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. Modernization 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 (Roger, 2003).

1.2 Sulfur dioxide

Sulfur dioxide (SO_2) is a colorless gas with a pungent, irritating odor characteristic of burning sulfur. This very reactive weak acid exists as a gas at normal ambient temperatures and pressures. It can be oxidised to sulfur trioxide. SO_2 can be oxidised to form acid aerosols. SO_2 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 (Public Health Service, 1998). Small sources include residential, commercial and industrial space heating as shown in Figure 1.1 and the Table 1.1 show summary of the chemical and physical properties of sulfur dioxide.

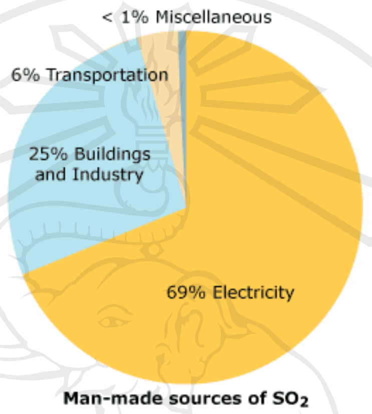

Figure 1.1 Sources of sulfur dioxide

(http://www.einstrumentsgroup.com/gas analyzers/combustion/ sulfur-compound-emissions.php)

Table 1.1 The chemical and physical properties of sulfur dioxide

Synonyms	bisulfite; sulfur oxide; sulfurous oxide; sulfurous acid anhydride; sulfurous anhydride
Molecular formula	SO_2
Structural formula	O=S=O
Molecular weight	64.06 g/mol
Air concentration units conversion	1 mg/m^3 = 0.38 ppm at 101.3 kPa
Color	Colorless in both liquid and gaseous forms.

Table 1.1 (continued)

Odor	Pungent, irritating odor, similar to burning sulfur. Odor thresholds of 0.1-5 ppm have been reported.
Melting point	-72.2°C at 101.3 kPa
Boiling point	-10.0°C at 101.3 kPa
Critical temperature	157.6°C
Vapour pressure	339 kPa at 21.1°C
Vapour density	2.26 g/l (air = 1)
Specific gravity	Liquid: 1.43 g/l at 0°C (water = 1)
Solubility in water	Very soluble in water (11.28 g/100 mL at 20°C). Rapidly converted to sulfurous acid (H_2SO_3), which is a dibasic acid with pH less than 3.
Solubility in other liquids	Acetone and other ketones, methanol, ethanol, acetic acid, diethyl ether, chloroform and sulfuric acid.
Stability	Extremely stable in heat – up to 2000°C. Complex reactions of SO_2 occur in the atmosphere.
Flammability	Does not burn.

Source: U.S. Department of Health and Human Services (Public Health Service), 1998.

1.2.1 Health and environmental effects

The major health concerns associated with exposure to high concentrations of SO_2 include effects on breathing, respiratory illness, alterations in pulmonary defenses, and aggravation of existing cardiovascular disease. Children, the elderly, and people with asthma, cardiovascular disease or chronic lung disease (such as bronchitis or emphysema), are most susceptible to adverse health effects associated with exposure to SO_2. EPA's health-based national air quality standard for SO_2 is 0.03 ppm (measured on an annual arithmetic mean concentration) and 0.14 ppm (measured over 24 hours). SO_2 is a precursor to sulfates, which are associated with acidification of lakes and streams, accelerated corrosion of buildings and monuments, reduced visibility, and adverse health effects (US Environmental Protection Agency, 2002).

1.2.2 Atmospheric reaction of 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 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 react 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 (Public Health Service, 1998).

1.3 Principles of gas and vapor separation (Lodge, 1989)

The techniques used to sampling and measure toxic gases and vapors in the field of industrial hygiene are very numerous and in principle include all the techniques of analytical chemistry. Many sampling methods for gases and vapors require that the contaminant be separated from the air sample prior to analysis. There are several physical or chemical mechanisms which can be utilized to carry this out.

1.3.1 Diffusion

Collisions between gas molecules results in random motion of the molecules in all directions. If there is a gradient in concentration of one component of a gas mixture (e.g the contaminant of interest), the random motion of all molecules will result in the net movement of the contaminant in the direction of decreasing concentration. This process is molecular diffusion, and several sampling devices take advantage of it. The concentration gradient is created using a very efficient collection surface, near which the number of contaminant molecules in the gas phase is very low compared to that in the surrounding gas.

1.3.2 Adsorption

When gases, vapors or solute substances are deposited on the surface of solid bodies in a reversible manner, this process is called adsorption. Activated charcoal and silica gel are examples of widely used adsorbents. The quantity of the substance which can be accepted by the adsorbents depends on the ambient conditions (pressure, temperature, concentration, humidity). The substances collected by this method can later be analyzed by a variety of methods.

1.3.3 Absorption

In this process a gaseous contaminant comes into contact with a solid surface or a liquid, penetrates and then dissolves in the solid or liquid phase. Two types of absorption are distinguished:

a) Physical absorption: In this process, the properties of the dissolved substance are not changed, and separation into the original components is possible by physical procedures.

b) Chemical absorption: In this process, the substance to be separated is absorbed irreversibly in a solution and then is altered by a chemical reaction with other components in the solution (conversion).

