CHAPTER 1

INTRODUCTION

1.1 Trace gas analysis

During a decade, the scientists pay attention and realize in toxic trace gas and aerosol as atmospheric problem. Since gas and aerosol play an important role in air quality related to photochemical smog, ozone depletion, global climate change, and health. Therefore, methods for air quality control have been required.

1.1.1 Trace gas sampling and analysis

Due to random movement of gas phase and it is not convenience to handle, most of atmospheric gases was sampling generally by flowing to some solid or liquid sorbent and convert to be the detectable species in liquid phase and then analyze such species by appropriate detector. For example, trace sulfur dioxide (SO_2) was flown into hydrogen peroxide solution (H_2O_2) reagent through midget bubbler as demonstrated in Figure 1.1. As a result, SO_2 convert to be sulfuric acid (H_2SO_4) and then was determined as sulfate by using ion chromatography (IC). Some organic vapors or gases were sampling by using a passive sampler and such species were determined by using chromatography or spectroscopy [1]. Although, such method is cheap, it takes a long time for batch determination. Some continuous methods for rapid analysis are required.

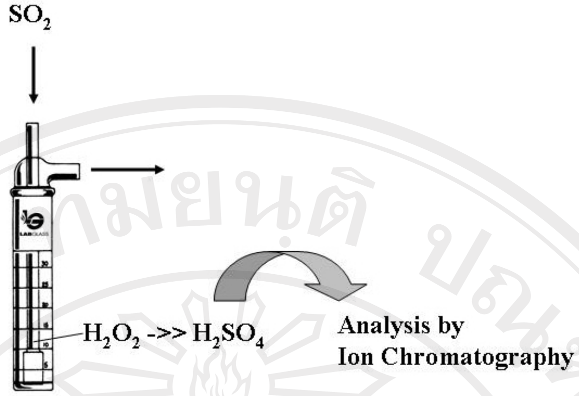

Figure 1.1 SO_2 purge into H_2O_2 through midget bubbler and then H_2SO_4 product was determined by using IC

1.1.2 Some online sampling devices for determination of trace gas in flow system

Most of those methods were developed based on diffusion of analyte gas into a flowing liquid. They can be classified as diffusion scrubber, wet denuder, and liquid drop.

- ***Diffusion scrubber***

A diffusion scrubber (DS) is a membrane based diffusion device which consists of tubular ion- exchanger or micro porous membrane insert in an inert jacket tube and scrubber liquid was flown continuously on another side of membrane for dissolve and transport the collected analyte gas or ionic species to detection device. A simple diffusion scrubber is depicted in Figure 1.2.

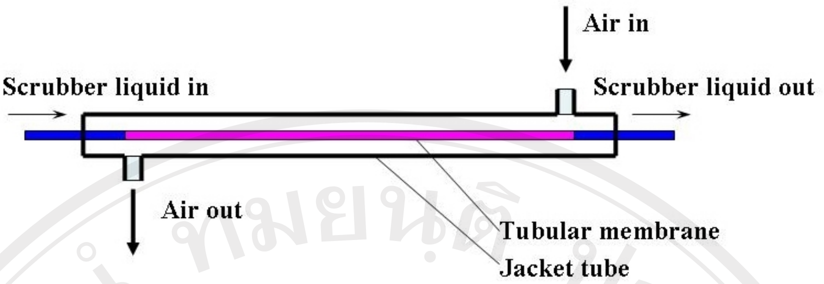

Figure 1.2 Schematic of a simple diffusion scrubber

Some automated gas sampling interface employing diffusion scrubber was developed as summarized in Table 1.1. Collection efficiency of DS depends on inlet pressure and geometry of the DS as studied by using IC [2, 3, 4]. A new designed DS was developed for collection of acid gas such as SO_2 by using formaldehyde as scrubbing liquid on another side of porous fluorocarbon membrane, after that developed color with pararosaniline reaction, change of color was detected by spectrophotometry [5]. Anion-exchange membrane was used in DS for nitric acid vapor sampling [6]. Not only detection by IC, but also fluorescent is sensitive technique couple with DS for gas determination. The method for HCOH, H_2O_2, SO_2 simultaneous sampling and sequential analysis was developed with simple micro porous polypropylene membrane and fluoromeric detection [7]. In addition, a device for field based H_2O_2 and HCOH detection [8] with highly sensitive single line FI system for H_2O_2 determination [9], and fully automated and highly sensitive fluorescent measurement employing GaN-UV light emitting diode (LED) with liquid core waveguide (LCW) for H_2O_2 [10] and HCOH [11] were developed.

