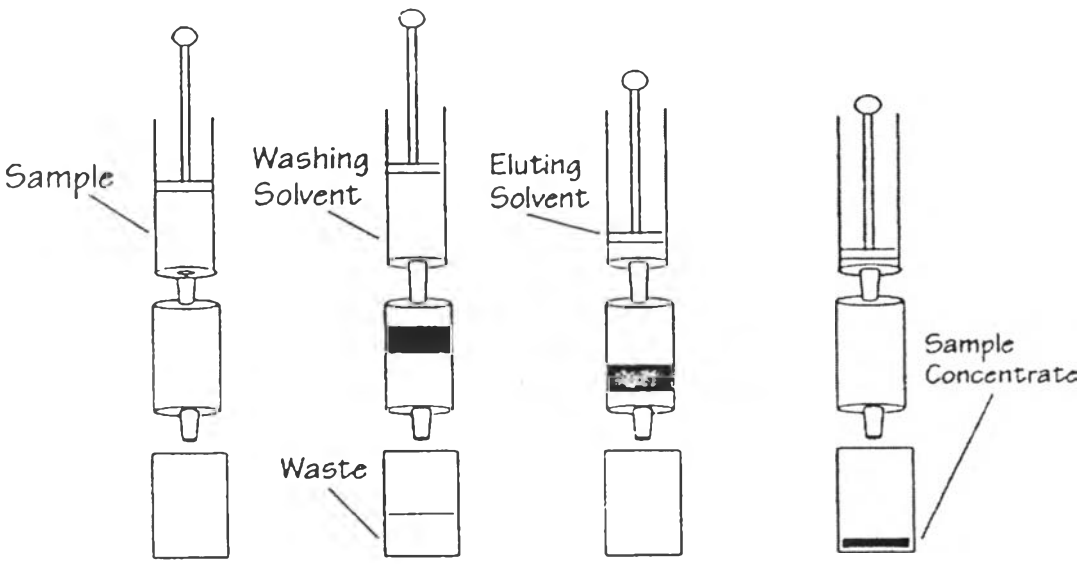


Figure 2.9 Solid phase extraction process. [3].

where the fiber is exposed, the analytes are desorbed and analyzed. The SPME system is as shown in Figure 2.10 The advantages of this method is that rapid, It is a solvent less technique, and is good for quick screening of both VOCs and SVOCS. SPME is a one-stop operation where extraction and enrichment take place simultaneously. However, SPME suffers from matrix effects. Changes in the sample matrix may affect quantitive results, due to the alteration of the distribution coefficent relative to that obtained for a pure sample [3].

2.2.4 Purge and Trap

Purge and trap is the most widely used , and the leading method for the analysis of trace volatile organics in water. It is used in diverse applications [2], such as, environmental, biological, pharmaceutical, and other types of analyses [31-33] because of its low detection limit and high precision. Purge and trap has gained widespread acceptance and was adopted by regulatory agencies as a standard method. Many Standard EPA methods are based on Purge and Trap. Figure 2.11 show a chromatogram obtained using a purge and trap procedure described in EPA method[2]. The detection limit suggested by EPA are listed in Table 2.2 [2].

Figure 2.12 show diagram of a tripical purge and trap system [2]. The purge and trap system consists of two major components: a purging device and a sorbent trap. There are three types of purging vessel commonly used: frit sparger, fritless sparger and needle sparger. Frit sparger creats fine gas bubbles which enhance mass transfer from matrix to gas phase to increase sensitivity. It can get clogged if sample is not clean. The typical size is 5 or 25 mL Fritless sparger is suitable for sample that contain particle, tend to foam and dirty, while needle sparger(typically 40 mL) is good for mixture of solid and liquid sample. The trap is typically a 25 cm long tube with an internal diameter of 0.267 cm.