1.4 Air monitoring techniques (WHO, 2000)

Air monitoring methodologies can be divided into four main generic types, covering a wide range of costs and performance levels. These are passive samplers, active samplers, automatic analyzers and remote sensors. The main advantages and characteristics of these monitoring technologies are summarized in Table 1.2.

1.4.1 Passive samplers

Passive samplers offer a simple and cost-effective method of screening air quality in an area. A sample integrated over a defined exposure time (typically a week to a month) is collected by molecular diffusion to a pollutant-specific absorbent material. The low unit costs permit sampling at a number of points in the area of interest. This is useful in highlighting “hot-spots” of high pollutant concentrations, such as major roads or emission sources, where more detailed studies may be needed. Careful survey design and attention to laboratory-based QA/QC of the sample analysis process is necessary to make best use of this technique.

1.4.2 Active samplers

Pollutants samples are collected either by physical or chemical means for subsequent analysis in a laboratory. Typically, a known volume of air is pumped through a collector such as a filter or chemical solution for a known period of time, which is then removed for analysis. There is a long history of active sampler measurements in many parts of the world, providing valuable baseline data for trend analyses and comparison. Sampling systems (for gases), sample conditioning, weighing systems (for SPM) and laboratory procedures are key factors influencing the quality of the final data.

1.4.3 Automatic analyzers

These can provide high-resolution measurements (typically hourly averages or better) at a single point for most of the criteria pollutants (SO_2, NO_2, CO and SPM), as well as for other important species such as VOC. The sample is analysed on-line and in real-time, usually by electro-optic methods: UV or IR absorption, fluorescence or chemiluminescence are common detection principles. To ensure the data from automatic analysers are accurate and reliable, a high standard of maintenance, operational and quality assurance/control procedures is invariably required.

1.4.4 Remote sensors

These are recently developed instruments which use long-path spectroscopic techniques to make real-time concentration measurements of a range of pollutants. The data are obtained by integrating along a path between a light source and a detector. Long-path monitoring systems can have an important role to play in a number of monitoring situations, particularly in proximity to sources. A high standard of operational, calibration and data screening/management practice is essential if meaningful data are to be produced by such systems.

Table 1.2 Advantages and characteristics of these monitoring technologies

Method	**Advantages**	**Disadvantages**	**Capital Cost**
Passive samplers	• Very low cost • Very simple • No dependence on mains electricity • Can be deployed in very large numbers • Useful for screening, mapping and baseline studies	• Unproven for some pollutants • In general only provide monthly and weekly averages • Labour-intensive deployment/analysis • Slow data throughput	US$10-70 per sample
Active samplers	• Low cost • Easy to operate • Reliable operation • Performance • Historical dataset	• Provide daily averages • Labour-intensive sample collection and analysis • Laboratory analysis required	US$1000-3000 per unit
Automatic analyzers	• Proven • High performance • Hourly data • On-line information	• Complex • Expensive • High skill requirement • High recurrent costs	US$10 000-15 000 per analyzer

Table 1.2 (continued)

Method	Advantages	Disadvantages	Capital Cost
Remote sensors	• Provide path or Range resolved data • Useful near sources • Multi-component measurements	• Very complex and expensive • Difficult to support, operate, calibrate and validate • Not readily comparable with point data • Atmospheric visibility and interferences	US$70 000 - 150 000 per sensor, or more

Source: Guidelines for Air Quality, WHO, Geneva, 2000.

1.5 Passive sampling

1.5.1 Principle

Analysis of data on air pollution in the global scale, passive samplers (also called diffusive samplers) can bring 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. No pumping of air is needed and therefore passive samplers are lightweight, cheap, robust and easy in operation (Krochmal and Kalina, 1997).

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 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. 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 (Gorecki and Namiesnik, 2002).

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 zero sink, which 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 nonporous membrane. Schematic diagrams of the two types of samplers are given in Figure 1.2 and some typical physical sampler configurations are shown in Figure 1.3.

(a) **(b)**

Figure 1.2 Schematic diagram of; (a) tube-type diffusion sampler, and (b) badge- type permeation sampler (Tadeusz and Jacek, 2002)

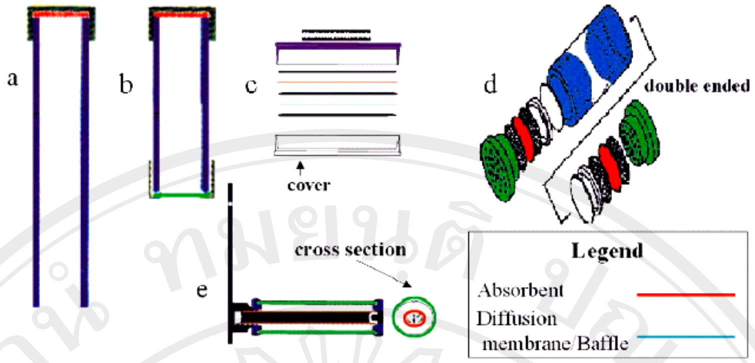

Figure 1.3 Example of different sampler configurations ; (a) opened-end diffusion tube, (b) shorter diffusion tube with diffusion membrane at opening, (c) badge-type with diffusion membrane at opening, (d) double-ended badge with baffles at opening, (e) cylindrical badge with tubular diffusion membrane (Roger, 2003).