Table 1.1 Some development of diffusion scrubber for automated gas sampling interface

Development	Detail	Ref #, Year
Study collection efficiency of the designed DSs	Hydrophilic fluorosulfonate cation exchanger membrane tube with diluted acid for ammonia gas and detect with IC*	[2], 1984
Membrane for atmospheric SO_2 sampling	Porous fluorocarbon membrane with HCOH for SO_2 and pararosaniline to form color and detect with spectroscopy	[5], 1986
DS with UV-VIS detection for nitric acid vapor	Use anion exchanger membrane tube with dilute sulfate (K_2SO_4) and detect with UV-VIS	[6], 1987
Simultaneous sampling and analysis for HCOH, H_2O_2, and SO_2	Microporous polypropylene with modified Nash reagent** for HCOH, HCHO solution +alkaline carbonate-bicarbonate buffer for SO_2 , and water + hydroxyphenylacetic acid buffer for H_2O_2 and detect with fluorometry	[7], 1988
Continuous sensitive method for SO_2 at ppbv level	Microporous polypropylene with H_2O_2 for SO_2 and detect with IC	[12], 1988
Study inlet effect of pressure to scrubber efficiency	Microporous polypropylene with H_2O_2 for SO_2 and detect with IC	[3], 1989
Field based measurement	Microporous polypropylene with water for H_2O_2, Dilute H_2SO_4 + modified Nash reagent for HCOH and fluorometric detection	[8], 1990
Various designs of DSs were developed	Nation ® membranes based DS were recommended for H_2O_2, and HCHO measurement	[4], 1991
Single line FIA for H_2O_2, pptv level highly by sensitive single line FI system for H_2O_2 determination	Mixed hematin-p-cresol solution was used for H_2O_2 to produce reaction product of 2,2-dihydroxy-4,4-dimethylbiphenyl and then detect with fluorometry	[9], 1992
Fully automated and highly sensitive instrument for H_2O_2,	Nafion with mixed hematin-p-cresol solution from peroxidase-like catalyst, for H_2O_2, and detect with LED-LCW*** fluorometry	[10], 2000
Fully automated instrument for HCOH	Nafion with 1,3-cyclohexanedione for HCOH and detect with LED-LCW fluorometry	[11], 2001

**IC is Ion Chromatography*

***LED-LCW is Light emitting diode with liquid core waveguide cell*

****Modified Nash reagent ; distilled 2,4 pentanedione, + ammonium acetate*

- ***Wet denuder***

Wet denuder is consequently diffusion based collection device. It provides a high efficiency gas collection. As a result, it is suitable for high air flow rate sampling. Wet denuder was designed and test for gas collection efficiency in both annular and parallel plate as demonstrated in Figure 1.3. Some developments and applications of wet denuder for gas sampling device are summarized in Table 1.2. Tested wet denuder was performed for SO_2 determination [13, 14]. It was developed to be an inexpensive analyzer [15]. Various designs of wet denuder were developed such as multiple parallel plate for high flow rate gas sampling [16], compact parallel plate from wetted cellulose acetate membrane for SO_2 [17] or soluble inorganic atmospheric trace gases [18]. Dasgupta and co-workers developed a fully automated field device for the measurement of acid gases and soluble anionic constituents of atmospheric particulate matter [19] and the method was developed further for atmospheric nitric and nitrous acid during the Atlanta Supersite study [20].

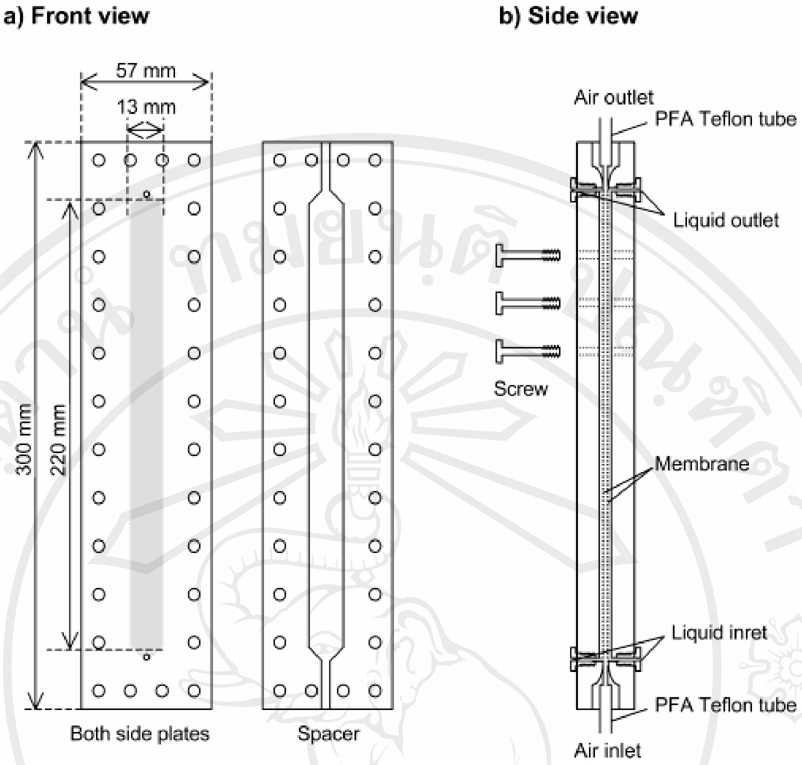

Figure 1.3 Wet denuder. a) Front view b) Side view

Table 1.2 Some development of wet denuder for automation atmospheric gas collection and analysis