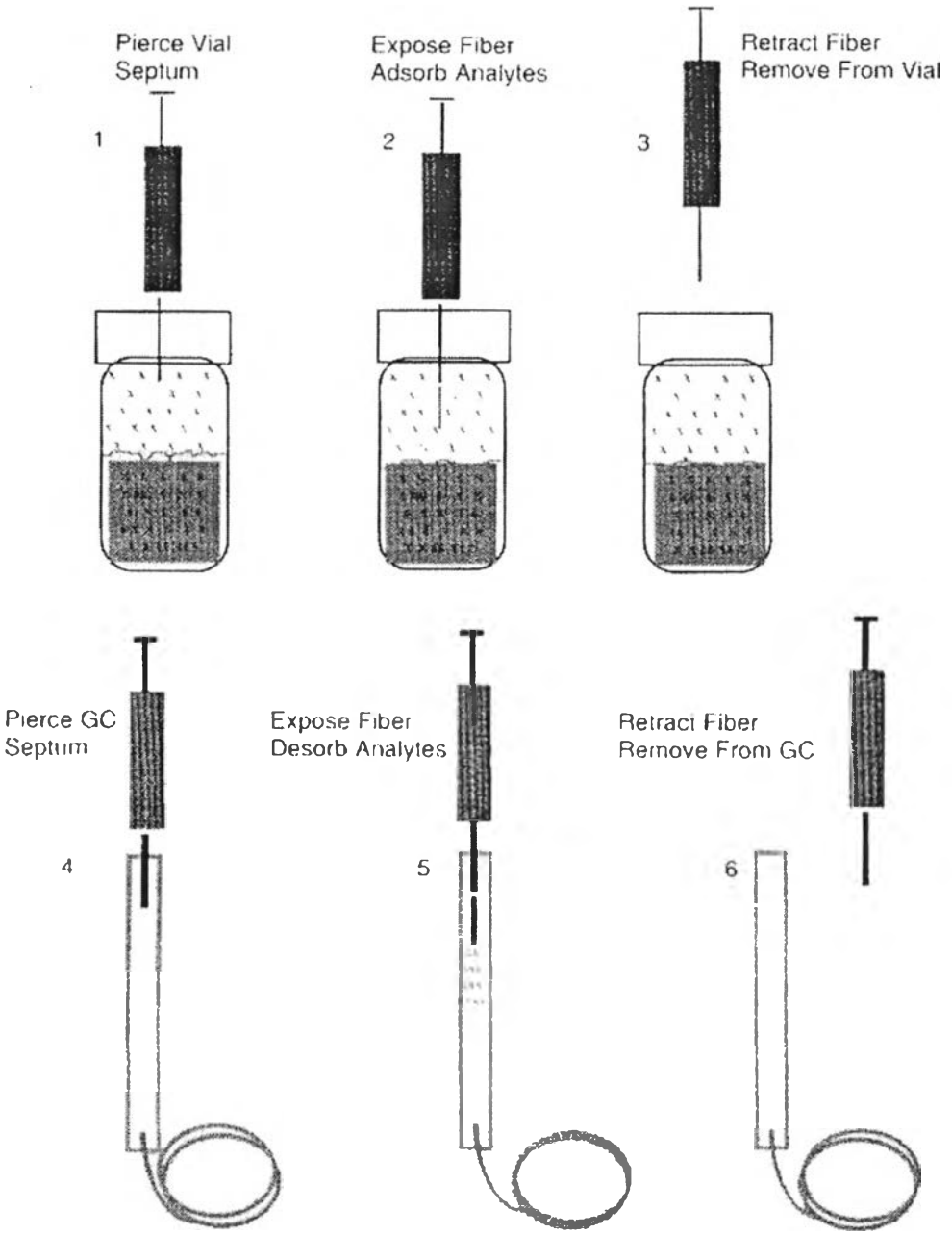


Figure 2.10 Step in a SPME headspace analysis [2].

