

**An Experimental Investigation on the Indoor Environmental  
Conditions on Diffusion Coefficient of VOCs in Building Materials**

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## Abstract

### **An Experimental Investigation on the Indoor Environmental Conditions on Diffusion Coefficient of VOCs in Building Materials**

**Yashar Farajollahi**

After the energy crisis in 1973, efforts were made to design constructions more airtight to be energy efficient. Since then, sick building syndrome (SBS) has been reported more often as a result of poor indoor air quality (IAQ). Among the proposed strategies to improve IAQ, source control is determined to be the most effective approach. Because of their large surface areas permanently exposed to the indoor environment, building materials are suspected of playing an important role in determining IAQ. Source-specific control, however, requires adequate knowledge about the extent of volatile organic compounds (VOC) emissions of materials so that in decision-making stages, only products with lower emission rates will be chosen and installed. Hence, knowing the characteristics of building materials (diffusion and partition coefficients) is necessary. Moreover, these data are needed as input parameters for VOC emission simulations, which presently suffer from the lack of a database of emission characteristics of materials. Therefore, this study has characterize building materials by measuring their diffusion coefficients ( $D$ ) in different environmental conditions.

Based on the twin-chamber method, an experimental set-up was developed to determine the  $D$  of five VOCs (octane, isopropanol, cyclo hexane, ethyl acetate, and hexane) for ceiling tile as the building material. By using Fick's law,  $D$  was calculated and linked to

physicochemical properties of VOCs. The method used also allowed us to investigate the influence of temperature, humidity, and the mixture of VOCs on  $D$ . Based on obtained results, a systematic parametric study was conducted to quantify the importance of investigated factors.

It was found that among different physicochemical properties, the  $D$  is positively related to vapor pressure. Additionally, no significant difference was observed between the  $D$  of a single VOC and that of a mixture of VOCs. Also, it was observed that temperature and humidity (in the range of a typical indoor environment) had a minor effect on the measured  $D$ .

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# List of Symbols

$A$	material area ( $m^2$ )
$C$	concentration of diffusing substance ( $mg/m^3$ )
$C_1$	VOC concentration in the primary (contaminated air supplied) chamber ( $mg/m^3$ )
$C_2$	VOC concentration in the secondary (clean air supplied) chamber ( $mg/m^3$ )
$C_{ad}$	VOC adsorbed phase concentration in the material ( $\mu g$ of adsorbed phase $VOC/m^3$ of material)
$C_{gas}$	VOC gas phase concentration in the near material surface air ( $\mu g/m^3$ )
$C_i(x)$	concentration of gas in the material pores at distance $x$ from surface ( $kg/m^3$ )
$C_{i=l}$	gas concentration at a distance $h$ from the surface ( $kg/m^3$ )
$C_m$	VOC material phase concentration in the material phase ( $\mu g/m^3$ )
$C_{s,i=1,2}$	concentration of air close to the surface of the material ( $kg/m^3$ )
$D$	diffusion coefficient ( $m^2/s$ )
$D_{eff}$	effective diffusion coefficient ( $m^2/s$ )
$D_{gas}$	VOC gas phase diffusion coefficient within the material ( $m^2/s$ )
$D_m$	VOC material phase diffusion coefficient ( $m^2/s$ )

$D_s$	VOC solid phase diffusion coefficient ( $\text{m}^2/\text{s}$ )
$d$	material thickness (m)
$f$	function describing sorption isotherm
$h$	utilized grid distance inside the material (m)
$J$	one-dimensional diffusion flux per unit area ( $\text{kg}/\text{m}^2 \cdot \text{s}$ )
$K$	VOC adsorbed / gas phase partition coefficient ( $\mu\text{gm}^{-3}/\mu\text{gm}^{-3}$ )
$k_B$	Boltzmann constant (J/K)
$K_g$	mass transfer coefficient between bulk air and air close to surface (m/s)
$K_m$	VOC material phase / gas phase partition coefficient ( $\mu\text{gm}^{-3}/\mu\text{gm}^{-3}$ )
$Kn$	dimensionless Knudsen number
$L$	pore diameter (m)
$MW$	molecular weight (g)
$m$	molar mass (kg)
$\dot{m}$	mass flow rate through the material (mg/s)
$p$	pressure (Pa)
$Q$	total discharge of fluid ( $\text{m}^3/\text{s}$ ),
$q_{i=1,2}$	chamber air flow ( $\text{m}^3/\text{s}$ )
$SS$	sum of squares
$T$	absolute temperature (K)
$t$	time (s)
$V$	chamber volume ( $\text{m}^3$ )
$\dot{V}$	ventilation rate ( $\text{m}^3/\text{s}$ )
$x$	distance along which diffusion takes place (m)

$Y_i(x)$	local concentration of compound inside the material at distance $x$ from surface ( $\text{kg/m}^3$ )
$Y_s$	surface concentration of adsorbed compounds ( $\text{kg/m}^3$ )
$y$	coordinate in which diffusion takes place (m)
$\alpha$	aspect ratio of the solid flakes
$\alpha_i$	average treatment effect of factor $A$ at level $a_i$
$\beta_j$	average treatment effect of factor $B$ at level $b_j$
$(\alpha\beta)_{ij}$	interaction effect of the $i^{\text{th}}$ level of factor $A$ and the $j^{\text{th}}$ level of factor $B$
$\nabla P$	pressure gradient vector (Pa/m)
$\varepsilon$	fraction of pores of the cross-sectional area
$\varepsilon_{ij}$	experimental error associated with each score
$\kappa$	permeability of the medium ( $\text{m}^2$ )
$\lambda$	mean free path of the diffusing molecules (m)
$\mu$	viscosity of fluid (Pa.s)
$\mu_T$	overall population mean
$\rho_b$	bulk density ( $\text{kg/m}^3$ )
$\sigma_{ii}$	collision diameter of the diffusing molecules (m)
$\tau$	tortuosity factor
$\phi$	volume fraction of the solid flakes
$\omega^2$	standard omega squared

# Chapter 1

## Introduction

### 1.1 Indoor Air Quality Concerns

Over the past several years, indoor air pollution and its impacts on human health have become a major global issue and have increasingly captured attention. After the energy crisis in 1973, efforts were made to design more airtight constructions in order to be efficient in terms of energy conservation (Stellman, 1998). That meant letting in a smaller proportion of fresh air from the outside and consequently minimizing the costs of heating and cooling of building enclosures. Although insufficient intake of fresh air in recently constructed buildings is not the only reason for poor indoor air quality (IAQ), sick building syndrome (SBS), obviously, has been reported more often since energy conservation policies were adopted and implemented. Buildings subject to complaints of occupants about symptoms are described as “sick buildings” (Godish, 1995; U.S. EPA, 1991).

Indoor environmental pollution has been ranked by the United States Environmental Protection Agency (EPA) as one of the top four environmental risks posing a significant threat to public health. It has been evidenced that indoor environments are more sensitive than outdoor air in even the most industrialized cities. At the same time, it has been shown that since people spend most of their time living and working indoors, they are



exposed to this high concentration of pollutants for 80% to 90% of their lifetime (U.S. EPA, 1995). Moreover, long-term exposure to even low levels of pollution, compared with short-term exposure to individual higher concentrations, could be more harmful and still does have an adverse impact on population health (Holmeberg, 1997).

In addition to the above mentioned health issues, the financial aspects of poor IAQ are estimated at tens of billions of U.S. dollars per year (Levin, 1999). Considering only office workers in the U.S., poor air quality could result in costs of \$12.4 to 24.8 billion/year because of absenteeism and \$1.5 to 3.1 billion/year due to reduced productivity of non-absent workers with respiratory illness. Obviously, sick buildings cost society more than what is gained through energy saving. Needless to say, the economic damage resulting from IAQ problems affect all stakeholders, including designers, builders, product manufacturers, building owners, occupants, and insurance institutions.

## **1.2 Indoor Air Contaminants and Their Origins**

It is impossible to completely cover all indoor contaminants and their sources within the scope of this study. However, the myriad known indoor air contaminants, whose existence in indoor environment leads to unacceptable IAQ and subsequent SBS, could be preliminarily classified into two main sources, namely interior air and exterior air (Brooks & Davis, 1992). Exterior sources contains thousands of contaminants including chemicals from industrial emissions, automobile exhaust, agricultural activities, atmospheric photochemical phenomena, and bioaerosols from natural microbial growth. Ventilation system intakes, ventilation through doors and windows, and infiltration

through the building envelope are possible pathways for exterior contaminants to find their way indoors. Apart from these outdoor contaminants present in indoor air, there are pollutant species unique to indoor environments, including volatile organic compounds (VOCs) and particulates from building materials, furnishings, appliances, office equipment, office/residential cleaning supplies, biological sources, indoor human activities, and defective ventilation systems (Pluschke, 2004).

### **1.2.1 Volatile Organic Compounds (VOCs)**

Volatile organic compounds are substances that contain carbon and different portions of other elements such as hydrogen, oxygen, fluorine, chlorine, bromine, sulfur and nitrogen. The boiling point of these compounds falls in the range of 50-100 to 240-260°C (WHO, 1989); under normal indoor conditions, therefore, they have high enough vapor pressure to significantly evaporate into indoor air.