Passive samplers are generally protected from the rain, sun, 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 (Roger, 2003).

The passive sampler has the following advantages

1. It is a cheap, lightweight, robust and simple technique, which is easy to operate and handle.
2. It does not require any power source, calibration and maintenance.

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

1.5.2 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 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 follows the equation 1.1. 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).

$$F_1 = -D_{12}\, dc_1 / dx \qquad 1.1$$

Where F_1 is the fux of gas (mol cm^{-2} s^{-1}), D_{12} is the diffusion coefficient of gas$_1$ in gas$_2$ (cm^{-2} s^{-1}), c_1 is the concentration of gas$_1$ in gas$_2$ (mol cm^{-3}) and x is the length of diffusion (cm). The quantity of gas transferred (Q_1mol) in t seconds for a cylinder of radius r is given by Equations 1.2 and 1.3.

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

Therefore

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

Where c_0 is the concentration experienced at the absorber surface, $(c_1-c_0)/L$ is the concentration gradient along the cylinder length (L), if an efficient absorber is used to remove gas_1 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 concentration. The unit of gas concentration in ambient air usually reported in $\mu g/m^3$ or ppbv.

Therefore

$$C = \frac{[Q * L]}{[A * t * D]} \qquad 1.4$$

Where

C = concentration measured by passive sampling tube (μg/m3)

Q = quantity of absorption products present in the sampler (μg)

L = diffusion length (m)

A = cross-sectional area (m^2) = πr^2

t = sampling time (s)

D = diffusion coefficient (m^2/s)

The diffusion coefficient of SO_2 in air must be corrected to average ambient temperature (K) and atmospheric pressure (Torr) during sampling period, according to equation (Fish and Durharn, 1971).

$$D = 0.004832 \ (T^{1.75} / P) \quad cm^{-2} \ s^{-1} \qquad 1.5$$

Where

D = diffusion coefficient (m^2/s)

T = temperature (K)

P = atmospheric pressure (Torr)

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

1.6 Literature Review

Diffusive sampling in the occupational environment dates back at least to the 1930 when qualitative devices were described, but the first serious attempt to apply science to quantitative diffusive sampling was in 1973 when Palmes described use of a diffusive device for measuring SO_2 predates the use for NO_2. Palmes' original SO_2 sampler was not however a Palmes tube as it later became, but a squat cylinder with a tube insert as diffusion barrier and a liquid sorbent as the collection element (Palmes and Gunnison, 1973). The sorbent was mercury (II) chloride solution. Palmes also developed similar samplers containing concentrated H_2S0_4 or silica gel for diffusive monitoring of water vapour. The colorimetric determination of SO_2 by complexing with mercury (II) chloride is commonly known as the West Gaeke procedure, and it is not surprising that West himself developed a sampler for SO_2 (and other analytes). Reiszner and West (1973) in the same year as Palmes, described a similar device using a liquid collection element, but incorporating a silicone membrane as a permeation barrier rather than an air gap as purely diffusive barrier. Since then, a wide variety of samplers have been described, some relying on diffusion through an air-gap, some, relying on permeation through a membrane, and some using both techniques, for the rate-controlling process in sampling (Jost, 1960; Tompkins *et al.*, 1977; Bamberger *et al.*, 1978). Many of these devices are commercially available.

The passive sampler was 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 type 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).

The theoretical basis for diffusive sampling is now well established. Diffusion and permeation processes can both be described in derivations of Fick's first law of diffusion, which result in expressions relating the mass uptake by the sampler to the concentration gradient, the time of exposure, and the sampler area exposed to the pollutant atmosphere (Moore, 1987). Expressions have also been derived for the application of Fick's law to diffusive sampling in the "real" world, i.e., taking into account nonsteady-state sampling, the effects of fluctuating concentrations, sorbent saturation, wind velocity and turbulence at the sampler surface, temperature, pressure, and so on (Bartley *et al.*, 1983, Pozzoli and Cottica, 1987). Except for sorbent saturation, which may lead to reduce (although sometimes predictable) uptake rates, these modifications to the basic Fick's law expression do not lead to significant errors for well-designed samplers. Such samplers may be regarded as truly integrating devices with accuracies similar to those of active samplers.

There are currently no national or international standards governing the application of sulfur dioxide diffusion tubes to ambient air monitoring. However, a number of different types of sample collection and analysis methods have been discussed in the scientific literature (WHO, 1999). The most widely used include using a diffusion tube with triethanolamine (TEA) as an absorbent, glycol as a desorbent, and spectrophotometry as the analytical method; potassium hydroxide/glycerol/ spectrophotometry; and sodium carbonate/glycerine/ion-exchange chromatography. In practice, the ion chromatographic technique has been informally accepted as the standard method for sulfur dioxide diffusion tube analysis.