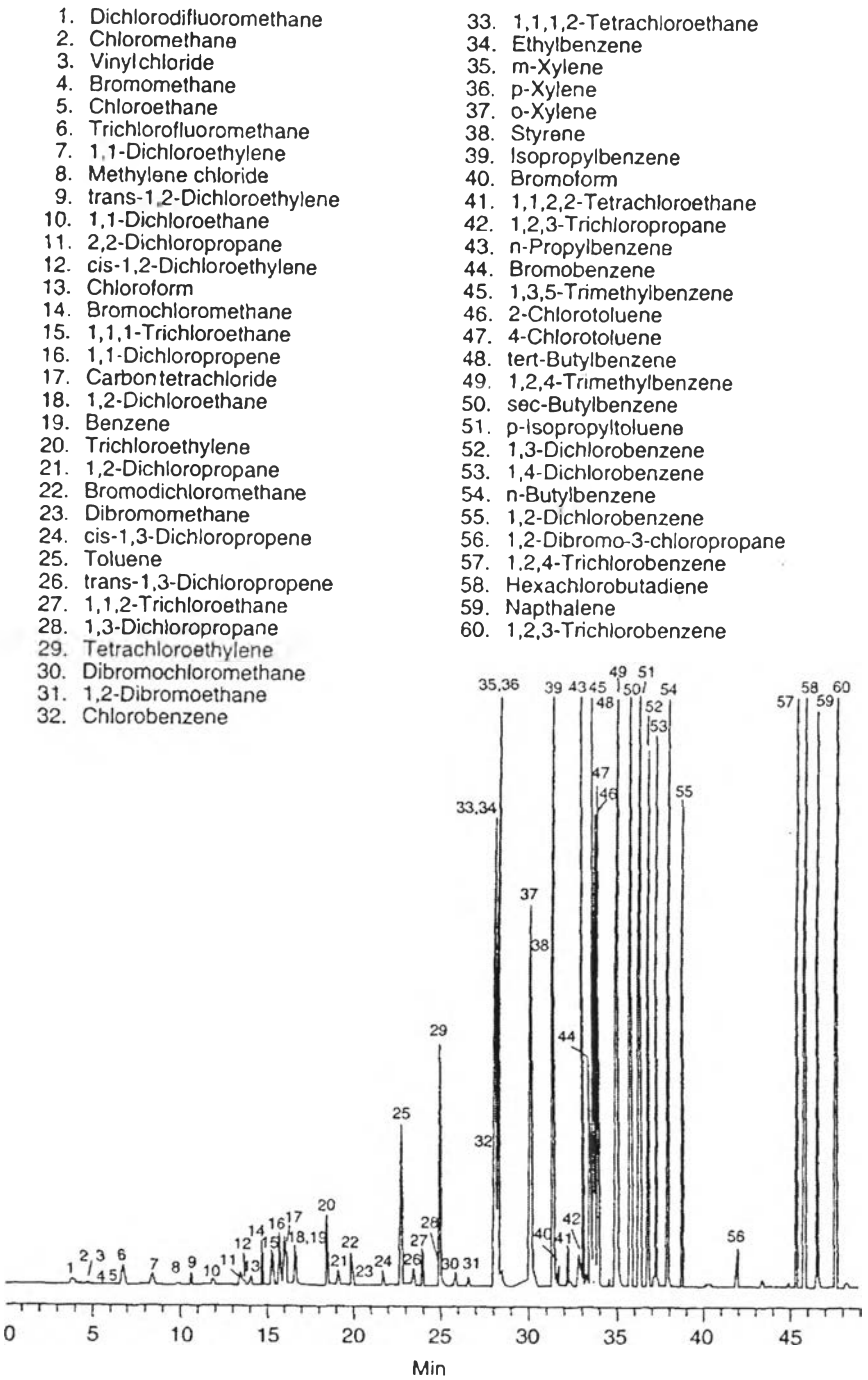


Figure 2.11 Chromatogram obtained using a purge and trap procedure as described in EPA method 524.2 [2].