VOCs in indoor environments include aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and oxygenated hydrocarbons such as aldehydes, alcohol, ketones, esters, ethers, and acids. The VOCs emitted from the wide variety of sources mentioned in the previous section are suspected to be the leading cause of SBS symptoms (Godish, 1995). First, many VOCs can cause both sensory irritation and central nervous system symptoms characteristic of SBS. Second, concentrations of these compounds in indoor air is significantly higher (2-100 times higher) than in outdoor environments. Finally, because VOCs are present in large numbers in indoor air, they may cause symptoms as a result of additive and/or multiplicative effects (Godish, 1995).

### **1.2.2 Building Construction Materials as Sources and Sinks of VOCs**

The following classification identifies four categories of building materials with respect to contaminant emission (Zhang, 2005):

1. Adhesives, sealants, and architectural coatings that outgas benzene, ethyl benzene, formaldehyde, hexane, styrene, tetra chloro ethylene, toluene, xylene, etc.
2. Particleboard and plywood that release benzene, formaldehyde, styrene, toluene, etc.
3. Carpet, resilient flooring, and wall-coverings that emit acetaldehyde, ethyl benzene, formaldehyde, styrene, toluene, xylene, etc.
4. Insulation, acoustical ceiling tile, and furnishings that generate benzene, chloroform, ethyl benzene, formaldehyde, hexane, methylene chloride, toluene, trichloroethylene, xylene, etc.

Because of their large effective surface areas exposed to the indoor atmosphere, building materials and interior furnishings are suspected of playing an important role in determining air quality in buildings. The worst aspect is permanent exposure of these materials to indoor environments. Building materials generate a surprising array of VOC emissions, especially in newly constructed or renovated buildings (Wolkoff, 1995; Haghghat et al., 1993). After installation of these materials, VOCs start to outgas continuously in two consecutive periods: the primary emission and the secondary emission (Wolkoff, 1995; Wolkoff, 1999). In primary emission, non-bound and free VOCs in the materials, which are generally low molecular weight VOCs used in the

production of accelerators, additives, antioxidants, plasticizers, solvents, and unreacted raw materials like monomers, escape from porous media during a relatively short period after installation. Thereafter, secondary emission occurs in which VOCs that were initially chemically or physically bound release into the indoor environment. In some cases, the secondary emission could take the entire life of the building materials to be released.

In conclusion, building materials have long-term/permanent direct effects on the ability to provide acceptable IAQ through sorption and desorption of VOCs, especially materials with large surface area and high adsorption capacity, such as carpet, wallpapers, ceiling tile, etc. In another words, building materials act as sources of and sinks for VOCs. That is, to attain equilibrium between adsorbed phase and gas phase, VOCs are always being transferred from one phase with a higher concentration to another phase with a lower concentration. Although such interactions between VOCs and building materials regulate the peak concentration of indoor contaminants, subsequent desorption of adsorbed pollutants delays removing them from indoor environments and prolongs their presence in indoor environments. Many studies have investigated the mechanism of sink and source behavior of building materials (see Haghghat and de Bellis, 1998).

### **1.3 Strategies to Improve IAQ**

In order to improve IAQ and, as result, to mitigate the potential health impacts caused by poor IAQ, the following strategies have been proposed:

Source-specific control is the most effective approach when contaminant sources are known. However, modifying pollutant sources, eliminating them from the site, or replacing them with materials with no or minimal emissions requires foresight and a knowledge of the characteristics of materials, furnishings, and office equipment (Godish, 1995; U.S. EPA, 1991).

The second possible approach to improving IAQ is to increase the ventilation rate, which leads to the dilution of pollutant concentrations in the indoor environment. This approach, however, results in additional costs because of the excess load that HVAC systems have to bear. For naturally ventilated buildings, this approach could be implemented by opening doors and windows, operating window or attic fans, or employing window air conditioners with the vent control open; however, this strategy is somewhat limited by weather conditions (Godish, 1995; U.S. EPA, 1991).

Another approach to improving IAQ is the use of air cleaners. However, the effectiveness of such devices to capture specific gaseous and particulate contaminants is not equally satisfactory. Nevertheless, this could be a useful adjunct to source-specific control and increased air exchange rate. In addition to these three approaches, education and communication have been identified as key components in both remedial and preventive IAQ management programs. By communicating and fully understanding the causes and consequences of IAQ issues, building inhabitants, management, and maintenance personnel can work more effectively together to avoid potential problems before they occur (Godish, 1995; U.S. EPA, 1991).

## **1.4 Motivations**

As described earlier, the importance of IAQ and related issues has motivated researchers to conduct studies and develop strategies to provide acceptable IAQ for public health enhancement. Better IAQ can be achieved through the implementation of the four approaches mentioned in the previous section, and in particular, by preventing health-affecting indoor air contamination problems from happening in the first place, which seems to be more logical than attempting to control it once it has manifested itself in the form of SBS symptoms and complaints.

Determined to be the most important source of VOCs in building enclosures (Lagoudi et al., 1995), building materials and furnishings should be the first target to be removed, treated, or modified. Source-specific control, however, requires adequate knowledge about the extent of VOC emissions of different materials and the interactions between pollutants and their sources so that in decision-making stages, only products with lower and safer emission rates will be chosen and installed. Moreover, understanding the processes involved in sink and source behavior of porous building materials, such as diffusion and adsorption, enables designers, manufacturers, consumers and other decision makers to develop strategies that improve IAQ and promote sustainable development. Also, knowing the characteristics of building materials is necessary for modeling and predicting VOC emissions. This involves diffusion coefficients and partition coefficients of individual VOCs that are input parameters for VOC emission modeling. Presently, such simulations suffer from the lack of a database of diffusion coefficients and partition coefficients. Once this information is available, building designers will be able to apply these physical models, predict indoor air quality, and select the most appropriate

mechanical ventilation system. Based on these data, manufacturers will be able to produce materials with diminished VOC emissions that meet requirements to deliver acceptable IAQ; and engineers will be able to design appropriate ventilation systems to remove contaminants efficiently.

Since the ultimate goal of such studies is to establish a link between emission test data and health data, by measuring the diffusion coefficient under different environmental conditions, this study is intended to characterize a building material as regards VOC emissions. This information, adjunct to information obtained from other building materials, helps decision makers to choose less harmful materials so that SBS could be expected to be minimized. Among the environmental factors that could considerably influence material source emissions and sink behavior are temperature and humidity. This investigation is aimed at developing an experimental procedure to measure VOCs diffusion coefficient and to study the impact of changing environmental conditions on the diffusion coefficients.

### **1.5 Objectives**

The objectives of the study were as follows:

- To develop an experimental set-up to determine the diffusion coefficient of building materials;
- To investigate the influence of environmental conditions (temperature and relative humidity) on the diffusion coefficient;

- To investigate the impact of a VOC as a single gas and as a mixture on the diffusion coefficient.
- To study the effects of the physical/chemical properties of VOCs and building materials on the diffusion coefficient.
- To quantify the effect of pressure differences on the measurement of diffusion coefficients and estimate the magnitude of associated error.

## **1.6 Thesis Outline**

Chapter 2 is a review of the literature, providing a brief description of the concept of sink/source behavior, its mechanism, and the processes involved; principles of diffusion; techniques used to measure diffusion coefficients; and relevant data. In Chapter 3, a modified experimental set-up used to determine the diffusion coefficient of VOCs in building materials is proposed, followed by a description of the experimental design and procedure. Chapter 4 reports on the analysis of achieved data using a statistical method, and provides a discussion of results Chapter 5 contains conclusions and recommends avenues for future research.



# Chapter 2

## Literature Review

### 2.1 Introduction

When building materials are installed in an indoor enclosure, a continuous interaction starts taking place between indoor air and exposed building materials. Over time, this may influence IAQ to a much higher extent than might be expected using traditional air quality models in which sink/source effects are not taken into account. On the other hand, these materials behave as a buffer due to their sink/source effects, and consequently reduce peak concentrations. That is, the direction of VOC transport varies sequentially which tends to smooth out abrupt changes of pollutant concentrations in room air; for instance, when new furniture is installed, paint is applied on a surface, or the ventilation rate is reduced at night and on weekends.

The physical mechanisms involved in sink behavior of building materials are similar to those that occur when VOCs are emitted from indoor furniture (source effect), but in reverse order. These mechanisms include (Axley, 1993):

- Bulk advection (convection) of VOCs from remote areas to areas containing the adsorbent (building material, furniture, etc.);
- Boundary layer diffusion (contaminants in room air diffuse to air close to the building material surfaces);

- Surface adsorption;
- Diffusion of contaminants within materials in vapor phase and solid phase.

The aim of underlying work of this thesis has been to investigate these mechanisms, and the processes involved in VOC emissions from building materials, and in particular, the last transport phenomenon which is the diffusion of VOCs within building materials. Once the building materials are characterized according to their diffusion coefficients, the results of further modelings may be more reliable and any potential variations in air quality could be more predictable.

As described in the previous chapter, among the strategies mentioned source control could be the wisest choice to enhance IAQ. This requires adequate information about the nature of the interactions between VOCs and building materials. However, unlike the adsorption process, which has been the subject of much research and has received significant attention from researchers, diffusion studies, especially studies of the influence of environmental conditions such as temperature and relative humidity, have suffered from the lack of a complete database resulting from insufficient investigations.

The main focus for the research for this study was to determine unknown material parameters (diffusion coefficients) in a physical model based on Fick's first law by conducting a set of experiments. Hence, this chapter begins with an introduction to process principles, followed by an explanation of the physical models used to describe VOC transfer within materials. Thereafter, different experimental methods used to measure these models' parameters are reviewed.

