CHAPTER 1

INTRODUCTION

1.1 Introduction to Formaldehyde and Passive Sampling

Volatile Organic Compounds (VOCs) have become major indoor air pollutants. Formaldehyde is one of the most serious pollutants among VOCs over the world, especially in newly decorated rooms. It comes from building materials, decorated materials, cigarette smoke, etc. Formaldehyde harms people's health seriously (Jones, 1999). It is pungent to the mucosa of the eye, nose and respiratory tract and acts as a lachrymator to cause sneezing and coughing even at a very low concentration. National Institute for Occupational Safety and Health (NIOSH) has announced that formaldehyde has the possibility of inducing cancers in human being.

Formaldehyde (gas) is reasonably anticipated to be a human carcinogen based on limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals (IARC 1982, 1987, 1995).

Formaldehyde is commonly found in pressed-wood products such as particle board, interior-grade plywood, and fiber board. It is also a major ingredient in urea-formaldehyde foam insulation, adhesives, dyes, inks and medicines and embalming fluids. Formaldehyde can be released into indoor air and, over time, may accumulate to problem levels causing mild to severe health disorders in sensitive individuals. Symptoms of formaldehyde exposure include: irritation of the eyes, nose, and throat; excessive thirst; headache; sneezing; shortness of breath; excessive phlegm and dermatitis. On December 4, 1987, the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) issued a comprehensive regulation covering

occupational exposure to formaldehyde at 29 CFR 1910.1048(see appendix). This rule reduced the permissible exposure limits (PELs) to 0.75 part formaldehyde per million parts of air as an 8-hour time-weighted average (TWA), and established a 2 ppm 15-minutes short term exposure limit (STEL) (Sexton *et al*., 1986).

A sensitive, simple, and cost-effective passive sampling methodology was developed to quantify indoor exposure to gaseous VOCs. Then, the passive sampling techniques fulfil many of the requirements listed above. They usually combine sampling, analyte isolation and preconcentration into a single step. Barring some exceptions described later, most passive sampling techniques require little or no solvent. In the context of this issue, it should be pointed out that passive methods usually simplify sample pretreatment and are very easy to implement. However, as passive sampling is usually carried out to determine time-weighted average (TWA) concentrations, its ‘‘response speed’’ is normally determined by the duration of the period for which TWA is being determined. This article presents a review of passive sampling techniques, including the principles and selected applications. The following two sections are based in large part on review papers summarizing the basic knowledge about passive sampling with the balance being mostly our own findings and ideas, so references to individual original papers are given only when necessary.

The first deployment of a 300 station passive monitoring network to determine relative atmospheric ozone (O_3) concentrations (Fox, 1873), during some past two decades, there has been an increasing interest to improve and use passive samplers to collect a number of gaseous air pollutants (Namiesnik *et al*., 1984; Cao and Hewitt, 1991).

Currently, passive samplers are being used to determine the air quality in: (1) the work place; (2) the indoor living environment; and (3) the ambient, outdoor environment including regional-scale air quality. Here, the emphasis of this review is on the outdoor, ambient environment and ecological responses. In this context, on a limited basis, passive samplers have also been evaluated for use in measuring the so called pollutant `gradients' and pollutant flux densities above and/or within vegetation canopies (Adema *et al*., 1993; Dammgen *et al*., 1996).

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. However, several conditions must be met for this approach to work. First, the receiving medium must act as a so-called ‘‘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, but it can be problematic when physical adsorption is responsible for analyte collection. In this case, only the linear portion of the adsorption isotherm should be utilized throughout the entire sampling process. Typically, this is accomplished by using high-capacity sorbents at low mass loadings (far from thermodynamic equilibrium). However, since adsorption is a competitive process, the linear range of the adsorption isotherm can be easily exceeded whenever other molecules are trapped in large amounts alongside the analyte molecules. A typical example is sorption of water by hydrophilic adsorbents. Accurate conversion of the amount of analyte trapped into its TWA concentration becomes impossible in such cases (Gorecki and Namiesnik, 2002).

The sorbent used to collect specific chemicals of ambient air will be specific in sampling method. A wide variety of synthetic absorbent can be used such as 1% sodium bisulfite solution coated on glass fiber or cellulose filter paper 2,4-dinitrophenylhydrazine(DNPH)-coatedsilicagel, 2- (hydroxymethyl)piperidine (2-HMP) coated on the surface of XAD-2.