Detail	Analyte species	Ref #, Year
Porous polypropylene membrane for 4 designs of denuder for SO_2 gas and test for collection efficiency	SO_2	[13], 1991
Borosilicate glass tube for inexpensive analyzer with wet efficient diffusion denuder	Atmospheric NO, N_2O gas	[15], 1991
Annular borosilicate glass tube parallel plate for efficiency and comparison between annular and parallel plate denuder for SO_2 collection.	SO_2	[14], 1993
A fabric screen was used for multiple parallel plates for high flow rate gas sampling	SO_2	[16], 1997
An inexpensive compact parallel plate diffusion denuder coupled capillary IC system for the determination of soluble ionogenic atmospheric trace gases	Chloride, nitrite, carbonate, sulfate	[18], 1999
Fully automated field instrument for the measurement of acid gases and soluble anionic constituents of atmospheric particulate matter	Acid gases and soluble anions in atmospheric particulate matter	[19], 2002
Continuously wetted cellulose acetate membrane-based parallel plate diffusion denuder. The device can remove soluble atmospheric gases such as SO_2 essentially quantitatively at flow rates up to1.7 LPM.	SO_2	[17], 2004

- ***Liquid drop***

A liquid drop was investigated to be a reproducible volume reaction vessel and adsorption gas sink by Dasgupta [21]. By adding various chemigenic reagent in liquid drop, specific chemical reaction, and detectors, trace atmospheric gas can be determined. Liquid drop was developed to be gas sampling device due to it can be regenerated. Renewable gas sampling interface for ammonia (NH_3) gas by using Berthelot reaction and measuring color changed with photodiode was investigated. Renewable liquid drop was developed for ppbv level of nitrogen dioxide determination by using Griess-Saltzman reaction with LED fiber optics contact to drop [22]. Not only renewable gas-liquid interface device, but also it can be a windowless optical cell. Windowless optical dynamics drop sensor for chlorine gas determination by using tetramethylbenzidine and measuring of color change of yellow product was demonstrated [23]. Moreover, a fluorescent detection was introduced for measuring in drop such as quenching of the native fluorescein mercuric acetate fluorescence as a near real-time fluorometric detection for hydrogen sulfide (H_2S) [24]. A sequential operation of liquid and reagent was developed to enhance sensitivity of detection such as sequential addition reagent in drop sensor for formaldehyde (HCHO) determination by measuring blue color product [25]. Circulation drop and preconcentration system was developed for trace atmospheric NH_3 by measure fluorescent from reaction with *o*-phthadialdehyde (OPA) [26]. Some developments of liquid drop sampling device for determination of some gases are shown in Table 1.3.

Table 1.3 Some liquid drop devices for gas sampling interface and analysis

Detail	Analyte species	Ref #, Year
SIA- electro osmotic pump control for precise generating a drop of Berthelot reagent* for NH_3 to form an indolphenol blue (photodiode spectrometric detection), and H_2O_2 for SO_2 (measure conductivity change due to H_2SO_4 produced)	NH_3, SO_2	[21], 1995
Gravity flow to form a drop of Griess-Saltzman reagent for NO_2 collection and absorbance detection with LED-fiber optic touch on drop	NO_2	[22], 1995
Syringe pump programming control to generate a drop of colorless tetramethylbenzidine as windowless optical cell, measured absorbance of yellow product on exposed to Cl_2	Cl_2	[23], 1995
A drop of alkaline fluorescein mercuric acetate for H_2S collection and detect with fluorometry by quenching with H_2S as a near real-time system	H_2S	[24], 1997
Manually dispense syringe as sequential reagent adding system in drop by using MBTH (3-methyl-2-benzothiazoline hydrazone) + $FeCl_3$ for HCHO, measuring blue color product	HCHO	[25], 1997
Flow system with circulating drop for NH_3 collection, then preconcentration ion in column and fluorescent detection by using o-phthaldialdehyde reagent and heating	NH_3	[26], 2000

**Berthelot reagent: phenol+ sodium nitroprusside +alkaline EDTA +sodium hypochlorite*

1.1.3 Atmospheric SO_2 gas determination

The method for determination of SO_2 in air was developed by Gaek and West [27]. Such West-Gaek 's method has been used for several years due to its specific chemical reaction and high sensitivity since 1980, the modified West-Gaek methods for SO_2 measurement without using mercury compound and with spectroscopic or fluorometric detection, were developed by Dasgupta and co-workers [28-30]. In addition, in 2001, rosaniline hydrochloride dye was developed to be used for SO_2 determination [31]. SO_2 in air could be trapped with specific reagents such as H_2O_2 to convert gas to be analytical ionic species, i.e. H^+ and SO_4^{2-}. The SO_4^{2-} ion was then determined by using ion chromatography [32]. Various sensors for measuring of SO_2 in air were also developed such as gold film conductometry [33] elipsometry based on thin film of silver [34], capacitive thin film [35], electrochemical solid state [36], porous gold solid polymer electrolyte [37]. Some commercial SO_2 sensors have been introduced with the prices of ~200 \$ US [38]. Automated and continuous methods for fast and sensitive measurement of SO_2 were investigated [39]. Most of continuous methods for SO_2 determination were performed by using gas sampling unit such as diffusion scrubber which fabricated from porous membrane and soaked with continuous liquid stream. The liquid stream was flow continuously to detection unit such as ion chromatograph [12], fluorometer [7], and spectrophotometer [40]. The procedure to take sampling liquid to detection unit was developed from flow injection (FI) [38, 39, 41, 42] sequential injection (SI) [40, 43] to microfabricated device [44].

