Measurement of Diffusion and Partition Coefficients of VOCs in Dry Building Materials

Zhong-Hong Zhang

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Abstract

Measurement of Diffusion and Partition Coefficients of Volatile Organic Compound in Dry Building Material

Zhong-hong Zhang

Building materials, as a source of contaminant, such as volatile organic compounds (VOCs), and a sink of those pollutants, can significantly affect indoor air quality (IAQ). Physical models have been developed to predict volatile organic compound emissions from building materials. These results are helpful in adopting strategies to control the pollutant source. Therefore, experimental methods have been established for measuring input parameters to these models, such as diffusion coefficient (*D*), partition coefficients (*K*). However, currently available data of diffusion and partition coefficients are limited. Moreover, the effects caused by the physicochemical properties of VOC are not completely observed. Hence, it is requisite that a comprehensive investigation on the relationship between diffusion and partition coefficients, and the physicochemical properties of VOC be conducted.

The twin chamber method was chosen in this research. The effects caused by physicochemical properties of VOC, such as molecular weight, vapor pressure, boiling point, and polarity, were investigated. Diffusion and partition coefficients of a single compound for gypsum board, ceiling tile, and carpet with SBR backing were determined; diffusion coefficients of toluene and isopropanol in a mixture, which consists of methanol, isopropanol, and toluene, for ceiling tile were measured.

The experimental results verified that the polarity of VOC is one crucial factor of which can affect *D* and *K*. The relationship of *D* and molecular weight found by Bodalal et al. cannot be verified by the presented study. Three reasons can be used to explain this phenomenon. Firstly, the results obtained by Bodalal et al. are probably not reliable because of the inter-dependence. Secondly, the effect of collision diameter of VOCs should be considered. Finally, the effect of the polarity on *D* was considered in the presented study. Moreover, the results from this presented study show that *K* increases with the increase of vapor pressure and *K* was significantly affected by polarity. The trend of *K* with vapor pressure is opposite to the conclusion drawn by Bodalal et al. The difference resulted from the polarity. In addition, the ratio of D_a/D_s were introduce into the results analysis. The ratios of D_a/D_s increase with the increase of polarity, which suggests that *D* obtained by Tiffonnet et al may be overestimation for polar compounds. The results showed that mixture affected the diffusive process since *D* obtained from a mixture test is smaller than that of a single compound test.

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Table of Contents

List of Figures

List of Tables

List of symbols

A	area of the sample (m^2)
C_0	air concentration into chamber(mg/m^3)
C_{ad}	VOC adsorbed phase concentration (mg/m^3)
C_{gas}	VOC gas phase concentration (mg/m^3)
C_m	VOC concentration in the material phase (mg/m^3)
C_1	VOC concentrations in the lower chamber (mg/m^3)
C_2	VOC concentration in the upper chamber (mg/m^3)
$C_{i=1}$	gas concentration at a distance h from the surface (mg/m^3)
$\overline{C}$	average concentration of air in two chambers (mg/m^3).
D_m	VOC material phase diffusion coefficient (m^2/s),
D_{gas}	VOC gas phase diffusion coefficient within the material (m^2/s)
$D°$	mean diffusion coefficient in the pores of the material(m^2/s) ,
E	emission rate of VOC produced by the diffusion cell (mg/s),
h	utilized grid distance inside the material (m)
k_a	adsorption rate constant (m/s)
k_d	desorption rate constant (s^{-1})
k_g	mass transfer coefficient between bulk air and air close to the surface (m/s),
K_m	VOC material phase/gas phase partition coefficient(mgm^{-3}/mgm^{-3})

K	VOC adsorbed /gas phase partition coefficient (mgm^{-3}/mgm^{-3}).
k	total amount of the diffusing substance
J	mass flow across the material($mg/m^2/s$)
L	thickness of the sample(m)
$\dot{m}$	mass flow rate through the material (mg/s)
M_t	total mass of a VOC that has entered or left the sample in time t (mg)
M_∞	corresponding mass at equilibrium(mg)
M	adsorbed VOC mass per unit area on the sink (mg VOC/m^2 of material)
$\dot{m}_{iC}$	mass flow into the primary chamber(mg/s)
$\dot{m}_{iA}$	mass flow out of the primary chambers(mg/s)
$\dot{m}_{iB}$	mass flow out of the secondary chambers(mg/s)
m_{ad}	VOC mass absorbed by testing material (kg)
m_{in}	VOC mass into upper chamber (kg)
m_{out}	VOC mass in air of both chambers (kg)
Δt_i	measurement interval(s)
t	time (s)
$\dot{V}$	airflow rate through the system(m^3/s)
V	volume of the sample material (m^3)
Δx	material thickness(m)
y	coordinate in which diffusion takes place (m)

ε	porosity of the material (m^3/m^3)
ρ	pore-phase gas density (mg/m^3)
τ	tortuosity factor of the porous network(dimensionless)

Chapter 1 Introduction

1.1 Indoor Air Quality (IAQ)

Beginning in the 1970's and instigated by the gas crunch, overall energy conservation captured global attention. North American national energy policies including governmental incentive programs initiated reducing building energy consumption. Energy saving measures to improve efficiency can include increasing insulation R factors and reducing infiltration through the building envelope. These actions improved energy conservation, however were in competition with natural ventilation and in some cases led to Sick Building Syndrome (SBS). The use of synthetic construction materials and furnishings can result in off gassing and further decrease indoor air quality.

Indoor air pollution can be two to five times higher than that of the outdoors (*EPA, 1991*) and people spend more than 90% of their life indoors (*Godish, 2001*). This can lead to a decreasing quality of living and health risks. Statistics Canada showed that 25% of the population has had an allergy or chemical sensitivity, while 10% of the adults and 20% of the children had asthma (*ITS, 1996*).

Indoor air pollution concentrations in a typical building generally do not exceed occupational limits, such as the Permissible Exposure Limits (PELs) set by OSHA and Threshold Limit Values (TLVs) set by American Conference of Government Industrial Hygienists (ACGIH) (*Reiser et al., 2002*). However, low concentrations of indoor contaminants do not mean that the risks to population health are low. Long-term multiple exposure to low concentrations could be more detrimental to the health than short term exposure to individual higher concentrations (*Holmberg, 1977*). Additive effects of indoor air chemistry also lead to detrimental effects on indoor occupants.

Although several strategies exist to avoid the health risks associated with Tight Building Syndrome (TBS), techniques to improve IAQ are limited. One method is to increase the volume flow rate of fresh air. Increasing the fresh air supply to a building increases the dilution of indoor air pollution. Another method is to control the source that emits pollutants, such as Volatile Organic Compounds (VOC). Increasing ventilation rates typically leads to higher operating costs, which places importance on controlling the source of indoor pollutants.

1.2 Indoor Air Contaminants and Building Materials

There are many different contaminants in indoor air that can adversely affect human health. The U.S. Environmental Protection Agency (EPA) divided the indoor pollutants into the following ten categories: biological contaminants, carbon dioxide, carbon monoxide, dust, secondhand smoke, lead, nitrogen oxide, pesticides, radon, and other volatile organic compounds (VOCs) (*EPA*).

Since hundreds of volatile organic compounds (VOCs) were detected indoors and their effects on indoor air quality were found, VOCs as dominant contaminants weakening indoor air quality is not doubtful (*Popa, 2002*).

In a recent study, 96% of VOCs found in a large office building resulted from construction and furnish materials. Also, due to large areas and long time/permanent exposure of building materials to indoor air, they play a major role in determining indoor air quality.

1.2.1 Volatile Organic Compounds (VOCs)

The World Health Organization defines the properties of VOCs according to the boiling point range between 50°C and 260°C, and the vapor pressure larger than 10^{-2} kPa (*WHO, 1989*). This translates into a molecular weight from 50 to 300.

Concentrations of volatile organic compounds are higher indoors than outdoors (*Salthammer et al., 1999*), and their effects on human health are diverse. Some pollutants cause acute effects, such as irritation, headache, asthma exacerbation, and chronic effects, such as cancer, organs damage, and central nervous system damage (*Maroni et al., 1995*). Some have low odour thresholds, so they easily provoke occupants' attention (*Knudsen, 1998*). Moreover, although in most cases, concentrations of indoor contaminants are at low levels, the prevalence of reported complaints from building occupants and a large number of pollutants present indoors suggest that VOCs are important pollutants in the indoor environment.

1.2.2 Building Materials as VOCs Sources and Sinks

VOCs emissions are classified into two types: the primary emissions and the secondary emissions (*Wolkoff, 1999*). The former means the VOCs emitted from materials are not bond or free and decay relatively fast. The latter means that VOCs given off are originally chemically or physically bound. They may take the entire life of building materials to be released (*Wolkoff and Nielsen, 1996*). Therefore, building materials have long-term/permanent effects on indoor air quality, especially those materials that have large surfaces and high absorption capacities, such as carpets, wallpapers, plywood, and etc.

Since once installed, building materials interact with VOCs through sorption and desorption processes, they act as sources of and sinks for VOCs. That is, building materials not only generate VOCs, but also absorb VOCs when the concentrations of other indoor sources are higher than those within materials. Accordingly, building materials play as buffers since they reduce the peak concentration of room air initially. However, the subsequent re-emission of adsorbed VOC within materials prolongs the presence of VOCs indoors (*Meininghaus et al., 2000*).

Building materials are classified into the following four categories according to their contaminant emission (*Spengler et al., 2001*):

1. Adhesives, sealants, and architectural coatings that generate benzene, ethylbenzene, formaldehyde, hexane, styrene, tetrachloroethylene, toluene, xylene, and etc.

2. Particleboard and plywood that emit benzene, formaldehyde, styrene, toluene, and etc.

3. Carpet, resilient flooring, and wallcovering that release acetaldehyde, ethylbenzene, formaldehyde, styrene, toluene, xylene, and etc.

4. Insulation, acoustical ceiling tile, and furnishings that produce Benzene, chloroform, ethylbenzene, formaldehyde, hexane, methylene chloride, toluene, trichloroethylene, xylene, and etc.

Most building materials emitting or off gassing VOCs are found from the above. Pollutants generated by the above building materials can cause acute and/or chronic effects on inhabitants or are suspected to cause acute or chronic effects (*Black, et al., 2002*). Increasing fresh airflow rate and adding filter can dilute or reduce concentrations of indoor contaminants, but the expenditures are costly. Therefore, source control, manufacturing low emission rate materials, and meeting minimum ventilation requirements are economic and logical strategies to enhance indoor air quality.

1.3 Diffusion and Partition Coefficients

Building materials, as one of the main sources emitting VOCs, should be pre-screened before they are installed in order to improve indoor air quality. Hence, it is very important to predict the VOCs emission rates of building materials that will be installed in buildings. The predictions are helpful to obtain information on indoor air quality control, such as selecting lower emission rates materials and supplying more information for designing HVAC systems.

Physical emission models are applied to predict emission rates of building materials. To obtain a successful model prediction, the availability and correctness of the model input parameters, such as diffusion coefficients, partition coefficients, and initial concentrations, are requisite. Diffusion and partition coefficients are two crucial parameters that determine the accuracy of an emission model for dry building materials. However, currently available data of diffusion and partition coefficients for building materials are limited; therefore, study of diffusion and partition coefficients for building materials is required. They are important parameters for researchers to predict emission rates for building materials. Prediction results give instructions on ranking building materials, selecting the low VOC emission materials, and encouraging manufacturers to improve product quality. On the other hand, engineers can set up appropriate ventilation system to efficiently remove VOC.

1.4 Objectives

The objectives of the proposed study are as follows:

- To develop an experimental set-up for determination of diffusion and partition coefficients.
- To study the effects of physicochemical properties of VOC and building materials on diffusion and/or partition coefficients.
- To investigate diffusion processes of a single compound within a material and VOC mixture within the material.

1.5 Thesis Outline

Chapter 2 reviews the physical emission models and literature related to measurements for diffusion and/or partition coefficients. Emphasis is focused on techniques of measuring diffusion and /or partition coefficients. Moreover, the merits and drawbacks of measuring methods are summarized. Chapter 3 describes an experimental set-up used to determine diffusion and partition coefficients, experimental plan and experimental procedures. Data analysis methods are presented in Chapter 4. Experimental results are outlined and discussed in this chapter. Chapter 5 draws conclusions of this study and provides recommendations for future work.

Chapter 2 Literature Review

2.1 Introduction

The awareness of the problems associated with indoor air quality is growing. This phenomenon strongly motivates people to take actions to improve indoor air quality. As mentioned in Chapter 1, there are two main ways, which can be used to provide better indoor air quality. One is to increase the air change rate, which can be realized by mechanical ventilation systems; the other is to control the source, that is, select materials with low VOC emission. Obviously, the first method is expensive. Therefore, controlling the source is a smart choice for improving indoor air quality. Predicting emission rates of materials is important for choosing materials of low VOC emission and known diffusion coefficients of specific contaminants also may give instructions to users and designers.

This chapter first reviews the models used to predict the building material VOC emission rates and the critical parameters used in these models. The importance of the model parameters has promoted the development of experimental methods to measure those parameters. The advantages and disadvantages of measuring methods of the model parameters are reviewed as well. The primary achievements and the limitations of the measurement methods are highlighted and analyzed.

2.2 Brief Review of Building Material VOC Emission Models

Two approaches are employed to describe the VOC mass transfer within dry building materials (*Huang, 2003*). The first one assumes that the material is a homogenous medium. Under this assumption, VOC existing within the material is called a material phase (*Little et al., 1994 and 1996*; *Cox et al., 2000*). The second treats the material as porous materials; VOC existing within the material are assumed as in a gas phase and an adsorbed phase (*Tiffonnet, 2000*; *Lee et al., 2002 and 2003*). Based on the assumptions, the physical emission models for dry materials can be classified as one-phase models and multi-phase models (*Huang, 2003*).

2.2.1 One-Phase Models

One-phase models are based on the assumption that the building material is homogeneous. In one-phase models, the VOC within the material is called the material phase in order to distinguish it from the gas phase. Little et al. (*1994*), Yang et al. (*1998 and 2001*), and Huang & Haghighat (*2002 and 2003*) used the one-phase models to predict VOC emission from dry building materials. Fick's second law is applied to describe the transient VOC diffusion within materials (Equation 2-1).

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial y^2} \qquad (2\text{-}1)$$

where:

C_m is the VOC concentration in the material phase (mg/m^3);

D_m is the VOC material phase diffusion coefficient (m^2/s);

y is the coordinate in which diffusion takes place (m);

t is the time (s).

Since VOC concentration levels in indoor air are much lower than their saturated levels, the Henry isotherm, which is a linear isotherm model, is generally adopted in the modelling of source and sink behaviour of building materials (*Axley, 1991*). In one-phase models, VOC concentration in material phase is assumed always proportional to VOC concentration in the gas phase. The partition coefficient (K_m) is used to describe the correlation. (Equation 2-2)

$$C_m = K_m C_{gas} \tag{2-2}$$

C_m is the VOC material phase concentration at the material surface (mg/m^3);

C_{gas} is the VOC gas phase concentration in the near material surface air (mg/m^3);

K_m is the VOC material phase/gas phase partition coefficient (mgm^{-3}/mgm^{-3}).

2.2.2 Multi-Phase Models

In multi-phase models, the VOC existing within the material is in a gas phase and adsorbed phase. The VOC mass transfer within the material is mainly controlled by gas phase diffusion process in the multi-phase models. Murakami et al. (*2000*), and Lee et al. (*2003*) apply the multi-phase models to predict VOC emission rate of

VOC from building materials. Fick's second law can be used to describe the transient VOC gas phase diffusion within the material (Equation 2-3).

$$\varepsilon \frac{\partial C_{gas}}{\partial t} = D_{gas} \frac{\partial^2 C_{gas}}{\partial y^2} - \frac{\partial C_{ad}}{\partial t}$$

(2-3)

where:

C_{gas} is the VOC gas phase concentration in the material (mg/m^3);

C_{ad} is the VOC adsorbed phase concentration in the material (mg/m^3);

D_{gas} is the VOC gas phase diffusion coefficient within the material (m^2/s);

ε is the porosity of the material (m^3/m^3).

At atmospheric pressure and low indoor VOC concentration, the linear adsorption isotherm is applied to describe the relationship between the gas phase concentration and the adsorbed phase concentration (Equation 2-4)

$$C_{ad} = KC_{gas}$$

(2-4)

where:

C_{gas} is the VOC gas phase concentration in the material (mg/m^3);

C_{ad} is the VOC adsorbed phase concentration in the material (mg/m^3);

K is VOC adsorbed /gas phase partition coefficient (mgm^{-3}/mgm^{-3}).

2.2.3 Effects of Diffusion and Partition Coefficients on Emission

Emission rates of VOC from dry materials are primarily controlled by a diffusion process within the materials. In order to employ a diffusion based model for predicting the emission rates of VOCs, it is requisite to obtain crucial parameters, such as the diffusion coefficient (*D*) and partition coefficient (*K*). A diffusion coefficient is "a kinetic coefficient specific to a given material and compound that describes the relationship between molecular flux and molecular concentration change" (*ASTM, F 1769-97*). It controls the rate of diffusion process. The definition of a partition coefficient in a one phase emission model "is used to describe the relationship between the concentration in the gas phase and the concentration in the solid phase" (*Bodalal et al., 1999*).

Diffusion and partition coefficients are two key model parameters. They can affect the accuracy of prediction of emission rates for building materials installed in buildings. Little et al. (1994) pointed out: that emission rates at the early time were proportional to the increasing of diffusion coefficients when partition coefficient and initial concentration are constants; at a constant initial concentration and diffusion coefficient, the emission rates decreases when the partition coefficient increases. Therefore, the availability and accuracy of the two input parameters have great impacts on the successful emission rates prediction. The two parameters provide a useful guide for improving material design and manufacturing procedures to reduce the emission of VOCs.

2.3 Techniques for Measuring Diffusion and/ or Partition Coefficients

Typically, techniques used to determine the VOC diffusion coefficient and/or partition coefficients are classified into the one-chamber method and the two-chamber method according to experimental set-up. Besides, the porosity test method is one of the methods used to measure diffusion coefficients. The two-chamber method is a promising approach for determination of the VOC diffusion coefficient and partition coefficient for dry building materials.

2.3.1 Techniques Used to Determine Diffusion coefficient and Partition Coefficient

2.3.1.1 Single Small-Scale Chamber Methods

A) Single small scale chamber method

Cox et al. (2001) used this gravimetric method to measure the diffusion coefficients of seven common VOCs for vinyl flooring (VF). The vinyl flooring (VF) was chosen as the sample because of its frequent use as one of main indoor sources. One of the VF samples cut in three different thicknesses was placed on a dynamic microbalance with high-resolution (0.1~0.5μg) in a chamber. The chamber was monitored by a temperature transducer, and the microbalance connected with a PC-based acquisition system (DAQ). First, clean air passed through the sample till the stable mass was obtained. The weight was recorded at this moment. Then, influent air containing a constant concentration of VOCs passed through the sample. The sample mass gaining over time was recorded till equilibrium was reached. This process was sorption. After that, the air stream was switched to clean air. That meant a desorption process began. The sample mass losing over time was monitored by the DAQ till equilibrium was established.

In this study, the data of sorption and desorption were monitored by a microbalance. *K* and *D* values can be determined.

K can be used to describe the relationship between VOC concentration in material phase and in gas phase (Equation 2-5).

$$K = \frac{C_m}{C_{gas}} \tag{2-5}$$

where:

C_m is the equilibrium concentration in material phase that can be obtained from the difference of the initial and equilibrium sample mass divided by the sample volume (g/m^3);

C_{gas} is the corresponding concentration of the sample in gas-phase (g/m^3).

The concentration of VOC can be written by Equation (2-6)

$$C_{gas} = \frac{E}{\dot{V}} \tag{2-6}$$

where:

E is the emission rate of VOC produced by the diffusion cell (mg/s);

$\dot{V}$ is the airflow rate through the system(m^3/s).

Rearranging Equation 2-5 and 2-6, *K* can be determined.

D can be determined by Equation (2-7). The equation is used to describe the rate of mass change in the sample due to Fickian diffusion process.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left\{ \frac{-D(2n+1)^2 \pi^2 t}{L^2} \right\} \qquad (2\text{-}7)$$

where:

M_t is the total mass of a VOC that has entered or left the sample in time t (mg);

M_∞ is the corresponding mass at equilibrium(mg);

L is the thickness of the sample (m).