Table 2.2 Detection Limits of the Volatile Organics in EPA Method 524.2

Analyte	MDL (μg/L)	Analyte	MDL (μg/L)
Benzene	0.04	1,3-Dichloropropane	0.04
Bromobenzene	0.03	2,2-Dichloropropane	0.35
Bromochlorobenzene	0.04	1,1-Dichloropropane	0.10
Bromodichlorobenzene	0.08	*cis*-1,2-Dichloropropene	N/A
Bromoform	0.12	*trans*-1,2-Dichloropropene	N/A
Bromomethane	0.11	Ethylbenzene	0.06
n-Butylbenzene	0.11	Hexachlorobutadiene	0.11
sec-Butylbenzene	0.13	Isopropylbenzene	0.15
tert-Butylbenzene	0.14	4-Isopropyltoluene	0.12
Carbon tetrachloride	0.21	Methylene chloride	0.03
Chlorobenzene	0.04	Naphthalene	0.04
Chloroethane	0.10	*n*-Propylbenzene	0.04
Chloroform	0.03	Styrene	0.04
Chloromethane	0.13	1,1,1,2-Tetrachloroethane	0.05
2-Chlorotoluene	0.04	1,1,2,2-Tetrachloroethane	0.04
4-Chlorotoluene	0.06	Tetrachloroethene	0.14
Dibromochloromethane	0.05	Toluene	0.11
1,2-Dibromo-3-chloropropane	0.26	1,2,3-Trichlorobenzene	0.03
1,2-Dibromoethane	0.06	1,2,4-Trichlorobenzene	0.04
Dibromoethane	0.24	1,1,1-Trichloroethane	0.08
1,2-Dichlorobenzene	0.03	1,1,2-Trichloroethane	0.10
1,3-Dichlorobenzene	0.12	Trichloroethene	0.19
1,4-Dichlorobenzene	0.03	Trichlorofluoromethane	0.08
Dichlorodifluoromethane	0.10	1,2,3-Trichloropropane	0.32
1,1-Dichloroethane	0.04	1,2,4-Trimethylbenzene	0.13
1,2-Dichloroethane	0.06	1,3,5-Trimethylbenzene	0.05
1,1-Dichloroethene	0.12	Vinyl chloride	0.17
cis-1,2-Dichloroethene	0.12	*o*-Xylene	0.11
trans-1,2-Dichloroethene	0.06	*m*-Xylene	0.05
1,2-Dichloropropane	0.04	*p*-Xylene	0.13

[a]This method uses purge and trap with GC-MS (with a wide-bore capillary column, a jet separator interface, and a quadrupole mass spectrometer).

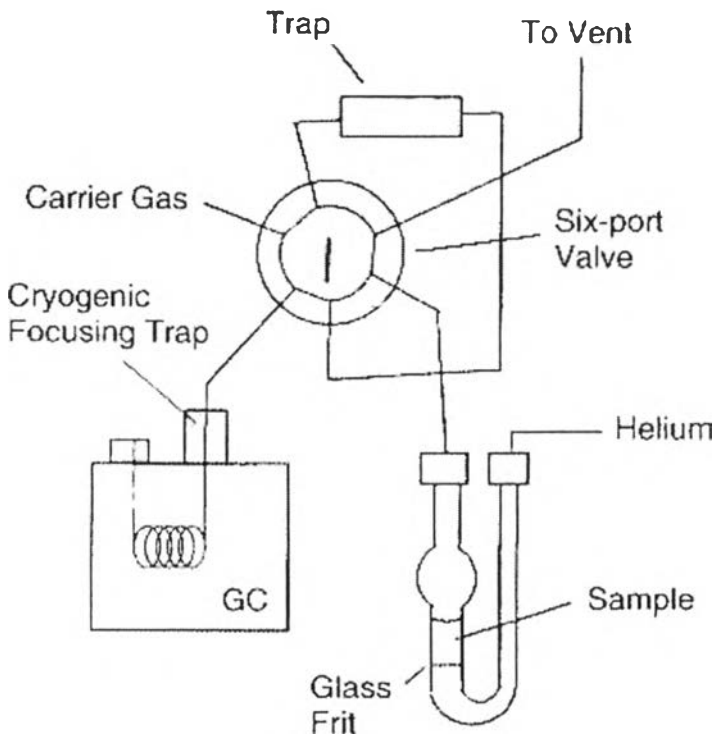


Figure 2.12 Schematic diagram of a typical purge and trap GC system [2].

It usually contain one or more layer of sorbents whose trapping abilities ranging from weakest at the inlet to strongest at the outlet to avoid from the reversible adsorption during desorption. There are three main processes in purge and trap: extraction (purging), simultaneous adsorption (trapping), and subsequent desorption (heating). Several milliliters of water sample is placed in the chamber then the purge gas (inert gas e.g. N_2) is turned on for exhaustive extraction. The inert gas is introduced into the bottom of purge chamber containing the sample to purge the organics from the water into a gas phase. To ensure good gas-water contact for maximum efficiency purging, the gas is dispersed into fine bubbles. This purged gas is then concentrated on a sorbent trap. Subsequently the organics are thermally desorbed and injected into a GC or a GC-MS. The extraction efficiency is effected by the properties of the analytes, the temperature, the flow rate, and the purge time. The sensitivity is improved by elevated temperatures, optimum flow rate and longer purge time. Typical extraction condition are: 11 minutes purging time, 25-40 mL/min flow rate. Trapping efficiency is also effected by the temperature and the properties of the analytes and sorbents. The trap consists of a one or more(typically3) commercial sorbents. It is designed to retain all of the purged organics, thus breakthrough needs to be eliminate. This is often achieved by using a lower trap temperature and selecting suitable sorbents. Desorption efficiency is effected by the temperature, the trap heating rate and the desorb-gas flow rate. Typical desorption condition are: 4 minutes desorption time, 5-10 ml/ min or 5 minutes at 4 ml/min[34]

