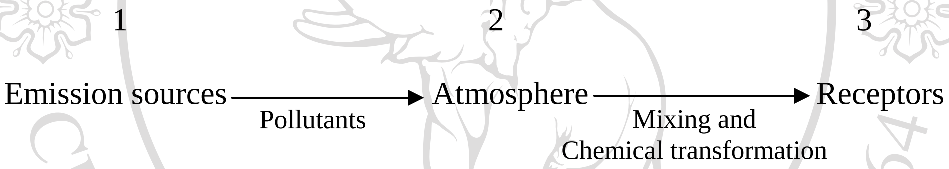
CHAPTER 1

INTRODUCTION

1.1 Air pollution

Air pollution may be defined as any atmospheric condition in which substances are presented at concentrations high enough above their normal ambient levels to produce a measurable effect on human, vegetation or materials. These substances may exist in the atmosphere as gases, liquid drops or solid particles. The air pollution problem can be simply depicted as system consisting of three basic components (Sernfeld, 1975):



Air transport is a term used to describe the mechanism by which air pollution moves from an emissions source to a receptor. A source is a location from which the pollutant emanates and a receptor is the place (soil, vegetation) where the pollutant is deposited. A receptor is adversely affected by polluted air. A receptor can be people, animals, vegetation, materials, and aquatic life. The wind is the transporter of air pollutants from sources and receptors. Air pollution can be man-made or naturally occurring. The main sources of air pollution are stationary and area sources (utilities and manufacturing industries), mobile sources, agricultural sources, and natural sources such as an erupting volcano, forest and prairie fires (Sernfeld, 1975).

1.2 Nitrogen dioxide

Nitrogen dioxide is one of the most important pollutants in ambient air because of it adverse effects on the human health and welfare, its contribution to the acidification of ecosystems and it role in the formation of photochemical oxidants (EPA, 1998). Besides these properties, NO_2 is one of the most important indicator pollutants for the urban air quality and it is the most toxic compound among the nitrogen oxides. Because of these reasons, it should be routinely monitored at urban setting to comply with present regulations on NO_2 aimed to protection of human health. Many countries and different international organizations such as EPA (Environmental Protection Agency), WHO (World Health Organization), the European Union Air Quality Framework and Daughter Directive, Word Bank, etc. published their own standard for this purpose (Lim *et al.*, 2005 cited by Ozden and Dogeroglu, 2007). Table 1.1 shows the general standard of air pollution.

Nitrogen dioxide is the chemical compound NO_2. It is one of the several nitrogen oxides. This reddish-brown gas has a characteristic sharp, biting odor. NO_2 is one of the most prominent air pollutants and a poison by inhalation. Nitrogen dioxide is toxic by inhalation. Symptoms of poisoning (lung edema) tend to appear several hours after one has inhaled a low but potentially fatal dose. Also, low concentrations (4 ppm) will anesthetize the nose, thus creating a potential for over exposure. Long-term exposure to NO_2 at concentrations above 40–100 µg/m³ causes adverse health effects.

Table 1.1 Ambient air standard

Pollutants	Average time	WHO Standards	US Standards	Thailand standards
Carbon monoxide (CO)	1 hour	30 mg/m^3	35 ppm (40 mg/m^3)	Not exceed 30 ppm (34.2 mg/m^3)
	8 hour	10 mg/m^3	9 ppm (10 mg/m^3)	Not exceed 9 ppm (10.26 mg/m^3)
Lead (Pb)	24 hour	0.5-1 ug/m^3		
	1 month			Not exceed 1.5 ug/m^3
	Quarterly		1.5 ug/m^3	
Nitrogen dioxide (NO$_2$)	Annual		0.053 ppm (100 µg/m^3)	
	24 hour	150 µg/m^3		
	1 hour			Not exceed 0.17 ppm (0.32 mg/m^3)
Ozone (O$_3$)	1 hour	150-200 µg/m^3	0.12 ppm (235 µg/m^3)	Not exceed 0.10 ppm (0.20 mg/m^3)
PM$_{10}$/TSP/SPM	Annual	60-90 µg/m^3	50 µg/m^3	Not exceed 0.10 mg/m^3
	24 hour	150-230 µg/m^3	150 µg/m^3	Not exceed 0.33 mg/m^3
Sulfur dioxide (SO$_2$)	Annual	40-60 µg/m^3		Not exceed 0.04 ppm. (0.10 mg/m^3)
	24 hour	100-150 µg/m^3	0.14 ppm (365 µg/m^3)	Not exceed 0.12 ppm (0.30 mg/m^3)

Source: Pollution Control Department, Ministry of Natural Resources and Environment, 2004

All combustion in air produces oxide of nitrogen (NO_x), of which NO_2 is major product. NO_x comes from the transportation, 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 (www. epa.gov) as shown in Figure 1.1 and Table 1.2 shows summary of the chemical and physical properties of nitrogen dioxide.