The validation test or calibration of the sampler can be tested in 2 techniques which are in exposure chamber and compare with the active sampling by control the condition according to test such as temperature, wind velocity, relative humidity and concentration of gas.

For desorption, whether thermal desorption or solvent desorption is used is mainly that depend on the choice of adsorbent material, the sampler design and the analytical method. The main advantages of thermal desorption over solvent desorption are high sensitivity and high desorption efficiency. However, solvent desorption is a simple method and also can be desorbed at the same time that suitable for paper adsorbent material.

The most of analytical procedures for determination aldehyde was High Performance Liquid Chromatography (HPLC) with UV detection (Potter and Karst, 1996), thermally desorbed and determined by a packed column gas chromatograph equipped with a flame ionization detector (FID) (Kinyanta *et al* 1991) and spectrophotometry after reaction with chromotropic acid (Balmat and Meadows, 1985).

In this study, experimental work aiming to optimize and adapt the method of the diffusion tube sampler for determination of formaldehyde in air using the 3M 3721 Formaldehyde Monitor. The thread seal tape is placed at the open end of the polypropylene (PP) tube in order to avoid wind speed effect. The method consists of formaldehyde exposure chamber, passive samplers and analysis by chromotropic acid method with spectrophotometer.

1.2 Formaldehyde Information

1.2.1 Physical and chemical properties

The chemical formula of formaldehyde is HCHO and chemical structure is shown in Figure 1.1. Its molecular weight is 30 g/mol. Boiling point is -19 °C. Density is 0.8153 at -20°C; 1.067 (air = 1.000). Vapor pressure is 400 mm Hg at -33°C.

Figure 1.1 Chemical structure of Formaldehyde
(http://en.wikipedia.org/wiki/Formaldehyde)

Formaldehyde is a flammable, colorless gas with a pungent, suffocating odor. It is highly soluble in water (up to 55%), acetone, benzene, chloroform, diethyl ether, and ethanol. The gas is stable in the absence of water, but it is incompatible with oxidizers, alkalis, acids, phenols, and urea. Explosive reactions occur with peroxide, nitrogen oxide, and performic acid. Anhydrous gaseous formaldehyde is not available commercially. Most formaldehyde is sold as aqueous solutions, known as formalin, containing 30% to 50% formaldehyde with 0.5% to 15% methanol as a polymerization inhibitor. Polymerization may also be inhibited by the addition of up to 100 mg/kg of stabilizers such as cellulose ethers (IARC 1982, 1995, ATSDR 1999). Its synonyms including polymeric forms from which formaldehyde can be generated are formalin, formic aldehyde, methaldehyde, methanal, methyl aldehyde, methylene glycol, methylene oxide, oxomethane, oxymethylene, paraform, paraformaldehyde, polyoxymethylene glycols, a-polyoxymethylene, a-trioxane, ß-trioxymethylene, tetraoxymethylene, a-polyoxymethylene and trioxane.

1.2.2 Source exposure

Formaldehyde is produced by the catalytic vapor phase oxidation of methanol with air. Most formaldehyde is marketed in an aqueous solution, called formalin, which contains 37 to 50% formaldehyde by weight. About half of the formaldehyde

produced in the U.S. is used to manufacture synthetic resins. These resins are often used to produce pressed wood products (hardwood plywood wall paneling, particle board, and fiber board) and Urea-formaldehyde foam insulation (UFFI). Urea-formaldehyde resins are used to coat materials, to produce paper products and to make foams for insulation. Other important uses include textile treating and molding of plastic materials. Formaldehyde is used for and furniture made with these pressed wood products. Combustion sources and environmental tobacco smoke. Durable press drapes, other textiles, and glues. In some medicines and also in embalming fluids. It is used in fur and leather tanning and also in the photographic industry (http://www.healthgoods.com/Education/Healthy_Home_Information/Indoor_Air_Quality/indoor_pollutant_formaldehyde.htm)

1.2.3 Levels in homes

Average concentrations in older homes without UFFI are generally well below 0.1 (ppm). In homes with significant amounts of new pressed wood products, levels can be greater than 0.3 ppm. Formaldehyde can be reduced by 1) use “exterior-grade" pressed wood products (lower-emitting because they contain phenol resins, not urea resins), 2) use air conditioning and dehumidifiers to maintain moderate temperature and reduce humidity levels and 3) increase ventilation, particularly after bringing new sources of formaldehyde into the home (IARC 1982, 1995, HSDB 2001).