Purge and trap method offers an improvement over static headspace extraction since no need to reach equilibrium, and is often referred as the dynamic head space analysis. It has high sensitivity and is suitable for quantitation and qualitation of a large number of compounds at trace analysis with detection limit at ppb to ppt level.

2.2.5 Membrane Extraction

Membrane-based separation has been recognized as a promising alternative to conventional sample preparation techniques. Membranes have received much attention because it can be used for selective extraction of organic from water or air. It has been used in for the extraction of a wide variety of analytes from difference matrix in many industrial applications. The first application of membranes in analytical chemistry appeared in the 60's. It has undergone significant developments in the last two decade and is still evolving. Membrane can be classified according to structure basis as porous and non-porous and according to geometry basis as flat and hollow. The basic concept of membrane separation is as shown in Figure 2.13. There are two sides of membrane, one is called the donor side which for feeding of sample, the sample is in contact with this side, and the other, permeate side. Sometime the permeate analyte is swept by another phase either a gas or liquid to increase permeate rate, It is called acceptor side. Membrane itself serve as a selective barrier, some components of the mixture can pass through by permeating to the other side [2].

Four types of membrane-based techniques has been used in sample preparation: dialysis, electrodialysis, membrane filtration and membrane extraction. In dialysis, a porous membrane is used and it allows only microsolute to permeate through, while the macrosolutes are blocked. An aqueous solution is used to receive the permeated analyte. The driving force of the dialysis technique is the concentration gradient between the two sides of the membrane. The selectivity of membrane depend on pore size. This technique has been used mainly in biomedical and food analysis. In electrodialysis, the dialysis is electrically driven. A pair of electrodes are placed on the two sides of the membrane. When a power supply is connected to the system, it creats an potential difference. So, the driving force is not only the concentration gradient but also the potential difference.

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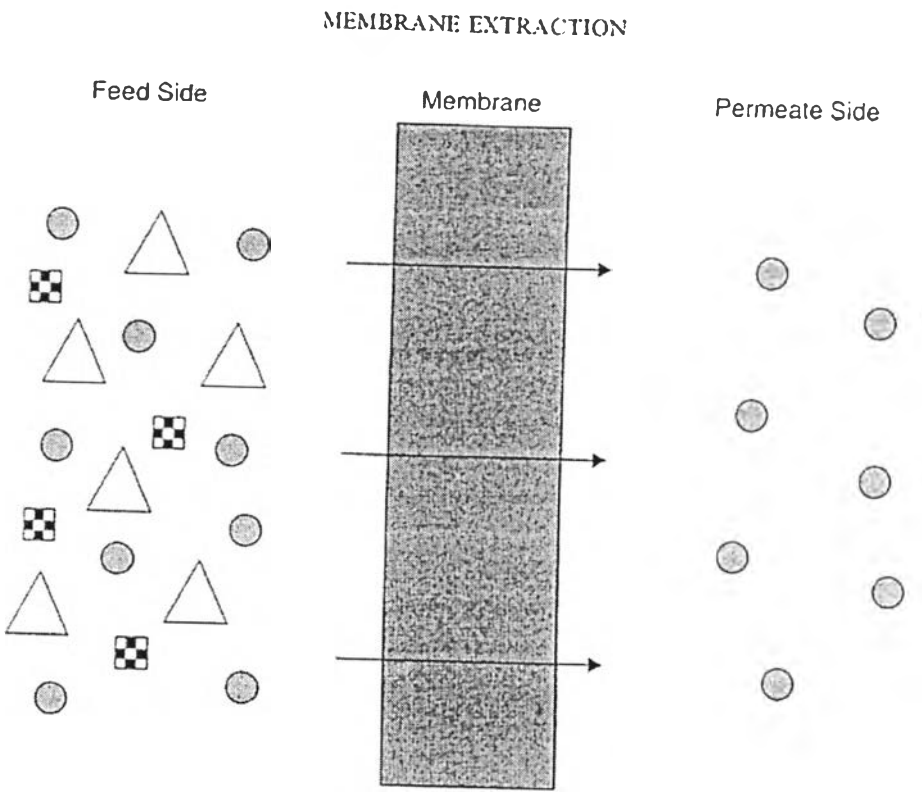

Figure 2.13 Concept of membrane separation; the circles are the analytes [2].