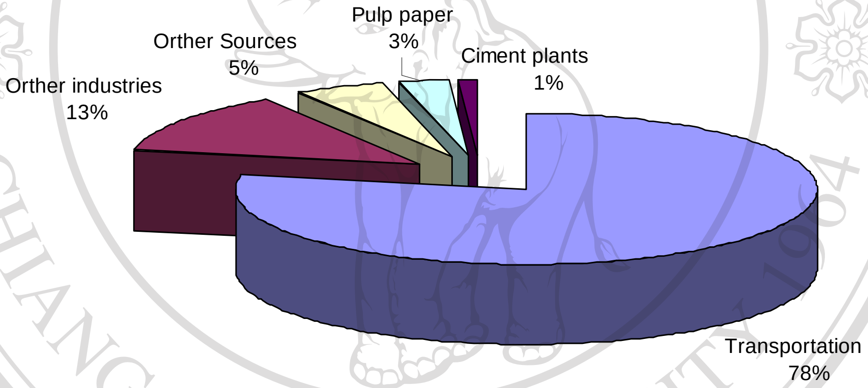


Figure1.1 Sources of nitrogen dioxide (NO_2)

Source: Environmental Canada, National Pollutant Release Inventory, 2004

Table 1.2 The chemical and physical properties of nitrogen dioxide

Item	Condition
Synonyms	dinitrogen tetroxide, nitrogen peroxide, nitrito
Molecular formula	NO_2
Structural formula	O=N=O
Molecular weight	46.05 g/mol
Color	reddish brown gas, or yellow-brown
Melting point	-11.2 ^oC
Boiling point	21.1 ^oC
Vapour density	3.3 g/l at 20^oC, 1 atm
Vapour pressure	1013 hPa
Critical temperature	158 ^oC
Specific gravity:	1.45 (liquid at 20 ^oC)
Flammability	Oxidizer

Source: Chemical Safety information-glossary (Oxford University), 2006

1.2.1 Atmospheric reaction of nitrogen

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 atmosphere from biological processes are nitrous oxide (N_2O) and nitrogen dioxide (NO_2).

Combustion processes release mostly nitrogen oxide (NO) and nitrogen dioxide (NO_2). 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 NO_x to indicate the uncertainty in chemical composition. Like sulfur, the modern global nitrogen cycle is very different from 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 (Environmental Canada, 2004 cited by Khaodee, 2006)

. The chemistry of atmospheric nitrogen in the troposphere is different from in the stratosphere. Nitrogen chemistry at both levels is driven by the photochemical dissociation of nitrogen dioxide, but the products formed depend on other substances with which the photochemically excited NO_2 molecules can react. At ground level the air is denser 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 the react with nitrogen oxides to from peroxyacetyl nitrates (PAN; $H_3COCOONO_2$), a product of photochemical smog (Foust, 2007) as shown in Figure.1.2.