## **2.2 Principles of Processes**

In this section, the most common physical processes involved in the sink/source effects of materials are briefly explained.

### **2.2.1 Adsorption**

Because of intermolecular forces, gas molecules are partially adsorbed to the surface of materials when they are in direct contact with each other. These attractive interactions, called London forces, are a process in which a monolayer or multilayer of molecules is formed and sticks to the surface of a material (Atkins, 1992). The strength of London forces varies with the type of substance; however, these physical bonds are basically weak. Thus, accumulated molecules on the surface of material start leaving the surface causing the “source behavior” of the materials.

In order to quantify adsorption processes at specific temperatures, adsorption isotherms, which determine the amount of adsorbed gas on a surface as a function of gas concentration, are used. The most common adsorption models are the linear adsorption isotherm, the Langmuir isotherm, the Freundlich isotherm, and the BET isotherm (Masel, 1996). Within the scope of indoor air studies, however, they may all be simplified to the linear adsorption isotherm since the level of VOC concentration is normally low.

### **2.2.2 Diffusion**

The most commonly used mechanisms to describe compound transport in a porous medium with negligible pressure differences are molecular diffusion, Knudsen diffusion, and surface diffusion. A brief description of these diffusion processes is presented here.

*Molecular diffusion:* When there is a concentration gradient in a fluid or solid, molecules are transferred from higher concentrations to lower concentrations to even out concentration differences. The process may be enhanced by low pressure and high temperature (Bird et al., 2002). According to Fick's first law, the one-dimensional diffusion flux per unit area,  $J$ , is proportional to the concentration gradient of the diffusing species,  $\frac{dC}{dx}$ , as shown below:

$$J = -D \frac{dC}{dx} \quad \text{Equation 2-1}$$

where  $D$  is the diffusion coefficient,  $C$  is the concentration of the diffusing species, and  $x$  is the distance along which diffusion takes place. The negative sign in Fick's first law equation implies that the diffusion flux is directed towards decreased concentration.

In a transition state where the concentration varies over time, Fick's second law for one-dimensional diffusion is given as:

$$\left( \frac{\partial C}{\partial t} \right)_x = D \left( \frac{\partial^2 C}{\partial x^2} \right)_t \quad \text{Equation 2-2}$$

*Knudsen diffusion:* When the diameter of material pores is smaller in comparison with the mean free path of the diffusing molecules, the collision between the molecules and the walls of the pores is more probable, and takes place more frequently than intermolecular collisions. This process is known as Knudsen diffusion, and the dimensionless Knudsen number,  $Kn$ , determines whether the process is dominated by Knudsen diffusion or molecular diffusion (Cussler, 1997).

$$Kn = \frac{\lambda}{L}$$

Equation 2-3

where  $\lambda$  is the mean free path of the diffusing molecules, and  $L$  is the pore diameter of the pores inside the porous material. When the Knudsen number is small compared to unity, of the order of  $Kn \leq 0.1$ , the process can be described as molecular diffusion. When the Knudsen number is near or greater than one, the continuum mechanics formulation of fluid mechanics is no longer a good approximation and the process should be described by Knudsen diffusion.

The mean free path is the average distance a molecule travels before it collides with another molecule. For monomolecular gases, the mean free path can be estimated using the following equation (Cussler, 1997):

$$\lambda = \frac{k_B T}{\sqrt{2} \pi \sigma_{ii}^2 p}$$

Equation 2-4

where  $\sigma_{ii}$  is the collision diameter of the diffusing molecules,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature and  $p$  is the pressure.

By using the kinetic theory of gases, the Knudsen diffusion coefficient can be expressed by the following correlation (Cussler, 1997):

$$D_{Kn} = \frac{d}{3} \left[ \frac{2k_B T}{m} \right]^{0.5}$$

Equation 2-5

where  $m$  is molar mass.

*Surface diffusion:* Surface diffusion, which occurs in the pores of porous materials, involves adsorption of gas molecules on the pore surfaces and subsequent diffusion in the

condensed phase resulting in additional flux (Hansson, 2003). Surface diffusion, however, is not as remarkable as molecular diffusion since mobility of the adsorbed phase is considerably smaller than that of the gas phase.

### **2.3 Diffusion in Porous Materials**

The mechanisms described earlier present a very idealized view of diffusion processes. In practice, diffusion in porous media is more complicated due to the complex structure of the material consisting of a random network of interconnecting pores of varying diameter and orientation (Kärger, 1992). Moreover, because of the non-straight form of the pores, the diffusion distance is much longer than in a homogeneous material, and the cross-sectional area is also much smaller. This makes it hard to determine the effective diffusion coefficient for porous materials.

Defining the effective diffusion coefficient in porous media may be done using two approaches which identify the principles for further modelings. The first approach assumes that the porous material is composed of pores and solid particles which are impermeable to the diffusing substances, and that diffusion occurs only in the pores of the material (Figure 2.1). In this case, the effective diffusion coefficient is defined as (Cussler, 1997):

$$D_{eff} = \varepsilon \frac{D_{gas}}{\tau} \quad \text{Equation 2-6}$$

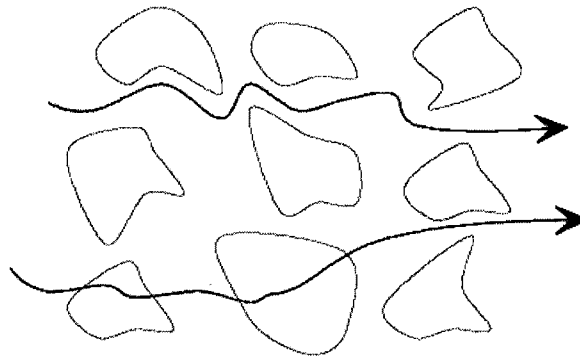
where  $\varepsilon$  is the fraction of pores of the cross-sectional area,  $D_{gas}$  is the diffusion coefficient within the pores, and  $\tau$  is the tortuosity factor. Tortuosity is dependent on the length of

the pores.

The second scenario assumes that the molecules are allowed to diffuse through the solid materials as well as the pores. In this case the effective diffusion coefficient,  $D_{eff}$ , is a function of the diffusion coefficient within the pores,  $D_{gas}$ , the diffusion coefficient within the solid phase of the material,  $D_s$ , the aspect ratio of the solid flakes,  $\alpha$ , and the volume fraction of the solid flakes,  $\phi$ .

$$D_{eff} = f(D_{gas}, D_s, \alpha, \phi)$$

Equation 2-7



**Figure 2-1: Diffusion in porous medium**  
The top arrow represents a case where a solid is impermeable to the diffusing molecules.  
The bottom arrow represents a case with a permeable solid.

Based on these two approaches, models for VOC transfer in building materials have been developed that will be discussed in the section 2.4.

In reality, VOC transport through a porous medium will be governed by various diffusion and sorption processes. Normal and Knudsen diffusion in gas phase of the material combined with surface diffusion in adsorbed phase on the pore surfaces will contribute to an integrated diffusion process. This process, at the same time, can be affected while

coupled with adsorption of VOC on the pore surface. For example, VOC adsorption on the pore surface reduces gas phase VOC concentration resulting in a reduced mass flow along the concentration gradient across the material. On the other hand, due to VOC adsorption on the pore surface, an additional transport process takes place in the form of surface diffusion (Meininghaus & Uhde, 2002).

By establishing a mass balance over the porous medium the effects of aforementioned processes can be lumped together in the following definition (Cussler, 1997):

$$\varepsilon \frac{\partial C_{gas}}{\partial t} + (1 - \varepsilon) \frac{\partial C_{ad}}{\partial t} = \varepsilon D_{gas} \frac{\partial^2 C_{gas}}{\partial y^2} + (1 - \varepsilon) D_s \frac{\partial^2 C_{ad}}{\partial y^2} \quad \text{Equation 2-8}$$

where,  $C_{gas}$  is the VOC gas phase concentration in the material ( $\mu\text{g}$  of gas phase VOC/ $\text{m}^3$  of air),  $C_{ad}$  is the VOC adsorbed phase concentration in the material ( $\mu\text{g}$  of adsorbed phase VOC per cubic meter of solid phase),  $D_{gas}$  is the VOC gas phase diffusion coefficient within the pores ( $\text{m}^2/\text{s}$ ),  $D_s$  is the VOC solid phase diffusion coefficient within the material ( $\text{m}^2/\text{s}$ ), and  $\varepsilon$  is the porosity of the material ( $\text{m}^3$  of air/ $\text{m}^3$  of material).

Equation 2-8 for an impermeable solid ( $D_s=0$ ) can be rewritten to:

$$\frac{\partial C_{gas}}{\partial t} = \frac{\varepsilon D_{gas}}{\varepsilon + \frac{\partial f}{\partial C_{ad}} (1 - \varepsilon)} \frac{\partial^2 C_{gas}}{\partial y^2} \quad \text{Equation 2-9}$$

where  $f$  is a function describing the  $C_{gas}$  vs.  $C_{ad}$  equilibrium relation (sorption isotherm).