Air sampling and analytical methods for sulfur dioxide that are used in practice by established agencies are reported. In general, standard air monitoring methods for sulfur dioxide are based on direct manual and automatic sampling technologies or integrated pump-and-tube and filter pack sampling approaches. Widely employed and accepted reference air monitoring methods and technologies for sulfur dioxide have been developed, tested and reported by the United States Environmental Protection

Agency (US EPA), National Institute of Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA).

The US EPA reference method for the determination of sulfur dioxide in the atmosphere is a colorimetric procedure based on a modified version of the pararosaniline method originally developed by West and Gaeke in 1956 (US EPA, 1982). This is a manual method in which a measured volume of air is bubbled through a solution of potassium tetrachloromercurate (TCM). The sulfur dioxide present in the air stream reacts with the TCM solution to form a stable dichlorosulfitomercurate complex. Once formed, this complex resists air oxidation and is stable in the presence of strong oxidants such as ozone and oxides of nitrogen. During subsequent analysis, the complex is reacted with acid-bleached pararosaniline dye and formaldehyde to form an intensely colored pararosaniline methyl sulfonic acid. The optical density of this species is determined spectrophotometrically and is directly related to the amount of sulfur dioxide collected. The total volume of air sampled, corrected to US EPA reference conditions (25°C, 760 mmHg), is determined from the measured flow rate and the sampling time. The concentration of sulfur dioxide in the ambient air is subsequently computed and expressed in micrograms per standard cubic meter ($\mu g/m^3$). The lower limit of detection of sulfur dioxide with this technique is approximately 25 $\mu g/m^3$ (0.01 parts per million (ppm) in an air sample of 30 liters (L) and 13 $\mu g/m^3$ (0.005 ppm) in an air sample of 288 L. Advantages of this technique are that it is specific for sulfur dioxide, it uses a simple and inexpensive apparatus, and it is suitable for sampling periods from 30 minutes to 24 hours. Disadvantages are that samples must be analyzed soon after collection and there are possible interferences from oxides of nitrogen and some metals. Other disadvantages include a relatively slow response time, the need for frequent periodic maintenance and the required use of wet chemical reagents.

US EPA equivalent methods used to monitor sulfur dioxide in the atmosphere must be capable of generating data comparable to data generated using the reference method. The monitoring systems designated as manual equivalent methods by the US EPA are colorimetric analyzers that use various modifications of the pararosaniline method described above. The two monitors are the technique I Automated Analysis System and the Technique II Automated Analysis System (US EPA, 2002). Both analyzers consist of an absorber column, a gas liquid separator, a mixing coil, and a flow-through colorimeter with a narrow band optical filter. The major difference between these analyzers and the reference method is that they can be operated continuously. The advantages of using these continuous colorimetric analyzers are they provide good sensitivity and specificity. In addition, data collected using these analyzers have a very good probability of correlating with data collected using the US EPA reference method because both methods are based on the same colorimetric principle. The disadvantages of using these analyzers are the relatively slow response time, the need for frequent periodic maintenance and the use of wet chemical reagents.

Development of passive sampler for determination of nitrogen dioxide, sulfur dioxide and ozone in ambient air, has been done by Khaodee (2006). In her work, standard US EPA method was chosen for the determination of SO_2 by spectrophotometry. It was found that the method provided low sensitivity with absorbance measurement from spectrophotometry.

Test kit is simple equipment. The method bases on measurement difference of color intensities of sample and standard according to Beer's law. Color comparison respected by human eyes or a spectrophotometry has to be distinguished. There was some examples of test kit which have been produced and implemented such as the test kit for determination of iodine in iodate salt (I-Kit) (Ruenwongsa *et al*., 1999). Other examples are the chloride and fluoride test kits (Norfun, 2003; Rugrai, 2003). Both kits were based on the change of color shade of the solution. After that chloride and fluoride in solutions were quantitated.

1.7 Methods for sulfur dioxide detection (Alberta Environment, 2003)

1.7.1 Ultraviolet fluorescence

This method is based on the characteristic fluorescence by the sulfur dioxide molecule when it is irradiated by ultraviolet light (Okabe *et al*., 1973). This fluorescent light is also in the ultraviolet (UV) region of the spectrum but at a different wavelength than the incident radiation. By monitoring the fluorescent wavelengths between 190 and 230 nm, there is very little quenching of the fluorescence by other components in the air. The light is detected with a photomultiplier tube producing a voltage proportional to the light intensity that is translated to concentrations by means of calibration factors. Either a continuous mechanically chopped or electronically pulsed UV light source is used. Instruments employing electronically pulsed UV light sources may cost more initially, but the pulsed UV light source lifetime is longer. Both water vapor and oxygen strongly quench the sulfur dioxide fluorescence at specific wavelengths. Water vapor may be removed with a permeation drier, although interference can be avoided by properly selecting the light sources and the optical filter. The effect of oxygen quenching is minimized by maintaining identical oxygen levels in calibration and sample gases. Polycyclic aromatic hydrocarbons exhibit strong fluorescence in the same spectral region as sulfur dioxide and may be removed by ambient or elevated temperature scrubbers. However, some aromatic scrubbers randomly allow breakthrough (Smith and Buckman, 1981). Advantages of the UV fluorescence analyzers for sulfur dioxide are high accuracy and low detection limits (usually 2 to 5 $\mu g/m^3$; 1 to 2 parts per billion (ppb).