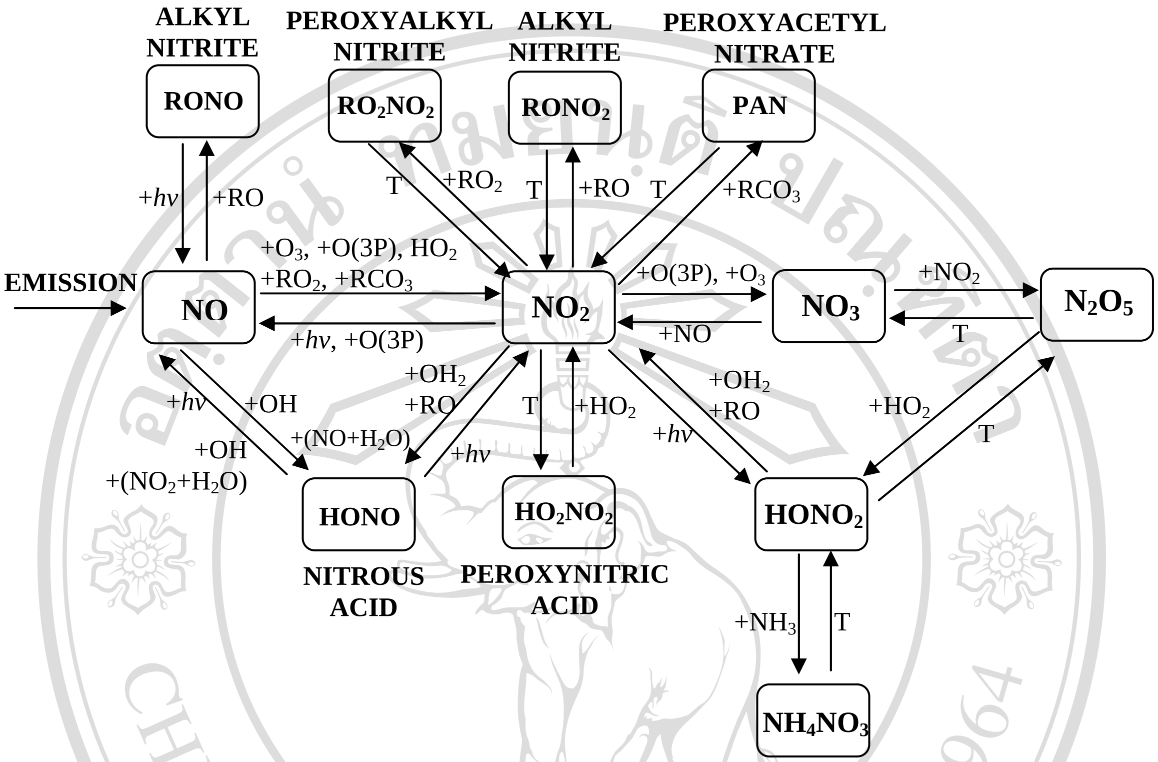


Figure 1.2 Chemical transformations of nitrogen oxides in the troposphere

Source: http://mtsu32.mtsu.edu:11233/Smog-Atm1.htm

1.3 Passive Sampling

Analysis of data on air pollution in the global scale 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 sophisticated, 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 use of passive samplers. Their sampling rate is controlled by the rate of diffusion of the substance through the air layer inside the samplers (Krochmal and Kalina, 1997). No pumping of air is needed and therefore passive samplers can be lightweight, cheap, robust and easy in operation. What is more, passive samplers can be mailed before and after exposure and stored for periods of at least several weeks.

A passive sampler operates by diffusing the sample gas from the atmosphere across the sampler volume, usually an inverted tube, to a skin or chemical absorbent according to Fick's law. Rate of pollutant gas absorption for a simple diffusion tube sampler is control by the diffusion path length and the internal cross-sectional area of the sampler (Roger, 2003).

1.3.1 Principle

Passive sampling will be defined in this article as any 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 analyte concentration can be easily determined, and this has its advantages. 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 (Gorecki and Namiesnik, 2002). 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

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 nonporous membrane. Schematic diagrams of the two types of sampler are shown in Figure 1.3 (Gorecki and Namiesnik, 2002)

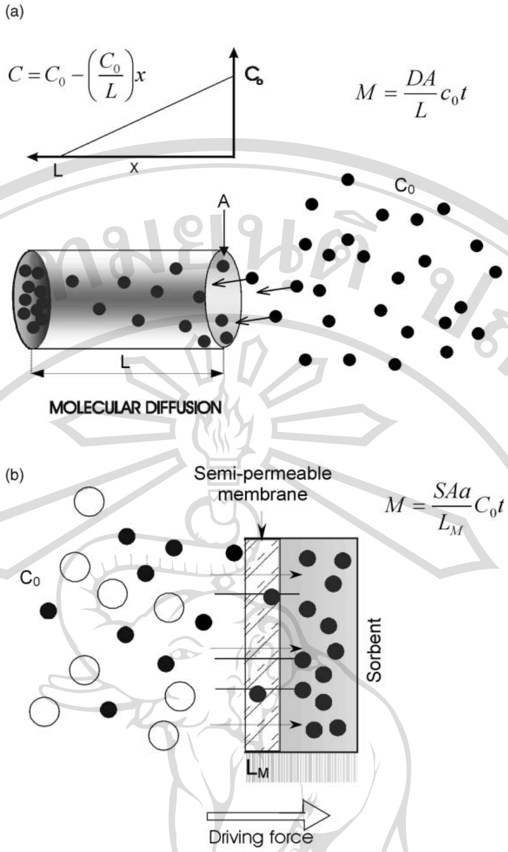


Figure1.3 Schematic diagrams of: (a) tube-type diffusion sampler, and (b) badge-type permeation sampler.

