CHAPTER 1

INTRODUCTION

1.1 Air pollution

Air pollution results from a variety of causes, not all of which are within human control. Dust storms in desert areas and smoke from forest fires and grass fires contribute to chemical and particulate pollution of the air. The source of pollution may be in one country but the impact of pollution may be felt elsewhere.

Modernisation and progress have led to air getting more and more polluted over the years. Industries, vehicles, increase in the population, and urbanization are some of the major factors responsible for air pollution. The following industries are among those that emit a great deal of pollutants into the air: thermal power plants, cement, steel, refineries, petrol chemicals, and mines.

Air pollution can cause health problems and it can also damage the environment and property. It has caused thinning of the protective ozone layer of the atmosphere, which is leading to climate change.

Nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and ozone (O_3) are the important gases found in the ambient air which exhibit documents adverse effects on health and welfare.

1.1.1 Nitrogen dioxide (NO_2)

Nitrogen dioxide is the most toxic of the nitrogen oxides. It is a brown toxic gas. All combustion in air produces oxides of nitrogen (NO_x), of which NO_2 is a major product. NO_x comes from the transportation sector, power generation, primary metal

production and incineration. Natural sources of NO_x include lightening and the aerobic activity of soil bacteria. These natural sources, however, are small compared to emissions caused by human activity as shown in Fig 1.1.

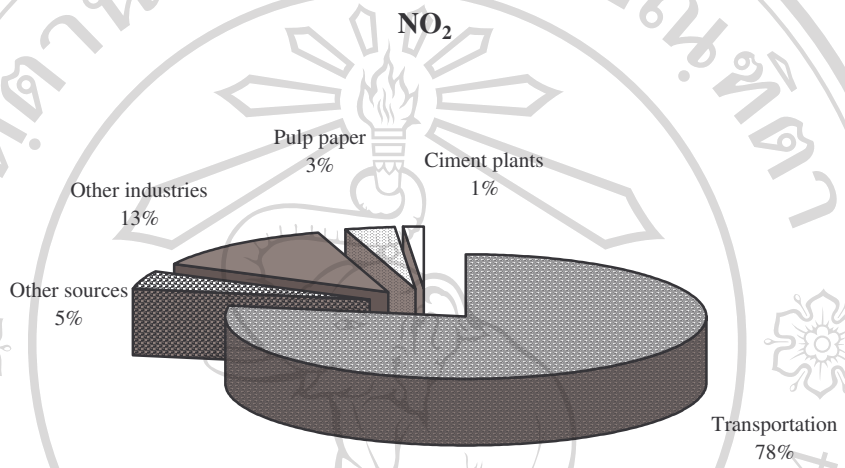

Fig 1.1 Sources of nitrogen dioxides (NO_2) in 2000 [(1)]

[(1)] Excluding natural sources such as bacterial activity, lightening and forest fires.

Source: Environment Canada, National Pollutant Release Inventory, 2004

Nitrogen dioxide can irritate the lungs and lower resistance to respiratory infection. Sensitivity increases for people with asthma and bronchitis. Nitrogen dioxide chemically transforms into nitric acid and, when deposited, contributes to lake acidification. Nitrogen dioxide, when chemically transformed to nitric acid, can corrode metals, fade fabrics and degrade rubber. It can damage trees and crops, resulting in substantial losses.

1.1.2 Sulfur dioxide (SO_2)

Sulfur dioxide is a colourless gas. It can be oxidised to sulfur trioxide. Sulfur dioxide can be oxidised to form acid aerosols. It is a precursor to sulfates, which are one of the main components of respirable particles in the atmosphere. SO_2 emitted from smelters and utilities, especially electrical generation. Other industrial sources include iron and steel mills, petroleum refineries, and pulp and paper mills (De Santis *et al*., 2001). Small sources include residential, commercial and industrial space heating as shown in Fig 1.2.

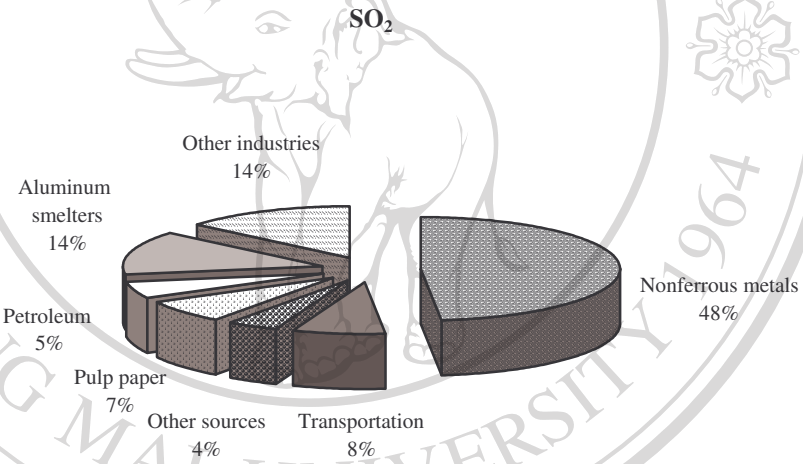

Fig 1.2 Sources of sulfur dioxide (SO_2) in 2000 [(1)]

[(1)] Excluding open sources such as forest fires.

Source: Environment Canada, National Pollutant Release Inventory, 2004

Health effects caused by exposure to high levels of SO_2 include breathing problems, respiratory illness, changes in the lung's defences, and worsening respiratory and cardiovascular disease. People with asthma or chronic lung or heart

disease are the most sensitive to SO_2. It also damages trees and crops. SO_2, along with nitrogen oxides, are the main precursors of acid rain. This contributes to the acidification of lakes and streams accelerated corrosion of buildings and reduced visibility. SO_2 also causes formation of microscopic acid aerosols, which have serious health implications as well as contributing to climate change.