1.2.4 Health effects

Because formaldehyde resins are used in many construction materials, including plywood, carpet, and spray-on insulating foams, and because these resins slowly give off formaldehyde over time, formaldehyde is one of the more common

indoor air pollutants. At concentrations above 0.1 mg/kg in air, inhaled formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes, headache, a burning sensation in the throat, and difficulty breathing. Large formaldehyde exposures, for example from drinking formaldehyde solutions, are potentially lethal. Formaldehyde is converted to formic acid in the body, leading to a rise in blood acidity, rapid, shallow breathing, hypothermia, and coma or death. People who have ingested formaldehyde require immediate medical attention (http://www.epa.gov/iaq/formalde.html).

In the body, formaldehyde can cause proteins to irreversibly bind to DNA. Laboratory animals exposed to large doses of inhaled formaldehyde over their lifetimes have developed more cancers of the nose and throat than are usual, as have workers in particle-board sawmills. However, some studies suggest that smaller concentrations of formaldehyde like those encountered in most buildings have no carcinogenic effects (IARC, 1973).

Symptoms of human exposure to formaldehyde include irritation of the eyes, the nose and the throat which lead to lachrymation, sneezing, shortness of breath, sleeplessness, tight chest, nausea and excess phlegm. Formaldehyde has been shown to cause dermatitis. Formaldehyde is an allergen and susceptible persons can become sensitized to the agent. Formaldehyde has been reported to cause menstrual disorders and secondary sterility in women. Formaldehyde is mutagenic in a variety of test systems. IARC reports that there is sufficient evidence that formaldehyde gas is carcinogenic to rats. IARC also reports that epidemiological studies provide inadequate evidence to assess the carcinogenicity of formaldehyde to man (IARC,

1982). Formaldehyde can react with hydrogen chloride to form bis-chloromethyl ether (BCME). Exposure to BCME may constitute a serious human lung cancer hazard (IARC, 1973).

1.2.5 Usage

Formaldehyde kills most bacteria, and so a solution of formaldehyde in water is commonly used as a disinfectant. It is also used to preserve biological specimens, and as a preservative in vaccinations. In medicine, formaldehyde solutions are applied topically to dry the skin, such as in the treatment of warts. Formaldehyde based solutions are used in embalming to disinfect and temporarily preserve human remains pending final disposition. Formaldehyde preserves or "fixes" tissue or cells by irreversibly connecting a primary amine group in protein with a nearby nitrogen in protein or DNA through a -CH2- linkage called a "Schiff's base

(http://www.urbandictionary.com/define.php?term=cross-link).

The primary uses for formaldehyde are for the production of ureaformaldehyde resins (23%), phenolic resins (19%), acetylenic chemicals (12%), polyacetal resins (11%), methylene diisocyanate (6%), pentaerythritol (5%), urea-formaldehyde concentrates (4%), hexamethylenetetramine (4%), melamine resins (4%), and miscellaneous products (chelating agents, trimethylolpropane, pyridine chemicals, nitroparaffin derivatives, textile treatings, and trimethylolethane) (12%). Urea-formaldehyde resins and phenolformaldehyde resins are used primarily as adhesives in the manufacture of particle board, fiberboard, and plywood, and for molding, paper treating and coating, textile treating, surface coating, and foams for insulation. The percentage of total formaldehyde production used in urea-formaldehyde resins and

phenol-formaldehyde resins have ranged between 20% and 26% each since the early 1960s (IARC 1982, 1995; IARC; ATSDR 1999).

1.2.6 Regulations

The regulations of concerning formaldehyde concentration were announced by many organizations. The last revised was in 1996 (OSHA 1996). Details are provided as follow:

a) Consumer Product Safety Commission (CPSC)

Formaldehyde and products containing 1% or more of formaldehyde are considered "strong sensitizers" and must contain a warning label.

b) Department of Transportation (DOT)

Formaldehyde is considered a hazardous material and special requirements have been set for marking, labeling, and transporting this material.

c) Environment Protection Agency (EPA)

Clean Air Act

Mobile Source Air Toxics: Listed as a Mobile Source Air Toxic for which regulations are to be developed.

d) The National Emissions Standards for Hazardous Air Pollutants (NESHAPS):

Listed as a Hazardous Air Pollutant (HAP)

e) New Source Performance Standards (NSPS): Manufacture of formaldehyde is subject to certain provisions for the control of VOC emissions.