1.7.2 Flame photometric detection

Flame photometric detection (FPD) is highly specific for sulfur compounds and is used to measure airborne sulfur dioxide. In FPD analyzers, the discrete light emission is measured from excited sulfur molecules after passing through a reducing-hydrogen flame. The emitted light is optically filtered to detect the specific 394 nm sulfur band with a photomultiplier tube. Typically, continuous FPD based sulfur dioxide analyzers have detection limits of 5 $\mu g/m^3$ (2 ppb), a lag time of 3 seconds, and a 10-second response time. Advantages of FPD systems include low maintenance, high sensitivity, very fast response and good selectivity for sulfur compounds (PACE, 1985). A disadvantage of the FPD systems includes the need for a compressed hydrogen source or hydrogen generator. In addition, although the FPD is insensitive to most non-sulfur species, it will detect sulfur compounds other than sulfur dioxide. Since the concentration of H_2S, mercaptans, and other organic sulfur compounds in typical urban air is less than 10 % of sulfur dioxide levels the potential interference is minimal. Particulate filters remove aerosol sulfates and other particulate matter to eliminate clogging and light scattering. Selective filters are available to reduce interference from other sulfur compounds (e.g. an H_2S filter for commercial instruments).

1.7.3 Gas chromatography with flame photometric detection

Gas chromatographs with flame photometric detectors (GC-FPD) are available commercially. An optimized chromatographic column is used to separate various sulfur compounds (i.e., COS, H_2S, CS_2, sulfur dioxide and RSH). The separated compounds are subsequently detected and quantified with the FPD. Typical detection limits for these systems are about 2 to 3 µg/m3 (1 ppb). Since compounds are separated by chromatography, measurements exhibit greater specificity and less bias due to interfering compounds than simple FPD systems. However, hydrocarbons may bias the results due to quenching effects if the hydrocarbon has the same retention time and is present at high concentrations (PACE, 1985). Major disadvantages of GCFPD systems are the need for compressed hydrogen gas, the need for highly trained technicians and the lack of continuous results since samples require up to 6 minutes to process.

1.7.4 Colourimetry

Colorimetric analyzers are based upon the reaction of sulfur dioxide with solutions of organic dyes to form colored species. Optical absorbance of the colored complex in solution, measured spectrophotometrically, is linearly proportional to the concentration of the colored species according to Beer's Law. Several examples of colorimetric methods for determining sulfur dioxide are described below. The pararosaniline method developed by West and Gaeke (1956) has been automated for monitoring sulfur dioxide in ambient air. Not only has this automated method been used by the US EPA, as mentioned earlier, but its use has also been suggested by a number of other agencies (e.g. Canadian Environmental Protection Service report no. EPS-1-AP-72-4 and ASTM "Standard Test Method for Sulfur Dioxide Content of the Atmosphere" method no. D2914-01) (ARPEL, 1998). In this method, sulfur dioxide is absorbed by aspirating a measured volume of air through a tetrachloromercurate (TCM) solution, resulting in the formation of a complex. EDTA is added to remove heavy metal interferences. Pararosaniline, formaldehyde and the sulfur dioxide complex react to form an intensely colored pararosaniline methyl sulfonic acid that is analyzed spectrophotometrically. The signal is translated to the sulfur dioxide concentration in the air sample by means of calibration data. Automation of the West-Gaeke method is rarely practical for continuous monitoring since some solutions require daily preparation. Typical features of some commercially available instruments are detection limits of approximately 13 μg/m^3 sulfur dioxide (5 ppb), lag time of 2 minutes and response time of 3 minutes. Advantages of these instruments include simplicity, high sensitivity and, with proper control, good specificity. Interferences by nitrogen oxides may be controlled by using a sulfamic acid reagent. Heavy metals may be complexed with EDTA in the scrubbing solution or with phosphoric acid in the dye solution. Ozone interference may be controlled by the use of a delay coil downstream of the absorber to allow time for ozone to decay, but this results in longer lag and response times. Major disadvantages of these instruments are the need for reagent and pump tubing replacement and frequent recalibration. Iodometric colorimetric analyzers employ regenerative chemical cartridges and detection by spectrophotometry. A sodium iodide solution passes through a reference cell to a set of electrodes generating iodine by electrolysis. The amount of iodine is reduced by reaction with sulfur dioxide in the sample stream and the reduction is measured spectrophotometrically. The iodine is regenerated to iodide in solution by a regenerative cartridge. The most sensitive operating range for this instrument is 5 to 500 μg/m^3 (2 to 200 ppb). Oxidizing gases interfere to give low results; reducing agents interfere to give high results. Interference from high concentrations of nitrogen oxides or ozone can be removed by introducing hydrogen into the air sample and passing the mixture over a platinum catalyst at 100°C.