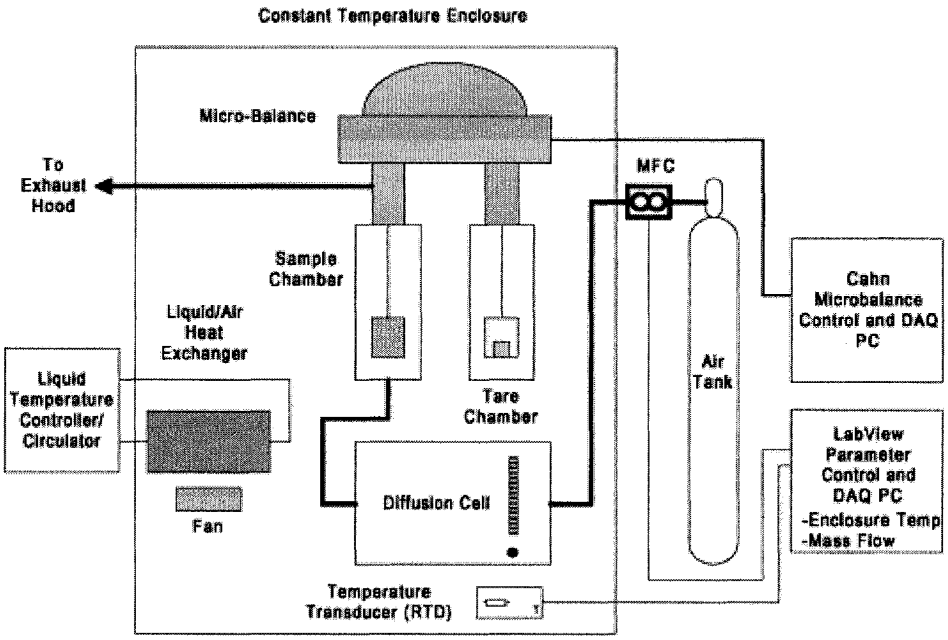


Figure 2. 1 Diagram of the microbalance test system (Cox et al., 2001)

Cox et al. (2001) concluded that there was a correlation of *K* and *D* with VOCs properties. Their results showed K decreased with increasing vapour pressure of compounds, while D increased with decreasing the molecular weight of compounds.

This method can be applied for other dry and diffusion-controlled materials besides VF. This approach is concentration independent (at low VOC concentration range), not complicated, but effective. However, C_m in Equation (2-5) is a mean value. This calculation is valid when the material is homogeneous. Equation (2-7) is valid under uniform initial distribution, equal surface concentration and a very thin sample. Because of these limitations, this method may not be applied to non-homogenous and thick materials. In addition, as the method weighs the mass of VOC periodically, only one VOC can be tested in one test.

B) Cup method

Hansson and Stymne (*2000*) and Kirchner et al. (*1999*) used the cup method to measure diffusion coefficients. Hansson and Stymne (*2000*) measured diffusion coefficients of toluene for three building materials, gypsum board, medium density fibreboard, and wood particleboard using a cup method at 20°C. Kirchner et al. (1999) used the same method to determine diffusion coefficients of n-octane and ethyl acetate for six building materials at 23°C. These materials were wallpaper with paste, PVC floor covering, carpet, acrylic paint on the woodchip paper, gypsum board, and aerated concrete. This approach is the simplest one in all of techniques used to measure diffusion coefficients. The diffusion cup method is based on the same principal as the wet cup method used to measure water vapour diffusion. A sample material was sealed at the top of a cup containing liquid toluene. The cup was placed under a control condition where the temperature was 20°C (*Hansson and Stymne, 2000*) and the relative humidity was less than 5%. Then, the sample was periodically weighed using a high resolution microbalance. The modified Fick's first law (Equation 2-8) was used to determine diffusion coefficients from the rate of VOC weight loss under steady state conditions.

$$D = \frac{\dot{m}}{A}\frac{L}{C} \qquad (2\text{-}8)$$

where:

D is the diffusion coefficient (m^2/s);

$\dot{m}$ is the mass flow rate through the material (mg/s);

A is the area of the sample (m^2);

L is the sample thickness(m);

C is the concentration of diffusing substance (mg/m^3).

One main advantage of this approach is that it is the simplest experimental and calculation procedure in measuring diffusion coefficients. However, as weights of samples are measured in this approach, only one VOC could be tested at one time. Moreover, since the saturated VOC concentration created by liquid VOC is applied, diffusion coefficients become concentration dependent and are overestimated.

2.3.1.2 Two Small-Scale Chamber Method

A) ASTM standard

A standard test method is applied to determine diffusion coefficient of organic vapor barriers using flame ionization (ASTM, 1997). A contaminated gas is introduced to one side of a planar sample. This contaminated gas is carried by a constant gas flow within a controlled temperature cell. Compounds that diffuse across the sample are swept by a carrier gas to a flame ionization detector (FID).

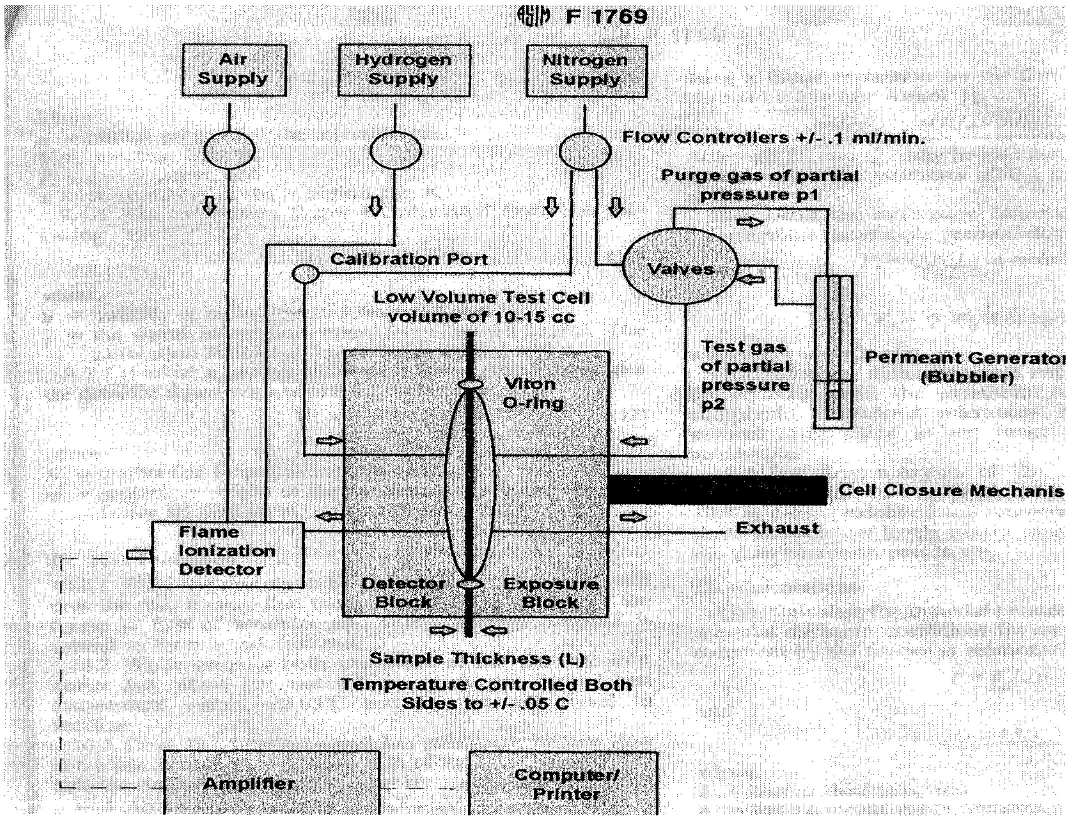


Figure 2. 2 Equipment Diagram (ASTM, 1997)

The compounds are detected by the flame ionization detector. Then, the resulting current signal from the detector is amplified and tabulated in accordance with the time of exposure. The diffusion coefficients for a given sample are determined by a non-linear regression using Fick's laws.

The VOC used in this method can be varied. Moreover, VOC mixture can be measured at one test. Small chamber volumes used in this standard effectively eliminate interference caused by measurement process. However, a steady state may not be reached in the course of the experiment. Experimental and calculation procedures are relatively complicated. In addition, equipments with high precision are required in this method. That is, cost is another drawback of this ASTM standard.

B) Diffusionmetric Method

Bodalal et al. (*2000*) used a diffusionmetric method to determine diffusion and partition coefficients of selected VOCs for three kinds of dry building materials. Bodalal et al. (*2000*) separated two identical chambers of 50 *l* in volume by a sample material. Air stream containing constant VOC was introduced to the high concentration chamber (see Figure 2-2). Gas samples were collected from the sampling port of each chamber through sorption tubes. The sample tubes were desorbed and analyzed by GC/FID system, and the concentrations of the samples were determined. In this experimental set-up, an electric fan was installed into each chamber. Some assumptions were made in this model. They included totally mixed chamber air, negligible convective resistance compared with diffusive mass transfer resistance, and instantaneous equilibrium of material surface concentration and concentration in the chamber air.

Fick's second law was used to describe the transient VOC diffusion within the material

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} \tag{2-9}$$

where:

D_m is the diffusion coefficient of material phase (m^2/s).

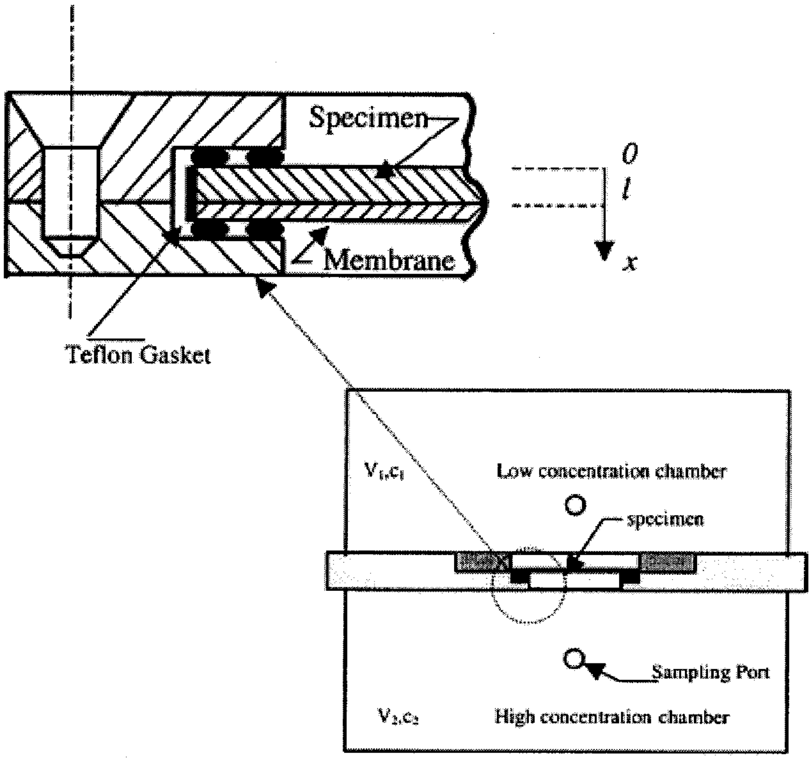


Figure 2. 3 Diffusionmetric apparatus (Bodalal et al., 2000)

Boundary conditions:

at $x = 0$, $C_m = KC_{gas}\Big|_{x=0}$ (2-10)

at $x = l$, $C_m = KC_{gas}\Big|_{x=l}$ (2-11)

Initial condition:

$t = 0$, $0 \le x \le 1$, $C_m = 0$ (2-12)

where:

K is the equilibrium partition coefficient (mg m^{-3}/mg m^{-3});

C_m is the surface concentration (mg/m^3);

C_{gas} is the gas concentration near surface (mg/m^3).

The chamber air concentration in low and high chambers can be determined by Eqs. (2-13) and (2-14), respectively,

$$C_{gas}\Big|_{x=0} = (DA/V_1)\int_0^t \left(\frac{\partial C_m}{\partial x}\right)_{x=0} dt$$

(2-13)

$$C_{gas}\Big|_{x=l} = C_{gas}\Big|_{t=0} - (DA/V_2)\int_0^t \left(\frac{\partial C_m}{\partial x}\right)_{x=l} dt$$

(2-14)

For determining D and K, Laplace-Carson Transformation was introduced in this model.

Bodalal et al. (2000) used the static chamber to measure D and K of toluene, nonane, decane, and undecane for the backing material of a carpet sample, of ethylbenzene, nonane, decane, and undecane for a flooring tile specimen, and of clcohexene, ethylbenzene, and decane for a plywood specimen. Correlations of *D* and *K* with the properties of VOCs were found. The diffusion coefficients decrease with the increasing of molecular weight of VOCs; the partition coefficients decrease with the increasing of vapor pressure of VOCs.

Controllable VOCs concentrations and no limitation of sample materials are two foremost advantages of the method. Moreover, the authors determined diffusion and equilibrium partition coefficients at transient conditions so the method approximately reflects typical indoor air situations. However, calculation procedures are relatively complicated. Risks of multiple solutions result from obtaining the diffusion and partition coefficients at the same time.

C) Twin chamber method

Meininghaus et al (*2000*) used two CLIMPAQ chambers to measure diffusion and partition coefficients of two VOCs for eight building materials. The eight materials were wallpaper with paste, PVC floor covering, acrylic paint on woodchip paper, gypsum board, and aerated concrete, solid concrete, and brick wall. Two VOCs were n-octane and ethyl acetate.

The sample materials were placed between the primary and the secondary chambers. Clean air was introduced into the secondary chambers, and the air stream containing a constant concentration of VOCs ventilated the primary chambers. The concentrations of the primary chambers, the secondary chambers, and the empty chamber were monitored by an Innova 1312 or Bruel & Kjer 1302.

Meininghaus et al. (*2000*) made some assumptions for this experiment. The air in chambers was assumed completely mixed. Namely, the surface concentration was the same as the concentration in the chamber air. The boundary layer effects caused by forced air convection resulting from installing fans were assumed to be neglected. Figure 2-3 is the schematic view of the experiment

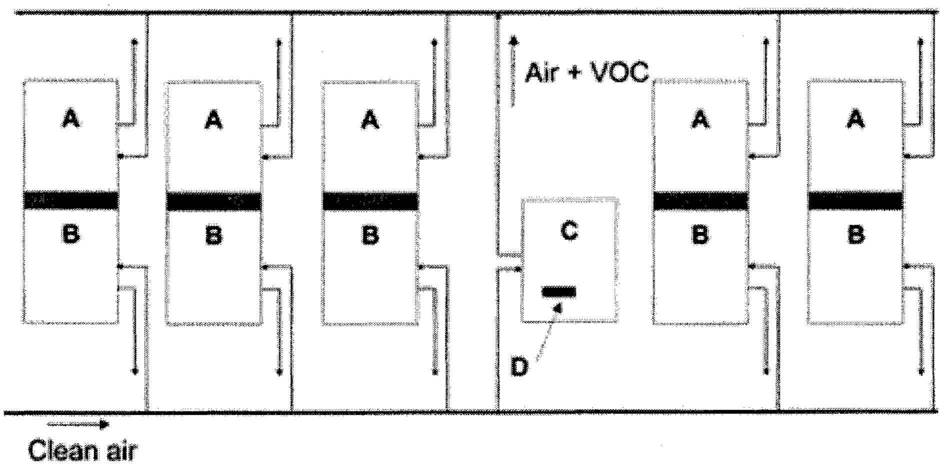


Figure 2. 4 Schematic of CLIMPAQ chamber (Meininghaus et al., 2000)

A: the CLIMPAQ containing VOC generator, B and C: primary chambers and secondary chambers, respectively.

Under steady-state conditions, diffusion coefficients for two VOC in eight building materials were determined using the modified Fick's first law of diffusion.

$$D = -\frac{m}{A}\frac{dx}{dc} = -\frac{\dot{V}\Delta x}{A}\frac{C_B}{C_B - C_A} \qquad (2\text{-}15)$$

where:

$\dot{V}$ is the volumetric air flow rate (m^3/s);

Δx is the material thickness(m);

A is the area of sample (m^2).

C_A and C_B are the VOC concentrations at steady-state condition in the primary and secondary chambers, respectively.

Meininghaus et al.(*2000*) calculated the sorption capacities S_A(mg m^{-2}/ mg m^{-3}). By taking into account the specimen mass per area (kg/m^2) and an air density, the partition coefficient k (kg air/ kg material) can be estimated. The calculation equations are listed as follows.

$$S_A = \frac{1}{A} \frac{\sum_{i=1}^{n} \left[\dot{m}_{iC} - \left(\dot{m}_{iA} + \dot{m}_{iB}\right)\right] \cdot \Delta t_i}{\left(\frac{C_A + C_B}{2}\right)} \tag{2-16}$$

$$C_{ad} = K \times C_{gas} \tag{2-17}$$

where:

$\dot{m}_{iC}$ is the mass flow into the primary chamber;

$\dot{m}_{iA}$ and $\dot{m}_{iB}$ are the mass flow out of the primary and secondary chambers, respectively;

C_{ad} is the sorbed mass divided by the mass of the sorbent at the equilibrium concentration(kg/kg_{mat});

C_{gas} is the concentration of the mass of VOC in air per mass of air(kg/kg$_{air}$);

K is the ratio of the VOC mass in material and in the air (kg/kg$_{mat}$ / kg/kg$_{air}$).

In this study, the results showed that PVC floor covering is diffusion-tight for observed compounds, n-octane and ethyl acetate. Diffusion coefficients of the seven materials were obtained. Also, Meininghaus et al. (*2000*) ranked the seven materials according to their diffusion coefficients. Gypsum board showed the highest diffusion coefficient, followed by aerated concrete, carpet, brick wall, solid concrete, wallpaper with paste, and acrylic paint on wallpaper.

No limitation of test materials, controllable concentration of investigated compounds, and relatively simple calculation procedures are the main advantages of this method. Because of the limitation of air sample collecting system, VOC mixture cannot be detected. The concentration difference of the specimen surface was used in modified Fick's first law equations. To obtain the validation of this application, the authors installed fans in chambers to obtain totally mixed chamber air. However, the influence on the boundary layer resulting from electric fans is neglected. Therefore, the diffusion coefficients may be underestimated.

D) Twin-compartment method

Hansson and Stymne (*2000*) proposed a twin-compartment method to measure diffusion and partition coefficients for toluene in three building materials: gypsum board, medium density fibreboard, and wood particleboard. A specimen separated two 62 ml cylinder chambers. They used clean air to flush the two compartments. Then, the air containing toluene in a step change concentration was introduced to the lower chamber, while clean air ventilated the upper chamber. The concentrations of toluene in the clean air, inlet air, and extract air from both chambers were continuously monitored by a quadrupole mass spectrometer till equilibrium was reached. This period took several hours.

A mathematical model was established to simulate transport processes. The processes include boundary layer diffusion, surface adsorption, vapour diffusion inside the material and interior sorption. In addition, it was assumed the chamber air was completely mixed. Equation (2-18) describes the conservation of mass within the air in the contaminated chamber.

$$V\frac{dC_1}{dt}=K_g A\left(C_{s,1}-C_1\right)+\dot{V}_1\left(C_0-C_1\right) \tag{2-18}$$

where:

V is the chamber volume (m^3);

C_1 is the bulk air concentration in lower chamber (mg/m^3);

$C_{s,1}$ is the air concentration close to surface of the sample (mg/m^3);

t is time(s). A is the material area covering the compartment (m^2);

k_g is the mass transfer coefficient between bulk air and air close to the surface (m/s);

$\dot{V}_1$ is the volumetric chamber air flow rate(m^3/s);

C_0 is the air concentration into chamber(mg/m^3).

Equation (2-19) describes the conservation of mass within the air in the clean chamber.

$$V\frac{dC_2}{dt} = K_g A(C_{s,2} - C_2) - \dot{V}_2 C_2 - gAC_2 \tag{2-19}$$

where, the subscript 2 designates the clean chamber; g is a rate constant for compound deletion.

Equation (2-20) models the adsorption of the sample material (both side).

$$C_{ad,s} = C_{gas,s} K_s \tag{2-20}$$

where:

$C_{ad,s}$ is the surface concentration of adsorbed compounds (mg/m^3);

K_s is the equilibrium constant for surface adsorption.