1.1.3 Ozone (O_3)

Ozone is a colorless gas at ambient temperature and pressure, and unstable especially at higher concentration. In the atmosphere the production of ozone is based on photochemical reactions of air pollutants (hydrocarbon and nitrogen oxides). When these pollutants build up to sufficiently high level, a chain reaction occurs from their interaction with sunlight in which nitrogen oxide is converted to nitrogen dioxide, and the later can absorb sunlight and breaks down oxygen atoms that combine with the air-oxygen to produce ozone. Although not directly emitted into the air, ozone is produced through a photochemical transformation of precursor pollutants: nitrogen oxides and volatile organic compounds. Human activity accounts for most of these pollutants, including transportation, industry and heating. Ozone is also emitted from germicide lamps, copy machine, printers, welding and other industrial process (Murad *et al*., 2002).

Ozone levels are generally higher in summer, during hot sunny weather. Concentrations are usually highest in late afternoon. Ozone is a pollutant that can travel large distances. Periods of high ozone levels can persist anywhere from a few hours to a few days, depending on weather conditions. The Table 1.1 shows the general standard of air pollution.

Table 1.1 Ambient air standard

Pollutants	average	Standard
1. Carbon monoxide (CO)	1 hr	Not exceed 30 ppm (34.2 mg/m^3)
	8 hr	Not exceed 9 ppm (10.26 mg/m^3)
2. Nitrogen Dioxide (NO_2)	1 hr	Not exceed 0.17 ppm (0.32 mg/m^3)
3. Ozone (O_3)	1 hr	0.10 ppm (0.20 mg/m^3)
4. Sulfur Dioxide[a] (SO_2)	1 year	Not exceed 0.04 ppm (0.10 mg/m^3)
	24 hr	Not exceed 0.12 ppm (0.30 mg/m^3)
	1 hr	Not exceed 0.3 ppm (780 µg/m^3)
5. Lead (Pb)	1 month	Not exceed 1.5 mg/m^3 (1500 µg/m^3)
6. Particulate Matter (< 10 µm)(PM - 10)	24 hr	Not exceed 0.12 mg/m^3 (120 µg/m^3)
	1 year	Not exceed 0.05 mg/m^3 (50 µg/m^3)
7. Particulate Matter (< 100 µm)	24 hr	Not exceed 0.33 mg/m^3 (330 µg/m^3)
	1 year	Not exceed 0.10 mg/m^3 (100 µg/m^3)

Remark : 1. Short term average standard (1, 8 and 24 hrs.) is to prevent acute effect on human health

2. Long term average standard (1 month and 1 year) is to prevent long term or chronic effect on human health

a 1- hr SO_2 Standard
* 1.3 mg/m^3 for Mae Moh area
* 0.78 mg/m^3, for elsewhere

Source :
1. Notification of National Environmental Board No. 10 , B.E 2538 (1995) under the Enhancement and Conservation of National Environmental Quality Act B.E.2535 (1992), published in the Royal Government Gäzette No. 112 Part 52 dated May 25, B.E.2538 (1995)
2. Notification of National Environmental Board No. 24, B.E. 2547 (2004) under the Enhancement and Conservation of National Environmental Quality Act B.E.2535 (1992), published in the Royal Government Gäzette No. 121 Special Part 104 D dated September 22, B.E.2547 (2004)

1.2 Atmospheric reaction of sulfur and nitrogen

1.2.1 Sulfur

The modern global sulfur cycle differs quite dramatically from the "pre-industrial" sulfur cycle from the large portion of anthropogenic sulfur added to the atmosphere each year. The anthropogenic sulfur is added in the form of SO_2 and is produced when fossil fuels containing sulfur are burned. The atmospheric reactions of SO_2 are very complex, and proceed through three different pathways to the sulfate ion (SO_4^{2-}). SO_2 can react with the hydroxyl radical to form an HSO_3 radical, which can react with another hydroxyl radical to form water and SO_3^{2-} or sulfuric acid (H_2SO_4). SO_2 also dissolves in water droplets where it can react with oxygen gas to form SO_4^{2-}. The third pathway to SO_4^{2-} is when SO_2 reacts with hydrogen peroxide to sulfuric acid. The ultimate fate of all sulfur in the atmosphere is to be oxidized to the SO_4^{2-}, usually as H_2SO_4. The most common base present in the atmosphere is ammonia (NH_3) which reacts with sulfuric acid to form ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$). Sulfuric acid, ammonium bisulfate and ammonium sulfate are all hydroscopic substances, readily dissolving in water. They wash out of the atmosphere during precipitation events.

1.2.2 Nitrogen

Atmospheric reactions of nitrogen are much more complex than the atmospheric reactions of sulfur. Ammonia (NH_3) is the most reduced form of nitrogen, and is released in small quantities from anaerobic degradation of organic matter containing nitrogen. Just like hydrogen sulfide (H_2S), ammonia reacts with the hydroxyl radical to form oxidized nitrogen species. Nitrogen oxides are released to the atmosphere from both natural and anthropogenic sources. The two most common

nitrogen gases released to the atmosphere from biological processes are nitrous oxide (N_2O) and nitrogen dioxide (NO_2). Combustion processes release mostly nitrogen oxide (NO) and nitrogen dioxide. The exact composition of nitrogen oxides emitted from combustion processes varies with temperature of the combustion process, and the nitrogen oxides from combustion are often referred to as NOx to indicate the uncertainty in chemical composition. Like sulfur, the modern global nitrogen cycle is very different than the "Pre-industrial" nitrogen cycle. The difference, again, is the large amount of nitrogen added to the atmosphere through combustion processes. The excess atmospheric nitrogen oxides contribute to acid rain in the same way that excess sulfur oxides do.