1.2 Soap bubble and applications

1.2.1 Soap bubble in everyday life

A soap bubble is formed from a layer of water sandwiched between 2 layers of soap, or surfactant, molecules [45]. Surfactant molecules have both hydrophobic and hydrophilic sites. They align to form a liquid–air interface. Hydrophilic site dissolve in water while the hydrophobic sites are squeezed to the surface.

Bubbles are part of our everyday life, used during bathing or hand-washing with soap. Children enjoy playing with soap bubbles as toys [46]. They are easy to create and fascinate us with their ever-changing, multi-colored iridescence. While bubbles are interesting for children, they are also elegant demonstration tools [47]. Multiple soap bubbles, attached together, have been used as structure models of chemical bonding [48]. Bubbles on water surfaces have little of restriction to their movement. As a result, bubbles are creative tools for study of paramagnetic and diamagnetic materials. Bubbles containing O_2, a paramagnetic gas, are attracted by magnets [49] while magnets will repel bubbles containing N_2, a diamagnetic gas.

1.2.2 Soap bubble as scientific device

Bubbles have been applied in various scientific devices relevant to gas flow. The burning velocity of methane was studied through soap bubbles [50]. The flame speed and unburned gas-velocity ahead of a flame were measured simultaneously in a soap bubble. Due to low restriction of soap bubble and a wall of cylinder tube, bubbles have been used in a meter for measuring flow rate of gas which are commonly used in gas chromatography [51]. In addition, the movement of bubbles has been used in engineering studies of flow visualization [52-55]. Moreover, the soap bubble was applied as a device for respirometer for measure heat of vaporization of hexane [56]; when a horizontally aligned, glass tube is used as a manometer arm connected to hexane flask, low gas pressure can be detected precisely.

1.3 Chiral separation membrane

Membrane technology has been used for separation process in various applications due to many of advantages such as appreciable energy saving, easily and continuous operation. There are various types of membranes depending on application and structural design [57]. Most of membranes for chiral separation applications are impregnated with cyclodextrin as chirality selection molecules.

According to the E.Schneiderman 's review [58], many chiral compounds were separated by using cyclodextrin(CD) as chiral selector molecule, immobilized in membrane. Cyclodextrins are non-reducing cyclic glucose oligosaccharides linked by α-1,4-glycosidic bonds, as a result, they arranged molecules like a bottomless bowl-shaped (truncated cone) as shown in Figure 1.4. The molecule stiffened by hydrogen bonding between the 3-OH and 2-OH groups around the outer rim. The exterior of these conically shaped compounds is hydrophilic, whereas the interior is a hydrophobic cavity. There are three types of cyclodextrins, α-, β-, and γ-cyclodextrins, as 6-, 7- or 8-D-glucopyranonsyl residues. Some properties of cyclodextrin are shown in Table 1.4 [59].

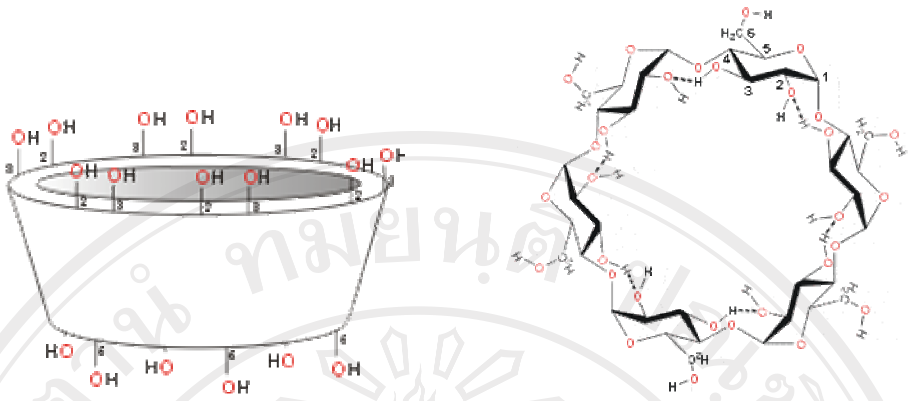

Figure 1.4 molecular structure of α-cyclodextrin

Table 1.4 Some properties of different cyclodextrins (CDs)

Molecular parameters	alpha-CD	beta-CD	gamma-CD
Number of glucose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Cavity diameter (nm)	0.57	0.78	0.95
Cavity height (nm)	0.79	0.79	0.79
Solubility in water at 25 ˚C (% w/v)	14.5	1.85	23.2

Various membrane types modified with CD for separation of some chiral compounds were reported [60-64]. The β -CD was used with modification in poly vinyl alcohol for D-4-hydroxyphenylglycine separation [65]. The chiral amino acids such as tryptophan or R,R-tartrate esters were separated by using beta-CD modified in cellulose membrane [66] or chitosan cross link [67]. Some organic compounds such as benzene derivetives were separated through α-CD modified in polyvinyl chloride membrane. In addition, α -CDs and β -CDs modified in polyvinyl acetate membrane, show significant usefulness for pervaporation for xylenes isomer vapor separation [68, 69]. Examples of cyclodextrin modified membrane for chiral separation are summarized in Table 1.5.