Equation (2-21) describes the conversation of adsorbed mass at the surface of the material on the contaminated side.

$$A\frac{dC_{s,1}}{dt} = A\frac{K_g}{K_s}(C_1 - C_{s,1}) + A\frac{D}{K_s h}(C_{i=1} - C_{s,1}) \tag{2-21}$$

where:

D is the gas diffusion coefficient (m^2/s);

h is the utilized grid distance inside the material (m);

$C_{i=1}$ is the gas concentration at a distance h from the surface (mg/m^3).

Equation (2-22) describes the interior sorption.

$$C_{ad}(x) = K \cdot C_{gas}(x) \tag{2-22}$$

where:

$C_{ad}(x)$ is the concentration of compound within the materials (mg/m^3);

$C_{gas}(x)$ is the gas concentration in the material pores (mg/m^3);

K is the equilibrium partition coefficient between the total concentration and the gas concentration(mg m^{-3}/mg m^{-3}).

Equation (2-23) describes conservation of compound mass within material.

$$\frac{\partial C_i}{\partial t} = \frac{D}{K}\frac{\partial^2 C_i}{\partial x^2} \tag{2-23}$$

Best fits of coefficients of *D* and *K* can be obtained simultaneously by a numerical technique.

VOC with controllable concentrations and variable types of materials can be applied into this method. However, it takes a long time to reach the steady state. Moreover, since *D, K* and *g* are simultaneously obtained by a least-squares regression analysis using the experimental data, the method may have a risk of multiple existences of best-fits of coefficients. The authors did not mention the basis of the guessed value, K_g, selection.

E) The Field and Laboratory Emission Cell (FLEC)

Meininghaus et al (*2002*) presented two experimental models using FLEC to determine diffusion coefficients. One is a one flow system; the other is a two-flow system. In the former, three opened VOC vials containing liquid VOC were placed in a glass chamber of 23.5 *l* in volume. The three vials were stored in the chambers for two days. Hence, concentrations with range from 20-770 $\mu g/m^3$ were established. The gypsum board was fixed to the top of the chamber. Then, the FLEC covered the gypsum board. Clean nitrogen with total flow of 100 ml per minute was introduced into the FLEC, and samples drawn from the FLEC were collected periodically using Tenax-adsorption tubes. The volume of a sample was 0.5 *l*. The collected samples were analyzed by GC/MS. In the latter, a test specimen separating two FLECs. Air flow containing VOCs was led to FLEC1, and clean air was introduced into FLEC2. The concentrations of VOCs were step-wised increased. Samples were collected from the inlet air flow of FLEC1 and both outlet flow of FLEC1 and FLEC2. The sampling time was variable according to different inlet VOCs concentrations. These samples were analyzed by GC/MS.

Under transient conditions, diffusion processes can be depicted by Fick's second law.

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \qquad (2\text{-}24)$$

where:

C is the concentration at position x and time t.

Equation (2-24) is independent of the sorption process. If the sorption process is considered, the above equation is replaced by the following one.

$$\left(\rho\varepsilon + \rho_{ad}\frac{\partial f}{\partial C_{ad}}\right)\frac{\partial C}{\partial t} = \rho D\frac{\partial^2 C}{\partial x^2} \tag{2-25}$$

where:

ρ is the pore-phase gas density (mg/m^3);

ε is the porosity of the sorbent;

f is a function describing C vs. C_{ad} equilibrium relation;

C_{ad} is the concentration of adsorbed phase (mg/m^3).

When a linear adsorption isotherm is given, Equation (2-25) can be rearranged to Equation (2-26)

$$\frac{\partial C}{\partial t} = D_{alt}\frac{\partial^2 C}{\partial x^2} \tag{2-26}$$

where: $$D_{alt} = \frac{\rho D}{\rho\varepsilon + \rho_{ad}\frac{\partial f}{\partial C_{ad}}} \tag{2-27}$$

Therefore,

$$C_{x,t} = \frac{k}{2\sqrt{\pi D_{alt}}} e^{-\frac{\Delta x^2}{4D_{alt}t}} \tag{2-28}$$

where:

$C_{x,t}$ is assumed to be the concentration of material surface measured in the FLEC;

k denotes the total amount of the diffusing substance.

Under steady-state conditions, Fick's first law is used to describe the diffusion process.

$$J = -D_{alt} \frac{dc}{dx} \tag{2-29}$$

Consequently, $D_{alt} = -\frac{\dot{V}_2 \Delta x}{A} \frac{C_2}{C_2 - C_1}$ (2-30)

where:

J is the mass flow across the material($mg/m^2/s$);

$\dot{V}_2$ is the ventilation of FLEC2(m^3/s);

C_2 is the concentration of the outlet of FLEC 2 (mg/m^3);

C_1 is the concentration of the outlet of FLEC 1 (mg/m^3).

In this study, Meininghaus et al.(*2002*) applied Fick's first law to determine diffusion coefficients, but D_{alt} in Equations (2-29) and (2-30) should be replaced by D. Since sorption and desorption processes reach equilibrium at a steady state condition, the diffusion coefficient is independent of the sorption process. In the one-flow system, the authors concluded that the more volatile compounds permeate through the gypsum board more quickly. In the two-flow system, a steady-state condition was observable. To simply the concentration profiles within FLECs(inlet to outlet), linear gradients within the FLECs were assumed. They concluded the assumption was demonstrated valid by comparing the results with existing literature data. However, since the authors compared the diffusion coefficients obtained from diffusion studies of VOC mixtures in a building material with those obtained from diffusion studies of single compound in a building material, further investigations should be considered. The authors also drew a conclusion that the same order of magnitude of diffusion coefficients (i.e., 1, 4 -dichlorobenezen) was found in both experimental set-ups. Moreover, the diffusion of less polar VOCs diffused fast in the gypsum board.

VOCs mixture can be measured at the same time, and sample materials are not limited. These are two main advantages of this method. However, in the one-flow system, the volume of FLECs is very small, so a large air sample has a risk of a pressure difference between the FLECs and the glass chamber. As a result, the assumption of pure diffusion process within materials will not be valid. In the two-flow system, over-simplification of the concentration profiles in FLECs may result in inaccuracy of diffusion coefficients estimation.

2.3.1.3 Porosity Test Method

Tiffonnet et al. (*2000*) proposed a methodology to determine diffusion coefficients:

mercury intrusion porosimetry (MIP) test. Diffusion coefficients of four VOC for seven building materials were determined by MIP. The seven materials are solid concrete, aerated concrete, gypsum board, brick, mortar, gypsum, and chipboard. The four VOCs are methane, ethyl acetate, n-octane, and n-dodecane. The process of diffusion transport within a material was analogously described by Fick's law. D_e as an effective diffusion coefficient was introduced and was computed from the equation:

$$D_e = D^\circ \frac{\varepsilon}{\tau} \tag{2-31}$$

where:

D° is the mean diffusion coefficient in the pores of the material(m^2/s) ;

ε is the connected-pore volume fraction (m^3/m^3);

τ is the tortuosity factor of the porous network(dimensionless).

Caniglia's mathematical model was applied to determine D_e, which considered the pore interconnections, the pore constrictions, and the pore random orientation. ε could be measured, and D° and τ could be calculated from the MIP. In this mathematical model, the pore interconnections, the pore constrictions, and the pore random orientation were considered.

The results showed that the diffusion coefficients decreased with the reducing of porosity of materials. Also, Tiffonnet et al. (*2000*) compared their results with those obtained by cup method and the CLIMPAQ method. It showed the results were in the same order of magnitude as other methods, but results obtained by Tiffonnet et al. (*2000*) were larger than those obtained in the cup method and the CLIMPAQ method.

This model has two main advantages. One is in its short experimental time. The other is that diffusion coefficients of various VOC at various temperatures can be determined by one test. However, due to the limitation of this method, it is simply suitable for homogeneous or single layer materials. In addition, interaction between the VOC and the building material are not considered in this model. Hence, diffusion coefficients may be inaccurate because of the possible influence caused by the interaction.

2.3.2 Sorption Tests Only Used to Determine Partition Coefficient

Sorption tests used to measure partition coefficients are classified as: the dynamic single small-scale chamber test (*Tichenor et al., 1990, Jorgensen et al., 1993, 1999, van der Wal et al., 1998, An et al., 1999, Won et al., 2001, Zhang et al., 2001, Popa, et al., 2002*), dynamic two chamber test (*Meininghaus et al., 1998, 2000a*), static small-scale chamber test (*Tiffonnet et al., 2002*), static two small-scale chamber test (*Boldalal et al., 1999*). Dynamic two-chamber test (*Meininghaus et al., 1998, 2000a*) and static two small-scale chamber test (*Boldalal et al., 1999*) were reviewed in section 2.3.1.2. In the dynamic single small-scale chamber test (*Tichenor et al., 1990, Jorgensen et al., 1993, 1999, van der Wal et al., 1998, An et al., 1999, Won et al., 2001, Zhang et al., 2001, Popa, et al., 2002*), air samples were analyzed using GC and partition coefficients were carried out using linear Langmuir equation (Equation 2-32).

$$\frac{dM}{dt} = k_a \cdot C_a - k_d \cdot M \tag{2-32}$$

where,

M is the adsorbed VOC mass per unit area on the sink (mg VOC/m^2 of material);

C_a is the VOC concentration in the chamber (mg VOC/m^3 of air);

k_a is the adsorption rate constant (m/s);

k_d is the desorption rate constant (s^{-1}).

When the transport processes in system reach equilibrium, the amount of VOC adsorbed and desorbed at the interface are the same. Hence, Equation (2-32) can be written as the following:

$$M = K \cdot C \tag{2-33}$$

where,

M is sorbed mass per unit area of sink (mg/m^2);

K is partition coefficient(mgm^{-2}/ mgm^{-3})(= k_a/ k_d);

C is the VOC concentration in the chamber (mg /m^3).

Equation (2-33) is similar to Henry isotherm, but it uses sorbed mass per unit area instead of sorbed VOC concentration. This expression may be more approporate to the expression of Henry isotherm for nonporous material where the effective surface area is the same as the physical surface area (*Tiffonnet et al., 2002*). However, the expression may not be appropriate to the expression of Henry isotherm for porous materials, such as gypsum board, ceiling tile. Since K comes from the ratio of k_a to k_d and the two parameters are coupled from one test, K has the risk to be unreliable. Meininghaus et al.(*2000b*) used a dynamic single chamber to determine partition coefficients of xylene and n-octane in wallpaper, carpet, acrylic paint, PVC, and aerated concrete gypsum. Except nonlinear isotherm for xylene in PVC, Henry isotherm was applied to calculate partition coefficients of others. Air samples were analyzed using microbalance. Since differences of VOC mass are directly read, the method is easier to carry out. However, sensitivity of the microbalance is one of the problems when low VOC concentration is introduced into this test. In addition, only one VOC can be tested at each test because of measuring weight periodically.

Tiffornet et al. (*2002*) used a static single chamber method to determine partition coefficients of acetone in paint, wood chipboard, and gypsum. The Henry isotherm was applied to acetone on paint in their test. For acetone in wood chipboard and gypsum, other isotherms were observed, such as the Brunauer type III or the low concentration part of type V, and type I or the low concentration part of type IV (Figure 2.5). The static single chamber method is easier to carry out as well. However, strong attention should be paid to the air sample volume drawn by the sample collector because a large volume may disturb transport process in the chamber. The authors used photoacoustic spectroscopy to take air samples. The volume drawn by photoacoustic spectroscopy was 3cm^3, which was relatively smaller than the chamber volume, and they returned the air sample to the chamber in order to minimize the effect caused by taking the air sample.

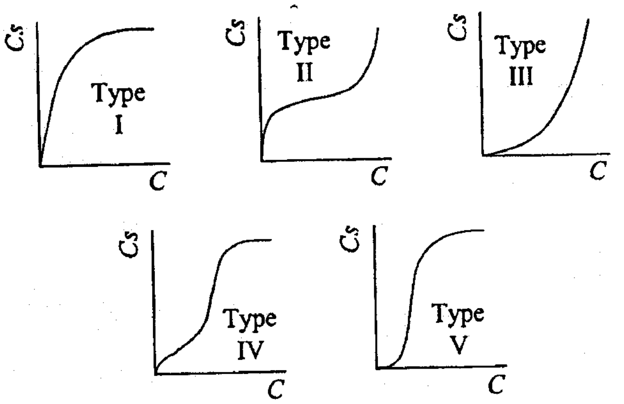


Figure 2. 5 Brunauer classification of the possible shape of sorption isotherms. (after Masel, 1996)

2.4 Conclusions

After the pertinent literature has been reviewed, significant discrepancy in the diffusion coefficient determined by different techniques is found. The reasons are due to different assumptions made in and techniques employed in the determination of the diffusion coefficients. When the materials and VOCs used in tests are not identical, it is impossible to compare the results.

Table (2-1) presents a summary of methods of diffusion coefficients measurement. The three types of physical models used to measure diffusion and/or partition coefficients, the one chamber method, the two-chamber method, and the porosity test method, were reviewed. Moreover, sorption tests only used to determine partition coefficients were briefly reviewed as well. One main merit of the one chamber method is easy to set up. However, Cox et al. (*2001*), Hansson and Stymne (*2000*), and Kirchner et al. (*1999*) used procedures to measure the VOC weight periodically, so only one VOC can be tested at one time. Since saturated VOC concentration is applied into the cup method, it leads to the risk of overestimation of the diffusion coefficient. A significant merit of the porosity test method is its short experimental time. However, it is only suitable for homogeneous and single layer material. Among these methods, the twin chamber physical model is still a relatively promising method for determining diffusion and/or coefficients of VOC in dry building material although it is difficult to set up. Controllable VOC concentration can be chosen in this method; the specimens are not limited. In the two chamber methods, transient conditions or steady state conditions are considered. Transient conditions are close to real indoor air situations, but they are difficult to translate. Steady state conditions are rarely found in real indoor air conditions, but estimates of diffusion coefficients are relatively easy. Hence, both of the application of steady state and transient methods may have their justifications.

Based on this literature review, the two-chamber method using a two-flow system and a steady state method was chosen for the study. Current works using twin chamber method are summarized as following.

It was found by Bodalal et al. (*2000*) that the diffusion coefficients decreased with the increase of molecular weight of VOCs and the partition coefficients increased with the decreasing of vapor pressure of VOCs. However, Bodalal et al. (*2000*) used regression technique to determine D and K. The results were obtained simultaneously through curve fitting. Therefore, D and K obtained in their study may be inaccurate. Meininghaus et al. (*2000*) focused on analyzing the influences of diffusion and sorption on indoor air quality by considering various wall materials. Hansson and Stymne (*2000*) used twin chamber method to study VOC diffusion and absorption properties of toluene in three different indoor materials. Meininghaus et al. (*2002*) did mixture tests using one flow and two flow systems. They concluded: that the less polar compound quickly diffused through gypsum board; the boiling points and molecular areas of chlorinated compounds affected diffusion coefficients.

Therefore, this research focus on studying the impacts caused by physicochemical properties of VOC, such as, molecular weight, vapor pressure, and polarity, on diffusion and partition coefficients. Moreover, the impacts caused by mixture test on diffusion coefficients are under investigation.

Table 2. 1 Summary of the diffusion coefficient measurement methods

Method	VOC measurement	Merits	Drawbacks
Single chamber method Cox et al., 2001; Hansson and Stymne, 2000	Microbalance	1.Simplest experimental procedure. 2.Simple analysis procedures 3.No limitation of test sample 4. Controllable VOC concentration (Cox et al. 2001).	1.Possible concentration dependence (Hansson and Stymne2000). 2.Only one VOC can be measured at one time
Twin-chamber method Bodalal et al., 2000; Meininghaus et al., 2000 and 2002; Hansson and Stymne, 2000	Photoacoustic spectroscopy (Meininghaus et al., 2000) GC/FID (Bodalal et al., 2000, and Meininghaus et al., 2002)	1.No limitation of test materials 2.Controllable VOC concentrations 3. More than one compound can be measured at one test (Meininghaus et al., 2002).	1.Risk of multiple solutions of coefficients 2. Relatively complicated experimental and analysis techniques
Porosity test method Tiffonnet et al., 2000		1. Short experimental time. 2. De of various VOC at different temperature can be determined at one time.	1. Limitation of materials (homogeneous or single layer materials). 2. Not simple calculation process 3. Lack of consideration of possible interaction between the VOC and the material.

Chapter 3 Measurement of diffusion and coefficients

3.1 Introduction

Three kinds of experimental techniques were reviewed in Chapter 2. These techniques were applied to measure diffusion (*D*) and/or partition (*K*) coefficients. Diffusion coefficients are determined by measuring weight periodically in single small scale chamber method (gravimetric method). Two main drawbacks of this method are: only one VOC can be tested in one test; diffusion coefficients are concentration dependent (the cup method). In the mercury intrusion porosimetry method, its main merit is short experimental period, but only homogenous and single layer materials can be tested. The two-chamber method is a relatively effective method used to determine diffusion and partition coefficients of VOC in dry building materials. The main merits of the method are no limitation of specimen and good control of the VOC concentration. Similar to or slightly higher concentrations than those in real indoor air can be obtained in the method. Experimental techniques used to investigate interaction of VOC and materials are roughly divided into one-flow and two- flow approaches. In the two- flow approach, diffusion coefficients can be measured based on observation during tests. Therefore, the two-chamber method with a two -flow system is selected in this study. Previous work carried out using twin chamber method were reviewed as well. Comprehensive work on the effects caused by physicochemical properties of

VOCs on diffusion coefficients have not been done. Therefore, the presented research focuses on investigations of the relationship between molecular weight, vapor pressure, and polarity of VOCs and *D* and *K*. Moreover, diffusion processes for a single VOC compound and VOC mixture within building materials are studied.

Experimental plans, set-up, and procedures are the three main sections of this chapter.

3.2 Test Plan

Three research plans were designed to achieve the objectives of the study. In the first plan, diffusion and partition coefficients of three kinds of VOCs through a given material were determined. It aimed to observe the correlation between physicochemical properties of VOCs and *D* and *K* for a given material. In the second plan, diffusion and partition coefficients of a VOC through three different materials were measured. The results of this research were used to rank the three materials according to their diffusion coefficients. In the third plan, VOC mixture through a specimen used in the first plan was carried out. This test was applied to analyze the difference between a diffusion coefficient obtained from a single compound test and a diffusion coefficient of the compound as part of a mixture.

3.3 Experimental Set-up

A two-flow approach was applied in this study. This approach allows for directly observing a mass flow across the material between two chambers and a good control of VOC concentrations (*Meinighaous et al., 2000*). Diffusion and partition coefficients can be determined based on the observations. Moreover, the VOC concentrations can be established at low concentrations comparable to or slightly higher than those in many buildings. To fulfill this aim, an experimental set-up consisting of a chamber assembly, an air (clean/contaminant) supply system, an air sample collection system, and an analytical system, was established. Figure 3-1 shows a schematic of the experimental setup.

3.3.1 Apparatus Descriptions

The chamber assembly includes two identical cylinder chambers of 2.7 l in volume and 0.13m in diameter. Each chamber has its own ventilating inlet and sampling outlet. Its internal wall is very smooth, which is helpful to reduce sink effects. A material specimen separateed two chambers, and the chambers were constantly ventilated by clean air and contaminated air, respectively. Air samples were collected from both sampling outlets and their concentrations were monitored periodically by data analysis system.