The chemistry of atmospheric nitrogen in the troposphere is different that the chemistry in the stratosphere. Nitrogen chemistry at both levels is driven by the photochemical dissociation of nitrogen dioxide (NO_2), but the products formed depend on other substances with which the photochemically excited NO_2 molecules can react. At ground level the air is more dense than in the troposphere, so the concentration of oxygen is much greater. Also at ground level are volatile organic carbon substances (from automobile traffic, solvents and industrial processes) that react with nitrogen oxides to form peroxyacylnitrates (PAN; $H_3COCOONO_2$), a product of photochemical smog as shown in Fig 1.3.

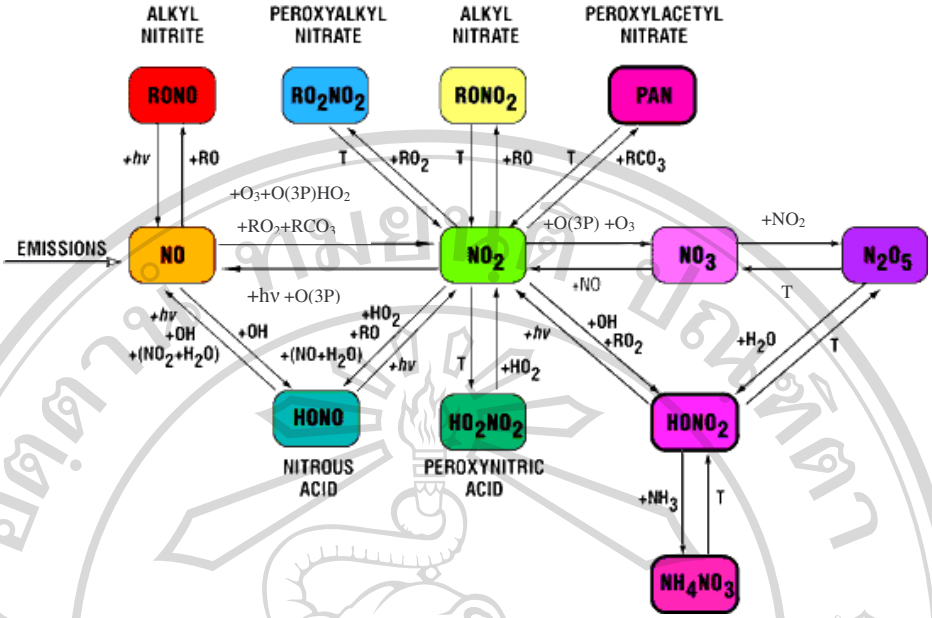

Fig 1.3 Different forms of nitrogen oxides in the troposphere important in the formation of photochemical smog.

Source: Environment Canada, National Pollutant Release Inventory, 2004

Stratospheric nitrogen chemistry includes ozone as a major player. The intense ultraviolet radiation 50 km from the earth's surface causes diatomic oxygen to dissociate into oxygen atoms. These single oxygen atoms react with oxygen molecules to form ozone. This sequences of reactions is known as the Chapman cycle, shown below

$$O_2 + h\nu \longrightarrow 2O^{\bullet}$$

$$O_2 + O^{\bullet} \longrightarrow O_3$$

$$O_3 + h\nu \longrightarrow O_2 + O^{\bullet}$$

Nitrogen oxides then react with ozone as shown in the two reaction schemes below:

Mechanism 1

$O_3 + NO \longrightarrow NO_2 + O_2$

$NO_2 + O^{\bullet} \longrightarrow NO + O_2$

Net $O_3 + O^{\bullet} \longrightarrow 2O_2$

Mechanism 2

$NO + O_3 \longrightarrow NO_2 + O_2$

$NO_2 + O_3 \longrightarrow NO + 2O_2$

Net $2O_3 \longrightarrow 3O_2$

1.3 Passive sampling

Analysis of data on air pollution in the global scale, passive samplers (also called diffusion samplers) can brings to the conclusion that the quality and availability of data is of high diversity. In some regions, for instance, in Europe and North America, air pollution monitoring networks are well developed whereas in many other parts of the world measurements of air pollution are conducted irregularly or not at all. One of the reasons why regular measurements are not conducted in many regions of the world is lack of suitable analytical methods. Modern air pollution monitoring equipment is very expensive and requires highly skilled operators. Development of new technology in this field is usually oriented towards achieving lower detection limits, higher accuracy and determination of wider range of pollutant species. Cost of equipment and simplicity of a method is rarely a matter of concern. One of the possibilities to develop a range of simple methods applicable for large-scale

monitoring is the use of passive samplers (Krochmal and Kalina, 1997). No pumping of air is needed and therefore passive samplers are lightweight, cheap, robust and easy in operation. Passive samplers can be mailed before and after exposure and stored for periods of at least several weeks.