Table 1.5 Cyclodextrin modified membrane for chiral separation

Membrane process	Membrane material	CD type	Compound model	Ref #
pervaporation	Polyacrylic acid	α,β,γ-CD	Xylene isomer	[59]
	Poly(vinyl alcohol)	β-CD	Xylene isomer	[69]
	TiO_2/Al_2O_3 ceramic nanofiltration membranes	β-CD	Xylene isomer	[70]
	Poly(vinyl acetal)	β-CD	Bezene /cyclohexane	[71]
	Nafion membrane	β-CD	Butanol isomer	[60]
	PDMS pervaporation membrane	β-CD	Linalool	[61]
ultrafiltration	YM1, PLBC, YM5 From Millipore Co.	α-CD and β-CD	o-, m- and p-nitrophenols D- and L- phenylalanine	[62]
electrodialysis	Sulfonated polysulfone nanofiltration membrane-ASP50	α-CD	D,L-tryprophan	[63]
	Poly(vinyl alcohol)	β-CD	D,L-4 hydroxyphenyl glycine	[65]
dialysis	Porous tubular ceramic membrane	β-CD	Chlorthalidone	[64]
	Nylon-6 membrane with chitosan cross-link	β-CD	Tryptophan	[67]
	Cellulose	β–CD	Tryptophan	[66]
	Poly(vinyl alcohol)	α-CD	Xylene isomer	[68]
liq./liq. extraction	Poly(vinyl alcohol)	α-CD and β-CD	Xylene isomer	[72]

1.4 Liquid membrane and separation process

1.4.1 Liquid membrane

Liquid membrane is one of highly selective membrane type and easily operated at laboratory scale. It contained a selectivity recognized molecule in liquid phase. In some liquid membranes, a liquid phase was immobilized or filled in a porous supporter, namely supported liquid membrane. Meanwhile, bulk liquid membrane does not appear as normal membrane. It is a selective liquid barrier between 2 parts, feeding and acceptor parts as shown for a simple system of this liquid membrane in Figure 1.5. Although, liquid membrane does not provide a good stability due to high pressure different between feeding and acceptor phases, it shows advantage on high selectivity between carrier in liquid phase and the target analyte.

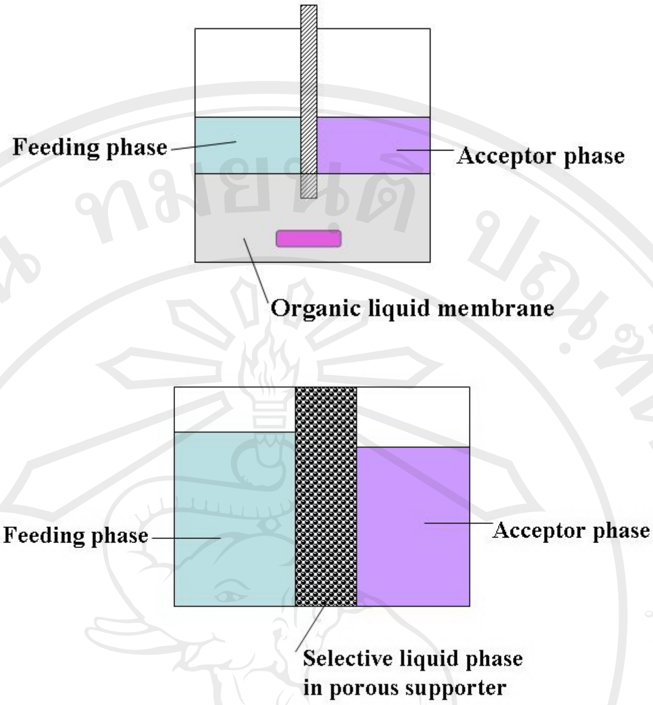

Figure 1.5 Liquid membrane a) bulk liquid membrane b) supported liquid membrane

The analyte molecule in feeding part can be transported through liquid membrane by interacting with specific carrier in liquid phase and such carrier moves to the other side and releases target molecule to acceptor part. The acceptor then moves to receive the new target analyte molecule continuously as demonstrated in Figure 1.6. There are 2 cases, symport and antiport mechanism. Only target molecule was transferred across membrane in symport system. While, in antiport system, there is some exchanged molecules in acceptor side move back to donor side and target analyte was transferred [73].