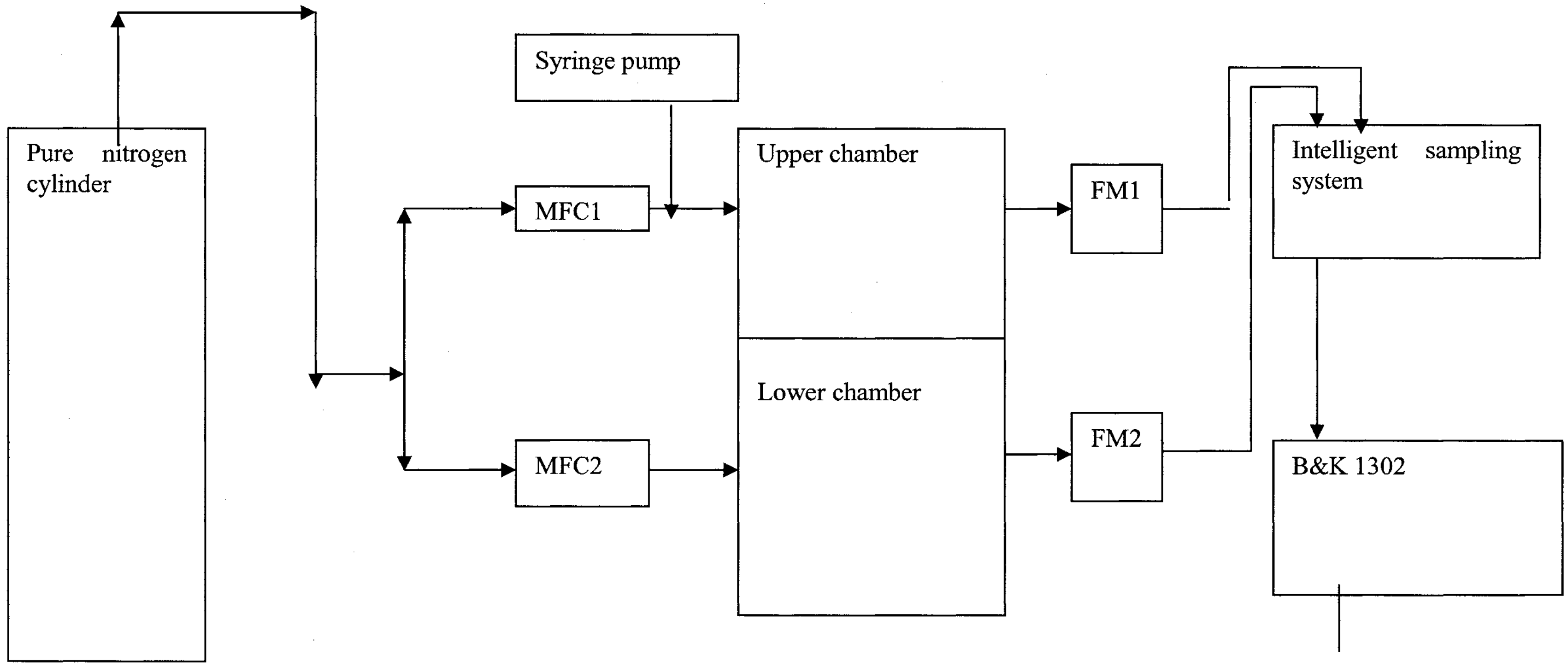
A commercially available compressed nitrogen (UHP 5.0) was used as a carrier gas. Two mass flow controllers (Matheson flow controller model 8270) were connected to the nitrogen compressed cylinder in order to control air flow rates. Before using, the flow controllers were calibrated using a flow calibrator (Bios DC 2).

A syringe pump (Fisher scientific) and a 25 μl gas tight syringe were used together as a contaminant generator. When gas flow rate was constant, the various VOC concentrations can be obtained by adjusting the injection rate parameter in the syringe pump. Also, once the injection rate was chosen, an injection period can be determined by setting the volume parameter in the syringe pump. The contaminant generator is connected to the upper chamber.

In single compound test, the air sample collection system consists of a sampling system, Intelligent Sampling System, and a multi-gas monitoring system. Two sampling outlets are connected to two channels of the sampling system. The sampling system automatically detects the channels according to the time interval chosen by a user. The outlet of the sampling system was connected to the inlet of the multi-gas monitor. In the VOC mixture test, air samples are collected through an air sample collection unit, which consists of sampling tubes (Tekmar Tenax TA stainless steel tubes), a vacuum pump (SKC Aircheck sampler model 224-43XR), and a flow controller (Matheson model 8270)(Figure 3-2).

In a single compound test, the multi-gas monitoring system (Bruel& Kjaer photoacoustic multi-gas monitor 1302) was used as an analytical system to measure the concentration. The multi-gas monitor was calibrated with toluene at Pacwill, California, U.S. and with methanol and isopropanol in the Indoor Air Quality (IAQ) lab, Concordia University. The calibration data are attached on Appendix II. In VOC mixture test, an analytical system consists of a thermal desorption unit (Aero trap desorber Tekmar 6000), GC/FID analyzer (Hewlett Packard 5890 series II), and the data acquisition system.

The whole test facility is in an environmentally controlled room at 23± 1°C.



MFC: mass flow controller; FM: flow meter

Figure 3. 1 Schematic experimental set-up (arrows indicate the direction of air flow)

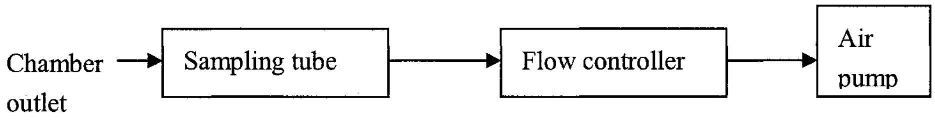


Figure 3. 2 Schematic the air sample collection unit of VOC mixture

3.4 VOCs , Materials, and Sampling Tubes Preparation

3.4.1 VOCs Preparation

Toluene, methanol, and isopropanol, which cover wide ranges of molecular weights, boiling points, and polarities, were chosen as target compounds. Three compounds at a given proportions were mixed in a ventilating hood. Molecular weights of the compounds are from 30 to 92; their boiling points are comparatively low (from 65 to 110□). Low boiling point is helpful to minimize sink effects in tubes and chambers. Table 3-1 lists the physical properties of VOCs.

3.4.2 Materials Preparation

Ceiling tile, gypsum board, and carpet with SBR backing were selected as test materials. The materials used in this study were chosen to represent major groups of building products often largely used in indoor surfaces.

Sample materials were cut into circular specimens with 0.13*m* in diameter, and placed in a clean chamber (Figure 3-3) at 23±1°C. Pure nitrogen ventilated the chamber for at least three weeks before testing. This allowed minimizing VOCs remaining within materials. The effectiveness of the cleaning was checked by drawing air sample from the chamber during the conditioning. Then, the conditioned specimens were placed into a glass container in order to keep the samples clean.

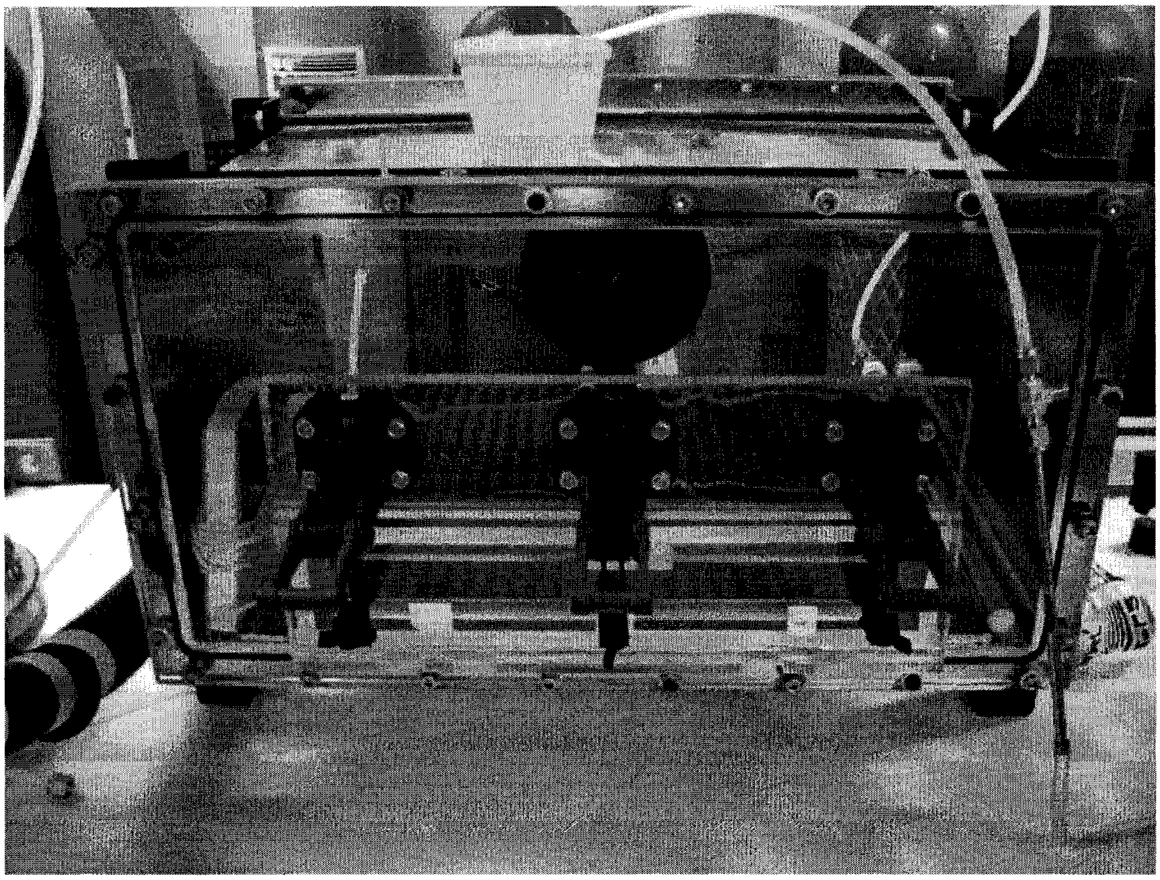


Figure 3. 3 ASTM chamber

The selection criteria of VOC and materials are summarized as following.

- The selected compounds are important to affect the indoor air quality.
- The selected compounds have a wide volatile range, namely they cover different boil points.
- The selected compounds have a wide molecular weight range.

- The test materials may be used for covering large indoor surfaces in common building construction.
- The test materials may have large sorption capacities.

Table 3. 1 Physicochemical properties of compounds (www.osha.gov, macro.lsu.edu , www.planet.nl)

Compound name	Chemical formula	Density (mg/µl) at 20°C	Molecular weight (g/mol)	Vapor pressure (mm-Hg) at 20°C	Boiling point (°C)	Polarity index (P)
Methanol	CH_3OH	0.792	32.4	97	65	6.6
Toluene	$C_6H_5CH_3$	0.867	92.14	25.64	110	2.4
Isopropanol	C_3H_7OH	0.786	60	33	82.2	4.3

3.4.3 Sampling Tubes Preparation

Blank Tekmar stainless steel tubes had been conditioned for three hours in a conditioner (Envirochemical) before use. Compressed helium (UHP 5.0) passed through the blank tubes while they were heated at 300°C. After conditioned, the tubes were checked by GC/FID and Aero Trap Desober (Tekmar 6000). The conditioned tubes were wrapped using aluminum foil. Then, the tubes were placed in containers and the containers were stored in a refrigerator.

3.5 Experimental Procedures

Before diffusion measurements were conducted, many operations had to be performed. These operations included cleaning the test apparatus, testing air leakage, and checking background contaminants level.

3.5.1 Cleaning the Chambers

The procedures for cleaning the chambers are given as follows:

- The two chambers were thoroughly cleaned using laboratory detergent and distilled water.
- The chambers were dried using clean lint free cloth and a dryer.
- Methanol was used to clean the test chambers, especially the inside seams.
- The chambers were thoroughly rinsed with distilled water again.
- The chambers were dried using clean lint free cloth.
- Clean air was introduced through the two chambers for at least ten hours.
- The concentration of the empty chamber was monitored and recorded using B&K 1302.

3.5.2 Testing Air Leakage

Air leakage is one of the primary factors that affect the accuracy of measurement of diffusion and partition coefficients. To assure the tightness of the test facility, Teflon tape was used to seal the edges of the specimen and three clamps were used to fix the chambers. The tightness of the chamber was checked by measuring the flow rates into the chamber and out of the chamber. When the difference between the flow rates coming into the chamber and out of the chamber was $\pm 0.2l/\min$, the chamber was considered tight to environment.

3.5.3 Preparation of Measurement

In this study, since pure diffusion within material is assumed, a sufficient gas flow rate should be supplied during the experimental procedure. Otherwise, a large sampling volume would create a huge pressure difference between two chambers. It would result in invalidation of pure diffusion assumption. Therefore, the sampling volume drawn by B&K 1302 should be measured in advance. The minimum sampling flow rate measured using a mass flow meter was 1.9 *l/min*. Therefore, 2 *l/min* in airflow rate to each inlet was thoroughly provided using a mass flow controller in the study. The preconditioned sample was picked up from the glass container storing conditioned specimens. Thickness of a specimen was measured using a calibrator; its weight was determined by a microbalance. After the measurement, edges of the specimen were sealed using Teflon film. Then, the specimen was placed between two chambers. The interface of two chambers was also sealed using Teflon film and the chambers were fixed using three commercially available clamps, which can withstand at least 10*psi*.

3.5.4 Background Contamination

The chambers and others apparatus were connected together according to Figure (3-1) except the connection of a syringe pump. Firstly, the Intelligent sampling system and B&K 1302 were turned on. Then, the airflow rate to each inlet was set 2 *l/min* by adjusting a mass flow controller. Thirdly, a flow meter was connected at each outlet of both chambers. This was for measuring the airflow rate out of chamber.

The concentrations of both outlets were monitored every two minutes using multi-gas monitor till the concentrations remained constant. The relationship of the VOC concentrations and time was plotted. The average concentration of VOC in background test was calculated using the concentration versus time curve. This value would be subtracted from the concentrations of VOC in diffusion and partition coefficients measurement.

3.5.5 Starting Test

When the background concentration was measured, a diffusion measurement would be started. Three parameters (injection rate, volume, and syringe diameter) in syringe pump were set to obtain the planned concentration of VOC and estimated injection period. The gas flow rate of each inlet was set 2 *l/min* by adjusting the mass flow controller. The syringe pump was connected to the inlet of upper chamber. Then, the syringe pump and the sampling system were run at the same time. The measurements were monitored till equilibrium reached. The concentrations of both outlets were recorded every two minutes and the airflow rates of both outlets were recorded every 14 minutes.

In mixture test, air samples were collected through both outlets when equilibrium reached (Figure 3-2). Airflow rate was controlled at 50*ml/min* using a flow controller. The sampling time for upper chamber was 10min; the sampling time for lower chamber was 30min. These samples were analyzed using a thermal desorber, GC/FID analyzer, and acquisition system(Hewlett Packard 5890 series II). The sampling tubes were desorbed by an Aero desorber Tekmar 6000 at a temperature

225°C for 10 minutes with its trap cooling down to -156°C, and then the trap was desorbed at a temperature of 240°C for 4 minutes with the outside CryoFocuser at a temperature of -156°C. Vocol (Supelco, Inc.) was used as the column of GC/FID analyzer. The column fused silica is 0.55*mm* in diameter and 105*m* in length. The GC/FID program was starting at 30°C, held for 2minutes, then with a heating rate of 10°C/min from 30°C to 200°C, held for 2 minutes. In the program, inlet/ detector were kept at 230°C.

3.6 Conclusion

In this research, two-chamber experimental set-up was chosen. The clean airflow and contaminant airflow were introduced into the upper and lower chambers, respectively. Diffusion and partition coefficients of a single compound in building materials, i.e., ceiling tile, were measured using multi-gas monitor; diffusion and partition coefficients of VOC in a mixture in ceiling tile were determined by using GC/FID.

Chapter 4 Data Analysis and Discussion

4.1 Introduction

Two approaches used to describe VOC transport in a dry material were reviewed in Chapter Two. One approach is using a one-phase model (*Little et al., 1994 and 1996 and Cox et al., 2000*), which assumes the material is homogenous. VOC existing within the material is in a material phase. The second is using a multiphase model (*Tiffonnet, 2000; Lee et al., 2002 and 2003*), which applies for porous media. VOC existing within materials are in a gas phase and an adsorbed phase. In this study, multi-phase approach is applied since most dry building materials are porous. Under steady-state conditions, Fick's first law of diffusion can be applied to describe VOC mass transfer in materials. Linear isotherm, i.e., Henry isotherm, is used to describe the relationship between VOC in absorbed phase and gas phase.

This chapter presents experimental measurement results and discussion. The diffusion and partition coefficients of toluene and isopropanol in ceiling tile and methanol for ceiling tile, carpet, and gypsum board were determined. The diffusion coefficients of isopropanol and toluene in a mixture in ceiling tile were measured. The relationship of physicochemical properties of VOCs versus diffusion or partition coefficients were analyzed; diffusion coefficients of methanol in different specimens were ranked according to their diffusion speed; the difference between diffusion coefficients of a single compound in ceiling tile and the compound as part of VOC mixture in ceiling tile were under investigation. The chapter includes three main sections: theory, data analysis method, and results and discussion.

4.2 Theory

Mass transfer in dry building materials results from diffusion due to concentration gradient, adsorption/ desorption due to surface force and/or capillary flow due to suction. In buildings without IAQ problems, the concentration for the individual compound is generally less than $100\mu g/m^3$ and for total volatile organic compounds (TVOC) is lower than $500\mu g/m^3$ (*Salthammer, 1999*). The saturation concentration is $97.36 g/m^3$ for n-octane and $473.45 g/m^3$ for ethyl acetate (*Kirchner et al., 1999*). Compared with the saturation concentrations, VOC concentration levels in indoor air are very low. Therefore, mass transfer in dry building materials is observed as gas phase diffusion, and adsorption /desorption in low concentration levels.

4.2.1 Mass Transfer in Materials

For dry building materials, mass transfer within a material is dominated by gas-phase diffusion and absorbed phase diffusion is neglected (*Tiffonnet et al., 2000*). Concentration gradient is assumed to be the only driving force for VOC transport; no chemical reaction inside the material is assumed; the dry material is assumed to have a homogeneous diffusivity. Under steady-state conditions, Fick's first law of diffusion can be used (Equation 4-1) to calculate diffusion coefficients for VOC in a material (Equation 4-2) (*Meininghaus et al., 2000*).

$$D = -\frac{\dot{m}}{A} \cdot \frac{dx}{dc} \tag{4-1}$$

where:

D is the diffusion coefficient (m^2/s);

$\dot{m}$ is the mass flow through the material (mg/s);

A is the area of the sample material (m^2).

4.2.2 Material/ Air Interface

Adsorption is determined as the accumulation of gas (adsorbate) on a solid (adsorbent). Solid molecules on the surface exert an attractive force to the surrounding gas since only one side of the outmost layer of solid molecules on the surface is bound to the inner layer of molecules by atomic and molecular forces (*Young and Crowell, 1962*). This attraction might have a physical or chemical characteristic (*Axley, 1991*). According to the different attractive force from the surface, adsorption can be classified as physical and chemical adsorptions. Physical adsorption relates relatively weak intermolecular Van der Waals forces and it is expected to be reversible, while chemical adsorption relates the interaction between the gas molecule and the solid surface and may not be reversible (*Ruthven, 1984*).

In this study, a material is functioning as an adsorbent and VOC as an adsorbate. It was assumed only physical adsorption occurs at the material/ air interface. At the interface, VOC interchanges between the adsorbed phase and the gas phase. The concentrations of absorbed phase and gas phase were assumed to be always at instantaneous equilibrium. This assumption was based on the observation of which the time scale for the surface adsorption and desorption to reach equilibrium was much smaller than that for diffusion process within the material (*Bodalal et al., 2000*). For isothermal conditions at atmospheric pressure, equilibrium relations between the concentrations of VOC in absorbed phase and in gas phase are identified as adsorption isotherms. Langmuir and BET are the most common isotherm models (*Masel, 1996*); however, at atmospheric pressure, for low VOC concentrations and isothermal conditions, all isotherms can be regarded as a linear isotherm (Equation 4-2).

$$C_{ad} = K \cdot C_{gas} \tag{4-2}$$

where:

C_{ad} is the VOC concentration in the absorbed phase(mg/m^3);

C_{gas} is the VOC concentration in gas phase (mg/m^3).

4.3 Data Analysis Method

4.3.1 Assumptions

In this study, several assumptions were made:

1) the air in chambers was assumed to be tally mixed. Since a large amount of airflow was introduced into the two chambers and the chamber volume is small, air in both chambers was identical in a short period of time;

2) the sink effects caused by tubes and chambers were ignored. The concentration of the outlet of an empty chamber was measured under an identical experimental

condition as a test. It was verified that difference between the VOC concentration measured at outlet and the VOC concentration introduced by a syringe pump was smaller than1 *mg/m*^{3};

3) the equilibrium between the surface concentration and the gas phase concentration always established instantaneously. This assumption was based on comparison between the time scale of diffusion processes within material and the surface adsorption and desorption. The former was much larger than the latter (*Bodalal et al., 2000*);

4) the concentration gradient in the material was assumed linear when the VOC concentration is at a low level (*Masel, 1996*).