1.3.1. Principle

Passive collection of a given air pollutant is achieved by chemical and physical sorption on a sorbent or filter impregnated with a sampling medium. In diffusional sampling the gas is passively transported to the sorbent by molecular diffusion. Passive sampling is sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potentials of the analyte between the two media. Net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling session is terminated by the user. In the former case, the amount of analyte collected by the sampler once equilibrium has been reached does not change with time provided that the analyte concentration in the sample medium does not fluctuate. This concentration can then be determined based on the ratio of analyte distribution between the two media involved or experimental calibration of the device. When sampling continues until the sampling session is terminated by the user, the amount of analyte collected by the sampler depends on both its concentration in the sampled medium and the exposure time. If the relationship between the sampling rate and analyte concentration is known, time-weighted average (TWA) analyte concentration can be easily determined, and this has its advantages. However, several conditions must be met for this approach to work. First, the receiving medium must act as a zero sink, that is it should not let the trapped

molecules be released even if the concentration of the analyte around the sampler decreases to zero. Second, the sampling rate (the amount of analyte collected by the sampler per unit time at constant concentration in the surrounding medium) must remain constant throughout the sampling session. This can be easily accomplished when the analyte is absorbed (for example into a liquid receiving phase) or chemisorbed.

The sampling process is similar for both types of samplers. Once they are exposed to the medium examined, they collect analyte molecules reaching the collecting medium by diffusion through a static layer of the examined medium contained in well-defined openings in the sampler, or by permeation through a non-porous membrane. Schematic diagrams of the two types of samplers are given in figure 1.4.

(a) (b)

Fig 1.4 Schematic diagram of; (a) tube-type diffusion sampler, and (b) badge-type permeation sampler (Tadeusz and Jacek, 2002).

Subsequently the pollutants can be examined by non-destructive optical method, or extracted or desorbed to quantify the pollutant of interest as appropriate

(Ferm,M., 1991; Krupa,S.V. and Legge., 2000). The sampling rate is controlled by the rate of diffusion of the substance through the air layer inside the sampler, according to Fick's law of diffusion.

However, after more than 20 years since the first paper on the principles of passive sampling was published by Palmes and Gunnison (1973) the potential advantages of passive samplers seem to be insufficiently exploited.

1.3.2 Theory

The passive sampling works based on the principle of Fick's law (Palmes and Gunnison, 1973). The details of operating principles are described by Gair *el al*. (1991).

$$F_1 = -D\,dC/dz \qquad \text{.....(1.1)}$$

Where F_1 is the flux of gas (mol cm^{-2} s^{-1}), D is the diffusion coefficient of gas (cm^{-2} s^{-1}), C is concentration of gas (mol cm^{-3}) and z is the length of diffusion (cm). The quantity of gas transferred (Q_1 mol) in t seconds for a cylinder of radius r is given by equations (1.2) and (1.3).

$$Q_1 = F_1(\pi r^2)t \quad \text{mol} \qquad \text{.....(1.2)}$$

Therefore

$$Q_1 = -D(c_1-c_0)(\pi r^2)t\,/L \quad \text{mol} \qquad \text{.....(1.3)}$$

Where c_0 is the concentration experienced at the absorber surface. Therefore, $(c_1-c_0)/L$ is the concentration gradient along the cylinder length (L), if an efficient absorber is used to remove gas then c_0 effectively becomes zero.

The negative sign is ignored as it arises from the direction of the flux flow from high to low concentrations.

The unit of gas concentration in ambient air usually reported in $\mu g/m^3$ or ppbv Therefore

$$\mathbf{C = [Q * L] / [A * t * D]} \quad \text{.....(1.4)}$$

Where

C = gas concentration ($\mu g/m^3$)

Q = quantity of gas transferred in sampling tube (μg)

L = length of diffusion tube (m)

A = cross-sectional area (m^2) = πr^2

t = sampling time (s)

D = diffusion coefficient ($m^2 s^{-1}$)

The diffusion coefficient of NO_2 and O_3 is $1.54 * 10^{-5}$ $m^2 s^{-1}$ and that of SO_2 is $1.27*10^{-5}$ $m^2 s^{-1}$.

The calculation of gas quantity presented in diffusion tube is depended on the final product after reacting with sampling medium. The details are shown in appendix A.

1.4 Literature Review

Passive sampler was firstly developed in America as an on-person air sampler by Palmes *et al.* (1976), for field studies related to occupational health. Later, a variety of passive samplers such as tube type (Palmes *et al*., 1976), badge type (Krochmal and Gorski, 1991) and high efficiency passive samplers were developed.

Out of these, two types, namely, the tube types and the badge type have become popular and are used widely in Europe and America because both the tube and badge types of samplers with slight modification serve satisfactorily. Different studies have shown a comparison of tube type and badge type samplers that tube type samplers are better than badge type samplers on account of their robustness and relatively higher precision (Van Reeuwijk *et al*., 1998). Some typical physical sampler configurations are shown in Fig 1.5.