Comparing this equation with Fick's second law of diffusion, an alternative effective diffusion coefficient can be defined as:



$$D_{eff} = \frac{\varepsilon D_{gas}}{\varepsilon + \frac{\partial f}{\partial C_{ad}}(1 - \varepsilon)} \quad \text{Equation 2-10}$$

The effective diffusion coefficient depends on the concentration, which is expressed by the  $\frac{\partial f}{\partial C_{ad}}$  term. When strong sorption occurs,  $D_{eff}$  becomes very small. When sorption is not significant,  $D_{eff}$  may depend on gas phase diffusion parameters.

## **2.4 Physical Models for VOC Transfer within Materials**

In order for us to be able to predict VOC emissions from building materials, physical models have been developed, and based on those, experimental methods have been designed to determine the properties of building materials, which are input parameters for these physical models. Based on assumptions about the physical status of VOCs in materials, physical models for VOC transfer within building materials are classified into one-phase models and multi-phase models (Haghighat et al., 2005).

### **2.4.1 One-phase Models**

In the one-phase model, the building material is assumed to be a single homogeneous medium within which VOC mass transfer takes place by diffusion (Figure 2.2.a), and Fick's second law is used to describes this process:

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial y^2} \quad \text{Equation 2-11}$$

where,  $C_m$  is the VOC material phase concentration in the material phase ( $\mu\text{g}/\text{m}^3$ ),  $D_m$  is the VOC material phase diffusion coefficient ( $\text{m}^2/\text{s}$ ),  $y$  is the coordinate in which diffusion takes place (m), and  $t$  is the time(s).

VOCs tend to be adsorbed or accumulated on the surface of material due to the intermolecular forces, mainly Van der Waal's forces (Hansson, 2003). Hence, at the material/air interface, the concentration of VOCs in the material phase is always higher than in the indoor gas phase concentration, and equilibrium is always established between these two concentrations. Since concentration levels of indoor air pollutants are much lower than their saturated concentration, it can be assumed that there is a linear equilibrium relationship between VOC concentration in the gas phase and VOC concentration in the material phase. At constant atmospheric pressure and isothermal conditions, therefore, the Henry isotherm can be used to describe this process (Axley, 1991; Cox et al., 2001):

$$C_m = K_m C_{gas} \quad \text{Equation 2-12}$$

where,  $C_m$  is the VOC material phase concentration in the material phase ( $\mu\text{g}/\text{m}^3$ ),  $C_{gas}$  is the VOC gas phase concentration in the near material surface air ( $\mu\text{g}/\text{m}^3$ ), and  $K_m$  is the VOC material phase/gas phase partition coefficient.

#### 2.4.2 Multi-phase Models

In multi-phase models, mass transfer occurs through porous material which consists of voids (pores) and solid parts; thus, the VOCs in these two parts are called gas phase and adsorbed phase on the pore surfaces, respectively (Figure 2.2.b). The governing equation for such models is given as:

$$\epsilon \frac{\partial C_{gas}}{\partial t} + \frac{\partial C_{ad}}{\partial t} = D_{gas} \frac{\partial^2 C_{gas}}{\partial y^2} \quad \text{Equation 2-13}$$

where,  $C_{gas}$  is the VOC gas phase concentration in the material ( $\mu\text{g}$  of gas phase VOC/ $\text{m}^3$ )

of air),  $C_{ad}$  is the VOC adsorbed phase concentration in the material ( $\mu\text{g}$  of adsorbed phase VOC/ $\text{m}^3$  of material),  $D_{gas}$  is the VOC gas phase diffusion coefficient within the material ( $\text{m}^2/\text{s}$ ), and  $\varepsilon$  is the porosity of the material ( $\text{m}^3$  of air/ $\text{m}^3$  of material).

As the above equation illustrates, two accumulation terms on the left side of the equation consider accumulation in both the gas phase and adsorbed phase; and on the right side of the equation, VOC transfer within the material is considered only by the gas phase diffusion (i.e., molecular and/or Knudsen diffusion) through the pores, whereas adsorbed phase diffusion is regarded as negligible. Further developments in multi-phase approaches consider both surface diffusion (adsorbed-phase diffusion) and gas-phase diffusion in the pores (Lee et al., 2005; 2003).

Similar to one-phase models, the linear adsorption isotherm can be applied in order to associate gas phase concentration with adsorbed phase concentration since indoor environments present low levels of pollutant concentration:

$$C_{ad} = KC_{gas} \quad \text{Equation 2-14}$$

where,  $K$  is the VOC adsorbed /gas phase partition coefficient.

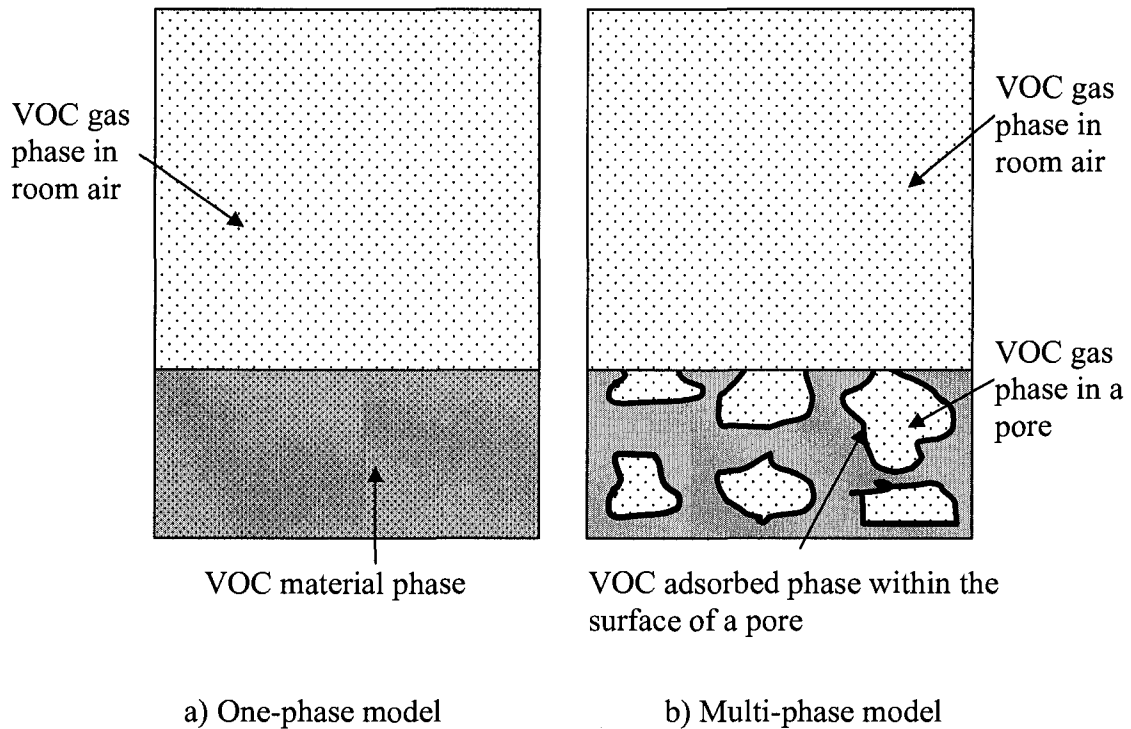


Figure 2-2: VOC within material and in room air

## **2.5 Diffusion Coefficient Measurement Methods**

Haghighat et al. (2002) carried out a comprehensive review of diffusion coefficient measurement techniques and classified them according to experimental set-up into three categories: the so-called cup method; the twin chamber method; and the porosimetry test method. A description of these approaches follows.

### **2.5.1 Cup Method**

The cup method is considered by ASHRAE (1997) to be the simplest method of measuring the diffusion coefficient of building materials. In this method, a sample of the building material tightly covers the top opening of a cup containing a liquid VOC. In a controlled environment, the cup is weighed periodically using a high-precision

microbalance, and the VOC weight loss is monitored over time. The diffusion coefficient can then be obtained from the rate of VOC weight loss at steady state:

$$D_{eff} = \frac{\dot{m} d}{A C} \quad \text{Equation 2-15}$$

where  $D_{eff}$  is the effective diffusion coefficient ( $m^2/s$ ) of the tested material,  $\dot{m}$  is the gas mass flow rate through the material ( $mg/s$ ) (calculated from the slope of the weight-loss curve),  $A$  is the material area ( $m^2$ ),  $d$  is the material thickness ( $m$ ), and  $C$  is the mass concentration of the diffusing substance ( $mg/m^3$ ).

This method offers the advantages of ease of use and simplicity of calculation. However, unrealistically high levels of VOC concentration created by the liquid VOC in the cup has been identified as the main drawback of this approach. For instance, the saturation concentration for n-octane and ethyl acetate at 23°C is 97.36  $g/m^3$  and 473.45  $g/m^3$ , respectively; whereas according to Seifert (1990), who developed the first notable guideline for indoor VOCs, TVOC (total volatile organic compounds) does not exceed 300  $\mu g/m^3$  in a residential enclosure with acceptable IAQ. Further, no individual compound should have a concentration of more than 10% of TVOC.

The high concentration issue can be resolved by placing desiccants in the cup to reduce vapor pressure to zero and create the desired low concentrations which are closer to reality. This modified set-up, known as the dry-cup method, delivers low constant concentrations to the chamber, but the test takes longer to complete since it involves a lower concentration gradient ASHRAE (1997).