Prevention of Accidental Release: Threshold Quantity (TQ) = 15,000 lb.

Urban Air Toxics Strategy: Identified as one of 33 HAPs that present the greatest threat to public health in urban areas.

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable Quantity (RQ) = 100 lb.

Emergency Planning and Community Right-To-Know Act

Toxics Release Inventory: Listed substance subject to reporting requirements

Reportable Quantity (RQ) = 100 lb.

Threshold Planning Quantity (TPQ) = 500 lb.

Resource Conservation and Recovery Act

Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on formaldehyde (not specifically gas) - U122, K009, K010, K038, K040, K156, K157

Listed as a Hazardous Constituent of Waste (not specifically formaldehyde gas).

f) The Occupational Safety and Health Administration (OSHA)

Permissible Exposure Limit (PEL) = 0.75 ppm.

Short-Term Exposure Limit = 2 ppm.

"Comprehensive Standards" for occupational exposure to formaldehyde have been developed.

1.2.7 Guidelines

Air quality guidelines have been published by WHO in 1987 and they were revised in 1997. Given the wealth of new studies on the health effects of air pollution that have been published in the scientific literature since the completion of the second edition of the Air quality Guidelines for Europe, including important new research from low-and middle income countries where air pollution levels are at their highest (WHO 2007).

American Conference of Industrial Hygienists (ACGIH)

Threshold Limit Value - Ceiling (TLV-C) = 0.3 ppm.

The National Institute for Occupational Safety and Health (NIOSH)

Recommended Exposure Limit (REL) = 0.016 ppm.

Immediately Dangerous to Life and Health (IDLH) = 20 ppm.

Ceiling Recommended Exposure Limit = 0.1 ppm (15 minute exposure)

Listed as a potential occupational carcinogen.

1.2.8 Workplace indoor monitoring

The primary OSHA exposure limits are known as the Permissible Exposure Limits (PELs) which are usually 8 hour time weighted average (TWA) values that are not to be exceeded for the work day. In addition, for some substances, OSHA has also established Short Term Exposure Limits (STELs) and Ceiling Limits (CL) that should not be exceeded at any time during a workday. OSHA has established their minimum requirements as follows:

a) Short Term Exposure Evaluation

A short term exposure limit (STEL) is usually defined as a 15 minute TWA exposure which should not be exceeded at anytime during the workday. When a compound has an assigned STEL, short term monitoring should be done for activities/areas that have the greatest potential for exposure. STEL monitoring is supplemental to eight hour TWA monitoring. Air samples must be taken in the employee's breathing zone.

b) Eight-hour exposure evaluation

Eight hour exposure evaluation (an 8 hr TWA) is done for the purpose of determining average employee exposure during a full shift. This is best done by taking consecutive full shift samples over a period of several days. Air samples must be taken in the employee's breathing zone.

c) Long Term Monitoring

Long term monitoring is used to monitor full shift exposures (typically 8 hours) and may employ either active or passive sampling systems. Equipment that can be used for long term sampling includes mechanical sampling systems (battery operated pumps), long term direct reading detector tubes (passive and active), passive dosimeters/badges (direct reading or analysis required). This equipment can be used for both personal and area monitoring (29 CFR Part 1910.1000).

1.3 Sampling and Analysis of formaldehydes

1.3.1 Passive Sampling

In the first instance the passive sampler was developed in America as an on-person air sampler by Palmes 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 of 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 (http://www.urbandictionary.com/ define.php?term=cross-link**).**

a) Fick's First Low of Diffusion

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.

The unidirectional flow of a gas1 through a gas2 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_1 is the rate of mass transfer of gas 1, $D_{1,2}$ 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 (ug) and t is the time, in seconds, for which the sampler is exposed. By rearrangement of Eq. (2.3), it is possible to determine the diffusion coefficient of a pollutant ***(D1,2*** if the mass of analyte collected **(M_1),** dimensions of the sampler ***(A/L),*** the exposure time (t) and the vapour phase concentration of the analyte **(C_1)** are all known.

$$D_{1,2} = \frac{M_1 L}{C_1 A t} \qquad (1.5)$$

The determination of diffusion coefficients are often considered to be unreliable, these can be calculated using several methods (Lewis, 1960; Gilliland, 1934; Wilke, *et al* (1955). In this work we use the estimation suggested by Wilke *et al* (1955).as described in equation.