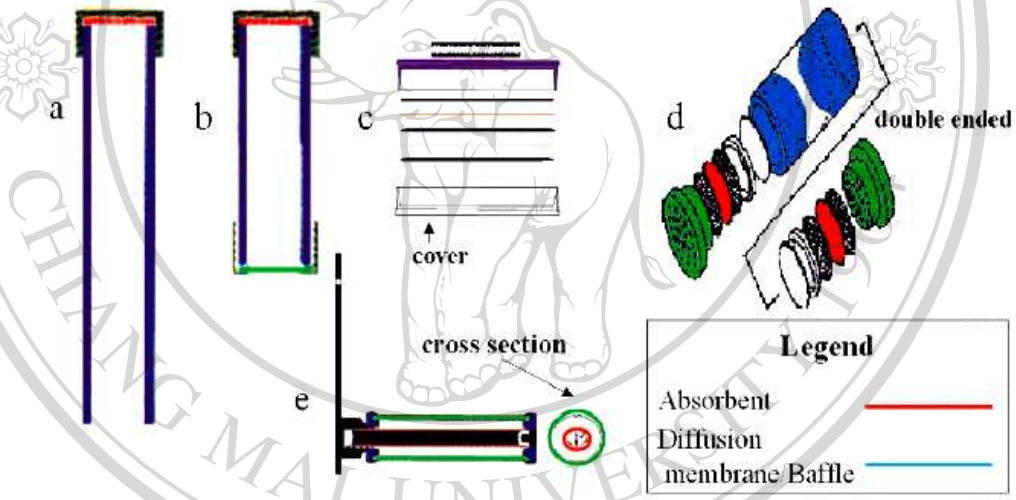

Fig 1.5 Example of different sampler configurations; (a) opened-end diffusion tube, (b) shorter diffusion tube with diffusion membrane at opening, (c) badge-type with diffusion membrane at opening, (d) double-ended badge with baffles at opening, (e) cylindrical badge with tubular diffusion membrane. (Roger, 2003)

The classical passive sampler is the tube type sampler first introduced by Palmes ang Gunnison (1973). Although simple to use, the Palmes tube requires a long process of optimization and validation. Indeed, the passive samplers must collect efficiently and selectively air pollutant while being resistant to meteorological factors,

such as temperature, humidity sunlight, precipitation and wind. The Palmes tube takes advantage of the small area-to-length ratio to minimise the influence from turbulence in the front of the tube. Nevertheless, there are conflicting result from number of some investigations on the possible sampling problems cause by wind conditions. The shortening of the effective diffusion length along the tube causes wind-induced turbulence at the face of the sampler. Gair and Penkett (1995) who found in their field experiment a reduction in the diffusion length between 7% and 38% which was depended on the increase of the wind velocity at the site. To overcome this problem of wind sensitivity, the passive sampler can be fitted with a porous membrane barrier (De Santis *et al*, 1997). The membrane presents a resistance to diffusion which must measured experimentally. This resistance can also vary under the low-wind speed effects and fluctuation in meteorological conditions. Another option is to use a protective shelter for the passive diffusion tubes, as recommended by Monn and Hangartner (1989), Krohmal and Kalina (1997), Tang (2000), Plaisance *et.al* (2001).

A further problem effects badge-type samplers. The disadvantage of having barrier is that since the membrane present an unknown resistance to diffusion and the increased boundary layer resistance under low wind speeds of badge samplers may also cause underestimates of pollutant gas concentrations. Membranes or baffles used at the sampler inlet reduce turbulent transfer of the pollutant to the sorbent, allowing shorter diffusion lengths. Here, the effective area of the pores in the membrane or baffle largely controls the rate of sampling. So the uptake can no longer be calculated as it can be done in the case of tube-type samplers (De Santis *et al*., 2001). However, one can use the relationship between wind speed and boundary layer resistance to correct air concentration estimates (Willems, 1993).

Gair *et al*., 1991 tested the contamination of unexposed tubes-type at room temperature. They found that the tube made from teflon show a significant increase in contamination of NO_2 when compared to acrylic tube. The result for the teflon tube may suggest that part or all of the contamination is caused by permeation of NO_2 through the sampler tubing. Another possible source of contamination is leakage around the sealing caps, however, it is unlikely that this contamination would be totally eliminate by storage in the freezer.

A variation in blanks was observed compared with the exposed tubes. Some of the caps were later made airtight by using parafilm as a sealant. The values in all these tubes were lower than the tubes without parafilm. Tate (2002) reported that the field blank values to be higher and more variable than in the expose tubes. He commented this to the contamination in the Ogawa passive samplers used for collection of NH_3. He used new cleaning procedures to reduce the blank variation, but the blank problems could not fully be solved by these cleaning procedures. The blank values were also found to be strongly depended on the analyte concentration in ambient air (Krochmol and Kalina, 1997). The tubes were contained inside the airtight plastic boxes during transportation and store in the refrigerator till the time of analysis. They found that no significant difference was noted between badge-type samplers stored at room temperature and in refrigerator. But the diffusion tube samplers and blank must be stored in a fridge at 4^{o}C prior to analysis to minimize background contamination. The tubes were not stored more than 3 weeks.

Influence of meteorological factors like sunlight, wind velocity, temperature and humidity of air on sampling rate have been minimized by an appropriate

modification of the sampler and calibration of the method under various conditions (Plasance *et al*., 2002).

Passive samplers are generally protected from the rain, sunlight, and mechanical damage during field deployment by a shelter of various designs. They provide a point of attachment to the monitoring site (pole, utility post or tree), and can be a simple flat shelter under which the sampler is attached. Recently, however, more attention has been paid to the shelter. The shelter used is an inverted tube or pipe cap with the samplers mounted inside with their inlets close to the bottom lip; they may hold one or a few samplers of various designs. Advantages and disadvantages of active and passive sampler were compared as shown in Table 1.2.

Table 1.2 the comparison of passive sampler with active analyzer (Varshney, 2003)

Characteristics	**Active anzlyzer**	**Passive sampler**
Power	Required	Not required
Calibration	Periodically	Validation once
Precision	High	Relatively low
Sampling duration	Small	Large
Accuracy	High	Relatively low
Temporal resolution	High	Low
Spatial measurement	Not suitable	Suitable
Concentration	Continuous real-time	Mean value
Skill required	High	Low
Cost	High	Low
Maintenance	Required	Not required
Size	Large	Small
Weight	Heavy	Light

All passive sampler parts are reusable. In addition, the passive samplers offer flexibility. They can be fixed to lamp-posts, traffic tunnels, in parks, office buildings, and on persons depending on the objective of the measurement. And it also remain stable over several months after sampling and can be conveniently transported before and after exposure. Moreover, they are ideally suited for developing a large spatial monitoring work even in remote areas lacking power source or elaborate infrastructure.