Employing this method, Kirchner et al. (1999) measured the diffusion coefficients of n-octane and ethyl acetate for six building materials including wallpaper with paste, PVC floor covering, carpet, acrylic paint on woodchip paper, gypsum board, and aerated concrete. In addition to these materials and chemicals, the diffusion of toluene in gypsum board, medium-density fiberboard, and wood particleboard were investigated in a study by Hansson and Stymne (2000). The diffusion coefficients were determined at a temperature of 20°C and relative humidity less than 5%.

### **2.5.2 Twin Chamber Method**

Basically, the twin chamber method involves two identical chambers between which the sample material is placed. The carrier gas with a constant level of VOC concentration is then introduced into one chamber, while a fresh air stream is supplied to another chamber. Samples are taken from outlets on both chambers and concentrations are continuously monitored until the system reaches steady state. Unlike the cup method, the twin chamber allows better control of the level of VOC concentration introduced into the chamber. Furthermore, this method is able to analyze unsteady-state conditions, and where analyzing facilities allow, several VOCs can be tested simultaneously.

Studies using the twin chamber approach are described below:

#### *A) CLIMPAQ method:*

Meininghaus et al. (1998) used pairs of CLIMPAQ-type small-scale chambers to quantify the diffusion properties of n-octane and ethyl acetate in eight building materials including wallpaper with paste, PVC floor covering, carpet, acrylic paint on woodchip paper,

gypsum board, aerated concrete, solid concrete, and brick wall. As illustrated in Figure 2.3, this experiment was performed by placing materials to be tested between a primary chamber, which is ventilated with VOC-containing air, and a secondary chamber, which is ventilated with clean air. The single VOC was constantly dosed using a VOC generator at a constant ventilation rate. Then, the stream was split and directed to all primary chambers, and VOC concentrations in the supply and exhaust air of each chamber were recorded. The volume of each chamber was 50 liter and the air exchange rate was set to  $2 \text{ hr}^{-1}$ . Temperature and relative humidity in the chambers were kept constant at  $24 \pm 0.5^\circ \text{C}$  and  $45 \pm 3\%$ , respectively. A fan was used in each chamber to ensure sufficient air mixing and avoid any concentration gradient inside the chamber.

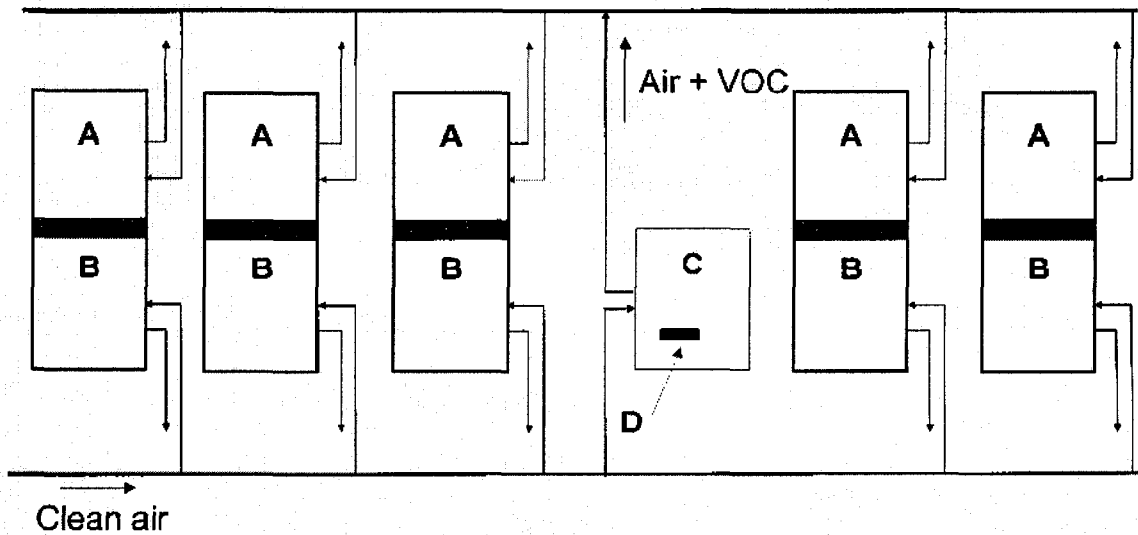


Figure 2-3: Schematic of a CLIMPAQ chamber (Meininghaus et al., 1998)

In order to calculate the diffusion coefficient of a given material, Fick's first law was utilized and then modified as described below:

$$D_{eff} = -\frac{\dot{m} \Delta x}{A \Delta c} = -\frac{\dot{V}d}{A} \frac{C_2}{C_2 - C_1}$$

Equation 2-16

where  $D_{eff}$  is the effective diffusion coefficient ( $m^2/s$ ),  $\dot{m}$  is the mass flow rate through the material ( $mg/s$ ),  $A$  is the area of specimen ( $m^2$ ),  $\dot{V}$  is the ventilation rate ( $m^3/s$ ),  $d$  is the material thickness ( $m$ ), and  $C_1$  and  $C_2$  are the VOC concentrations under steady-state conditions in the primary (contaminated air supplied) and secondary (clean air supplied) chambers respectively ( $mg/m^3$ ).

The assumptions made in this study, similar to the previous case, include: 1) the concentration gradient inside the material is considered as linear and one-dimensional; 2) the diffusion coefficient is independent of concentration; and 3) the concentration gradient in the modified Fick's first law is considered as the concentration difference of the material surfaces. That is, the resistance to diffusion in the boundary layer on both sides of the material was ignored, which means that the surface concentration was assumed to be equal to the chamber air concentration. This requires the chamber air to be completely mixed. Subsequent studies showed that these assumptions may lead to a significant underestimation of the diffusion coefficient (Haghighat et al. 2002, Lee 2000).

*B) Diffusionmetric method:*

Using the diffusionmetric apparatus shown in Figure 2.4, Bodalal et al. (2000) conducted a study to determine diffusion and sorption properties for four VOCs (toluene, nonane, decane, and undecane) through the backing material of a carpet specimen, for four VOCs (ethyl benzene, nonane, decane, and undecane) through a floor tile specimen, and for three VOCs (cyclo hexane, ethyl benzene, and decane) through a plywood specimen.



Experiments were performed in static situation where the boundaries of the system were closed. The system consisted of two identical 50 l chambers, separated by a specimen. At a temperature of  $23 \pm 1^\circ C$  and relative humidity of  $50 \pm 5\%$ , a single VOC or VOC mixture was introduced into a chamber, and gas samples were drawn out of each chamber periodically through sampling ports and collected in adsorbent tubes. Then, samples were analyzed using a GC/FID system to determine the VOC concentration.

The researchers modeled the whole process using Fick's second law of diffusion and solved it analytically considering the following initial and boundary conditions:

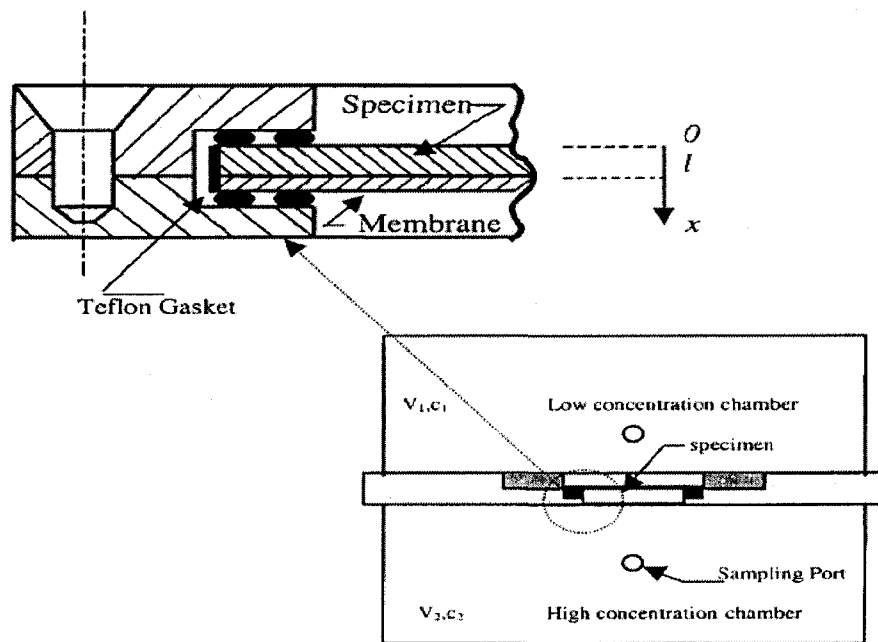


Figure 2-4: Diffusionmetric apparatus (Bodalal et al. 2000)

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} \quad (\text{Fick's second law}) \quad \text{Equation 2-17}$$

the boundary condition at the material surface in the low concentration chamber side is:

$$C_{m,1} = Kc_1 \quad \text{at} \quad x = 0 \quad \text{Equation 2-18}$$

the boundary condition at the material surface in the high concentration chamber side is:

$$C_{m,2} = Kc_2 \quad \text{at} \quad x = d \quad \text{Equation 2-19}$$

and initial conditions are:

$$C = 0 \quad \text{at} \quad t = 0 \quad \text{and} \quad 0 \leq x \leq d \quad \text{Equation 2-20}$$

where,  $D_m$  is the diffusion coefficient of a VOC in the material phase ( $\text{m}^2/\text{s}$ ),  $C_m$  is the VOC concentration in the material phase ( $\text{mg}/\text{m}^3$ ),  $c$  is the VOC concentration in the chamber air ( $\text{mg}/\text{m}^3$ ),  $d$  is the specimen thickness (m), and  $K$  is the equilibrium partition coefficient between the specimen and the air ( $\text{mg m}^{-3}/\text{mg m}^{-3}$ ).