1.7.5 Infrared Absorption

Fourier transform-infrared analyzers (FT-IR) with path lengths of 1 km or more have been designed to monitor a wide range of pollutants in ambient air including sulfur dioxide, CO, NO, NO_2 and O_3. This method is based on absorption of incident electro-magnetic radiation at characteristic infrared wavelengths by sulfur dioxide across long distances. By monitoring the magnitude of infrared light absorption by sulfur dioxide over the path length, sulfur dioxide can be detected at low ppb levels. Computerized Fourier transformations of the absorption signals are used to separate the sulfur dioxide signals from instrumental noise by superimposing repetitive infrared scans until an absorption peak is resolved. A Michelson interferometer modulates the absorption frequency range so it can be measured. The application of infrared absorption to the monitoring of sulfur dioxide in ambient air has not yet gained wide acceptance as a routine monitoring method.

1.7.6 Coulometry

Coulometric analyzers are based on the reaction of sulfur dioxide with a halogen, formed directly by electrolysis of a halide solution. Typically, an inner chamber (into which air samples are introduced) is contiguous with an outer chamber. Both contain solutions of potassium bromide and bromine in dilute sulfuric acid. The potential difference between the chambers, relative to a reference potential, is measured by the reference electrodes. As absorbed sulfur dioxide reduces the bromine in the inner chamber, the amplifier produces a current to restore the bromine until the potential difference returns to zero. The current needed to replace the depleted halogen is proportional to the amount of sulfur dioxide absorbed in solution, and hence to the sulfur dioxide concentrations. maintenance (reagent consumption is negligible since halides are regenerated and evaporated water is replaced by condensation from air or from a reservoir), and simplicity of operation. The major disadvantage of using this technique is the necessity of using selective filters to eliminate interfering species. Interfering species are those that oxidize halides, reduce halogens, or complex with either. They consist primarily of sulfur compounds (i.e., H_2S, mercaptans, and organic sulfides, disulfides) with sensitivities comparable to that of sulfur dioxide. Other, less important interferences are O_3, NO_x, chlorine, ethylene, aldehydes, benzene, chloroform, other nitrogen or halogen-containing compounds, and other hydrocarbons. Interferences can be minimized by selective filters such as heated silver gauze filters to remove H_2S, O_3, NO_x, chlorine, carbon disulphide, ethylene, aldehydes, benzene, and chloroform, but will not remove mercaptans.

1.8 Ultraviolet and Visible Spectroscopy

The ultraviolet region of the spectrum is generally considered to range from 200 to 400 nm and the visible region from 400 to 800 nm. The corresponding energies for these regions are about 150 to 72 and 72 to 36 kcal mol^{-1}, respectively. Molecular absorption spectroscopy is based on the measurement of the transmittance (T) or the absorbance (A) of solution contained in transparent cells having a path length of b cm. It is difficult, if not impossible, to measure actual absorbance of light. Instead, we measure transmittance or the fraction of light that is able to pass through a solution of molecules. A spectrophotometer measures the intensity of light entering a sample and compares this to the intensity of light emerging from the sample. The quantitatively was described the absorption as follows the equation 1.6 and 1.7. The Figure 1.4 shows transmittance of light in a spectrophotometer.

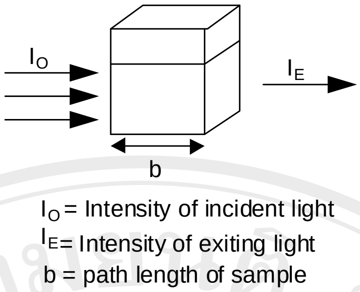

Figure 1.4 Transmittance of light in a spectrophotometer

$$\text{Transmittance} = I_0/I_E \qquad 1.6$$

$$\text{Absorbance} = -\log T = -\log I_0/I_E \qquad 1.7$$

When no light is absorbed, $I_E = I_O$, T = 1.00 and A = 0. When 90% of the light is absorbed, T = 0.1 and A = 1. Beer then showed that absorbance was linearly related to concentration. These two men are given credit for the Lambert-Beer Law.

$$A = abc \qquad 1.8$$

Where is a constant which takes into account the specific properties of the molecules which are absorbing photons, b is sample path length, usually given in centimeter units, and c is concentration of solution. Note that Absorbance is unit less, so the units of the constant a must be the inverse of the units of path length and concentration. For example, if b is in centimeter units and c is in mg/mL units, then a must be in $ml*mg^{-1}*ml^{-1}$ units. When b has $M^{-1}*cm^{-1}$ units, we call it the molar absorption coefficient (formerly called the extinction coefficient) and designate it as ε. This means the concentration of the solution must be expressed in molarity units. Also, some chemists will use l instead of b to denote path length. In these cases, equation 1.9.

$$A = \varepsilon lc \qquad 1.9$$

A spectrophotometer can be either single beam or double beam. In a single beam instrument, all of the light passes through the sample cell. I_o must be measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference, the other beam passes through the sample. Some double-beam instruments have two detectors, and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam.

The basic parts of a spectrophotometer are a light source (often a tungsten lamp for the visible wavelengths, or a deuterium lamp in the ultraviolet), a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light,and a detector. The detector is typically a photodiode. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. The Figure 1.5 show diagram of spectrophoto meter (single beam) and the Figure 1.6 show diagram of spectrophotometer (double beam).