Absorbing solution used in passive samplers

Ozone

The earliest measurements of ground-level ozone were made by the Swiss chemist Schofinbein in the mid-1800s, using passive exposure of "test papers" impregnated with potassium iodide (cited in London, 1985). Other ozone samplers with different chemical absorbents have been developed for field use since the 1960s. Absorbents used today for ozone sampling are, nitrite (Brauer and Brook, 1995; Koutrakis et al., 1993; Tang and Lau, 2000; Ray, 2001), indigo compounds (Cox and Malcolm, 1999; Werner, 1989; Grosjean *et al*.,1995; Bytnerowicz *et al*.,1993) and 1,2-di(4-pyridyl)ethylene (DPE) (Hauser and Bradley,1966; 1990; Gerosa *et al*., 2001).

Nitrogen dioxide

The most commonly used absorbent solution for NO_2 is triethanolamine (TEA) where the gas is converted to nitrite ions. This has been used in open diffusion tubes (Palmes *et al*., 1976) or in membrane-covered badges (Mulik *et al*., 1989). A lack of specificity of TEA towards NO_2 can cause problems as sulfur dioxide (SO_2) is also absorbed, acidifying the TEA reagent and reducing collection efficiency.

Limiting exposure of the sampler to 1 or 2 weeks can reduce this interference by SO_2 (Heal and Cape, 1997; Ferm and Svanberg, 1998), and reduce suspected loss of NO_2 due to photodegradation of TEA in bright conditions (Tang *et al*., 2000). Potassium iodide (KI) has also been used in passive samplers for NO_2 in conjunction with sodium hydroxide (NaOH) to maintain high surface alkalinity of the reagent surface, required for long-term exposure (Ferm and Rodhe, 1997). Sodium carbonate (Na_2CO_3)/1% glycerine-impregnated filter paper has also been used in a badge-type sampler with a fine stainless mesh diffusion membrane for sampling both NO_2 and NO_x (De Santis *et al*., 2001). A new collection medium (Chemix TM) has been developed (Maxxam Analytics Inc.) for their badge-type sampler and was reported as a quantitative all-season sampler (Tang *et al*., 1999).

Sulfur dioxide

Passive monitoring for SO_2 dates back to 1945 in the UK, using lead peroxide candles, this method was re-approved by the American Society for Testing and Materials. Other absorbents used for the passive sampling of SO_2 are sodium tetrachloromercurate solution (Na_2HgCl_4) within a permeation device (Reiszner and West, 1973), potassium carbonate (K_2CO_3) (Dunikowski, 1986; Orr *et al*., 1987), TEA in a diffusion tube or badge (Ferm and Svanberg, 1998; Krochmal and Kalina, 1997) and sodium hydroxide-impregnated filter paper in a badge-type sampler (Ferm and Svanberg, 1997; Ayers *et al*., 1998; Carmichael *et al*., 1995).

1.5 The using of passive sampling in Thailand

There are some numbers of researches about passive sampling of pollutant gases in Thailand. Detail is shown in Table 1.3. However, limitation of using sampler is still there and more study is still needed in order to improve its efficiency and apply in wider ranges of monitoring site.

Table 1.3 The using of passive sampler in Thailand

Researcher	Type	Pollution	Absorbing solution	Analysis method	Remark
Assc. Prof. Dr. Winai Soomboon (King Mongkut's University of Technology Thonburi)	Badge	NO_2	NaOH/NaI	Spectrophotometry	Compared the efficiency of membrane barrier
		SO_2	NaOH	IC	
Assc. Prof. Dr. Wanida Jinsart (Chulalongkorn University)	Badge	NO_2	NaOH/NaI in MeOH	Spectrophotometry	Modified the passive sampler from the millipore container
		SO_2	NaOH	IC	
Dr. Hathairatana Garivait	Badge	NO_2	-	FIA	Used the commercial passive sampler to make the pollution mapping
		SO_2	-	IC	
		O_3	-	IC	
		NH_3	-	Spectrophotomety	
Mr. Hiroyuki Kurumiya (Jica, Japan)	Tube	NO_2	Triethanolamine	Spectrophotometry	Modified the easily passive sampler for determination pollution in Bangkok
		SO_2	NaOH		
		O_3	KI+Phosphate		

1.6 Analytical methods

The purpose of this study is to focus the analytical methods, ion chromatography and spectrophotometry, that are available for measuring NO_2, SO_2 and O_3. The intent is not provided an exhaustive list of analytical methods. Many of the analytical method used for environmental samples are the method approved by federal agencies and organization such as the Environmental Protection Agency (EPA) and the National Institute for Occupational Safety and Health (NIOSH).

1.6.1 Ion chromatography

Ion-exchange processes are based upon exchange equilibria between ions in solution and ions of like sign on the surface of an essentially insoluble, high-molecular-weight solid. Synthetic ion-exchange resins were first produced in the mid-1930s for water softening, water deionization, and solution purification. The most common active sites for cation-exchange resins are the sulfonic acid group $-SO_3^-H^+$, a strong acid, and the carboxylic acid group $-COO^-H^+$, a weak acid. Anionic exchangers contain tertiary amine groups $-N(CH_3)_3^+OH^-$ or primary amine group $-NH_3^+OH^-$; the former is a strong base and the latter a weak one.