Based on the described experimental set-up, the correlation of  $D$  and  $K$  with VOC properties was investigated. The authors showed that the diffusion coefficient for a given material is inversely proportional to the molecular weight of the VOCs. They also found that partition coefficients increase with VOC vapor pressure.

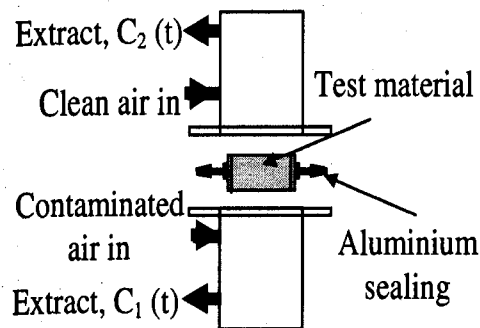
The assumptions made in this model were: first, that by running a fan inside both chambers and making the air completely stirred, convective resistance can be neglected as compared with diffusive mass transfer resistance; and second, that there is an instantaneous equilibrium between material surface concentration and concentration in chamber air.

Quantification of diffusion and partition coefficients in transient conditions is considered to be an advantage of this method since it reflects real-life applications. However, the calculation procedure is fairly complicated because the diffusion coefficient and partition

coefficient are coupled and calculated simultaneously. So there could be a risk of having multiple solutions.

*C) Twin-compartment method:*

Hansson and Stymne (2000) proposed an experimental set-up in which the diffusion and absorption properties of toluene in three building materials were evaluated by fitting a simple mathematical model to the experimental data. Material to be tested was placed between two 62 ml cylindrical stainless steel compartments. Compartments were identically equipped with inlet and outlet streams (Figure 2.5). One chamber was conditioned with clean air and the other flushed with VOC-containing air. The toluene concentration of inlet air, clean air, and extracted air from both compartments was continuously measured using a quadrupole mass spectrometer. The analysis was continued until no changes were observed in the toluene concentrations of both chambers.



**Figure 2-5: Twin compartment (Hansson and Stymne, 2000)**

Establishing the mass balance equations for both chambers, the authors developed a mathematical model which incorporates boundary layer diffusion, surface adsorption,

vapor diffusion inside the material, and interior sorption. Accounting for mass transport processes, the mass conservation equation for the contaminated compartment can be expressed as:

$$V \frac{dC_1}{dt} = K_g A (C_{s,1} - C_1) + q_1 (C_0 - C_1) \quad \text{Equation 2-21}$$

where  $V$  is chamber volume (m<sup>3</sup>),  $C_1$  is chamber bulk air concentration (kg/m<sup>3</sup>),  $C_{s,1}$  is the concentration of air close to the surface of the material (kg/m<sup>3</sup>),  $t$  is time (s),  $A$  is the exposed area of the specimen (m<sup>2</sup>),  $K_g$  is the mass transfer coefficient between bulk air and air close to the surface (m/s),  $q_1$  is the chamber air flow (m<sup>3</sup>/s), and  $C_0$  is the chamber inlet concentration (kg/m<sup>3</sup>).

Similarly, establishing the mass conservation equation for the air in the clean chamber results in:

$$V \frac{dC_2}{dt} = K_g A (C_{s,2} - C_2) + q_2 C_2 - g A C_2 \quad \text{Equation 2-22}$$

The subscript 2 designates the clean chamber, and  $g$  is a rate constant for compound depletion (m/s) (i.e., an irreversible sink in the clean compartment).

The adsorption process at the surfaces of both sides of the specimen is modeled by the reversible linear adsorption isotherm described earlier:

$$Y_s = C_s \cdot K_s \quad \text{Equation 2-23}$$

where  $Y_s$  is the surface concentration of adsorbed compounds ( $\text{kg/m}^3$ ),  $C_s$  is the concentration of air close to the surface of specimen ( $\text{kg/m}^3$ ), and  $K_s$  is the equilibrium constant for surface adsorption.

The following equation illustrates the conservation of adsorbed mass at the surface of the specimen on the contaminated side:

$$A \frac{dC_{s,1}}{dt} = A \frac{K_g}{K_s} (C_1 - C_{s,1}) + A \frac{D}{K_s h} (C_{i=1} - C_{s,1}) \quad \text{Equation 2-24}$$

where  $D$  is the gas diffusion coefficient ( $\text{m}^2/\text{s}$ ),  $h$  is the utilized grid distance inside the material (m), and  $C_{i=1}$  is the gas concentration at a distance  $h$  from the surface ( $\text{kg/m}^3$ ).

Similar to the Equation 2.21, we can drive an equation for conservation of adsorbed mass on the clean side of material.

The diffusion process inside the material is regarded as one-dimensional according to Fick's second law.

$$\frac{\partial C_i}{\partial t} = \frac{D}{K_i} \frac{\partial^2 C_i}{\partial x^2} \quad \text{Equation 2-25}$$

Also, interior sorption is treated as an instantaneous and reversible process following Henry's law:

$$Y_i(x) = C_i(x) \cdot K_i \quad \text{Equation 2-26}$$

where  $Y_i(x)$  is the local concentration of a compound inside the material at distance  $x$  from the surface ( $\text{kg/m}^3$ ),  $C_i(x)$  is the concentration of gas in the material pores ( $\text{kg/m}^3$ ),

and  $K_i$  is the equilibrium partitioning coefficient between the gas concentration and the total concentration.

The parameters  $D$ ,  $K_i$  and  $g$  in the model can be determined by solving the system of equations numerically. However, since the values of these parameters are obtained simultaneously to yield best fit to the experimental data, it is probable the method will result in multiple sets of best-fit. In addition,  $K_g$  was evaluated based on a guesstimate, and  $K_s$  was obtained from earlier studies.

### **2.5.3 Porosimetry Test Method**

Using the Mercury Intrusion Porosimetry (MIP) test, Tiffonnet et al. (2000) and Blondeau et al. (2000) computed the diffusion coefficient for methane, ethyl acetate, n-octane, and n-dodecane. Their study was intended to make a comparison between calculated diffusivities and measured values in order to assess the methodology's applicability to building materials.

Their approach consisted of carrying out MIP tests, and then determining the tortuosity factor based on a mathematical model proposed by Carniglia (1986). In that model, the author showed that the parameters presented in calculating the effective diffusion coefficient (Equation 2.6), can be measured ( $\epsilon$ ) or computed ( $D$  and  $\tau$ ) from porosimetry tests. The proposed model took into account pore interconnection, pore constriction, and pore random orientation.

Results obtained using this model have showed agreement with measured values. Despite significant discrepancies observed between measured data and predicted data, they are in

the same order of magnitude. Applicability, however, is limited to homogeneous and single layer materials. Therefore, the model is not useful in evaluating the diffusion coefficient of non-porous materials and furniture such as carpet, or material assembly such as painted gypsum board. Further, the influence of possible interactions between the VOC and the building materials is not considered in this model, which may lead to inaccurate results. On the other hand, the test can be completed within 2 hours, which is much shorter than the relatively long periods required by other methods to be stabilized and reach steady-state conditions. Testing various VOCs at different temperatures in just one run could be another advantage of this method.

In a subsequent study, the authors concluded that the diffusion coefficient is proportional to the porosity of the materials (Blondeau et al. 2003). Furthermore, obtained data were greater than those measured by the cup method or the CLIMPAQ method.

## **2.6 Influence of the Environmental Conditions on Diffusion Coefficient**

Among the environmental parameters, indoor air temperature and relative humidity are believed to have effects on VOC emissions from building materials (Haghighat and de Bellis, 1998). Although this subject has received particular attention from researchers, an independent assessment of the influence of the environmental conditions on emission parameters such as diffusion coefficient and partition coefficient is still lacking. Investigating the diffusion coefficient and/or partition coefficient individually can be an effective approach to better know the impact of environmental conditions on the emission characteristics of the building materials. That is, the results avoid having a risk of interdependence (Zhang, 2005).

Accordingly, Zhang et al. (2007) developed a method, so-called C-history, to measure variations of the diffusion coefficients and the partition coefficients of formaldehyde in dry building materials with temperature. For all four tested materials, they reported trends of decrease in partition coefficient and increase in diffusion coefficient with increasing temperature, respectively. Haghghat et al. (2002) pointed out that small differences in temperature may result in minor effects on diffusion coefficients. Also, Won and Shaw (2004) demonstrated a correlation between diffusion coefficient and molecular weight, air temperature, and initial concentration through fitting the following equation to all the measured data from experiments:

$$D = (b_1 + b_2 \cdot MW)(b_3 + b_4 \cdot T)(b_5 + b_6 \cdot C_0) \quad \text{Equation 2-27}$$

where  $D$  is the diffusion coefficient ( $\mu\text{m}^2/\text{h}$ ),  $MW$  is molecular weight,  $T$  is air temperature ( $^{\circ}\text{C}$ ),  $C_0$  is the initial concentration of a chemical in a paint sample ( $\text{g/L}$ ), and  $b_1$ ,  $b_2$ ,  $b_3$ ,  $b_4$ ,  $b_5$ , and  $b_6$ , are correlation constants.

Equation 2-27 was used to investigate the VOC emission from solvent-based paint and is solely valid for non-polar compounds (alkanes and alkyl benzenes).