1.3.2 The theory of passive sampling

Most passive samplers are operated by diffusion. Diffusive samplers rely on the movement of contaminant molecules across a concentration gradient that can be defined by Fick's first law of diffusion. In other words, chemical will diffuse from an area of high concentration in the air to an area of low concentration on the sampler and flux (mass/unit area/unit time) for an individual chemical (Gorecki and Namiesnik, 2002) follows the equation.

The unidirectional flow of a gas1 through a gas 2 is given by Fick's law

$$F_1 = -D_{1,2}\left(\frac{dc_1}{dx}\right) \qquad (1.1)$$

Fick’s first law of diffusion states that the rate of mass transfer of gas 1 in gas 2 can be expressed by

$$W_1 = -D_{1,2}\,A\left(\frac{dc}{dx}\right) \qquad (1.2)$$

Where W_I is the rate of mass transfer of gas 1 μg/s, $D_{1,2}$ is the diffusion coefficient of gas 1 in gas 2 (cm^2/s), A is the cross-sectional area of the diffusion path (cm^2) and dc/dx is the instantaneous rate of change in concentration along the diffusion path, (x is the position in the diffusion path). If C_1-C_0 is the change in concentration along the diffusion path length, L, (negative, as the diffusion path is in the direction of decreasing concentrations), then the equation becomes

$$W_1 = D_{1,2}\,\frac{A}{L}\left(C_1 - C_0\right) \qquad (1.3)$$

Where L is the diffusion path length (cm), C_1 is the concentration of gas 1 in the exterior atmosphere ($\mu g/cm^3$) and C_0 is the concentration of gas 1 in the air space directly above the sorbent surface. If the sorbent used in the sampler acts as a perfect sink, then the concentration of C_0 tends towards zero, and by multiplying both sides of the equation by time (t) the equality can be written as

$$M_1 = D_{1,2} A \frac{C_1 t}{L} \qquad (1.4)$$

Where M_1 is the total mass of the substance taken up by the sorbent (µg) and t is the time, in seconds, for which the sampler is exposed.

The atmospheric concentration of NO_2 in the measurement period is calculated, as described in Palmes *et al.* (1976) cited by Glasius *et al.*, 1999, using Fick's first law. The diffusion coefficient is expressed as

$$D_T = D_{298}(T)^{1.75} \times (298.15)^{-1.75} \qquad (1.5)$$

Where D_T is the diffusion coefficient (cm^2s^{-1}) of NO_2 through air at T (K), D_{298} is the diffusion coefficient of NO_2 through air at 298.15 K (0.154 cm^2s^{-1}) and T is the average temperature (K) in the measuring period (Glasius *et al.*, 1999).

Sampling rate (SR) in term of DA/L is expressed in cm^3/min (the same as sample flow rate in dynamic devices). Consequently, it is often considered to be the sampling rate (SR). For a device with a defined geometry and at constant temperature (Plaisance *et al*, 2004), SR= DA/L should be constant for a given analyte. Thus, as long as the exact geometry of the sampler (A and L) is known, it should be possible to calculate C_0 based on the literature value of D. The coefficient of proportionality D (cm^2/s) is the diffusion coefficient of nitrogen dioxide in air (0.154 cm^2s^{-1}).

However, several factors make this approach impractical. The values of the molecular diffusion coefficient for a given compound often differ between literature sources, and the data on the temperature dependence of D are often incomplete. Other factors include analyte losses through sorption to various parts of the sampler, as well as collection efficiency lower than 100%. Thus, most often in practice, it is necessary to calibrate each sampler, during sampling the flux of gas through all sections of the passive gas sampler is equal, i.e., gas is not adsorbed on the walls. The total air resistance can be calculated by summing all resistances that influence diffusive transport of the gas to the sampling filter. The Teflon filter over the inlet prevents turbulent diffusion inside the sampler. Equation 1.6 is used to calculate total air resistance (Ayera *et al*, 1998).

$$\text{Total air resistance (m}^{-1}\text{)} = \left[\frac{LR}{AR} + \frac{LF}{AF} + \frac{LN}{AN} + \frac{LBL}{AR}\right] \quad (1.6)$$

$$C_o = \frac{Q}{tD}\left[\frac{LR}{AR} + \frac{LF}{AF} + \frac{LN}{AN} + \frac{LBL}{AR}\right] \quad (1.7)$$