4.3.2 Equations Used to Determine *D* and *K*

In this study, multi-phase approach is applied. VOC within the material is assumed to be in gas phase and/or absorbed phase. The VOC mass transfer within the material is mainly controlled by a gas diffusion process. D is a proportionality of flux and concentration gradient. Modified Fick's first law (Equation 4-3) can be applied to determine the diffusion coefficient under a steady-state condition.

$$D = -\frac{\dot{m}}{A} \cdot \frac{dx}{dC} = -\frac{\dot{V}\Delta x}{A} \cdot \frac{C_1}{C_1 - C_2} \tag{4-3}$$

where:

D is the diffusion coefficient (m^2/s) of the gas phase;

$\dot{m}$ is the mass flow through the material (mg/s);

A is the area of the sample material (m^2);

$\dot{V}$ is the volumetric flow rate through the material(m^3/s);

dx can be approximated as the thickness of the sample Δx (m);

dC can be approximated as the difference of VOC concentrations in two chambers ΔC (mg /m^3);

C_1 and C_2 are the VOC concentrations in the lower and upper chamber, respectively (mg /m^3) .

K ($mg \cdot m^{-3} / mg \cdot m^{-3}$) is a coefficient that describes the relationship between the concentrations of absorbed phase and gas phase. At atmospheric pressure, for low VOC concentration, linear isotherm, i.e., Henry isotherm, can be used to describe the relationship between the VOC concentrations in absorbed phase and in gas phase (Equation 4-2). Therefore, K can be calculated by the concentration of the absorbed phase divided by the concentration of gas phase. The VOC mass absorbed by material can be calculated from a mass balance within the chamber assembly (Equation 4-4).

$$m_{ad} = m_{in} - m_{out} \tag{4-4}$$

where:

m_{ad} is the VOC mass absorbed by testing material (mg);

m_{in} is the VOC mass into upper chamber (mg);

m_{out} is the VOC mass in air of both chambers (mg).

The mass of absorbed phase can be obtained by numerical integration (Equation 4-5)

$$m_{ad} = \sum_{1}^{n} \left[\dot{m}_{1i,in} - \left(\dot{m}_{1i,out} + \dot{m}_{2i,out} \right) \right] \cdot \Delta t_i = \sum_{1}^{n} \left[\dot{V}_{1i,in} \cdot C_{1i,in} - \left(\dot{V}_{1i,out} \cdot C_{1i,out} + \dot{V}_{2i,out} \cdot C_{2i,out} \right) \right] \cdot \Delta t_i$$

(4-5)

where:

i is the number of single measurement;

$\dot{m}_{1i,in}$, $\dot{m}_{1i,out}$, and $\dot{m}_{2i,out}$ are mass flow rates into the upper chamber, out of the upper chamber, and out of the lower chamber, respectively (mg/s);

$\dot{V}_{1i,in}$, $\dot{V}_{1i,out}$, and $\dot{V}_{2i,out}$ are volumetric flow rates into the upper chamber, out of the upper chamber, and out of the lower chamber, respectively (m^3/s);

$C_{1i,in}$, $C_{1i,out}$, and $C_{2i,out}$ are VOC concentrations into the upper chamber, out of the upper chamber, and out of the lower chamber, respectively (mg/m^3);

Δt_i is measurement time interval (s).

The concentration of gas phase is normalized by averaged the concentrations of both chamber air. This normalization is based on the assumption, which the concentration gradient within the test material is linear. To rearrange Equation (4-2) and (4-5), *K* can be determined by Equation (4-6).

$$K = \frac{C_{ad}}{C_{gas}} = \frac{1}{V} \cdot \frac{m_{ad}}{\overline{C}} = \frac{1}{V} \cdot \frac{\sum_{1}^{n} \left[\dot{V}_{1i,in} \cdot C_{1i,in} - \left(\dot{V}_{1i,out} \cdot C_{1i,out} + \dot{V}_{2i,out} \cdot C_{2i,out} \right) \right] \cdot \Delta t_i}{(C_1 + C_2)/2}$$

(4

-6

)

where:

V is the volume of the sample material (m^3);

$\overline{C}$ is the average concentration of air in the two chambers (mg/m^3).

4.3.3 Calculation Procedures

In a single compound test, the average background concentration was firstly calculated from a concentration- time curve. Then, the average background concentration was subtracted from the concentrations of both outlets in a test. When corrected concentrations versus time were plotted, the concentrations at a steady state condition could be determined from the plot and the average concentrations of both chambers air could be calculated. The diffusion coefficient was determined using Fick's first law (Eq. 4-3) and the partition coefficient was calculated using Eq. (4-6). In the mixture test, the concentrations of both chambers air under a steady state condition were determined by GC/FID and the acquisition system. The diffusion coefficients of each compound in a mixture were also calculated using Fick's first law(Eq. 4-3).

4.4 Results and Discussion

This section deals with the results obtained from the measurements of the diffusion and partition coefficients of single volatile organic compound (VOC) and VOC mixture through dry building materials. The results are presented in three subsections. The results of the diffusion measurements of a single compound for ceiling tile, gypsum board, and carpet with SBR backing are presented in subsection 4.4.1. The subsection 4.4.2 presents the results of VOC mixture in the ceiling tile. Finally, subsection 4.4.3 discusses the results of the diffusion measurements.

4.4.1 *D* and *K* for a Single Compound in a Building Material

In a single compound test, the diffusion and partition coefficients of toluene, isopropanol, and methanol for ceiling tile were determined; the diffusion and partition coefficients of methanol in gypsum board and carpet with SBR backing were measured. Tested VOCs and their physicochemical properties are listed in Table (4-1); the results of diffusion measurements and parameters related to the measurements are listed in Table (4-2). All experimental data are attached in Appendix I.

Table 4. 1 The physicochemical properties of tested VOCs

Compound name	Chemical formula	Molecular weight	Vapor pressure (mm-Hg) at 20°C	Boiling point (°C)	Polarity index (P)	D_a (10^6*m^2/s)
Methanol	CH_3OH	32.4	97	65	6.6	15.9
Toluene	$C_6H_5CH_3$	92.14	25.64	110	2.4	8.4
Isopropanol	C_3H_7OH	60	33	82.2	4.3	10

D_a: Schifftner (2002)

Table 4. 2 Tested materials and D and K of single compounds in tested materials

Materials	Thickness (10^2*m)	VOC compound	Injected concentration (mg/m^3)	Diffusion coefficients (10^6*m^2/s)		Partition coefficients (mgm^{-3}/mgm^{-3})	
					Average		Average

Ceiling tile	1.17	Toluene	26.2	7.04 6.95	7.00	840 852	846
	1.13	Isopropanol	31.44	1.56 1.56	1.56	1390 1408	1399
	1.13	Methanol	30.82	1.94 1.96	1.95	3692 3668	3680
Gypsum board	1.29			2.57 2.55	2.56	3571 3668	3620
Carpet with SBR backing	0.351			0.91 0.90	0.91	9890 9889	9890

4.4.2 *D* of Toluene, Methanol, and Isopropanol Mixture in Ceiling Tile

Air samples were collected from the outlets of both chambers when equilibrium reached, then, sent to the analytical unit to determine their concentrations. Likewise, diffusion coefficients of VOC in the mixture were calculated using Fick's first law. The results are listed in Table (4-3).

Table 4. 3 Diffusion coefficients of toluene, methanol, and isopropanol in ceiling tile

Material name	Compound name	Inject concentration (mg/m^3)	Diffusion coefficient (10^6*m^2/s)	
				Average
Ceiling tile	Toluene	26.01	2.37 2.28	2.33
	Isopropanol	3.93	0.324 0.327	0.326
	Methanol *	11.88		
	Toluene	4.33	1.53 2.25	1.89
	Isopropanol	27.51	0.380 0.360	0.370
	Methanol *	7.92		

*: The Tekmar tube is low affinity of methanol, so methanol is not included in this mixture test.

4.4.3 Discussion

The diffusion and partition coefficients measured with a single compound and a mixture and the physicochemical properties of the tested materials and VOCs can be found in Tables (4-2) and (4-3).

4.4.3.1 Relationship Between Molecular Weight and Vapor Pressure of VOC and *D*, *K* measured with a single compound

The clear tendency of the diffusion coefficients of different VOCs for a given material, i.e., ceiling tile, obtained in this study with molecular weight, vapor pressure, and polarity of VOCs cannot be found (Figures 4-1, 4-2 and 4-3). However, the partition coefficients of different VOCs through given materials are proportional to the increase of vapor pressure, the increasing of polarity, and the decrease of molecular weight of VOC (Figures 4-4, 4-5 and 4-6).

Diffusion coefficients of methanol through different materials can be ranked according to diffusion speed. Gypsum board possesses the highest diffusion coefficient among the three tested materials, followed by ceiling tile and carpet.

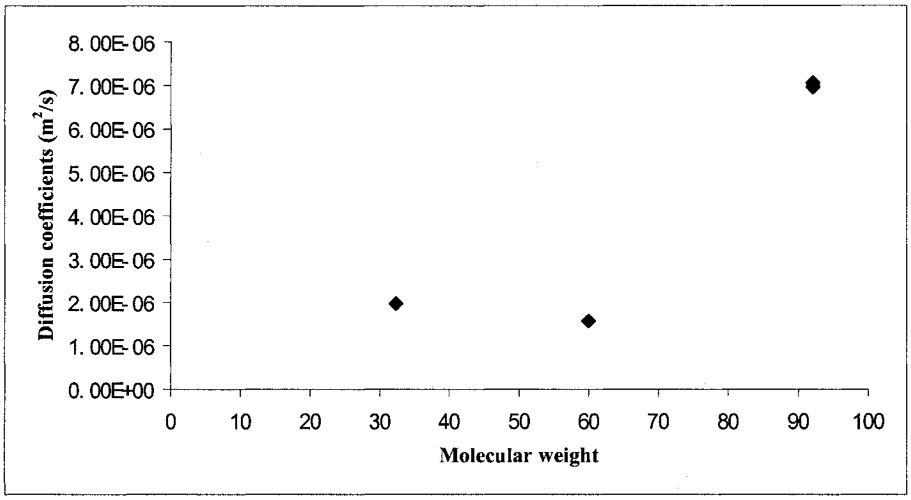


Figure 4. 1 Diffusion coefficients versus molecular weight

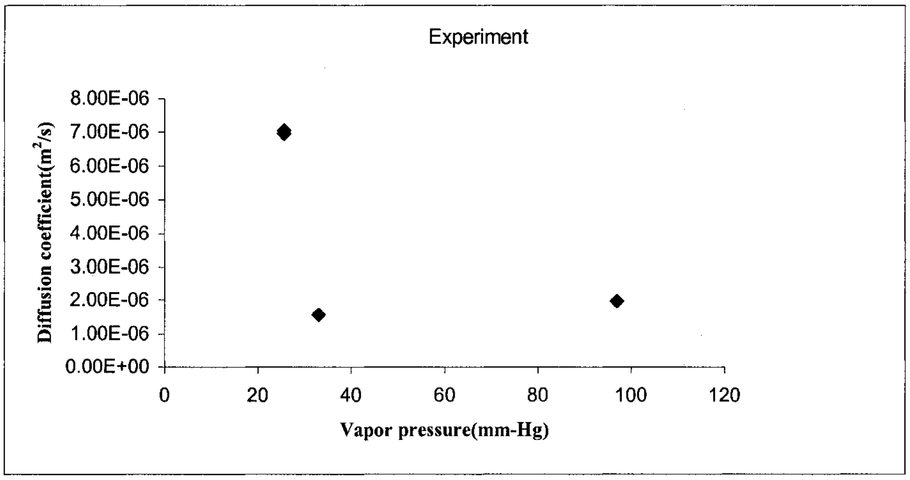


Figure 4. 2 Diffusion coefficients versus vapor pressure

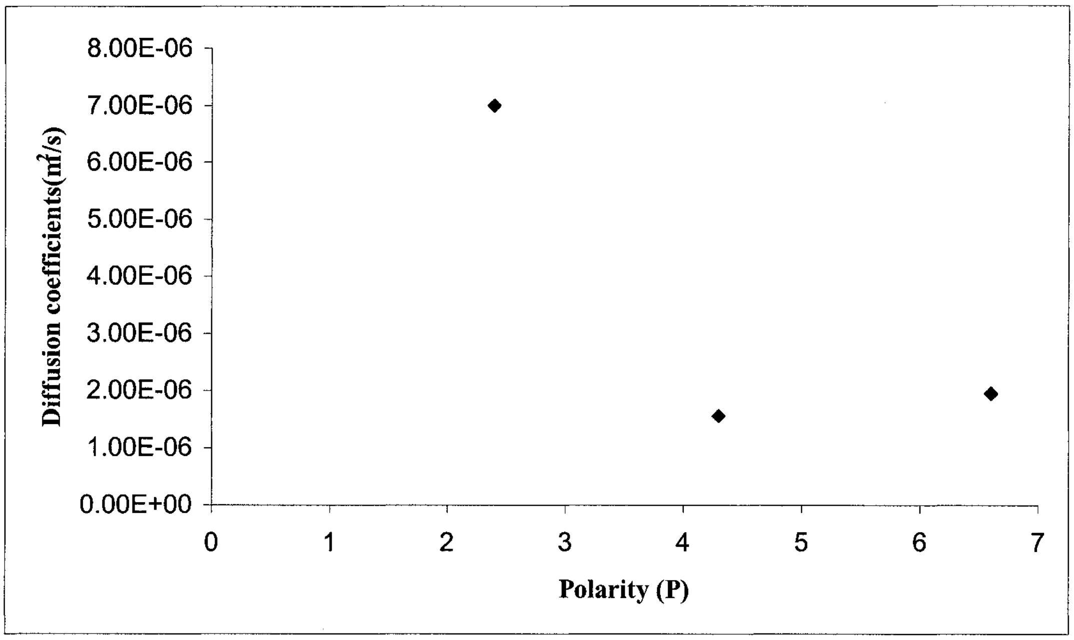


Figure 4. 3 Diffusion coefficients versus polarity

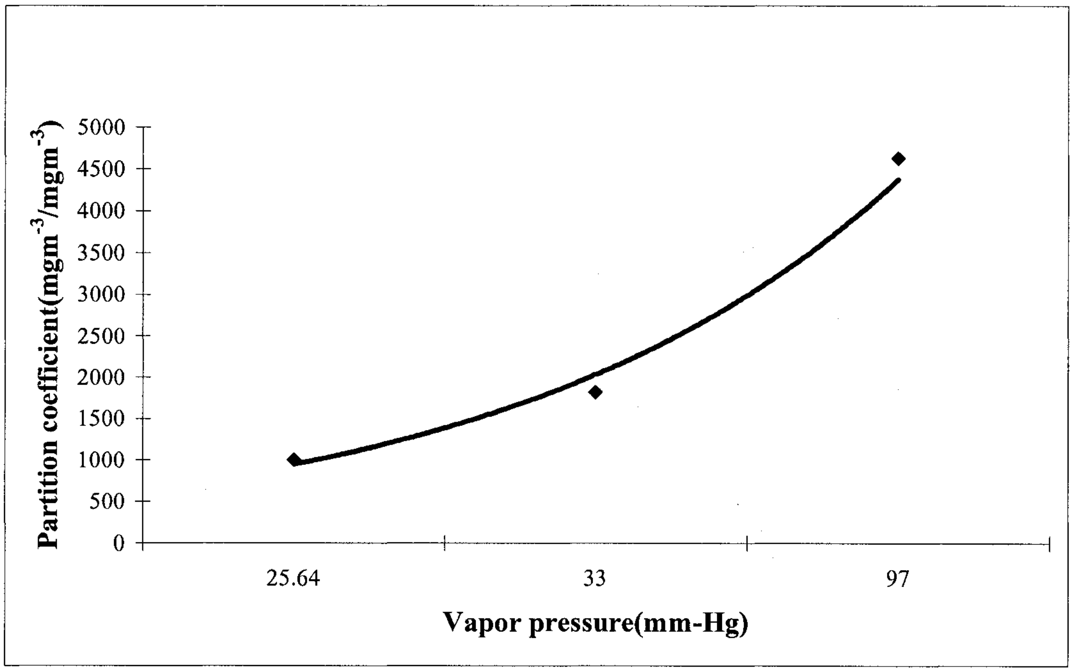


Figure 4. 4 Partition coefficient versus vapor pressure

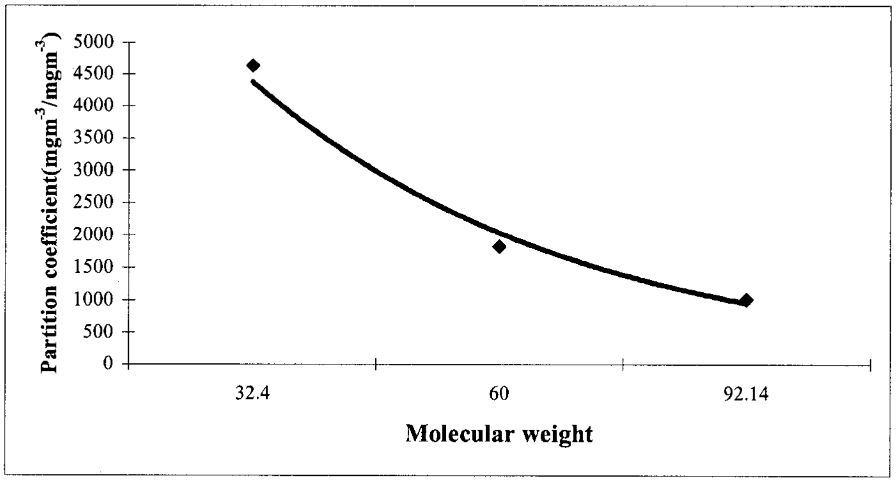


Figure 4. 5 Partition coefficients versus molecular weight

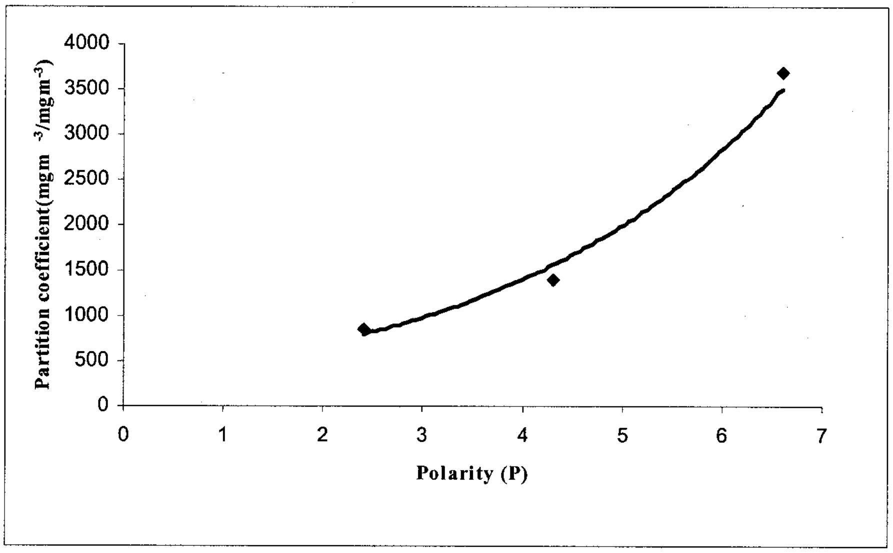


Figure 4. 6 Partition coefficients versus polarity

4.4.3.2 Comparisons of D and K Measured with a Single Compound and a Mixture

From Tables (4-2) and (4-3), differences between diffusion coefficients of a VOC in a single compound test and a mixture test can be observed. In the first mixture test, in which the volume proportion of toluene, methanol, to isopropanol were 60%, 30%, to 10%, respectively, the inlet concentration of toluene was set to 26.01*mg/m*^{3}, while the inlet concentration of isopropanol was 3.93*mg/m*^{3}. Under this condition, the diffusion coefficients of toluene and isopropanol in ceiling tile were 2.33E-06 m^2/s, 3.26E-07m^2/s, respectively. The two diffusion coefficients were smaller than those in a single compound test. In the second mixture test, which the volume proportion of toluene, methanol, and isopropanol were 10%, 20%, and 70%, respectively, the inlet concentration of isopropanol was set to 27.51*mg/m*^{3}, while the concentration of toluene was 4.33*mg/m*^{3}. Under this condition, the diffusion coefficients of toluene and isopropanol were 1.89E-06 m^2/s, 3.70E-07 m^2/s, respectively. They were also smaller than those in a single compound test. Moreover, with the increase of VOC concentration, its diffusion coefficient slightly went up. The results showed that mixture affected the diffusive process. Mixture, concentration change of tested VOC, and their physicochemical properties like polarity and molecular structure, may be the factors affecting the results. Further investigations are needed.