When a sulfonic acid ion-exchanger is brought in contact with an aqueous solvent containing a cation M^{x+}, an exchange equilibria is set up that can be described by

$$\underset{\text{solid}}{xRSO_3^-H^+} + \underset{\text{solution}}{M^{x+}} \rightleftharpoons \underset{\text{solid}}{(RSO_3^-)_xM^{x+}} + \underset{\text{solution}}{xH^+}$$

where $RSO_3^-H^+$ represents one of many sulfonic acid groups attached to a large polymer molecule. Similarly a strong base exchanger interacts with the anion A^{x-} as shown by the reaction

$$xRN(CH_3)_3OH^- + A^{x-} \rightleftharpoons [RH(CH_3)_3^+]_xA^{x-} + xOH^-$$

solid solution solid solution

As an example of the application of the mass-action law to ion-exchange equilibria, we will consider the reaction between a singly charged ion B^+ with a sulfonic acid resin held in a chromatographic column. From a neutral solution, initial retention of B^+ ions at the head of the column occurs because of the reaction

$$RSO_3^-H^+(s) + B^+(aq) \rightleftharpoons RSO_3^-B^+(s) + H^+(aq)$$

Here, the (s) and (aq) emphasize that the system contains a solid and an aqueous phase. Elution with a dilute solution of hydrochloric acid shifts the equilibrium to the left, causing part of the B+ ions in the stationary phase to be transferred to the mobile phase. These ions then move down the column in a series of transfers between the stationary and mobile phase. The diagram of IC system is showed in Fig 1.6.

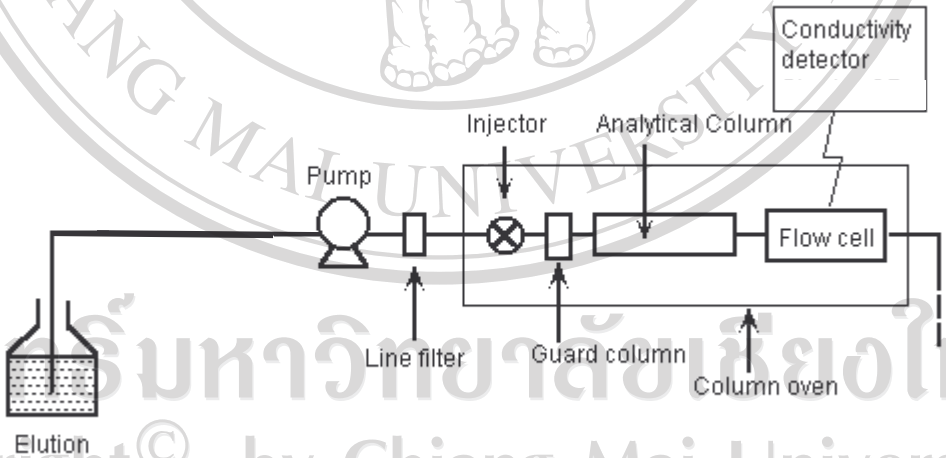

Fig 1.6 The diagram of ion chromatographic system

(http://www.shodex.com/english/illust/i0055)

A) Inorganic applications of ion-exchange chromatography

The mobile phase in ion-exchange chromatography must have the same general properties that are required for other types of chromatography. That is, it must dissolve the sample, have a solvent strength that leads to reasonable retention times, and interact with solutes in such way as to lead to selectivity. The mobile phases in ion-exchange chromatography are aqueous solution that may contain moderate amounts of methanol or other water-miscible organic solvents these mobile phases also contain ionic species, often in the form of a buffer. Solvent strength and selectivity are determined by the kind and concentration of these added ingradients. In general, the ions of mobile phase compete with analyte ion for the active sites on the ion-exchange packing.

B) Ion-exchange chromatography with eluent suppressor column

At note earlier, the widespread application of the ion chromatography for the determination of inorganic species inhibited by the lack of good general detector, which would permit quantitative determination of ion on the basis of chromatographic peak areas. Conductivity detectors are an obvious choice for this task. They can be highly sensitive, they are universal for changed species, and, as a general rule, they respond in a predictable way to concentration changes. Furthermore, such detectors are simple, inexpensive to construct and maintain, easy to miniaturize and ordinarily give prolong, trouble free service. They only limitation to conductivity detector proved to be serious one, which delayed their general use. This limitation arises from the high electrolyte concentration required to elute most analyte ion in the reasonable time. As a consequence, the conductivity from the mobile phase components tends to swamp that from analyte ions, thus greatly reducing the detector sensitivity.

For anion separations, the suppressor packing is the acid form of cation-exchange rasin. Here, sodium bicarbonate or carbonate may serve as the eluting agent. The reaction in suppressor is then

$$Na^{+}_{(aq)} + HCO_3^{-}{}_{(aq)} + Resin^{-}H^{+}_{(s)} \longrightarrow Resin^{-}Na^{+}_{(s)} + H_2CO_{3(aq)}$$

Here, the largely undissociated carbonic acid does not contribute significantly to the conductivity.

In recently designed commercial instrument, regeneration of supperssor solutions is performed automatically with electrogenerated hydrogen or hydroxyl ions so that interruptions in the use of instruments for regeneration are not required (Douglas *et al*., 1998).