There is a thin stagnant air layer outside the sampler through which gases are transported by laminar, instead of turbulent, diffusion. The thickness of this laminar boundary layer denoted as *LBL*. It depends on the wind speed and the turbulence of the ambient air and is about l-2 mm. The thickness of the steel net and the membrane filter are denoted *LN* and *LF* respectively. *L* is the length of the ring. The cross section areas are denoted with A and have the same indexes. Fluxes of the gas through all the sections during sampling are equal, i.e. nothing is adsorbed on the walls. In this case ambient concentration Co can be calculated by adding all concentration differences over all sections. Ferm (1991), cited by Ayera *et al* (1998) measured the laminar boundary layer thickness under the range of ambient atmospheric and suggested the mean value of the order 1.5×10^{-3} m for *LBL*.

Nitrogen dioxide in the atmosphere is captured in the sampler as nitrite (NO_2^-). The quantity of NO_2^- in the sampler is proportional to the NO_2 concentration outside the sampler, the diffusion coefficient, the dimensions of the sampler and the sampling time (Van Reeuwijk H, 1998). Concentrations are calculated from the quantity of nitrite captured in the sampler by using the following equation. 1.7

$$C = \left[\frac{Q*L}{A*t*D}\right] \tag{1.8}$$

Where

C = the ambient air NO_2 concentration (µg/m^3)

Q = quantity of NO_2^- captured in the sampler (µg)

L = length of diffusion tube (m)

A = cross-sectional area (m^2)

t = sampling time (s)

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

1.3.3 Development of passive samplers

Passive sampling was firstly developed in the US as 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 type and the badge type have become popular 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)

Influence of meteorological factors like temperature, relative humidity and wind velocity on the sampling rate of nitrogen dioxide the greatest effect is observed for the wind velocity with significant increase of sampling rate (Plasance *et al*., 2004). 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 with 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 passive diffusion tubes, as recommended by Krohmal and Kalian (1997), Plaisance *et al.* (2002).

A further problem effects badge type samplers. The disadvantage of having barrier is that since the membranes present an unknown resistance to diffusion and the increased boundary layer resistance under low wind speeds of the badge samplers may also cause underestimates of pollutants gas concentrations. Membrane or baffles used at the sampler inlet reduce turbulent transfer of the pollutant to the sorbent, allowing shorter diffusion lengths. Here, the effective areas of the pores in the membrane largely control the rate of sampling. So 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 tube type at the room temperature. They found the tube mead from Teflon show a significant increase in the 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 though 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 be storage in the freezer.

A variation in blanks was observed with the exposed tubes. Same of the caps were later made airtight by using parafilm as a sealant. The values in all these tube were than the tubes without parafilm. Tate (2002) reported that filed blank values to be higher and more variable than in the expose tube. He commented this to the contamination in the Ogawa passive sampler 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.

However, after exposure samplers are usually mailed back to the laboratory which performs analyses. Therefore, it is essential that samplers can be stored for sometime after exposure without significant losses of absorbed substances. 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 (Krochmal and Kalina, 1997).

The most commonly used absorbent sink for NO_2 is triethanolamine (TEA) where the gas is converted to nitrite ion. 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 of 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 one or two weeks can reduce this interference by SO_2 (Heal and Cape, 1997; Ferm and Svanberg, 1998), and suspected loss of NO_2 due to photo degradation of TEA in bright condition (Tang *et al*., 2001).

Potassium iodide (KI) has also been used in passive sampler 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% glycerin-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).

Ayers *et al.* (1998) used passive diffusion samplers of 10 mm length and tested under ambient condition in Australia for NO_2 and SO_2 at exposure times of one to four weeks. The passive diffusion samplers were found to provide quantitative measurement of these gases. Heal *et al*. (1999) used passive diffusion samplers of 7.1 cm length. It was found that four weeks exposure gave significantly lower NO_2 concentrations than the average of four parallel one week exposures indicating that net effective NO_2 uptake decreased with exposure time.

Glasius *et al*. (1999) used diffusion tube monitoring of NO_2 in Denmark and Italy. They found that the measurement of NO_2 with chemiluminescence and diffusive sampling showed good agreement between the methods (no significant difference). In the year 2001, Bush *et al*. (2001) reported NO_2 concentrations in UK monitored by diffusion tubes. They found that average of NO_2 concentrations calculated from diffusion tube measurements showed a 10% difference from chemiluminescence measurement data.