4.4.3.3 Comparison of D and K from the Experiments and Literatures

After study of VOC diffusion in soil under transient and steady state conditions has been conducted (*Batterman et al., 1996*), it is concluded that diffusion coefficients under transient and steady state conditions are different. Transient condition is closer to real indoor air condition than steady state condition, but the transient condition is difficult to interpret. In the course of literature review, diffusion coefficients under both conditions were found. Diffusion coefficients in this presented research were obtained under steady state conditions.

When the tested materials and VOC are not identical, direct comparison is impossible. The same VOCs and material used to obtain diffusion coefficients in this study cannot be found in the course of literature review. However, comparisons of the ratio of diffusion coefficient in air (D_a) to diffusion coefficients of material (D_s) can also provide cross-comparison of the diffusion coefficients among different VOCs.

Table 4-5 shows the ratios of D_a to D_s. In the previous review on diffusion coefficients (*Haghighat et al., 2002*) showed that the ratios of D_a to D_s of gypsum board range from 5.6 to 7.52 in the twin chamber method. The ratio of D_a to D_s of gypsum board obtained in this study is 6.21. The result obtained in this research shows good agreement with the ratios found in literature. In CLIMPAQ method, the ratios of carpet are 17.1 and 18.8, respectively (*Haghighat et al., 2002*). The ratio of D_a to D_s of carpet is 17.53, which is much closer to the literature data.

The ratios of D_a to D_s for different VOC obtained from Tiffonnet et al. (*2000*) were almost constant for the same material (*Haghighat et. al., 2002*). That means the authors did not consider interaction between gas molecular and materials. However, the different ratios of D_a to D_s among toluene, methanol, and isopropanol for ceiling tile in the present study were found. That is, interactions between gas molecular and materials exist. Hence, the diffusion coefficients obtained by Tiffonnet et al. (*2000*) may be overestimation for polar compounds.

Diffusion coefficients in air considered the effects caused by molecular weight and boiling point in an estimate equation (Equation 4-7) (*Perry et al., 1973*).

$$D_a = \frac{BT^{3/2}\sqrt{(1/M_1)+(1/M_2)}}{\mathrm{Pr}_{12}^2 I_D} \tag{4-7}$$

where:

D_a is diffusion coefficient in air, m^2/s;

B is $(10.85 - 2.50\sqrt{1/M_1 + 1/M_2}) \times 10^{-4}$;

T is absolute temperate, K;

M_1, M_2 are molecular weights of components 1 and 2, respectively;

$r_{12} = (\frac{(r_0)_1 + (r_0)_2}{2})$ is collision diameter, angstroms;

r_0 is $1.18V_b^{1/3}$;

V_b is molal volume of liquid at normal boiling point, cc./gmole;

I_d is collision integral for diffusion, function of kT/ε_{12};

$\frac{\varepsilon_{12}}{k} = \sqrt{\left(\frac{\varepsilon_1}{k}\right)\left(\frac{\varepsilon_2}{k}\right)}$;

k is Boltzmann constant 1.38E-06 erg/K;

ε_{12} is energy of molecular interaction, ergs.

Polarity was not considered in the estimation of D_a. However, Figure (4-7) shows the ratios of D_a to D_s of the ceiling tile increase with the increasing of polarities of VOCs. Moreover, the relationship between D_a/D_s and polarity of VOC can be verified by data in literature. The polarity index of n-octane and ethyl acetate are 0.4 and 4.3, respectively. In the CLIMPAQ method, D_a/D_s of ethyl acetate is larger than that of n-octane for concrete, wall-paper with paste, carpet, acrylic paint on woodchip paper, and gypsum board (*Haghighat et al., 2002*). Therefore, polarity is an important factor that should be considered in diffusion measurements.

Table 4. 4 Tested VOCs and the ratios of *D* in air to *D* of materials

Diffusion coefficients (m^2/s)						Ratios (D_a/D_s)		
Material	VOC	For air (D_a*10^6)	For a single compound ($D_{ss}*10^6$)	For a mixture ($D_{sm}*10^6$)		D_a/D_{ss}	D_a/D_{sm}	
Ceiling tile	Methanol	15.9	1.95	---	---	8.15	---	---
	Isopropanol	10	1.56	0.326	0.37	6.41	30.67	27.03
	Toluene	8.4	7	2.33	1.89	1.2	3.60	4.44
Gypsum board	Methanol	15.9	2.56			6.21		
Carpet with SBR backing			0.907			17.53		

D_a (Schifftner, 2002)

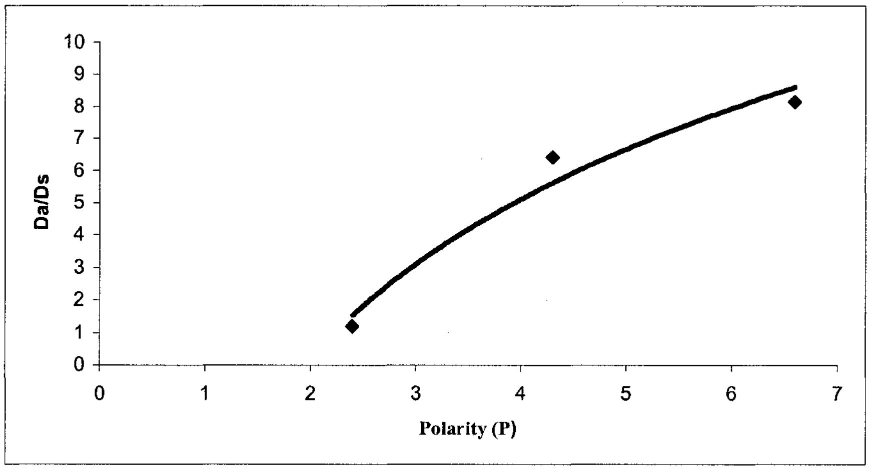


Figure 4. 7 D_a/D_s versus polarity

Bodalal et al (2000) said "it was found that the values of the diffusion coefficients for a given material are inversely proportional to the molecular weights of the

VOCs". However, the conclusion cannot be verified in this presented research. Diffusion coefficients of methanol and isopropanol through ceiling tile show that diffusion coefficients increase with the decreasing of VOC molecular weight for the given material. However, the diffusion coefficient of toluene in ceiling tile does not respect the similarity. Bodalal et al. (*2000*) applied a least-squares regression technique using experimental data to obtain diffusion and partition coefficients. As *D* and *K* were obtained through curve fitting at the same time, the *D* and *K* have a risk of multiple solutions. However, the diffusion and partition coefficients in this research were obtained separately, so the results avoid having a risk of inter-dependence. Therefore, the diffusion and partition coefficients obtained by Bodalal et al.(*2000*) are probably not reliable. Further investigations are required. Moreover, the molecular structure and polarity of the VOC may be the factors affecting diffusion coefficients. Since toluene is aromatic-hydrocarbon and methanol and isopropanol are aliphatic- alochol, their functional groups and molecular structure are different. From Equation (4-7), diameter of VOC molecule and collision diameter of air to VOC can be estimated. Diameter of air molecule is 3.617 Angstroms (*Perry et al., 1973*). The difference of molecular weight of toluene and isopropanol, which are 92.14 and 60, respectively, is significant. However, the difference of collision diameters (r_{12}) of toluene to air and isopropanol to air, which are 4.70 Angstroms, 4.32 Angstroms, respectively, is not large. Moreover, the value ($\frac{1}{r_{12}^2}$) of toluene to air and isopropanol to air, which are 0.045, 0.054, respectively, are much closer. Hence, collision diameters may affect diffusion coefficients, not only the molecular weight. This may explain in this study, toluene did not follow the rule found by Bodalal et al. (*2000*). Besides, polarity may be one of factors affected diffusion coefficients. Bodalal et al (2000) selected VOCs with similar polarity, so they did not consider the effects of polarity on *D*. However, three VOCs with different polarities were chosen in the presented study. The results obtained in the study showed polarity affected *D*. In addition, the value of diffusion coefficients for a given materials did not show clear trend of the diffusion speed with polarities of VOCs (Figure 4-4). The reason is that *D* is affected by molecular weight, boiling point, and polarity. However, which factor dominates the effect cannot be observed in this presented study. Further investigations are needed. Meininghaus et al. (*2002*) stated "diffusion of less polar VOCs in gypsum board can be fast". This statement cannot be verified in this study and further investigations are also required.

Likewise, since the identical VOCs and test materials cannot be found in the course of literature review, direct comparison is impossible. However, in this presented research, the partition coefficients increase with the increasing of vapour pressures of VOCs (Figure 4-2), which is opposite to the relationship found by Bodalal et al.(*2000*). Since Bodalal et al.(2000) selected VOCs with similar polarities in their research, they did not consider the effect of polarity on *K*. However, VOCs with wide ranges of polarity were chosen in the presented study. The results show *K* are proportional to the polarities of VOCs (Figure 4-6). Therefore, polarity significantly affects *K*. The trend can be verified using the data obtained by

Meininghaus et al.(2000).

Partition coefficient is an equilibrium coefficient of sorption and desorption processes. The amount of VOC adsorbed by material surface depends on the physicochemical properties, such as, volatility, polarity, and environmental parameter, such as, room temperature, as well as their affinity of material surface (*Alevantis et. al., 1996*). The results obtained in this study show that polarity is a crucial factor that greatly affects partition coefficients.

Chapter 5 Conclusions and Recommendations

5.1 Summary

The objective of this study was to conduct experimental investigation on the diffusion measurement of VOC for dry building materials by selecting a two-chamber method with two-flow system. Strong attention was paid to the relationships of the physicochemical properties of VOCs and diffusion and partition coefficients. These provided much information of accurately predicting diffusion and/or partition coefficients.

In this presented research, three different VOCs through a given material were under investigations; a VOC in three types of building materials were observed; a VOC mixture in a building material was investigated. Volatile organic compounds considered in this study included toluene, methanol, and isopropanol; building materials included ceiling tile, gypsum board, and carpet with SBR backing. Diffusion coefficients were determined by Fick's first law of diffusion; partition coefficients were calculated based on the difference between the mass flow into upper chamber and out of upper and lower chambers. To reach the validation of the method used in this study, a few assumptions were made. These assumptions included: totally mixed chamber air; ignored sink effects caused by tube and chamber system; the instantaneous equilibrium between the surface concentration and the gas phase concentration; and the linear concentration gradient in the material .

Five diffusion and partition coefficients for a single compound were calculated; diffusion coefficients for a mixture were determined. Moreover, the relationships between physicochemical properties of VOCs and diffusion coefficients, partition coefficients were analyzed. In addition, diffusion speeds of a VOC through three kinds of building materials were ranked.

5.2 Conclusions

The conclusions of this thesis study are summarized as following:

- Since diffusion and partition coefficients were obtained separately in the analysis of the experimental data, they were not inter-dependent unlike a previously proposed method (*Bodalal et al, 2000*), which obtain both properties simultaneously through curve fitting.

- Diffusion coefficients of different VOCs at a given material were not always proportional to the decreasing of molecular weight of VOCs. In this study, diffusion coefficient of toluene in ceiling tile was an exception since it did not respect the rule stated by Bodalal et al. (*2000*).

- The ratio of diffusion coefficient in air (D_a) to diffusion coefficient in material (D_s) provided cross-comparisons of diffusion coefficients among the different VOCs. D_a/D_s increases with the increasing of polarity of VOCs.

- In diffusion measurements, the interaction between VOC and building materials should be considered.

- Polarity significantly affects partition coefficients.
- Polarity of VOC is a crucial factor that affects partition coefficients and the ratio of D_a to D_s.
- Diffusion coefficients of methanol through different materials can be ranked. Gypsum board showed the highest diffusion coefficient among the three test materials, followed by ceiling tile and carpet.
- Diffusion coefficient of a VOC measured in a single compound test is different from it obtained from a mixture test. The diffusion coefficients of isopropanol and toluene in a mixture test are smaller than those obtained in a single compound test.

5.3 Recommendations

- In a mixture test, the effects of constituents, concentrations, and physicochemical properties of VOCs on material properties, need to be further investigated. The results showed that the mixture affected the data of diffusion coefficients. However, which factors dominate the difference between diffusion coefficients for a single compound and a mixture is not clear.
- Further investigation should be made on the effects caused by environmental parameters, such as temperature and humidity. The results in this study were obtained at a constant temperature and humidity. Effects of environment

parameters have not been considered in this study. Haghighat et al.(*2002*) pointed out that minor effect on diffusion coefficients can be caused by little differences of temperature. However, since temperature and humidity vary from one location to another and season by season, relationships between environment parameters and diffusion and partition coefficients will provide some information for accurately predicting of emission rate of building material.

- More building materials popularly used indoors and volatile organic compounds frequently found indoors should be considered in diffusion measurements. If a database of diffusion and partition coefficients can be established, it will give useful information to researchers and users.

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Appendix I

Experimental Data for Single Test

- **Toluene through ceiling tile**

Table I. 1 Experimental data of toluene concentrations of both chambers air

Time(min)	C_B(mg/m^3)*	C^1_2(mg/m^3)*	C_2(mg/m^3)	C^1_1(mg/m^3)*	C_1(mg/m^3)
	2.26	0	0	0	0
	2.26	4.1	1.84		
0	2.26	4.1	1.84	2.34	0.08
2	2.26	4.4	2.14	2.34	0.08
4	2.26	4.4	2.14	2.43	0.17
6	2.26	5.42	3.16	2.43	0.17
8	2.26	5.42	3.16	2.35	0.09
10	2.26	6.78	4.52	2.35	0.09
12	2.26	6.78	4.52	2.81	0.55
14	2.26	8.38	6.12	2.81	0.55
16	2.26	8.38	6.12	2.62	0.36
18	2.26	14.3	12.04	2.62	0.36
20	2.26	14.3	12.04	2.94	0.68
22	2.26	16.3	14.04	2.94	0.68
24	2.26	16.3	14.04	3.13	0.87
26	2.26	17.9	15.64	3.13	0.87
28	2.26	17.9	15.64	3.67	1.41
30	2.26	18.3	16.04	3.67	1.41
32	2.26	18.3	16.04	3.85	1.59
34	2.26	18.3	16.04	3.85	1.59
36	2.26	19.5	17.24	3.97	1.71
38	2.26	19.5	17.24	3.97	1.71
40	2.26	19.5	17.24	4.28	2.02
42	2.26	19.5	17.24	4.28	2.02
44	2.26	18.6	16.34	4.34	2.08
46	2.26	18.6	16.34	4.34	2.08
48	2.26	19.6	17.34	4.34	2.08
50	2.26	19.6	17.34	4.38	2.12
52	2.26	18.7	16.44	4.38	2.12
54	2.26	18.7	16.44	4.17	1.91
56	2.26	20.2	17.94	4.17	1.91
58	2.26	20.2	17.94	5.09	2.83
60	2.26	20.1	17.84	5.09	2.83
62	2.26	20.1	17.84	4.97	2.71

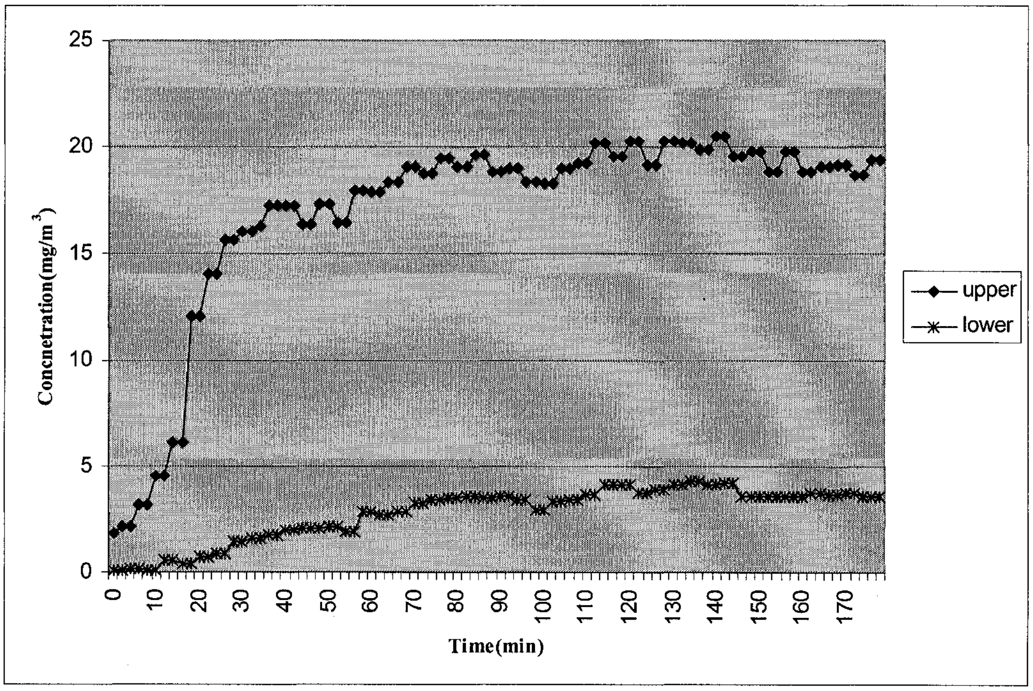
64	2.26	20.6	18.34	4.97	2.71
66	2.26	20.6	18.34	5.11	2.85
68	2.26	21.3	19.04	5.11	2.85
70	2.26	21.3	19.04	5.48	3.22
72	2.26	21	18.74	5.48	3.22
74	2.26	21	18.74	5.65	3.39
76	2.26	21.7	19.44	5.65	3.39
78	2.26	21.7	19.44	5.74	3.48
80	2.26	21.3	19.04	5.74	3.48
82	2.26	21.3	19.04	5.8	3.54
84	2.26	21.9	19.64	5.8	3.54
86	2.26	21.9	19.64	5.74	3.48
88	2.26	21.1	18.84	5.74	3.48
90	2.26	21.1	18.84	5.8	3.54
92	2.26	21.2	18.94	5.8	3.54
94	2.26	21.2	18.94	5.68	3.42
96	2.26	20.6	18.34	5.68	3.42
98	2.26	20.6	18.34	5.22	2.96
100	2.26	20.5	18.24	5.22	2.96
102	2.26	20.5	18.24	5.59	3.33
104	2.26	21.2	18.94	5.59	3.33
106	2.26	21.2	18.94	5.7	3.44
108	2.26	21.5	19.24	5.7	3.44
110	2.26	21.5	19.24	5.88	3.62
112	2.26	22.4	20.14	5.88	3.62
114	2.26	22.4	20.14	6.35	4.09
116	2.26	21.8	19.54	6.35	4.09
118	2.26	21.8	19.54	6.35	4.09
120	2.26	22.5	20.24	6.35	4.09
122	2.26	22.5	20.24	5.98	3.72
124	2.26	21.4	19.14	5.98	3.72
126	2.26	21.4	19.14	6.17	3.91
128	2.26	22.5	20.24	6.17	3.91
130	2.26	22.5	20.24	6.38	4.12
132	2.26	22.4	20.14	6.38	4.12
134	2.26	22.4	20.14	6.51	4.25
136	2.26	22.1	19.84	6.51	4.25
138	2.26	22.1	19.84	6.39	4.13
140	2.26	22.7	20.44	6.39	4.13
142	2.26	22.7	20.44	6.48	4.22
144	2.26	21.8	19.54	6.48	4.22
146	2.26	21.8	19.54	5.87	3.61
148	2.26	22	19.74	5.87	3.61
150	2.26	22	19.74	5.83	3.57
152	2.26	21.1	18.84	5.83	3.57
154	2.26	21.1	18.84	5.86	3.6
156	2.26	22	19.74	5.86	3.6
158	2.26	22	19.74	5.84	3.58
160	2.26	21.1	18.84	5.84	3.58
162	2.26	21.1	18.84	6	3.74
164	2.26	21.3	19.04	6	3.74
166	2.26	21.3	19.04	5.9	3.64

168	2.26	21.4	19.14	5.9	3.64
170	2.26	21.4	19.14	6.02	3.76
172	2.26	20.9	18.64	6.02	3.76
174	2.26	20.9	18.64	5.83	3.57
176	2.26	21.6	19.34	5.83	3.57
178	2.26	21.6	19.34	5.87	3.61

* C_B is the average concentration of background contamination.