In the same study (Won & Shaw, 2004), relative humidity was found to have no effect on emissions of VOCs belonging to two non-polar groups of compounds, namely alkanes and alkyl benzenes. In another study based on porosimetry test method, Bouilly et al. (2006) investigated the influence of humidity on VOC effective diffusivity in materials using both the VOC molecular diffusivity in air and the pore size distribution of the material as input of a mathematical model. This model computes the effective diffusion



coefficient of the corresponding VOC/material system. From the results obtained, no effect was observed from humidity on the diffusivities in both particle board and gypsum. However, a considerable decrease in the acetone diffusivity in mortar was found with increasing relative humidity from 50% to 80%.

## **2.7 Relation between Physical Properties and Diffusion Coefficient**

According to the reviewed literature, diffusion coefficients measured by aforementioned techniques were then related to the physicochemical properties of VOCs. Using a diffusion-controlled emission model, He et al. (2005) reported on decrease of diffusion coefficient of four alkanes emitted from six carpets as molecular weight increases. For same functional group Cox et al. (2001) conducted the diffusionmetric test and concluded that diffusion coefficients of alkanes correlate well with molecular weight. Meininghaus et al. (2002) found a clear correlation of the calculated diffusion coefficient with the boiling point of the corresponding halogenated aromatic compounds. They also conducted a multiple linear regression of the known substance properties (boiling point and molecular area) to test whether other physical properties of same group of compounds also influence the diffusion coefficient. For their bilinear model, they found reasonably high dependency (correlation factor = 0.929) of diffusion coefficient on mentioned physical properties. Besides, they confirmed that the diffusion of less polar compounds in gypsum board can be fast. In addition to this study, these researchers also studied the interaction of a single VOC with an indoor material in presence of other VOCs. Jørgensen & Bjørseth (1999) concluded that this interaction may not be influenced by the presence of other VOCs. That is, whether it is tested as a single

compound or in a mixture of compounds, a VOC shows similar emission behavior. This might be interpreted by the abundant amount of adsorption sites compared with the relatively small number of adsorbing VOCs (Meininghaus et al., 2002).

## **2.8 Summary and Conclusions**

This Chapter reviews the related studies dealing with the measurement of building materials typically used in indoor environments. It began with an introduction to sink/source behavior in building materials, a discussion of the influence that these behaviors may have on IAQ, and the importance of the issue of IAQ. Some fundamental concepts involved in sink/source behavior were then reviewed, and various mechanisms of diffusion and adsorption were summarized. Physical models to predict VOC emission from building materials were also classified into one-phase models and multi-phase models. Input parameters of these models can be found to yield best fit to the experimental data. Finally, the major techniques used to measure the diffusion coefficients of building materials were explained, and influence of environmental factors on the results of these measurements reported in the literature was discussed. A summary of measurement methods based on Lee (2003) is shown in Table 2.1.

The literature survey indicates that environmental conditions have an impact on the VOCs diffusion coefficient. However, more fundamental studies are needed to examine the effects and to have a practical measurement of VOCs diffusion coefficient in building materials. It is believed that the observed discrepancies in effective diffusion coefficients obtained by different methods result from the different diffusion mechanisms applied and/or the difference in boundary conditions. For instance, as the material specimen is

subjected to saturated VOC concentrations in the cup method, the effective diffusion coefficients obtained are significantly higher than those measured by the twin chamber approach.

**Table 2-1: Summary of measurement methods (Lee, 2003)**

<b>Method</b>	<b>Test procedure</b>	<b>Merits</b>	<b>Drawbacks</b>
<b>Cup method</b> Kirchner et al. (1999); Hansson et al. (2000)	<ul style="list-style-type: none"> <li>• Specimen placed over liquid contained in a cup, in a controlled environment</li> <li>• Periodic measurement of weight loss using microbalance</li> <li>• Calculation of <math>D_e</math> using Fick's 1<sup>st</sup> law</li> </ul>	<ul style="list-style-type: none"> <li>• Simple experimental procedure</li> <li>• Simple calculation technique</li> <li>• No limitation on material type</li> </ul>	<ul style="list-style-type: none"> <li>• Possible overestimation of <math>D_e</math> due to high VOC concentration (wet cup test)</li> <li>• Only one VOC in one test</li> <li>• Long experimental time</li> </ul>
<b>Twin chamber method</b> Meininghaus et al. (1998); Hansson and Stymne (2000); Bodalal et al. (2000)	<ul style="list-style-type: none"> <li>• Specimen placed between two identical chambers</li> <li>• Introduction of VOCs at a constant concentration in one chamber, and clean air in the other chamber</li> <li>• Periodic measurement of VOC concentration of air in both chambers air using GC</li> <li>• Calculation of <math>D_e</math> using Fick's 1<sup>st</sup> or 2<sup>nd</sup> law</li> </ul>	<ul style="list-style-type: none"> <li>• Controllable VOC concentration</li> <li>• No limitation on materials</li> <li>• VOC mixture can be tested: <math>D_e</math> of various VOCs can be obtained from one test</li> </ul>	<ul style="list-style-type: none"> <li>• Relatively complicated experimental and analysis procedures</li> <li>• Long experimental time to reach steady-state conditions</li> <li>• Possible multiple existence of best-fits of coefficients (Twin-compartment and diffusionmetry methods)</li> </ul>
<b>Porosimetry test method</b> Tiffonnet et al. (2000); Blondeau et al. (2000)	<ul style="list-style-type: none"> <li>• Porosity and pore size distribution measurement using MIP test</li> <li>• Carniglia's mathematical model</li> </ul>	<ul style="list-style-type: none"> <li>• Short experimental time (max. 2 hours)</li> <li>• <math>D_e</math> of various VOCs at various temperatures can be computed from one test</li> </ul>	<ul style="list-style-type: none"> <li>• Homogeneous materials only</li> <li>• Relatively complicated analysis procedure</li> <li>• No consideration of the possible interaction between the VOC and the material</li> </ul>

Based on this review of available methods, the twin chamber method would be selected in order to achieve the study goals. Regardless of complications in the experimental set-

up, this approach is promising for measuring the diffusion coefficients of dry building materials. It offers the advantage of allowing researchers to control the level of VOC concentration, selecting any kind of material without limitation, and simultaneously testing VOCs in a mixture.

# Chapter 3

## Experimental Set-up and Methodology

### 3.1 Introduction

As noted earlier, an experimental procedure was needed to determine the diffusion coefficient of VOCs in building materials, as well as to evaluate the influence of environmental conditions on those coefficients. In addition, experiments conducted for this study were intended to provide a database of input parameters for modeling purposes; the study has, therefore, taken into account that the experimental design covers the whole range of possible environmental conditions. The possibility of controlling the concentration of the VOC and keeping it at a relatively low level close to actual indoor environments was considered to be the main advantage of choosing the two-chamber method. The experimental design for this type of study, as well as the experimental set-up and procedure, are described in the following sections.

### 3.2 Experimental Design

In order to achieve the objectives described in Chapter 1, a plan was proposed to investigate the influence of temperature, relative humidity, and the mixture of VOCs on diffusion coefficients. Five VOC compounds were selected: octane, isopropanol, cyclo hexane, ethyl acetate, and hexane. The temperature levels were: 15, 23, 31 and 39°C, and the selected relative humidity levels were: 0%, 20%, and 40% (all at 23°C).

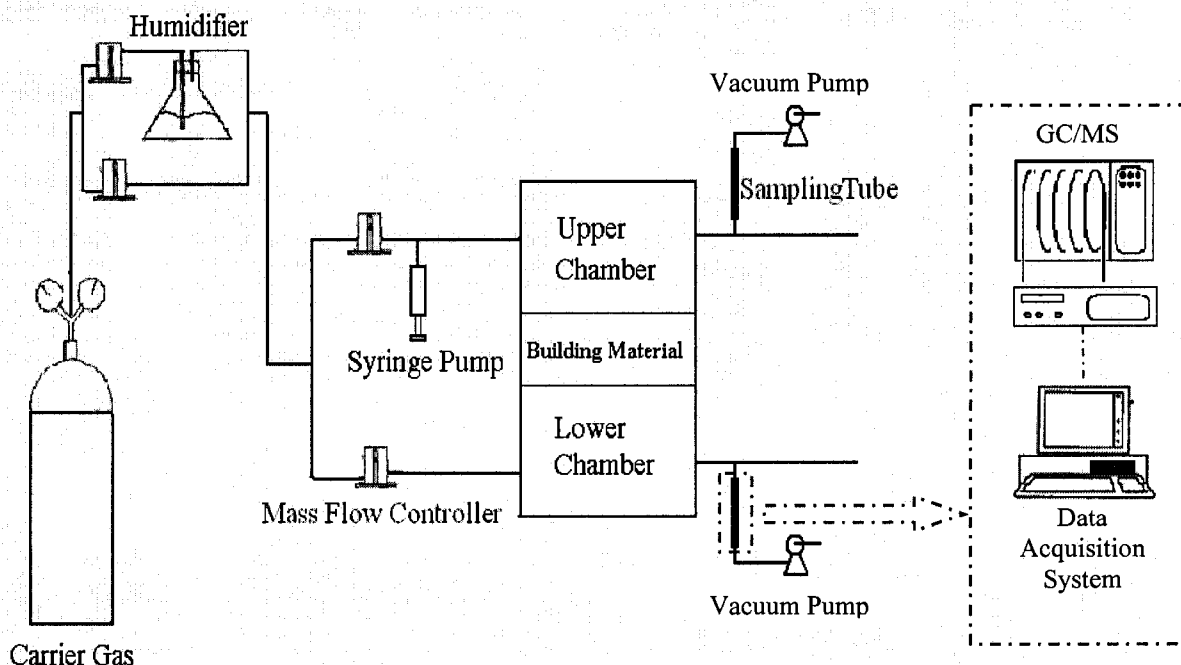
Considering all the possible combinations of these factors yields 12 series of experiments. This enables us to perform a systematic analysis involving full factorial design which consists of 2 factors (temperature and relative humidity) at three different levels of humidity and four different levels for temperature. Ceiling tile was chosen as the target material.