This technique is more complicated, and its analytical applications are few. In membrane filtration, a porous membrane is used with a pressure applied on the feed side of the membrane. Liquid phase together with microsolute are pass through the membrane. This mechanism is like the general filtration where the membrane acts as filter paper. The dialysis, electrodialysis and membrane filtration are based on size exclusion. The analytical applications of membrane filtration has been in the fermentation process. The membrane extraction is an extraction techniques, and is not size dependent. The mechanism is base on a solution-diffusion principles.The solute first dissolve into the membrane, and then diffuse through it. The driving force is still a concentration gradient across the two sides of membrane. There are many analytical application using this technique especially in water quality analysis [35]. The membrane can be porous or non-porous. This technique has been applied to extract VOCs, SVOCs and polar, ionizable compound from a variety of matrices. A major advantage of membrane extraction is that it can be used in conjunction with a instrument for continuous on-line analysis. Typically, a mass spectrometer or GC is used as the detection device. Figure 2.14 shows the schematic diagrams of these systems [2].

2.3 On-line Analysis

Most of the above mentioned techniques provide excellent analytical results, but are mainly used as laboratory methods. They can not be used for continuous on-line monitoring, which is important for drinking water, wastewater and groundwater monitoring. All the conventional methods provide sensitive and reliable measurements but may take a few hours, days to get results after samples collection. The data can not be used for taking corrective action immediately. The delay between sample collection and

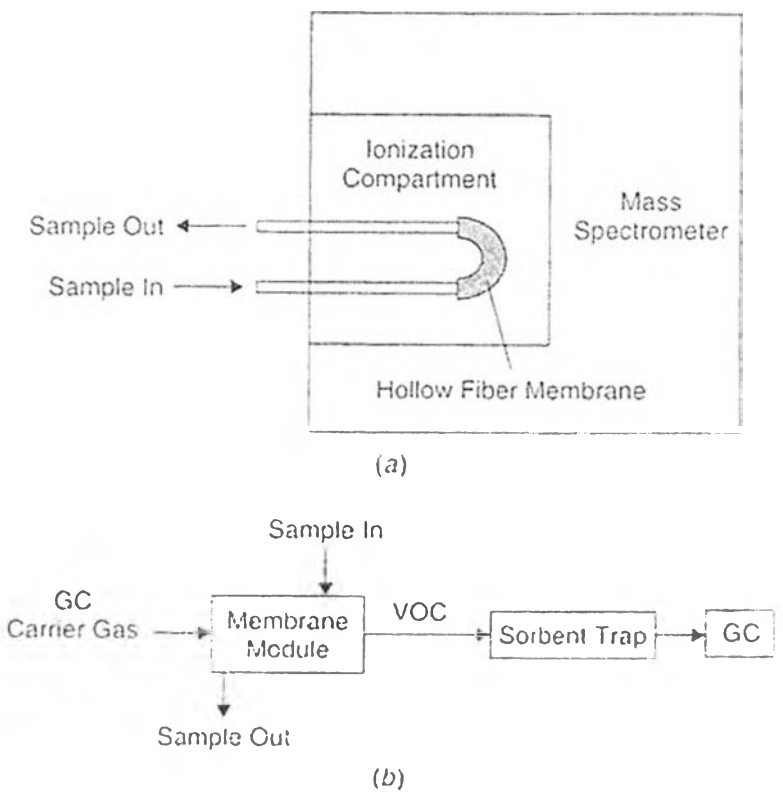

Figure 2.14 Mass introduction mass spectrometry [2].