$$D = \frac{0.00837 \times T^{3/2} \times \sqrt{\frac{M_1 + M_2}{M_1 \times M_2}}}{P \times (V_1^{1/3} + V_2^{1/3})^2 \times \left(1 + \frac{C}{T}\right) \times 1000} \qquad (1.6)$$

$$C = \left(\frac{2\sqrt{V_1^{1/3} \times V_2^{1/3}}}{V_1^{1/3} + V_2^{1/3}}\right)^3 * \sqrt{C_1 \times C_2} \qquad (1.7)$$

where *D*) diffusion coefficient ($m^2 s^{-1}$), *T*) absolute temperature (K), *M*1) molecular weight of air 28.96 g mol^{-1} (*8*), *M*2) molecular weight of formaldehyde 30.026 g mol^{-1},V_1)molar volume of air at boiling point 33.082 cm^3 mol^{-1} (*8*), V_2) molar volume of formaldehyde at boiling point 36.842 cm^3 mol^{-1} (*22*), *P*) total pressure (atm), and *C*) Sutherland constant, calculated from the expression the constants *C*1 and *C*2 can be obtained from the absolute boiling temperatures: *C*1) 1.47 x Tb_1, *C*2) 1.47 x Tb_2 for air Tb_1) 78.67 K (*8*), for formaldehyde Tb_2) 253.95 K (*13*).

The diffusion coefficient of formaldehyde in air, calculated with eq. 6 was **1.6 x 10^{-5}** $m^2 s^{-1}$ at a temperature of 298 K (Gillettr, *et a.,* 2000).

b) Diffusion uptake rate (Sampling rate, SR)

The term 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,

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 formaldehyde in air. Its value (0.16 cm^2 /s) is reported in literature (Kring *et al* 1982).

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.

Whose work, 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 eq. 1.8 is used to calculate total air resistance

$$\text{Total air resistance } (m^{-1})) = \frac{LR}{AR} + \frac{LF}{AF} + \frac{LN}{AN} + \frac{LBL}{AR} \qquad \textbf{(1.8)}$$

$$C_o = \frac{Q}{tD} \left(\frac{LR}{AR} + \frac{LF}{AF} + \frac{LN}{AN} + \frac{LBL}{AR} \right) \qquad \textbf{(1.9)}$$

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,

A, is the total area of all pores in the filter. If only membrane is used the member ***LN/AN*** from eq. (2.9) must to be dropped out. For the boundary layer theory is that the boundary layer thickness is **5 x 10^{-3}** m indoors (Gillettr, *et al.* 2000).

c) Application of passive sampler data in vegetation response assessment

Table 1 provides some examples of the use of passive samplers in studies relevant to ecological response assessment. With the exception of two studies (Nosal, 1984; Runeckles and Bowen, 1999), all others have used the passive sampler data to primarily examine the spatial and temporal variability in pollutant concentrations and derive ordinal estimates of flux or possible geographic locations at ecological risk. In some cases the geographic distribution of visible foliar injury to vegetation has been used to corroborate the latter conclusion (Brace and Peterson, 1998). Nevertheless, there has been very little progress made in developing satisfactory numerical relationships of cause and effect, particularly through the use of multipoint (growth characteristics) models.

Table 1.1 Application of passive samplers in air pollution-vegetation effects related studies.

Air pollutant	Study location	Reference
1. Ammonia	1.Giesegaard, Denmark	Schjoerring (1995)
	2.Sumava Mountains, Czech Republic	Adema *et al*. (1993)
2. Nitrogen dioxide, sulfur ioxide	Rural areas of Poland	Krochmal and Kalina (1997)
3. Nitrogen dioxide, ozone	Alpine Valley, Chamonix, France	Marcoux *et al*. (1998)
4. Nitrogen dioxide, ozone and sulfur dioxide	Drayton Valley, Alberta, Canada	Peake (1998)
5. Ozone	1. Carpathian Mountains, Europe	Bytnerowicz *et al.* (1998)