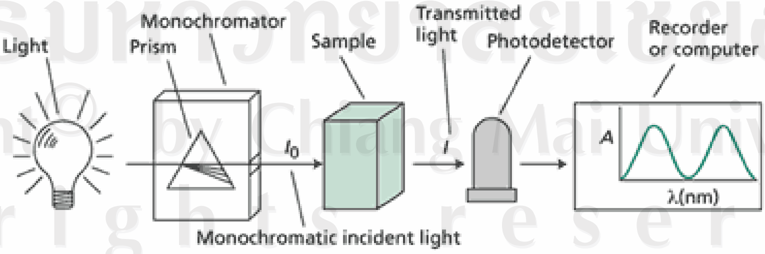

Figure 1.5 Diagram of spectrophotometer (single beam)

(http://4e.plantphys.net/article.php?ch=2&id=66)

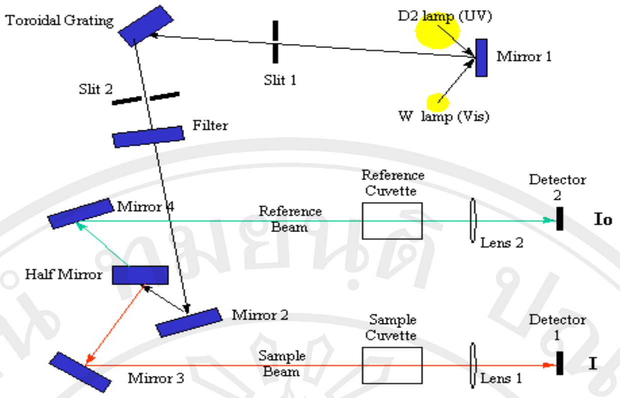

Figure 1.6 Diagram of spectrophotometer (double beam)

(http://bouman.chem.georgetown.edu/S02/lect10/lect10.htm)

1.9 Luminescence spectroscopy

Luminescence is the emission of light by a substance. It occurs when an electron returns to the electronic ground state from an excited state and loses it's excess energy as a photon. Luminescence spectroscopy is a collective name given to three related spectroscopic techniques.

- Molecular fluorescence spectroscopy
- Molecular phosphorescence spectroscopy
- Chemiluminescence spectroscopy

1.9.1 Molecular fluorescence spectroscopy

Fluorescence is a type of electromagnetic spectroscopy which analyzes fluorescence from a sample. It involves using a beam of light, usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light of a lower energy, typically, but not necessarily, visible light. A complementary technique is absorption spectroscopy.

Molecules have various states referred to as energy levels. Fluorescence spectroscopy is primarily concerned with electronic states and vibrational states. Generally, the species being examined will have a ground electronic state (a low energy state) of interest, and an excited electronic state of higher energy. Each of these electronic states has various vibrational states. Photons of light are small of energy, each with an energy proportional to its frequency; photons of high frequency light have higher energy than those of low frequency light. These can be absorbed by molecules, with the molecule gaining the energy of the photon, or emitted by molecules, with the photon carrying some of the energy of the molecule away. Typically, the different frequencies of fluorescent light emitted by a sample, when the excited light is held at a constant wavelength are measured. This is called an emission spectrum. An excitation spectrum is measured by recording the sum of the fluorescent light emitted at all frequencies as function of the frequency of the monochromatic incident light. The Figure 1.7 show schematic of a fluorometer**.**

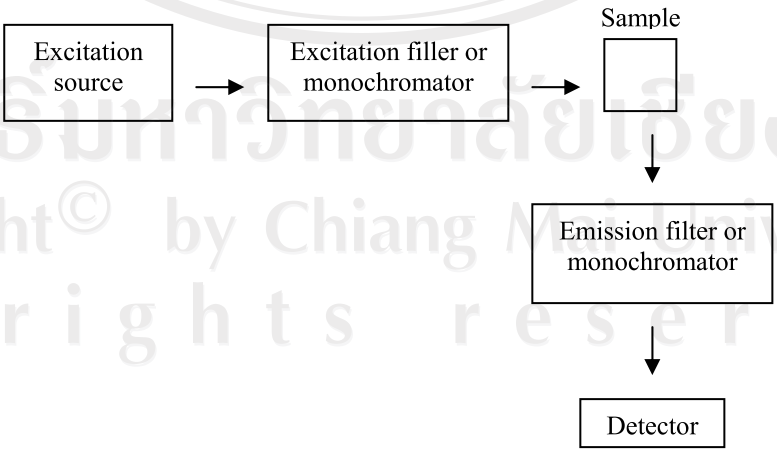

Figure 1.7 Schematic of a fluorometer with 90° geometry

(http://www.chemistry.adelaide.edu.au/external/soc-rel/content/images/fluo-sch.png)

The light from an excitation source passes through a filter or monochromator, and passes through the sample. Here some of it probably is absorbed, making some of the molecules in the sample fluoresce. A part of the fluorescent light is then focused on a filter or monochromator, which often is placed at a 90° angle to the excitation light. The light is then detected by a detection device. Various light sources may be used as excitation sources, including lasers, photodiodes, and lamps; xenon arcs and mercury vapor lamps in particular. Filters or monochromators may be used in fluorimeters. A monochromator transmits light of an adjustable wavelength with an adjustable tolerance. The monochromator can then select which wavelengths to transmit. Another form of monitor using the principle of fluorescence has been developed, and this provides a satisfactory alternative to the FPD sulfur analysers. Fluorescence is a process where by light energy of a given wavelength is absorbed and then reemitted at a different wavelength, i.e.

$$AB + h\nu \rightarrow AB^* \rightarrow AB + h\nu' \qquad 1.10$$

The change in wavelength occurs because the molecule that is excited remains in that state for some finite period of time. This is sufficient for some of the energy to be dissipated in the form of vibration or rotation within the molecule. This results in the emission of light of a lower energy, and hence a longer wavelength.