1.6.2 Spectrophotometry

In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight (or white light) as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. The component colors of the visible portion can be separated by passing sunlight through a prism, which acts to bend the light in differing degrees according to wavelength. Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. **Wavelength** is defined on the left below, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters). **Frequency** is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz). Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible

wavelength is red and the shortest is violet. When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. The diagram of spectrophotometric system is shown in Fig 1.7.

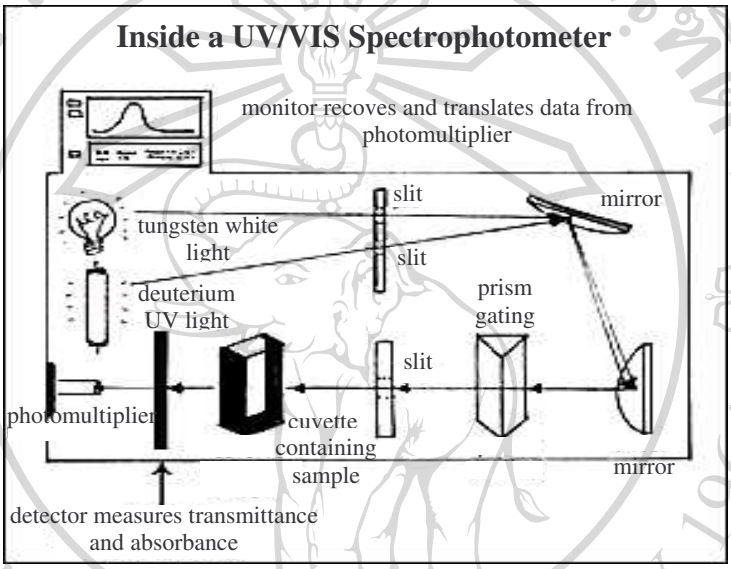

Fig 1.7 The diagram of UV-VIS spectrophotometric system (http://www.skipwagner.net/smbiotech/graphics/insideUV_VIS)

UV-Visible Absorption Spectra

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the

degree of absorption at each wavelength. Fig 1.8 shows the visible spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

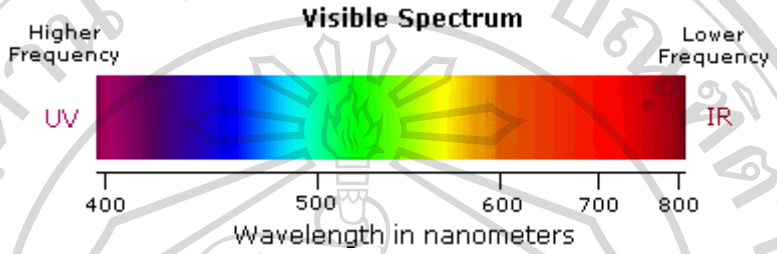

Fig 1.8 The visible spectrum

(http://www.chemicool.com/img1/graphics/spectrometer1)

The resulting spectrum is presented as a graph of absorbance (A) versus wavelength. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation. Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). Beer's law was developed in 1852 by J. Beer. The quantitatively was described the absorption as;

$$\textbf{Log } (I_o/I) = A = \varepsilon cl$$

where **A**= absorbance, **c** = sample concentration in moles/liter, **l** = length of light path through the sample in cm, $\mathbf{I_o}$ = the intensity of light entering the sample, **I** = the intensity of light leaving the sample, **ε** = molar absorptivity

The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths so conjugation becomes the major structural feature identified by this technique. The example of spectrum from spectrophotometry is shown in Fig 1.9.

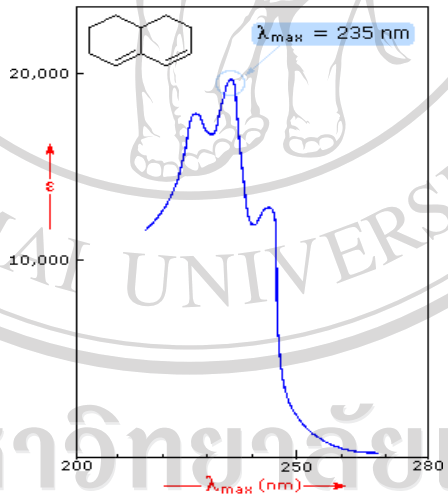

Fig 1.9 The example of spectrum from spectrophotometry

(http://www.chemicool.com/img1/graphics/spectrometer1)

1.7 Research Objectives

In this study, laboratory and field calibrations of passive samplers against instrumental monitors are needed for optimizing sampler configuration. Such tests are also used for development of sampler sensitivity. Selection of absorbent is based on minimization of potential interferences by reactive gases and environmental factors, which may vary between sampling locations. Considerations of sampler configuration to be used are based on the minimization of residence time of any inter-reactive gases within the sampler.

The main objectives of this study were development of passive samplers for determination of NO_2, SO_2 and O_3 in ambient air by ion chromatography and spectrophotometry, and also to apply the optimum passive sampler to determine levels of NO_2, SO_2 and O_3 in Chiang Mai ambient air. The accuracy of passive samplers was compared with active sampler of Pollution Control Department (PCD) monitoring stations.

Rapidly growing cities like Chiang Mai are in need of wide spread and effective air quality monitoring programs to have better control plans for air pollution in order to reduce the risks from it. As there are only two active monitoring stations in Chiang Mai, they are probably not sufficient or reliable information about the air quality of Chiang Mai. It is feasible to have sufficient numbers of sampling sites with passive sampling technique because of it's cost effective. Thus, the passive sampling can be alternative method to monitor the environmental situation especially air pollution based on pollution gases in ambient air.