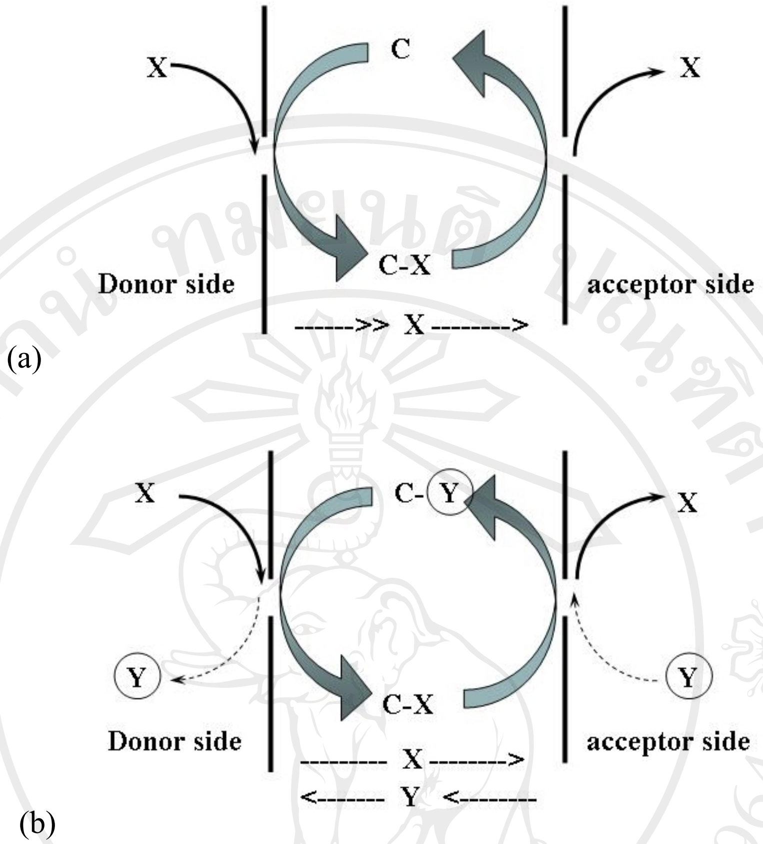

Figure 1.6 Moving of carrier molecule in liquid membrane- a) symport b) antiport mechanism

1.4.2 Liquid membrane for gas separation

There are various applications of using supported liquid membrane (SLM) for gas separation as summarized in Table 1.6. SO_2 permeated through liquid membrane which using water molecule as carrier in micro porous poly (vinylidene difluoride) [74]. Various carriers and solid supports for oxygen removal or oxygen enrichment for various applications such as enrichment for medical use since 1960, were reviewed [75]. Triethylene glycol which contained AgBF4 was modified in poly tetrafluoroethylene (PTFE) micro porous membrane to specific to propylene vapor from propylene/ propane mixed gas [76]. Moreover, CO_2 was separated from others mixed gas by using ionic liquid which contained various types of carriers in various solid supports; such as diglycolamine or triethylene glycol in PTFE, or potassium carbonate in vinyl alcohol and acrylate copolymer, and etc [77-82].

Table 1.6 Supported liquid membrane for gas separation

Analyte/ gas	Carrier	Solid support	Ref #, Year
SO_2 from N_2	water	poly(vinylidene difluoride)	[74], 1999
O_2 enrichment	micro-encapsulated liquid membranes	polyethyleneoxide	[75], 2001
Propylene/propane mixed gas	Triethylene glycol TEG/$AgBF_4$	Polytetrafluoroethylene (PTFE) microporous membrane	[76], 2003
CO_2 from CO_2/CH_4 mixed gas	Diglycolamine (DGA) or triethylene glycol (TEG)	Hydrophilictreated polytetrafluoroethylene (PTFE)	[77], 2001
CO_2 from CO_2/N_2 mixture	bis(trifluoromethanesulfonyl)amide $[Tf_2N]^-$, trifluoromethane-sulfone $[CF_3SO_3]^-$	Porous hydrophilic polyethersulfone (PES)	[78], 2004
H_2, O_2, and CO	Ionic liquids ([C4-mim] $[NTf_2]$, $[C_{10}\text{-mim}]$ $[NTf_2]$, $[N_{8881}][NTf_2]$, $[C_8Py][NTf_2]$)	Nanofiltration (NF) membranes	[79], 2006
CO_2 in process of crude natural gas,	Nano size ionic liquids dispersed in polymer	Poly(vinylidene fluoride)(PVDF)	[80], 2006
CO_2 separation from CO_2/N_2	Aqueous potassium carbonate (K_2CO_3)	Poly vinylalcohol and poly acrylate copolymer (PVA–PAA)	[81], 2007
CO_2 from CO_2/He gas pair	1-*n*-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	Tuffryn® (polysulfone) and Supor® (polyethersulfone) polymeric porous	[82], 2007

1.4.3 Liquid membrane for chiral compound separation

In pharmaceutical industry, chiral drug which is compound that contains an asymmetric center (chiral atom or chiral center) and thus can occur in two nonsuperimposable mirror-image forms (enantiomers) [83] which are identical chemical and physical properties, but the activity of such compounds in biological and chemical reaction are different [84]. Various of racemic drugs such as Mirtazapine, were separated by using Cuprophan (regenerated cellulose) hollow fibers membrane contained R,R- and S,S-dihexyltartrate as chiral selector [85]. In addition, enantiomer amino acids were separated through liquid membrane by using various types of chiral selectors or liquid membrane carriers impregnated in various supported modules. The interesting carrier in liquid membrane for enantiomer amino acid separation were investigated such as chiral phosphoric acids [86], poly (γ-methyl-l-glutamate) [87], N-decyl-(l)-hydroxyproline [88]. D, L-lactic acid was separated by using N-3,5-dinitrobenzoyl-l-alanine-octylester [89] or N-3,5 dinitrobenzoyl and alanineoctylester [90] or adamantyl-carbamoyl-11- octadecylthioether-quinine, on polysulfone hollow fibers, [91] as chiral selector. Examples of liquid membranes for chiral compound separations are shown in Table 1.7.