	2. Western Washington, USA	Brace and Peterson (1998)
	3. New Hampshire, Vermont, USA	Manning *et al*. (1996)
	4. National Parks, USA	Ray (1996)
	5. Frazer Valley,British Columbia, Canada	Runeckles and Bowen (1999)
	6. Krakow region, Poland	Godzik (1997)
	7. Carpathian Mountains, Kiev region, Ukrain	Blum *et al*. (1997)
6. Sulfur dioxide	8. New Brunswick, Canada	Cox (1997)
	Whitecourt, Alberta, Canada	Nosal (1984); Legge *et al*. (1988)

d) Comparative advantages and limitations of passive samplers versus active (continuous) monitors

Table 1.2 provides a summary of the comparative characteristics of passive samplers and active monitors for quantifying ambient air pollutants. In general, passive samplers are relatively simple, portable and, as previously stated, inexpensive to deploy in the field. They do not require electrical power to operate. All these features make passive samplers very attractive for use in regional scale relative air quality measurements. However, the sampler preparation must be done under great care (e.g. use of pure absorbents and clean air preparation facilities). Since the pollutant in question is either collected by chemical absorption or by physical adsorption, subsequent laboratory

analysis is required to quantify the air constituent. Most passive samplers allow the measurement of integrated total or average pollutant concentrations over a sampling duration of several hours, one to several days or even weeks. Depending on the frequency of collection of such samples, laboratory analysis costs can be high. Nevertheless, in most cases the total cost here will still be lower compared to the initial costs for purchasing, installing temperature controlled shelters and operating a continuous monitor. However, two problems associated with the use of passive samplers must be clearly addressed a priori: (1) interferences of the absorbent by the chemical constituents in the atmosphere, other than the pollutant of interest, e.g. several passive samplers used for measuring ambient ozone concentrations either over or underestimate the values in comparison to the continuous monitor (Zhou and Smith, 1997); and (2) can be subject to wind turbulence effects. At low face velocities the sampler absorbent can become starved and, thus, not satisfactorily collect the actual air concentration of the pollutant (Koutrakis *et al*., 1993).

Table 1.2 Comparative characteristics of passive samplers and active (continuous) monitors for quantifying ambient air pollutant concentrations

Feature	Passive Sample	Active Sampler
1. Usage history	Since late 1800s	Mostly since the 1950s
2. Complexity of field deployment	Low (+)	High (-)
3. Construction/deployment cost	Low (+)	High (-)
4. Field labor requirement	Low (+)	High (-)
5. Field maintenance costs)	Low (+)	High (-)
6. Laboratory analysis costs	Moderate to high (-)	None to moderate (+/-)

7. Time resolution of pollutant levels	Low (-)	High (+)
8. Electricity requirement for field deployment	None (+)	Needed (-)
9. Measurement specificity (other pollutants) Interference	possible (+/-)	Interference none (+)
10. Meteorology	high (-)	Low (+)
11. Minimum detection limit (in fine-time resolution)	Relatively high (-)	Relatively low (+)
12.Integrated measurement value inter-comparison Differs from	active (-)	- (+)
13. Regional (spatial) scale usage cost	Low (+)	High (-)
14. Relevance to vegetation effects relationships	Low (-)	High (+)
15. Detection of short-term (e.g. 1 or 2 h) episodes and regulatory noncompliance, where appropriate	Low (-)	High (+)

Source: Krupa (1998); (+), advantage; (-), disadvantage

In contrast, under high face velocities, some samplers are known to be subjected to interferences from other pollutants, as in the case of NO_2 (Heal and Cape, 1997). To avoid these problems, many commercially available passive samplers use protective,

miniature shelters coupled with diffusion barriers in front of the absorption surface (Monn and Hangartner, 1990; Zhou and Smith, 1997).

The disadvantage of having barrier is that since the membrane presents 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 absorbent, 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*. (1990) tested the contamination of unexposed tubes-type at room temperature. They found that the tube made from Teflon showed 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 eliminated by storage in the freezer.

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*., 2004).To overcome the problem of wind sensitivity and of low

resolution retention time, passive samplers characterized by a large ratio of cross-sectional area to length of diffusion path have been developed (De Santis *et al*., 2001).

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. (Krochmal and Kalina, 1997)

1.3.2 Formaldehyde passive samplers

The most widely used measurement method for formaldehyde and other lower carbonyls is based on pumped sampling through acidified 2,4- dinitrophenylhydrazine (DNPH)-coated silica gel cartridges, where they are converted to stable hydrazones (Potter and Karst 1996). The latter are then extracted with acetonitrile and analysed by High Performance Liquid Chromatography (HPLC) with UV detection.