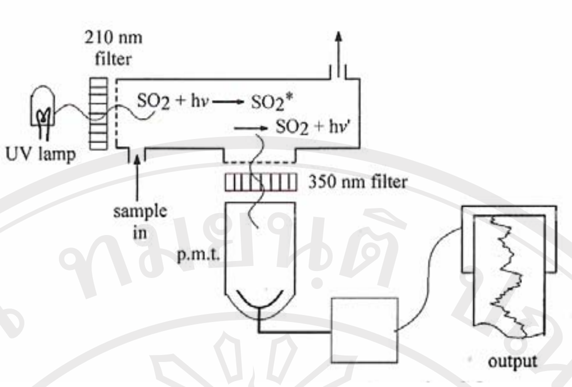

Figure 1.8 Fluorescence analyser for SO_2

This phenomenon has been utilised in the development of a monitor for SO_2. As shown in Figure 1.8 a UV lamp provides a source of radiation, either continuous or pulsed, which is filtered to admit a narrow band of light into the cell, centred at about 210 nm. The fluorescent radiation is measured at right angles to the incident beam, using a photomultiplier. Unlike the FPD analyser, the fluorescence system is specific for SO_2. Sample air must be dry and free of dust to avoid fouling of the cell. There is also the potential for interference from fluorescent organic compounds that may be present in the air, but these can also be removed with an appropriate pre-filter.

1.9.2. Chemiluminescence

Chemiluminescence occurs when a chemical reaction produces an electronically excited species which emits a photon in order to reach the ground state. The number of chemical reactions which produce chemiluminescence is small. However, some of the compounds which do react to produce this phenomenon are environmentally significant. Chemiluminescence is defined as the emission of ultraviolet, visible, or near-infrared radiation through the chemical excitation of a reacting species. In most cases of chemiluminescence, a chemical reaction results in an excited product that emits radiation upon relaxation to its ground electronic state. In general form, chemiluminescence reactions can be expressed as follows equation 1.11 and 1.12.

$$A + B \rightarrow C^* + D \qquad 1.11$$

$$C^* \rightarrow C + h\nu \qquad 1.12$$

Gas phase chemilumininescent reactions have been observed for over a century since Salet first observed the blue emission from sulfur compounds burned in a hydrogen flame. In the past twenty-five years, chemiluminescence has been extensively used in analytical instrumentation. Two very desirable features of detectors for the emitted light are high sensitivity and high selectivity toward a particular class of compounds.

Instrumental monitoring methods a wide range of instrumental methods have been reported for the monitoring of air pollutants. Chemiluminescence is the emission of light energy that results from some chemical reactions.The reaction between NO and O_3 is an example as follows equation 1.13 and 1.14.

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad 1.13$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad 1.14$$

These reactions produce a continuum of radiation in the range 500 to 3000 nm. The reaction between O_3 and ethylene is also chemiluminescent, with an emission in the region of 435 nm. Both of these phenomena have been used to produce continuous monitors for NO_x and O_3, respectively.

A typical layout of a chemiluminescence analyser for NO_x is shown in Figure 1.9 Ozone is generated by the UV irradiation of clean air and mixed in a reaction chamber with the sample air. Light from the reaction passes through an optical filter and is detected with a photomultiplier tube.

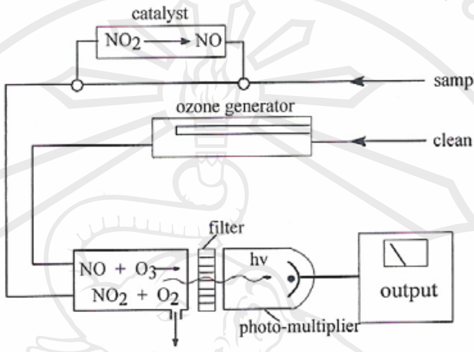

Figure 1.9 Chemilunminenscence detector for NO_x

Clearly, NO_2 in the sample will not be detected in this system. However, this can be reduced to NO by means of a heated catalyst, such as a stainless steel or molybdenum. If this is included in the system the instrument can respond to NO and NO_2, i.e. NO_x. In commercial analysers the converter is either incorporated as shown in Figure 1.10 with automatic valves to switch continuously between operation with and without the catalyst, or two separate channels with individual reaction chambers and detectors are used.

1.10 Research Objectives

This research work is aimed to modify a method for determination of SO_2 in air by passive sampler and construct a SO_2 test kit based on color differentiation.