Since 2004 Environmental Chemistry Research Laboratory, Chemistry Department Faculty of Science, Chiang Mai University has been developed various passive samplers for monitoring of some pollutant gases in ambient air. Khaodee, (2006) developed passive samplers for determination of NO_2, SO_2 and O_3 in ambient air. The NO_2 values obtained from the passive sampler and analysed by IC and spectrophotometry, were strongly correlated with values from active analyzer. Pongsai and Detsri (2008) tested different membranes placed at the open end of diffusion tubes for monitoring of ozone in ambient air. They found that the values obtained from Teflon membrane were very closed with values from active analyzer with the difference of 9-29%. Borisuttichun (2008) constructed SO_2 test kit using passive sampling technique. Concentrations of SO_2 obtained from the SO_2-kit are agreeable to those from the fluorescence technique.

1.4 Test kit

Test kit is an equipment for measurement of color intensity by comparing colors of sample and standard solutions. The color charts are made by measuring the light absorbed by solution of varying concentration. Color comparison is respected by human eyes or a spectrophotometer. An apparatus or device used to monitor specific chemical residuals, levels, constituents. Kits usually contain reagents, vials, color comparators and other materials needed to perform tests.

(http://www.southshoregunitepools.com/resources/pool_glossary2.htm)

Ruenwongsa *et al*. (1999) and Norfun, (2003) produced and implemented the test kit for determination of iodine salt and chloride and fluoride test kit. Both kits were based on the change of color shade of solution.

1.4.1 Determining sample size for validation of standard color chart of nitrogen dioxide (Glenn D, 2008)

A) Sample size criteria

In addition to the purpose of the study and population size, three criteria usually need to be specified to determine the appropriate sample size: the level of precision, the level of confidence or risk, and the degree of variability in the attributes being measured. Each of these is reviewed below.

(i) The level of precision

The level of precision, sometimes called sampling error, is the range in which the true value of the population is estimated to be. This range is often expressed in percentage points, (e.g., ±5 percent).

(ii)The confidence level

The confidence or risk level is based on ideas encompassed under the Central Limit Theorem. The key idea encompassed in the Central Limit Theorem is that when a population is repeatedly sampled, the average value of the attribute obtained by those samples is equal to the true population value. Furthermore, the values obtained by these samples are distributed normally about the true value, with some samples having a higher value and some obtaining a lower score than the true population value. In a normal distribution, approximately 95% of the sample values are within two standard deviations of the true population value (e.g., mean).

In other words, this means that, if a 95% confidence level is selected, 95 out of 100 samples will have the true population value within the range of precision specified earlier. There is always a chance that the sample obtained does not represent the true population value.

B) Strategies for determining sample size

There are several approaches to determining the sample size. These include using a census for small populations, imitating a sample size of similar studies, using published tables, and applying formulas to calculate a sample size. Each strategy is discussed below.

(i)Using a census for small populations

One approach is to use the entire population as the sample. Although cost considerations make this impossible for large populations, a census is attractive for small populations (e.g., 200 or less). A census eliminates sampling error and provides data on all the individuals in the population. In addition, some costs such as questionnaire design and developing the sampling frame are fixed, that is, they will be the same for samples of 50 or 200. Finally, virtually the entire population would have to be sampled in small populations to achieve a desirable level of precision.

(ii) Using a sample size of a similar study

Another approach is to use the same sample size as those of studies similar to the one you plan. Without reviewing the procedures employed in these studies you may run the risk of repeating errors that were made in determining the sample size for another study. However, a review of the literature in your discipline can provide guidance about "typical" sample sizes which are used.

(iii) Using published tables

A third way to determine sample size is to rely on published tables which provide the sample size for a given set of criteria.

(iv) Using formulas to calculate a sample size

Although tables can provide a useful guide for determining the sample size, you may need to calculate the necessary sample size for a different combination of levels of precision, confidence, and variability.

1.5 Research Objectives

This study aims to optimize condition of passive sampler for determination of nitrogen dioxide in ambient air by spectrophotometry. An accuracy of the developed passive sampler will be tested by comparing the NO_2 values with those obtained from chemiluminescence technique of Pollution Control Department (PCD) air quality monitoring station. After that the optimized passive sampler will be applied for construction of the NO_2 test kit.