C^1_l, C^1_2 are the concentrations of lower and upper chambers before subtracting C_B, respectively.

Figure I. 1 A plot of concentrations of toluene versus time



- ## Methanol through ceiling tile

Table I. 2 The methanol concentrations of both chambers air

Correction equation: $C_l=0.25C_{lread}+0.066$

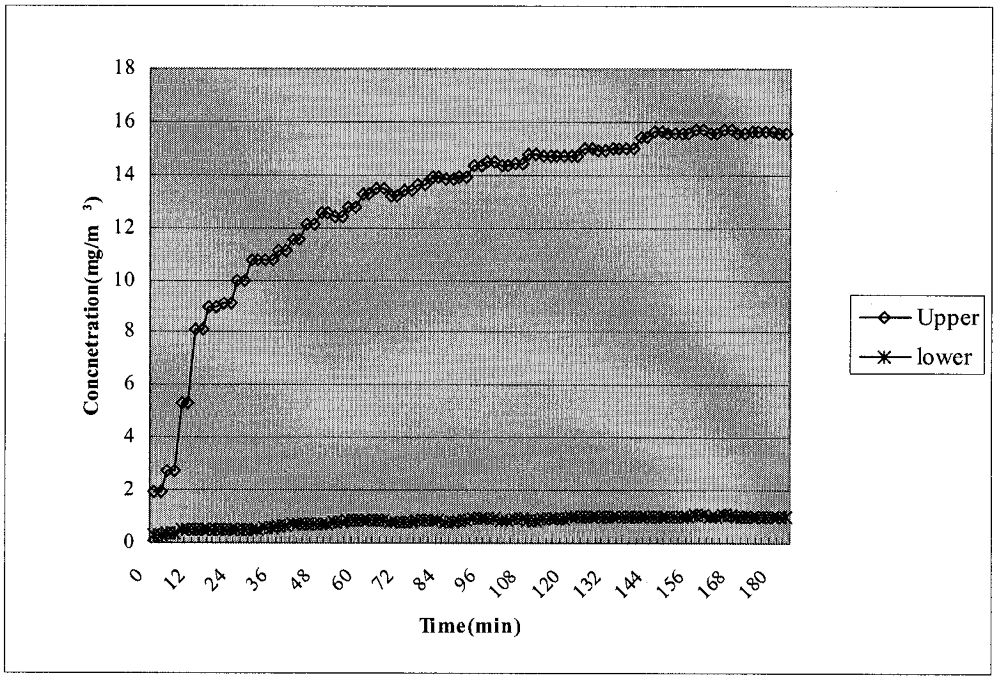
Time(min)	C2read(mg/m3)	Clread(mg/m3)	C2(mg/m3)	Cl(mg/m3)
0	7.58	1	1.961	0.316
2	7.58	1	1.961	0.316
4	10.6	1.29	2.716	0.3885

6	10.6	1.29	2.716	0.3885
8	21.1	1.7	5.341	0.491
10	21.1	1.7	5.341	0.491
12	32.1	1.76	8.091	0.506
14	32.1	1.76	8.091	0.506
16	35.5	1.67	8.941	0.4835
18	35.5	1.67	8.941	0.4835
20	36.2	1.76	9.116	0.506
22	36.2	1.76	9.116	0.506
24	39.7	1.82	9.991	0.521
26	39.7	1.82	9.991	0.521
28	42.8	1.8	10.766	0.516
30	42.8	1.8	10.766	0.516
32	42.9	1.94	10.791	0.551
34	42.9	1.94	10.791	0.551
36	44.1	2.3	11.091	0.641
38	44.1	2.3	11.091	0.641
40	46	2.48	11.566	0.686
42	46	2.48	11.566	0.686
44	48.1	2.53	12.091	0.6985
46	48.1	2.53	12.091	0.6985
48	50	2.73	12.566	0.7485
50	50	2.73	12.566	0.7485
52	49.5	2.95	12.441	0.8035
54	49.5	2.95	12.441	0.8035
56	50.8	3.17	12.766	0.8585
58	50.8	3.17	12.766	0.8585
60	52.8	3.12	13.266	0.846
62	52.8	3.12	13.266	0.846
64	53.7	3.13	13.491	0.8485
66	53.7	3.13	13.491	0.8485
68	52.4	2.97	13.166	0.8085
70	52.4	2.97	13.166	0.8085
72	53.5	3.01	13.441	0.8185
74	53.5	3.01	13.441	0.8185
76	54.1	3.26	13.591	0.881
78	54.1	3.26	13.591	0.881
80	55.5	3.24	13.941	0.876

82	55.5	3.24	13.941	0.876
84	55	3.03	13.816	0.8235
86	55	3.03	13.816	0.8235
88	55.5	3.23	13.941	0.8735
90	55.5	3.23	13.941	0.8735
92	57.1	3.49	14.341	0.9385
94	57.1	3.49	14.341	0.9385
96	57.8	3.52	14.516	0.946
98	57.8	3.52	14.516	0.946
100	57.2	3.32	14.366	0.896
102	57.2	3.32	14.366	0.896
104	57.5	3.33	14.441	0.8985
106	57.5	3.33	14.441	0.8985
108	58.8	3.26	14.766	0.881
110	58.8	3.26	14.766	0.881
112	58.4	3.35	14.666	0.9035
114	58.4	3.35	14.666	0.9035
116	58.6	3.56	14.716	0.956
118	58.6	3.56	14.716	0.956
120	58.6	3.65	14.716	0.9785
122	58.6	3.65	14.716	0.9785
124	59.6	3.72	14.966	0.996
126	59.6	3.72	14.966	0.996
128	59.4	3.62	14.916	0.971
130	59.4	3.62	14.916	0.971
132	59.6	3.69	14.966	0.9885
134	59.6	3.69	14.966	0.9885
136	59.8	3.72	15.016	0.996
138	59.8	3.72	15.016	0.996
140	61.3	3.75	15.391	1.0035
142	61.3	3.75	15.391	1.0035
144	62.4	3.86	15.666	1.031
146	62.4	3.86	15.666	1.031
148	62.1	3.8	15.591	1.016
150	62.1	3.8	15.591	1.016
152	62.1	3.81	15.591	1.0185
154	62.1	3.81	15.591	1.0185
156	62.6	4	15.716	1.066

158	62.6	4	15.716	1.066
160	62	3.86	15.566	1.031
162	62	3.86	15.566	1.031
164	62.5	3.94	15.691	1.051
166	62.5	3.94	15.691	1.051
168	62.1	3.85	15.591	1.0285
170	62.1	3.85	15.591	1.0285
172	62.4	3.81	15.666	1.0185
174	62.4	3.81	15.666	1.0185
176	62.4	3.89	15.666	1.0385
178	62.4	3.89	15.666	1.0385
180	62.1	3.85	15.591	1.0285
182	62.1	3.85	15.591	1.0285

Figure I. 2 A plot of concentrations of methanol versus time



- ## Isopropanol through ceiling tile

Table I. 3 The isopropanol concentrations of both chambers air

Correction equation: C_I=0.306 $C_I$read +0.079

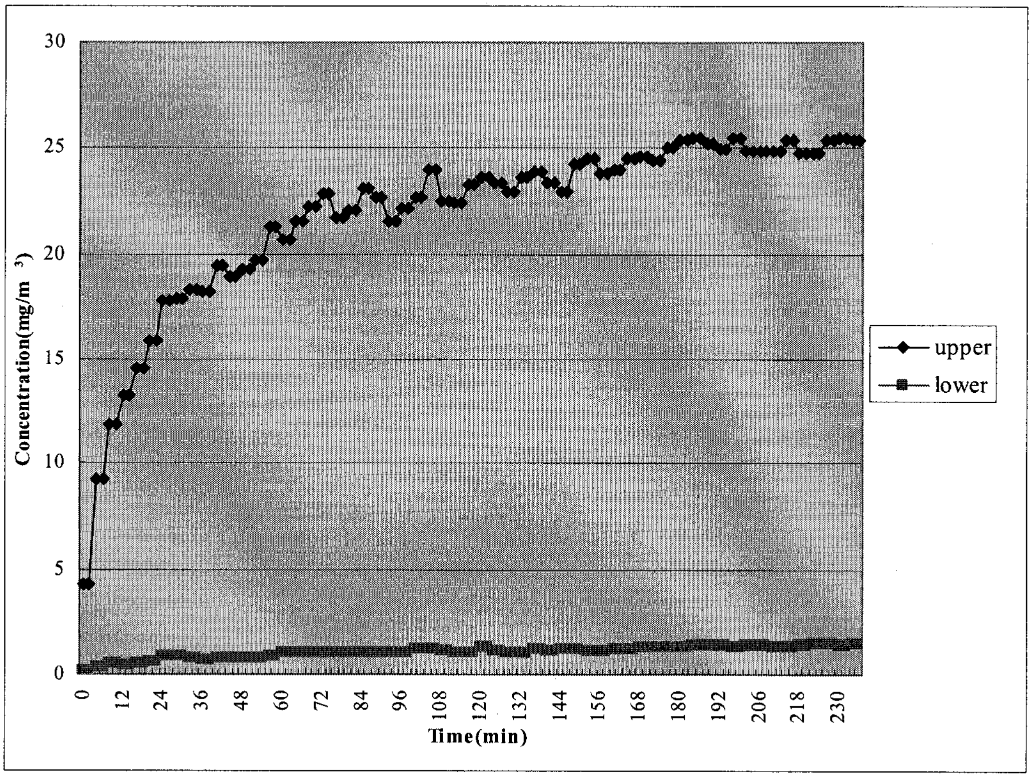
Time(min)	C_2read(mg/m3)	C_1read(mg/m3)	C_2(mg/m3)	C_1(mg/m3)
0	13.8	3.33E-01	4.3018	1.81E-01
2	13.8	3.33E-01	4.3018	1.81E-01
4	30	9.90E-01	9.259	3.82E-01
6	30	9.90E-01	9.259	3.82E-01
8	38.4	1.49E+00	11.8294	5.35E-01
10	38.4	1.49	11.8294	5.35E-01
12	43	1.20E+00	13.237	4.46E-01
14	43	1.2	13.237	4.46E-01
16	47.2	1.55E+00	14.5222	5.53E-01
18	47.2	1.55	14.5222	5.53E-01
20	51.7	1.66	15.8992	5.87E-01
22	51.7	1.66	15.8992	5.87E-01
24	57.8	2.57	17.7658	8.65E-01
26	57.8	2.57	17.7658	8.65E-01
28	58.2	2.64	17.8882	8.87E-01
30	58.2	2.64	17.8882	8.87E-01
32	59.6	2.24	18.3166	7.64E-01
34	59.6	2.24	18.3166	7.64E-01
36	59.4	2.16	18.2554	7.40E-01
38	59.4	2.16	18.2554	7.40E-01
40	63.3	2.24	19.4488	7.64E-01
42	63.3	2.24	19.4488	7.64E-01
44	61.7	2.33	18.9592	7.92E-01
46	61.7	2.33	18.9592	7.92E-01
48	62.6	2.34	19.2346	7.95E-01
50	62.6	2.34	19.2346	7.95E-01
52	64.1	2.38	19.6936	8.07E-01
54	64.1	2.38	19.6936	8.07E-01
56	69.2	2.7	21.2542	9.05E-01
58	69.2	2.7	21.2542	9.05E-01
60	67.3	3.13	20.6728	1.04E+00
62	67.3	3.13	20.6728	1.04E+00
64	70.1	3.15	21.5296	1.04E+00
66	70.1	3.15	21.5296	1.04E+00
68	72.4	3.26	22.2334	1.08E+00
70	72.4	3.26	22.2334	1.08E+00

72	74.3	3.03	22.8148	1.01E+00
74	74.3	3.03	22.8148	1.01E+00
76	70.7	3.15	21.7132	1.04E+00
78	70.7	3.15	21.7132	1.04E+00
80	71.8	3.17	22.0498	1.05E+00
82	71.8	3.17	22.0498	1.05E+00
84	75.2	3.21	23.0902	1.06E+00
86	75.2	3.21	23.0902	1.06E+00
88	73.7	3.07	22.6312	1.02E+00
90	73.7	3.07	22.6312	1.02E+00
92	70	3.05	21.499	1.01E+00
94	70	3.05	21.499	1.01E+00
96	72.1	3.12	22.1416	1.03E+00
98	72.1	3.12	22.1416	1.03E+00
100	73.9	3.64	22.6924	1.19E+00
102	73.9	3.64	22.6924	1.19E+00
104	78	3.69	23.947	1.21E+00
106	78	3.69	23.947	1.21E+00
108	73.2	3.39	22.4782	1.12E+00
110	73.2	3.39	22.4782	1.12E+00
112	73	3.19	22.417	1.06E+00
114	73	3.19	22.417	1.06E+00
116	75.8	3.25	23.2738	1.07E+00
118	75.8	3.25	23.2738	1.07E+00
120	77.1	3.93	23.6716	1.28E+00
122	77.1	3.93	23.6716	1.28E+00
124	76.1	3.56	23.3656	1.17E+00
126	76.1	3.56	23.3656	1.17E+00
128	74.8	3.27	22.9678	1.08E+00
130	74.8	3.27	22.9678	1.08E+00
132	76.9	3.29	23.6104	1.09E+00
134	76.9	3.29	23.6104	1.09E+00
136	77.9	3.67	23.9164	1.20E+00
138	77.9	3.67	23.9164	1.20E+00
140	76.1	3.57	23.3656	1.17E+00
142	76.1	3.57	23.3656	1.17E+00
144	74.7	3.78	22.9372	1.24E+00
146	74.7	3.78	22.9372	1.24E+00

148	79.1	3.65	24.2836	1.20E+00
150	79.1	3.65	24.2836	1.20E+00
152	79.7	3.54	24.4672	1.16E+00
154	79.7	3.54	24.4672	1.16E+00
156	77.6	3.45	23.8246	1.13E+00
158	77.6	3.45	23.8246	1.13E+00
160	78.2	3.82	24.0082	1.25E+00
162	78.2	3.82	24.0082	1.25E+00
164	79.8	3.84	24.4978	1.25E+00
166	79.8	3.84	24.4978	1.25E+00
168	80	3.99	24.559	1.30E+00
170	80	3.99	24.559	1.30E+00
172	79.5	4.13	24.406	1.34E+00
174	79.5	4.13	24.406	1.34E+00
176	81.5	3.96	25.018	1.29E+00
178	81.5	3.96	25.018	1.29E+00
180	82.6	3.99	25.3546	1.30E+00
182	82.6	3.99	25.3546	1.30E+00
184	82.9	4.19	25.4464	1.36E+00
186	82.9	4.19	25.4464	1.36E+00
188	82	4.4	25.171	1.43E+00
190	82	4.4	25.171	1.43E+00
192	81.2	4.29	24.9262	1.39E+00
194	81.2	4.29	24.9262	1.39E+00
196	83.1	4.1	25.5076	1.33E+00
198	83.1	4.1	25.5076	1.33E+00
202	81	4.4	24.865	1.43E+00
204	81	4.4	24.865	1.43E+00
206	81	4.16	24.865	1.35E+00
208	81	4.16	24.865	1.35E+00
210	81	4.06	24.865	1.32E+00
212	81	4.06	24.865	1.32E+00
214	82.7	4	25.3852	1.30E+00
216	82.7	4	25.3852	1.30E+00
218	80.8	4.25	24.8038	1.38E+00
220	80.8	4.25	24.8038	1.38E+00
222	80.7	4.51	24.7732	1.46E+00
224	80.7	4.51	24.7732	1.46E+00

226	82.7	4.48	25.3852	1.45E+00
228	82.7	4.48	25.3852	1.45E+00
230	83	4.41	25.477	1.43E+00
232	83	4.41	25.477	1.43E+00
234	82.6	4.57	25.3546	1.48E+00
236	82.6	4.57	25.3546	1.48E+00
238	82.6	4.57	25.3546	1.48E+00

Figure I. 3 A plot of concentrations of isopropanol versus time



Methanol through gypsum board

Table I. 4 The methanol concentrations of both chambers air

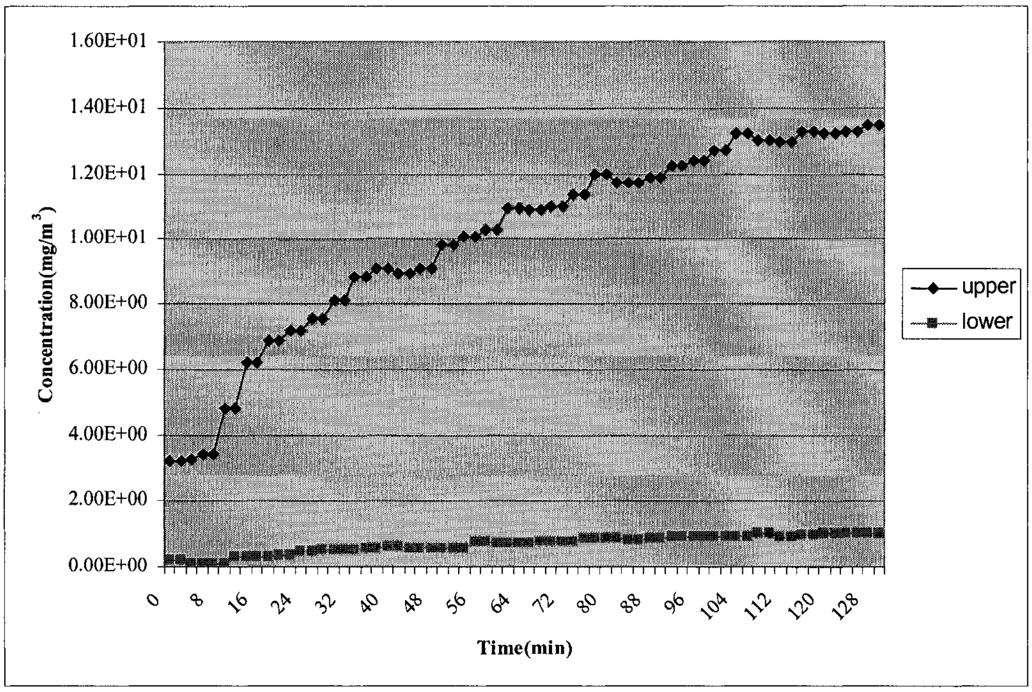
Correction equation: $C_1=0.25C_{1read}+0.066$

Time(min)	C_2read(mg/m3)	C_1read(mg/m3)	C_2(mg/m3)	C_1(mg/m3)
0	12.5	4.76E-01	3.19E+00	1.85E-01
2	12.5	4.76E-01	3.19E+00	1.85E-01
4	12.8	2.11E-01	3.27E+00	1.19E-01
6	13.3	2.11E-01	3.39E+00	1.19E-01
8	13.3	1.89E-01	3.39E+00	1.13E-01
10	19	1.89E-01	4.82E+00	1.13E-01
12	19	1	4.82E+00	3.16E-01

14	24.5	1	6.19E+00	3.16E-01
16	24.5	1.02	6.19E+00	3.21E-01
18	27.2	1.02	6.87E+00	3.21E-01
20	27.2	1.12	6.87E+00	3.46E-01
22	28.5	1.12	7.19E+00	3.46E-01
24	28.5	1.61	7.19E+00	4.69E-01
26	29.8	1.61	7.52E+00	4.69E-01
28	29.8	1.84	7.52E+00	5.26E-01
30	32.2	1.84	8.12E+00	5.26E-01
32	32.2	1.86	8.12E+00	5.31E-01
34	35.1	1.86	8.84E+00	5.31E-01
36	35.1	2.11	8.84E+00	5.94E-01
38	36.1	2.11	9.09E+00	5.94E-01
40	36.1	2.31	9.09E+00	6.44E-01
42	35.4	2.31	8.92E+00	6.44E-01
44	35.4	2.03	8.92E+00	5.74E-01
46	36	2.03	9.07E+00	5.74E-01
48	36	2.03	9.07E+00	5.74E-01
50	38.9	2.03	9.79E+00	5.74E-01
52	38.9	2.09	9.79E+00	5.89E-01
54	40	2.09	1.01E+01	5.89E-01
56	40	2.77	1.01E+01	7.59E-01
58	40.9	2.77	1.03E+01	7.59E-01
60	40.9	2.55	1.03E+01	7.04E-01
62	43.5	2.55	1.09E+01	7.04E-01
64	43.5	2.59	1.09E+01	7.14E-01
66	43.2	2.59	1.09E+01	7.14E-01
68	43.2	2.81	1.09E+01	7.69E-01
70	43.8	2.81	1.10E+01	7.69E-01
72	43.8	2.87	1.10E+01	7.84E-01
74	45.2	2.87	1.14E+01	7.84E-01
76	45.2	3.28	1.14E+01	8.86E-01
78	47.6	3.28	1.20E+01	8.86E-01
80	47.6	3.18	1.20E+01	8.61E-01
82	46.5	3.18	1.17E+01	8.61E-01
84	46.5	3.11	1.17E+01	8.44E-01
86	46.5	3.11	1.17E+01	8.44E-01
88	47.2	3.28	1.19E+01	8.86E-01
90	47.2	3.28	1.19E+01	8.86E-01
92	48.6	3.47	1.22E+01	9.34E-01
94	48.6	3.47	1.22E+01	9.34E-01
96	49.3	3.52	1.24E+01	9.46E-01
98	49.3	3.52	1.24E+01	9.46E-01
100	50.5	3.35	1.27E+01	9.04E-01
102	50.5	3.35	1.27E+01	9.04E-01
104	52.6	3.55	1.32E+01	9.54E-01
106	52.6	3.55	1.32E+01	9.54E-01
108	51.7	3.82	1.30E+01	1.02E+00
110	51.7	3.82	1.30E+01	1.02E+00
112	51.5	3.52	1.29E+01	9.46E-01
114	51.5	3.52	1.29E+01	9.46E-01