Monitoring at DuPont is performed by sampling with impingers containing 1% aqueous sodium bisulfite or with silica gel tubes. The collected formaldehyde is measured spectrophotometrically after reaction with chromotropic acid (Balmat and Meadows, 1985). A method utilizing diffusive sampling of formaldehyde in air has been developed. A glass fiber filter, impregnated with DNPH and phosphoric acid and mounted into a modified aerosol-sampling cassette, was used for sampling by controlled diffusion. The formaldehyde hydrazone formed is desorbed and determined by HPLC with UV detection (Livin *et al*., 1986). The passive sampler consists of a

modified dual filter holder in which the upper stage serves as the diffusion barrier, the lower stage includes a DNPH-coated filter and DNPH-coated C_{18} cartridges which collects formaldehyde used a Teflon filter as the diffusion barrier to improve the detection limit (Grosjean and Williams ,1992).

A tube-type passive sampling method has been developed and assessed for the quantification of formaldehyde vapours in indoor air. The procedure involves collection of formaldehyde vapours in a Palmes diffusion tube containing a paper support impregnated with an acidified solution of DNPH. After sampling, quantification of the trapped Formaldehyde-DNPH is achieved by HPLC analysis with UV detection at 350 nm. To validate the procedure, permeation devices were used to generate formaldehyde-containing atmospheres, 81-2975 ppb, in a 20 dm^3 chamber so that experimentally derived sampling rates could be calculated and compared with the theoretical value (Gibson and Brokerhof, 2001). The formaldehyde is collected on silica gel particles coated with 1-methyl-1-(2,4-dinitrophenyl)hydrazine (MDNPH) and phosphoric acid. The formaldehyde hydrazone (HCHO-MDNPH) and the N-methyl-2,4-dinitroaniline (MDNA) formed are extracted with acetonitrile and determined by HPLC with UV detection at 365 nm (Bertoni. *et al*, 2005).

A formaldehyde exposure chamber was developed by Geisling. *et al* (1982). Validation studies were conducted by exposing the sampling devices for 1 week to dry formaldehyde gas generated by passing trioxane vapor over an acid catalyst bed. In these tests, formaldehyde concentrations ranged from 0.05 to 0.80 ml/m^3. Reproducibility was excellent, with relative standard deviations averaging 5.4% for five constant concentrations.

1.3.3 Analysis method

Several methods can be used for either indirect or direct determination of the concentration of this gas in the atmosphere, such as spectrophotometric, colometric and chromatographic. The most of analytical procedures for determination formaldehyde was analyzed by spectrophotometry after reaction with chromotropic acid (Balmat and Meadows, 1985). Thermally desorbed and determined by a packed column gas chromatograph equipped with a flame ionization detector (FID) (Kinyanta et al 1991) and High Performance Liquid Chromatography (HPLC) with UV detection (Potter and Karst 1996).

1.3.4 Type of sorbent

Bisulfite solution was used to absorbed formaldehyde gas by treated on glass-fiber filter and analyzed by the chromotropic acid (CTA) method by Geisling *et al*. (1982). A glass fiber filter, impregnated with DNPH and phosphoric acid and mounted into a modified aerosol-sampling cassette, was used for sampling by controlled diffusion. The formaldehyde hydrazone formed is desorbed and determined by HPLC with UV detection (Livin *et al*., 1986). Formaldehyde permeates the membrane and reacts with 2-(hydroxymethyl)piperidine (2-HMP) coated on the surface of XAD-2 (Manufacturers name for a class of polymeric resin beads used to isolate HOCs from water) . The passive sampler consists of a modified dual filter holder in which the upper stage serves as the diffusion barrier, the lower stage includes a DNPH-coated filter and DNPH-coated C_{18} cartridges which collects formaldehyde used a Teflon filter as the diffusion barrier to improve the detection limit (Grosjean and Williams ,1992).The formaldehyde is collected on silica gel particles coated with 1-methyl-1-(2,4-dinitrophenyl)hydrazine (MDNPH) and phosphoric acid. The formaldehyde

hydrazone (HCHO-MDNPH) and the N-methyl-2,4-dinitroaniline (MDNA) formed are extracted with acetonitrile and determined by HPLC with UV detection at 365 nm (Bertoni. *et al*, 2005).