chemical analysis introduces errors. Some analytes may degrade, which may change both chemical and physical properties or contamination can occur during this period. Change in properties may make the contaminants undetectable. To obtain high accuracy, precision and reliable information, extensive quality control steps are needed which make the process more expensive. Recently there has been much effort in the development of continuous, on-line measurement techniques which integrate a sampling interface, analysis, and a control and data analysis system to be done on-line. The instrument also need to be automated. On-line monitoring offers several advantages. They can provide better quality data at lower cost, and eliminate errors that can be brought about by contamination which are introduced during discrete sample collection, storage and transportation. On-line method also provide real-time or near real-time information because there is no delay between sampling and analysis step [36-38]. The analytical results can be fed back for process control. The turn around time is of the order of a few minutes or even a few seconds for most on-line methods. This method is valuable in monitoring and implementing in process control [16,25,36]

Over the last few years, methods have been developed for on-line water monitoring, including, membrane introduction mass spectrometry (MIMS) [1,39-41], pulse introduction membrane extraction (PIME) [37,42], and gas injection membrane extraction (GIME) [35,43] which offer some excellent opportunities. In membrane introduction mass spectrometry (MIMS), a selective membrane interfaces water sample and vacuum of ionization source was used for analyte permeation. The permeated VOCs were directly pulled in by the vacuum in the MS for analysis. This technique can be used in continuous, on-line water monitoring. The MIMS increases the analysis sensitivity, improve the detection limit and combines the separation, concentration and analysis into

one step. However, there is a problem for interpretation of chromatograms which most of them are complicate [1].

Membrane coupled with GC has been developed for the measurement of VOCs in water. An adsorbent or a cryogenic trap can be an interface for a membrane-GC system. Over the last few years, an on-line membrane extraction microtrap system (OLMEM) has been developed for continuous introduction of VOCs from a liquid stream directly into GC. This system has demonstrated low detection limit (ppb level), high sensitivity and the ability to continuously monitor VOCs in water. The disadvantage has been its long response time, since the measurement were made at equilibrium state which takes a fairly long time to reach. This evident come from the boundary layer effect which occur from continuous passing water sample to contact with membrane.

A non-steady state, Pulse Introduction Membrane Extraction (PIME) method was developed, which was a modification of OLMEM system mentioned above. This is suitable for the analysis of small volume individual samples as well as for continuous on-line monitoring. The aqueous sample is introduced as a pulse into the membrane. An eluent stream is used for transporting the sample to the membrane module. The analyte that permeate through are stripped by countercurrent gas stream to concentrate in microtrap and desorbed to GC for analysis. This technique can reduce boundary layer effect and shorten response time since it can have the measurement without waiting for steady state.The continuous monitoring approach can be done by introducing a series of pulses from a flowing aqueous stream. The disadvantage is some degree of low sensitivity since the dispersion and dilution increase from aqueous eluent will lower permeate flow rate which result in the increase in lag time also [37,42].

Gas Injection Membrane Extraction (GIME) is the most advanced of membrane based techniques to address the issue of boundary layer effect and sample dispersion. This

is shown in Figure 2.15.An aqueous sample is introduced using N_2 stream, which injects the sample into the membrane. The membrane serves as a selective barrier for organic analyte to permeate through. On the permeate side, a counter-current gas stream strips the organic and transport them to a microtrap which concentrate and desorb the analytes into the GC for analysis. N_2 stream pushes the aqueous sample through membrane, the liquid boundary layer never fully develops. After the sample permeates through, the N_2 stream cleans the membrane surface, which refreshes the membrane fresh for the next sample. This phenomena results in much faster permeation, and therefore shorter lag time.[35,43]

The dispersion of analytes is an important parameters for short residence time and sensitivity of the system. The major causes of dispersion are convective and diffusive mixing of the sample with the carrier gas. This technique shows no convective mixing with N_2 stream, moreover higher N_2 flow rate generate higher flux rate. This technique provides short lag time, improved sensitivity, and high precis

2.4 Sorbents in Environmental analysis

Sorbents are utilized in both air and water analysis, such as, purge and trap and thermal desorption based air monitoring. A variety of sorbents are used in this field. The proper sorbent means the one that can retain a specific or group of analytes for a specified sample volume, however it must also be able to release the analytes during the desorption process. A material that traps, and then releases a group of compounds efficiently will help provide high recoveries, sharp chromatographic peaks for good resolution, and allow accurate quantification of those analytes.