116	52.7	3.6	1.32E+01	9.66E-01
118	52.7	3.6	1.32E+01	9.66E-01
120	52.6	3.89	1.32E+01	1.04E+00
122	52.6	3.89	1.32E+01	1.04E+00
124	52.8	3.85	1.33E+01	1.03E+00
126	52.8	3.85	1.33E+01	1.03E+00
128	53.6	3.88	1.35E+01	1.04E+00
130	53.6	3.88	1.35E+01	1.04E+00

Figure I. 4 A plot of concentrations of methanol versus time



• Methanol through carpet with SBR backing

Table I. 5 The methanol concentrations of both chambers air

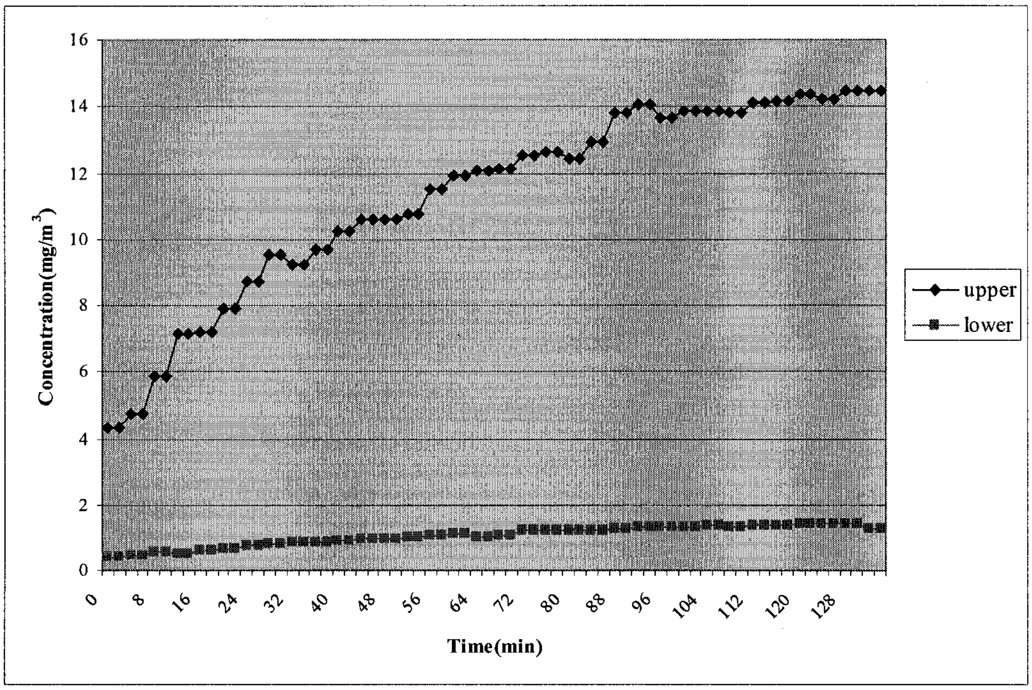
Correction equation: $C_1=0.25C_{1read}+0.066$

Time(min)	C_2read(mg/m3)	C_1read(mg/m3)	C_2(mg/m3)	C_1(mg/m3)
0	17	1.43	4.316	0.4235
2	17	1.43	4.316	0.4235
4	18.6	1.53	4.716	0.4485
6	18.6	1.53	4.716	0.4485
8	23.1	2.01	5.841	0.5685
10	23.1	2.01	5.841	0.5685
12	28.3	1.76	7.141	0.506
14	28.3	1.76	7.141	0.506
16	28.5	2.24	7.191	0.626
18	28.5	2.24	7.191	0.626

20	31.3	2.38	7.891	0.661
22	31.3	2.38	7.891	0.661
24	34.5	2.89	8.691	0.7885
26	34.5	2.89	8.691	0.7885
28	37.8	2.91	9.516	0.7935
30	37.8	2.91	9.516	0.7935
32	36.6	3.16	9.216	0.856
34	36.6	3.16	9.216	0.856
36	38.4	3.14	9.666	0.851
38	38.4	3.14	9.666	0.851
40	40.8	3.48	10.266	0.936
42	40.8	3.48	10.266	0.936
44	42.2	3.58	10.616	0.961
46	42.2	3.58	10.616	0.961
48	42.1	3.59	10.591	0.9635
50	42.1	3.59	10.591	0.9635
52	42.8	3.79	10.766	1.0135
54	42.8	3.79	10.766	1.0135
56	45.9	4.02	11.541	1.071
58	45.9	4.02	11.541	1.071
60	47.4	4.17	11.916	1.1085
62	47.4	4.17	11.916	1.1085
64	48	3.89	12.066	1.0385
66	48	3.89	12.066	1.0385
68	48.2	4.02	12.116	1.071
70	48.2	4.02	12.116	1.071
72	49.9	4.64	12.541	1.226
74	49.9	4.64	12.541	1.226
76	50.2	4.53	12.616	1.1985
78	50.2	4.53	12.616	1.1985
80	49.4	4.59	12.416	1.2135
82	49.4	4.59	12.416	1.2135
84	51.6	4.64	12.966	1.226
86	51.6	4.64	12.966	1.226
88	55	4.84	13.816	1.276
90	55	4.84	13.816	1.276
92	56	5.11	14.066	1.3435
94	56	5.11	14.066	1.3435
96	54.3	4.96	13.641	1.306
98	54.3	4.96	13.641	1.306
100	55.1	5.03	13.841	1.3235
102	55.1	5.03	13.841	1.3235
104	55.1	5.24	13.841	1.376
106	55.1	5.24	13.841	1.376
108	54.9	4.99	13.791	1.3135
110	54.9	4.99	13.791	1.3135
112	56.1	5.22	14.091	1.371
114	56.1	5.22	14.091	1.371
116	56.3	5.3	14.141	1.391
118	56.3	5.3	14.141	1.391
120	57.3	5.36	14.391	1.406

122	57.3	5.36	14.391	1.406
124	56.7	5.37	14.241	1.4085
126	56.7	5.37	14.241	1.4085
128	57.6	5.48	14.466	1.436
130	57.6	5.48	14.466	1.436
132	57.6	4.85	14.466	1.2785
134	57.6	4.85	14.466	1.2785
136	58	4.87	14.566	1.2835
140	58	4.87	14.566	1.2835
142	58	4.87	14.566	1.2835

Figure I. 5 A plot of concentrations of methanol versus time



Appendix II

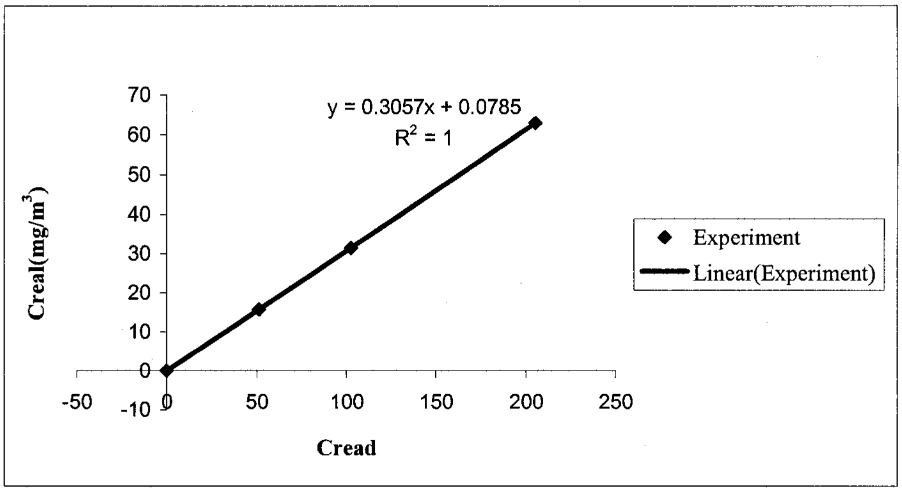
Multi-gas monitor calibration with methanol and isopropanol

1 Multi-gas monitor calibration on methanol

1.1 **Table II. 1Experimental data of injection concentrations of isopropanol and its read value**

Injection concentration(mg/m^3)	Read value	Average read value
0	-0.234	-0.258
	-0.25	
	-0.248	
	-0.3	
15.72	51.10	51.13
	51.00	
	51.30	
31.44	102.12	102.63
	102.23	
	102.20	
	103.97	
62.88	205.20	205.4
	206.00	
	205.00	

1.2 **Figure II. 1 Calibration curve for GC with methanol**

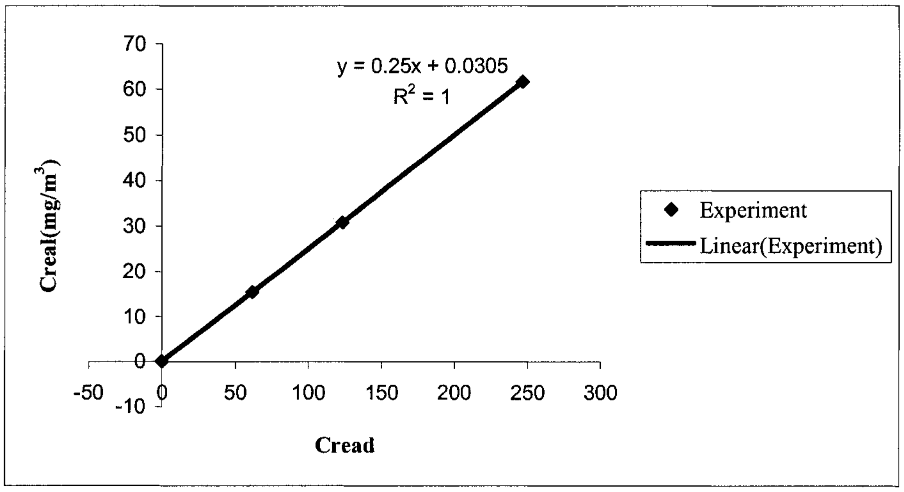


2. **Multi-gas monitor calibration with methanol**

2.1 **Table II. 2Experimental data of injection concentrations of methanol and its read value**

Injection concentration(mg/m^3)	Read value	Average read value
0	-0.215	-0.263
	-0.268	
	-0.255	
	-0.243	
	-0.335	
15.41	61.50	61.39
	61.20	
	61.50	
30.82	123	123.31
	123	
	124	
	123.24	
61.64	245.67	246.31
	246.00	
	247.26	

2.2 **Figure II. 2Calibration curve for GC with isopropanol**

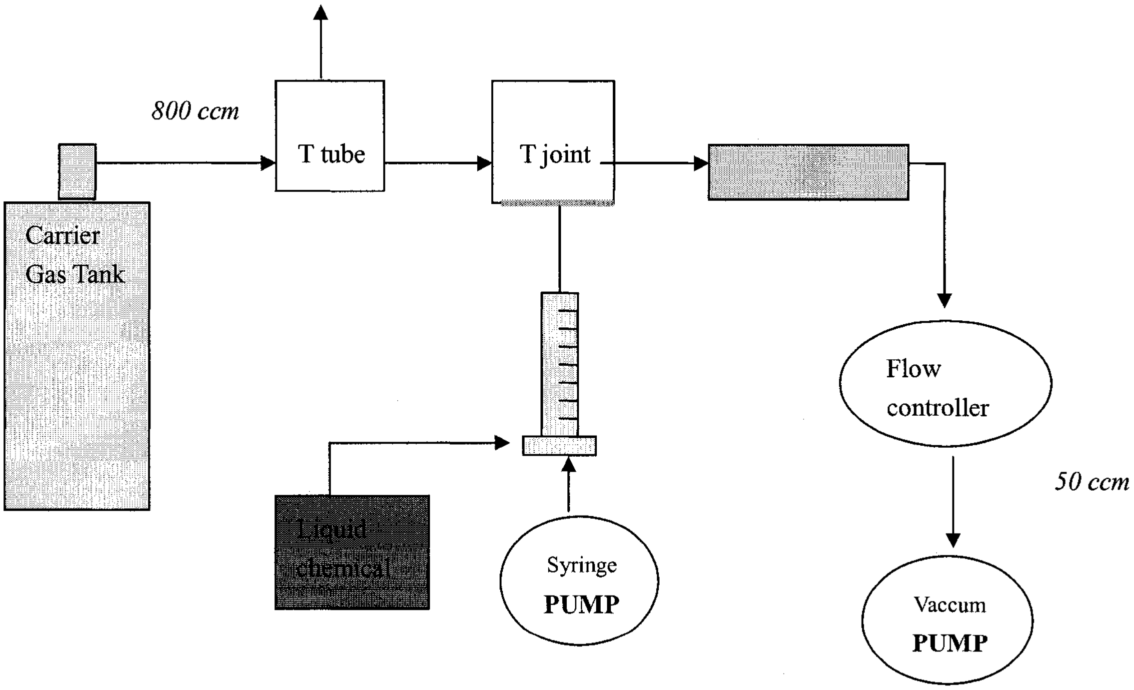

y = 0.25x + 0.0305
$R^2 = 1$
Creal(mg/m^3)
70
60
50
40
30
20
10
0
-10
-50
0
50
100
150
200
250
300
Cread
◆ Experiment
Linear(Experiment)

Appendix III

Experimental data of GC calibration with toluene, isopropanol, and methanol and air sample analysis

1. GC calibration with toluene, isopropanol, and methanol

1.1 **Figure III. 1Schematic figure of sample collecting for GC calibration**



GC calibration procedures

- To set carrier gas flow rate as 800ccm and absorbing flow rate as 50ccm.

- To slowly inject 0.1 μl liquid toluene into T joint.
- To collect air sample for 5 minutes.
- To determine retention time of toluene by analyzing the air sample using GC/FID analyzer.
- To determine retention time of isopropanol and methanol by repeating above procedures.
- To mix toluene, methanol, and isopropanol with different proportion.
- To inject mixture into T joint
- To collect and analyze air samples
- To record peak area.
- To plot peak area-mass

1.3 **Table III. 1 Experimental data of mixture test**

Injection compound	Volume (μl)	Density (mg/μl)	Mass (mg)	Peak area
Methanol*	0.1	0	0	0
		0.1584	0.01584	566601
		0.2376	0.02376	392840
		0.396	0.0396	276334
Isopropanol	0.1	0	0	0
		0.0786	0.00786	1.37E+07
		0.1572	0.01572	1.41E+07
		0.5502	0.05502	9.71E+07
Toluene	0.1	0	0	0.00E+00
		0.0867	0.00867	2.90E+07
		0.2601	0.02601	4.40E+07
		0.5202	0.05202	1.85E+08
		0.867	0.0867	2.59E+08

*: Since the absorbent in Tekmar tube is low affinity of methanol, the data of methanol in the calibration is not trustable. Methanol is not taken consideration in the GC calibration.

1.4 Calibration Curve

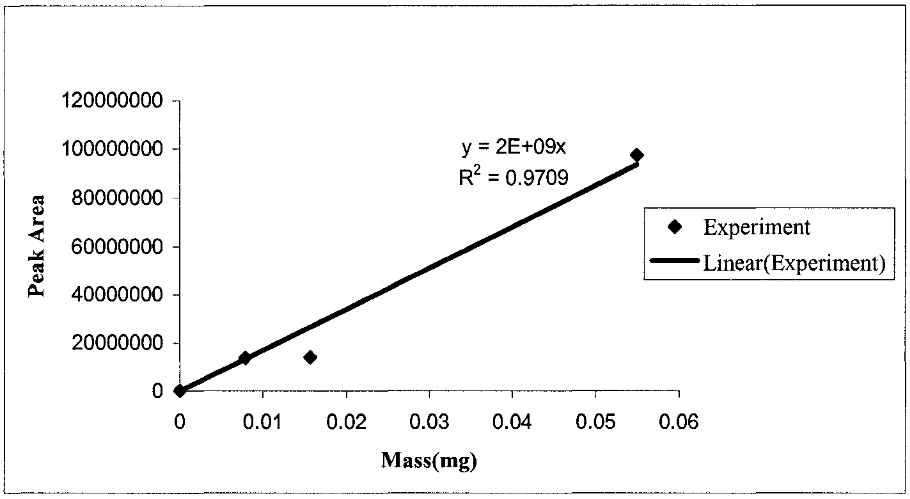


Figure III. 2 GC calibration with isopropanol

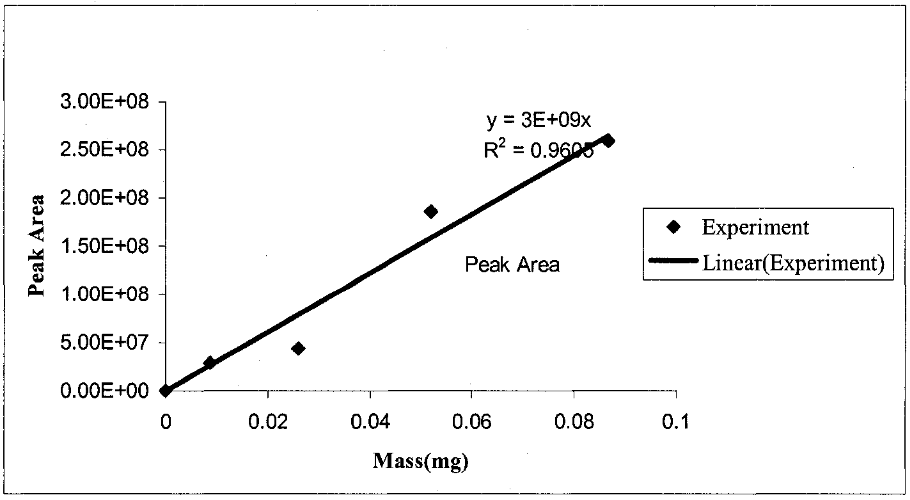


Figure III. 3 GC calibration with toluene

2. Experimental data for mixture test

The thickness of ceiling tile is 1.17E-02 m; its the surface area is 1.37E-02 m^2.

Table III. 2 Experimental data of mixture test

Mixture		Peak area		Mass (mg)		Volume (ml)		Concentration (mg/m^3)		
		Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper	D (m^2/s)
T 60% M 30% I 10%	T	2.28E+06	2.64E+07	0.000761507	0.0088	450	400	1.692238519	22	2.37239E-06
		4.10E+06	2.52E+07	0.001366667	0.0084	840	350	1.626984127	21.96	2.27808E-06
	I	18336	1434154	0.000009168	0.000717077	450	400	0.020373333	1.792693	3.27271E-07
		34892	1290242	0.000017446	0.000645121	840	350	0.020769048	1.843203	3.24453E-07
T 10% M 20% I 70%	T	105359	491561	3.51197E-05	0.000163854	1000	238	0.035119667	0.688461	1.53037E-06
		21195	68660	0.000007065	2.28867E-05	950	225	0.007436842	0.101719	2.24568E-06
	I	22944	414957	0.000011472	0.000207479	1000	238	0.011472	0.871758	3.7965E-07
		2231	42234	1.1155E-06	0.000021117	950	225	0.001174211	0.093853	3.60704E-07

T: toluene, M: methanol, I: isopropanol