1.3.5 Calibration system for passive samplers

In 1982 Geisling was constructed the formaldehyde exposure chamber for validation the passive sampler by exposing the sampling devices for 1 week to dry formaldehyde gas generated by passing trioxane vapor over an acid catalyst bed. In these tests, formaldehyde concentrations ranged from 0.05 to 0.80 ml/m^3. Reproducibility was excellent, with relative standard deviations averaging 5.4% for five. Elbert *et al*. (1982) constructed the dynamic contaminant generation system consists of three parts: a vapor generation chamber, a mixing manifold and a badge exposure chamber. It was developed by Du Pont and manifold for laboratory validation of the Pro-Tek C-60 Formaldehyde badge. The generation system was constructed entirely of two inert substances, glass and Teflon FEP-fluorocarbon resin tubing. The concentration of formaldehyde in air was generated using a standard diffusion tube containing solid paraformaldehyde kept at 70 °C. Dry air was passed over the diffusion tube and later diluted and mixed with humidified air in the mixing manifold. The final contaminant – mixing was monitored for humidity with hygrometer.

Formaldehyde generated with a Freeland manifold was developed by Freeland (1977) and analysis with chromotropic acid method used for calibration badge type sampler (Balmat and Meadows, 1985). Formaldehyde test were generated by injection of aqueous solution of formalin and using a syringe pump into a steam of prepurified nitrogen heated 150 °C. The formaldehyde-laden steam was mixed with charcoal-

filtered air whose temperature, humidity, volume and flow rate were maintained with a Miller-Nelson (Dillon, 1994). Pure air for both the concentrated vapor stream and dilution air branches was generated by a Whatman Zero Air Generator using house compressed air. It was still necessary to install leak-tight indicating Drierite and charcoal canisters after the generator to indicate when the purified air was sufficiently dry and free of organic vapor for use (Shih and Shane, 1999).

In this work, Formaldehyde gas was generated using a formaldehyde solution. The air was passed into the formaldehyde tube and later diluted and mixed with humidified air in the mixing chamber referred from (Thammakhet *et al*, 2006) Toluene standard gas was generated from its liquid form using the diffusion cell which was connected to a glass chamber where the analyte was diluted by incoming air from an air pump.

1.4 Spectrophotometer for formaldehyde determination

The instrument used in ultraviolet-visible spectroscopy is called a UV/vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the *transmittance*, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log(\%T) \qquad (1.10)$$

The basic parts of a spectrophotometer are a light source (often an incandescent bulb for the visible wavelengths, or a deuterium arc 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 or a CCD. Photodiodes

are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

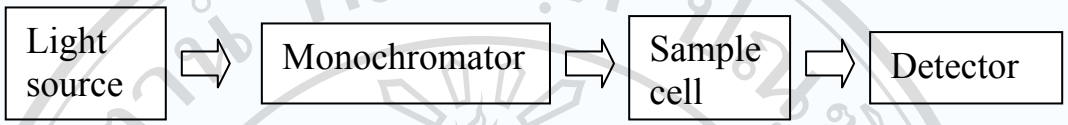

Diagram of spectrophotometer.

A spectrophotometer can be either *single beam* or *double beam*. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.

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 (photodiodes), 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.

Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a **cuvette**. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, *L*, in the Beer-Lambert law.) Test tubes can also be used as cuvettes in some

instruments. The best cuvettes are made of high quality quartz, although glass or plastic cuvettes are common. (Glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths.)

Ultraviolet-visible spectrum

An ultraviolet-visible spectrum is essentially a graph of light absorbance versus wavelength in a range of ultraviolet or visible regions. Such a spectrum can often be produced by a more sophisticated spectrophotometer. Wavelength is often represented by the symbol λ. Similarly, for a given substance, a standard graph of extinction coefficient ε vs. wavelength λ may be made or used if one is already available. Such a standard graph would be effectively "concentration-corrected" and thus independent of concentration. For the given substance, the wavelength at which maximum absorption in the spectrum occurs is called $\boldsymbol{\lambda_{max}}$.

Woodward-Fieser rules are a set of empirical observations which can be used to predict λ_{max}, the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones (http://en.wikipedia.org/wiki/Ultraviolet-Visible_spectroscopy)

1.5 Research objectives

1.5.1 To develop the passive samplers for determination of indoor formaldehyde.

1.5.2 To construct an exposure chamber for validation of the developed passive samplers.

1.5.3 To analyses formaldehyde indoors by developed passive samplers and spectrophotometry.