Table 1.7 Examples of supported liquid membranes for chiral separations

Carrier compound	Solid support	Permeant	Ref #,Year
R,R- and *S,S* dihexyltartrate (DHT)	Cuprophan(regenerated cellulose) hollow fibers	Norephedrine-HC1, Ephedrine- HCl, Mirtazapine, Phenylglycine, and other drugs	[85], 1996
Tri-(2-ethylhexyl) phosphate (TEHP) and dihexyl ether (DHE)	Porous PTFE	D-, L-Tryptophan. phenylalanine and tyrosine	[86], 1999
Poly(γ-methyl-L-glutamate) (PMLG)	Porous polyacrylonitrile (PAN)	Amino acid D-,L-tryptophan	[87], 2001
N-3,5-dinitrobenzoyl-L-phenylalanine-octylester	Microporous polypropylene tubes	D,L-lactic acid and D,L-alanine	[90], 2002
N-decyl-(l) hydroxyproline	Microporous polypropylene	Phenylalanine and methionine	[88], 2005
Adamantyl-carbamoyl-11- octadecylthioether-quinine or -quinidine	Polysulfone hollow fibers	DNB-D,L-leucine.	[91], 2006
N-3,5-dinitrobenzoyl-l-alanine-octylester	Polypropylene polymeric hollow fiber	D-,L-lactic acid	[89], 2005
Modified trioctyl methylammonium chloride (Aliquat^{TM} 336)	PTFE filters	D-, L-lactic acid	[92], 2007

For bulk liquid membrane, although it is suitable for laboratory operation, it is easy setup and does not need to immobilize in solid support. In 1996, 6 types of chiral azophenolic crown ethers were synthesized and prepared for chiral recognition in bulk liquid membrane for chiral ethylamine and ethanolamine derivatives separation [93]. Beta-cyclodextrin (CD) was used as chiral mobile carrier in bulk liquid membrane for chiral enrichment of racemic chlorthalidone [94]. Sodium dodecyl sulfate (SDS) was added to stabilize oil in water emulsion and partitioning of xylenes in aqueous solution and interaction with alpha cyclodextrin as mobile carrier in bulk liquid membrane [95].

1.4.4 Soap bubble film as liquid membrane

In 1987, Amstrong used water based liquid membrane, modified with α-,β-, and γ- cyclodextrins for o-, and p- nitroanilines and other enantiomer or isomer compounds for enrichment application [96]. Soap bubble film, which is a sandwich layer of surfactant and water molecule containing surfactant micelle as carrier dissolved in water layer, has been considered as one of liquid membranes [51]. Permeation of the non-polar vapor molecule such as hexane through sodium dodecyl sulfate (SDS) soap bubble was studied [97]. Micelle of surfactant molecules in solution plays an important role in transfer of heptane through SDS film. With a reason in that soap liquid film is easily regeneration, effective low cost membrane and does not need to immobilize selective liquid phase in solid support, it is interesting tool for some vapor separation applications.

1.5 Membranes in flow systems for gas determination

The supported liquid membrane has been applied for preconcentration or extraction of sample prior analysis by using normal detector in flow system as shown in Table 1.8. As a result, it improved sensitivity and selectivity of detection.

Table 1.8 Application of supported liquid membrane for preconcentration or extraction prior to determination in flow system

Detail	Ref #, Year
Micro porous membrane liquid-liquid extraction (MMLLE) for anionic surfactants in detergent determination by using FIA spectroscopy	[98], 2001
Automated system for supported liquid membrane (SLM) extraction and micro-porous membrane liquid–liquid extraction (MMLLE) with HPLC-UV for Trace Polar (2-aminobenzimidazole) and non-polar (fungicide thiophanate methyl) ionisable compounds determination in water sample	[99], 2002
Continuous-flow liquid membrane extraction (CFLME) and C-18 pre-column for high sensitivity and selective sample enrichment for determination of sulfonyl ureas in water sample prior to LC–UV	[100], 2003
Possibility of micro-porous membrane liquid–liquid extraction technique as a preconcentration of sulfonylurea herbicides in water sample prior to analyze with capillary electrophoresis (CE)	[101], 2003
Supported liquid membrane for extraction and enrichment of tricyclic antidepressants from water and urine samples for reversed-phase high performance liquid chromatography with UV detector	[102], 2004
Development of a simple SLM technique for extraction and purification of glyphosate and AMPA from fruit juices before HPLC-UV	[103], 2005
Selective immuno-supported liquid membrane (ISLM) extraction or enrichment and analysis of 2,4,6-trichlorophenol with fluorescence detection	[104], 2005

1.6 Solid phase micro extraction (SPME) coupled with gas chromatography for vapor permeation study

SPME is a sampling tool kit made from fiber coated with a solid sorbent, or a liquid polymer, or mixed of both materials. With a small size of fiber and thin coated sorbent layer, SPME provides solvent free technique, fast, economical and versatile sampling. After sampling process, SPME fiber is inserted directly into injector unit of gas chromatograph for desorption and analysis. SPME has been used in many applications such as forensics and toxicology science, environmental and biological analysis [105].