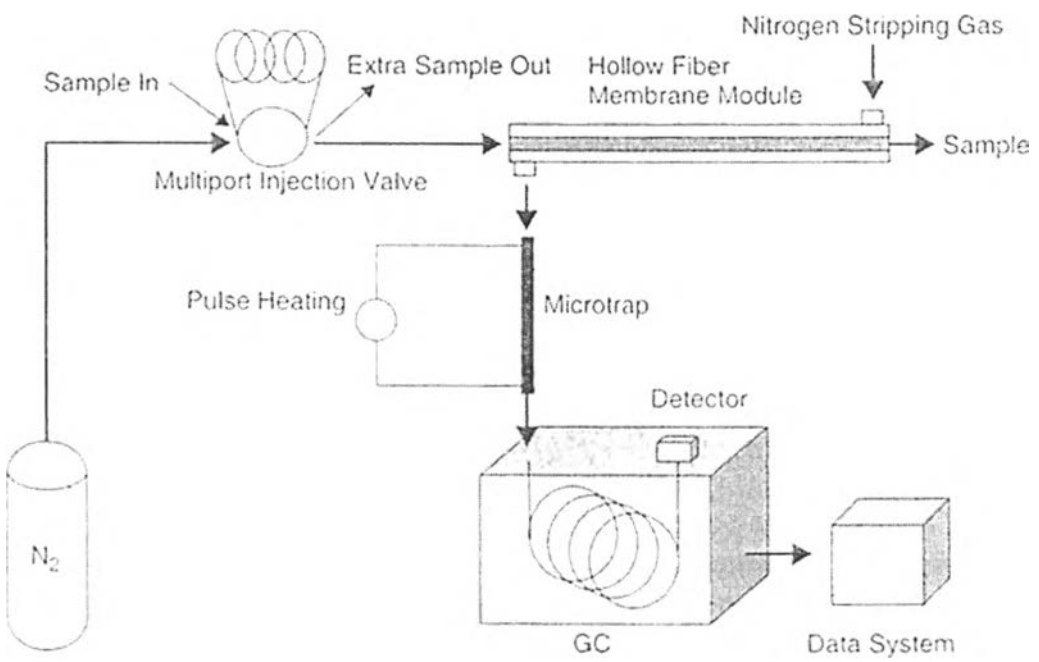

Figure 2.15 Schematic diagram of gas injection membrane extraction [2].

A wide variety of sorbents are available from many suppliers and manufactures. The commonly used sorbents are : Tenax TA, Tenax GR, Carbotrap, CarbotrapC, Carbotrap F, Carboxen 569, Carbosieve SIII and Glass Beads. Tenax TA is a porous polymer based on 2,6-diphenyl oxide. It has been specifically designed for the trapping of volatiles and semi-volatile from liquid or solid matrices. Due to its low affinity for water, Tenax TA is useful for the analysis of VOCs from high moisture content samples. It has high temperature limit at 350°C. Tenax GR is a composite of Tenax TA and 30% graphite carbon. It has a higher retention volume for most compounds and is twice as dense. Carbotrap is a graphitized carbon black for the trapping of a wide range of organic volatiles, its upper temperature limit is 400 °C. The difference between different types of Carbotraps are their surface area. It also has low affinity to water. Carboxen 569 is a carbon molecular sieve sorbent designed for small chlorinated and other C2-C5 VOCs. It has low affinity to water, 400 °C temperature limit. Carbosieve SIII is a large surface area carbon molecular sieve sorbent which is ideal for trapping the small airborne molecules. It has high affinity for water, 400 °C temperature limit. Glass Beads are most useful for the trapping of large molecular weight compounds. It will not retain any of the light volatiles, aromatics or other medium boiler [44-46].

Both Tenax and Carbotrap type sorbents can be used to determine VOCs in water samples since they are hydrophobic. For the microtrap mentioned before, the desorption temperature reached by a pulse of electric current between 300-400 °C. At this temperature, Tenax begins to breakdown and is not suitable for the microtrap application.

Carbotrap is in a, hydrophobic sorbent with 400°C as the high temperature limit. Carbotrap C was found to be suitable because of its optimum trapping and desorption without artifact formation. It is also hydrophobic enough for application with water samples. However, there continues to be the need for more efficient sorbents with higher

sorption capacity, faster desorption kinetic that can be used to make even smaller sorbent traps. Nano-scale material being developed hold much promise, because they have high active surface area for adsorption, and fast desorption. The large surface area may provide high BTV, which may lead to high sensitivity. So, surface area increase coupled with decreased trap size may lead to the next generation microtrapping technology.