The SPME assembly for GC application was produced commercially by SUPELCO. The commercial SPME consists of holder which is available for both manual and automatic operation, and sorbent coat fiber as shown in Figure 1.7.

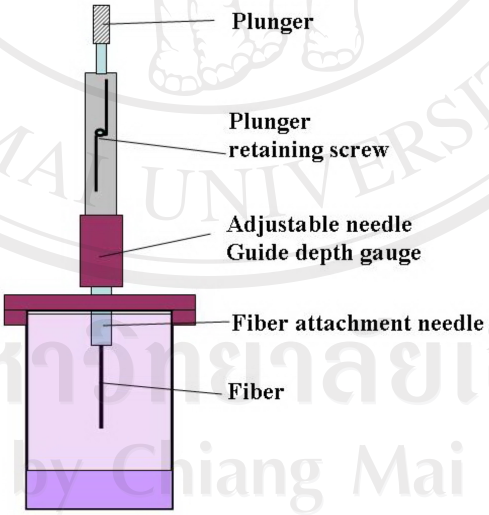

Figure 1.7 Commercial SPME for manual sorption injection

The SPME can be performed for sampling in three modes namely direct extraction, head space, and membrane protected SPME as demonstrated in Figure 1.8. For vapor determination, SPME fiber can be sampling directly in vapor stream.

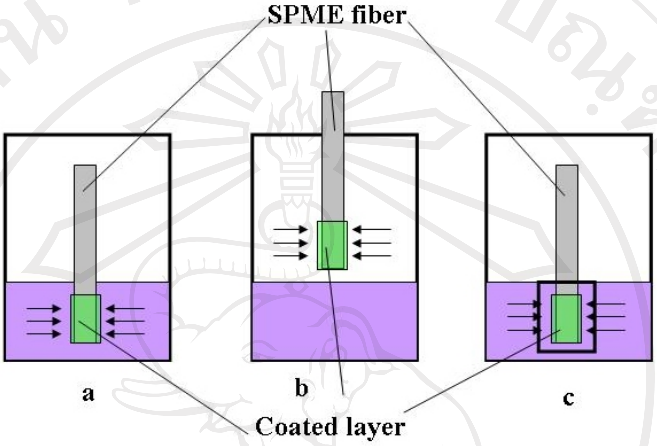

Figure 1.8 Modes of SPME sampling a) direct extraction b) head space SPME c) membrane protected SPME [106]

The fiber for SPME is important for sample type in that partition process of sample to sorbent layer. In this research, the 100 um PDMS was selected due to it's suitable for general volatile organic vapor.

The principle of SPME involves partitioning of analytes between the sample matrix and the polymeric phase on the fiber [106]. The equilibrium conditions can be described as:

$$n = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \qquad [1.1]$$

where n is the mass of analyte extracted by the coating,

K_{fs} is a fiber coating-sample matrix distribution constant,

V_f is the fiber-coating volume,

V_s is the sample volume,

and C_0 is the concentration of a given analyte in the sample.

In some analysis systems, K_{fs} is relatively small compared to coating volume, V_f ($V_f << V_s$). As a result, the capacity of the fiber is much less than capacity of the sample, the relationship can be simplified as:

$$n = K_{fs} V_f C_0 \qquad [1.2]$$

From equation 1.2, when $K_{fs}V_f$ is much larger than V_s, the extracted analyte (mole) is independent of Vs. When the K_{fs} and V_f are controlled to be the same during the whole analysis process, therefore, the SPME fiber can be inserted directly to the analyte vapor for quantitative analysis.

Some basics in gas chromatography and SPME sampling system

Gas chromatography is device which is widely used for determined gas or vapor. The gas components can be separated and qualitatively analyzed based on different partition ability of gas components on carrier gas and solid support stationary phase in column. With a reliable of GC, some technical methods and procedures of GC for chiral gas or vapor separation such as column, detector, carrier gas, and temperature programming, were reported and can be picked up such experimental conditions for vapor determination. The sample vapor component sampling by using SPME can be introduced through GC injection port.

In gas chromatography, the extracted amount (n) of analyte in the fiber can be considered as:

$$n = fA \qquad [1.3]$$

where f is specific calibration factor of analyte;

A is the peak area of analyte obtained by GC.

From Equation 1.2 and 1.3, the concentration of analyte in the permeation study can be expressed as [107]:

$$C_0 = \frac{fA}{K_{fs}V_s} \qquad [1.4]$$

When the same SPME sampling condition and GC condition are the same, the peak areas from GC are comparable. The concentration of permeated vapor in permeation study is related to corresponding peak area obtained by GC.

1.7 Aims of the research

The aims of these studies are as follows:

1. To develop a bubble soap film in flow system for gas sampling interface
2. To study conductometry on hollow sphere shape cell as soap bubble
3. To perform bubble soap film applied for continuously SO_2 gas sampling and analysis system
4. To perform soap bubble film for gas permeation and exploiting on the use of soap film as separation devices
5. To investigate permeation of chiral vapor, α- pinene as model compounds, through soap film which cooperated with α-cyclodextrin as chiral recognition compound