The second design was intended to compare the diffusion of a compound as part of a mixture with diffusion of a single compound through a specimen. Hence, all the VOCs used in the mixture in the first plan were individually tested at 23°C and 20% of relative humidity so that the difference could be measured by comparison to respective mixture tests.

In addition, VOC species were selected to be representative of the whole range of physicochemical properties of VOCs such as boiling point and polarity. That is, each represents a different boiling point or polarity. Thus, another goal of the study, which is to observe how physicochemical properties of VOCs affect diffusion coefficients, could be achieved.

### **3.3 Experimental Set-up**

A two-flow technique was used to satisfy the aims of this study. In an overview, this set-up consisted of four main components including a chamber assembly, air supply system, air sample collection system, and analytical system. Figure 3.1 is a diagram of the experimental set-up.



**Figure 3-1: Schematic diagram of the experimental set-up**

The chamber assembly consisted of two identical cylindrical chambers; the material specimen was placed between their open ends and separated them. The volume and diameter of each cylinder was 2.7 liter and 0.13 m, respectively. In order to minimize the potential sink effect, the internal wall of the chambers had a smooth surface texture so that adsorption of VOCs into the walls would be negligible. Each chamber was equipped with an inlet and an outlet port through which the chambers were continuously ventilated with fresh air or contaminated air.

The air supply system included a cylinder containing carrier gas coupled with a humidifier. Carrier gas was supplied by commercially compressed nitrogen (UHP 5.0) with a purity grade of 99.999%. A portion of pure nitrogen was blown into the distilled water to be humidified. This humidified portion was then mixed with the dry portion at a specific ratio so that the desired level of humidity could be achieved. The ratio was

manually adjusted by employing valves for both the humidified and dry streams to obtain the required flow rate and humidity. The relative humidity of nitrogen was measured using a humidity meter (Testo 625), and the flow rate of nitrogen using a mass flow meter (Matheson mass flow controller model 8270) which was set to deliver 4.2 l/min. The mass flow meter was calibrated with a primary flow meter (Bios model DryCal DC-Lite). Subsequently, the carrier gas was split into two streams with equal flow rates. One stream was directed to the inlet of the lower chamber to ventilate it while the other stream (contaminated with VOC) was directed to the inlet of the upper chamber. By adjusting the rate of VOC injecting into the second stream, the desired level of VOC concentration was achieved. A syringe pump (kdScientific) coupled with a 250  $\mu$ l Hamilton gas tight syringe was used to inject the VOC and generate contaminated air.

Subsequently, samples from both chamber outlets were periodically collected in two separate prepacked thermal desorption tubes (Supelco Air Toxics stainless steel sampling tubes). Each sampling tube was connected to a vacuum pump (Gilian personal air sampler model GilAir-3) that had been adjusted to draw out a flow of 50 cc/min from outlet stream for one minute. The two vacuum pumps were operated simultaneously to prevent any pressure difference across the sample.

In the analyzing unit, samples were analyzed using a thermal desorber (Perkin Elmer model TurboMatrix 350) and GC/MS analyzer (Perkin Elmer model Clarus 500).

The entire experimental set-up was kept in a controlled chamber at the desired temperatures.



### **3.4 Preparation of VOCs, Material Specimens, and GC/MS Apparatus**

#### **3.4.1 VOC Preparation**

It was decided to select VOCs representing a wide range of molecular weights, boiling points, and polarities. Accordingly, octane, isopropanol, cyclo hexane, ethyl acetate, and hexane were selected. Table 3.1 lists the physicochemical properties of these compounds.

**Table 3-1: Physicochemical properties of VOCs (www.osha.gov, macro.lsu.edu, physchem.ox.ac.uk†)**

VOC	Chemical Formula	Boiling Point (°C)	Molecular weight (g)	Density (g/ml)	Polarity Index	Vapor pressure <sup>†</sup> (mm-Hg) at 20 °C
Octane	C <sub>8</sub> H <sub>18</sub>	125.52	114	0.703	0.1	11
Isopropanol	C <sub>3</sub> H <sub>8</sub> O	82.3	60	0.785	4.3	33
Cyclo hexane	C <sub>6</sub> H <sub>12</sub>	80.74	84	0.779	0.0	77
Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	77.1	88	0.897	4.3	76
Hexane	C <sub>6</sub> H <sub>14</sub>	69	86	0.661	0.06	130

The diffusion coefficient of each compound was measured individually as well as in a mixture. In the mixture test, in order to prepare a solution with an equal partial concentration of each compound, the compounds were mixed together in pure form (GC or HPLC grade) at a specific ratio (based on their density) in a volumetric flask and then diluted to the desired level with methanol as solvent. The procedure of calculation is described in Appendix A.

### **3.4.2 Material Preparation**

Ceiling tile, commonly used as a material in building structures, was selected for this study. It was cut into circular specimens of 0.13 m in diameter. Before each test, the specimen was baked in an oven at 60-70°C to release the residual VOCs within the material followed by conditioning with pure nitrogen for an hour to minimize the remaining VOCs. To ensure that all possible contamination had been removed from the tile, background contamination was checked by sampling air from both outlet ports before starting the injection.

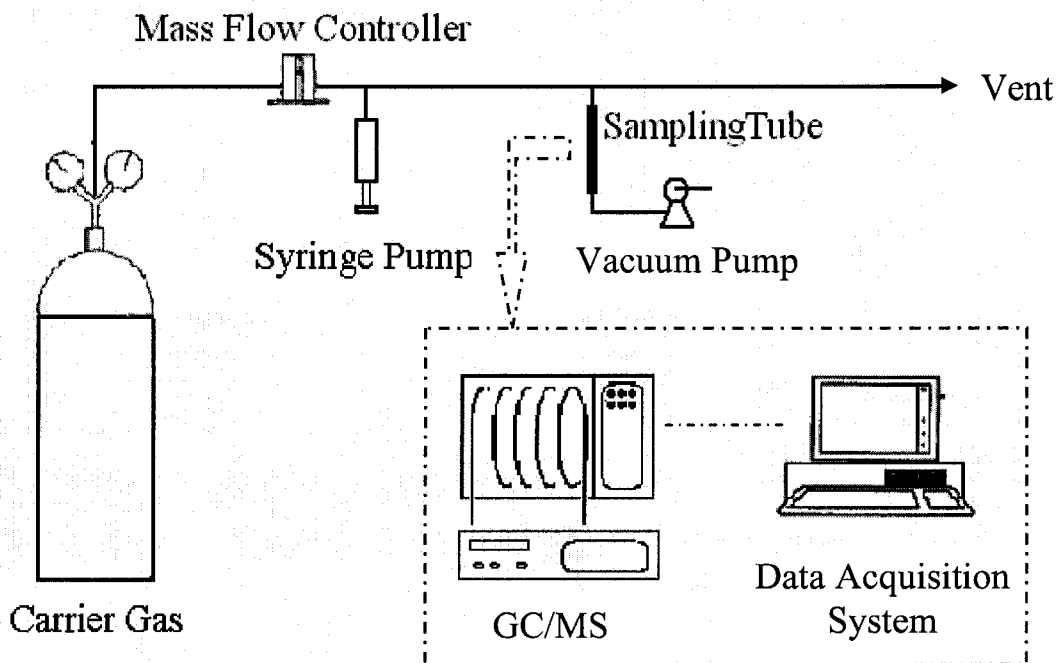
### **3.4.3 Sampling Tubes**

Before testing, sampling tubes (Supelco Air Toxics stainless steel sampling tubes) were preconditioned by passing a 50 cc/min flow of compressed helium (UHP 5.0) through the tubes for 10 min at 350°C. Conditioned tubes were wrapped with aluminum foil and then stored in the refrigerator to prevent any contamination.

### **3.4.4 GC/MS Calibration and Method Development**

Before starting the experiment, an analytical system was calibrated for each compound. To do so, a set-up was designed as illustrated in Figure 3.2. Using a syringe pump, the solution of VOCs prepared for the test was smoothly injected at a set rate into a flow of pure nitrogen with a constant flow rate of 2.1 l/min. At the sampling port designated to connect the sampling tube and the vacuum pump, samples were collected with the same sampling volume as in the diffusion measurement test (i.e., vacuum flow rate of 50 cc/min for a sampling time of one minute), and then analyzed using GC/MS. A method was developed for the thermal desorber and GC/MS analyzer as follows. First, in the

thermal desorber unit, the sampling tubes were desorbed at a temperature of 300°C for 10 minutes while the temperature of the trap was set at -20°C. Subsequently, the trap was desorbed at 300°C for 5 minutes. The temperature of the transfer line that connects the thermal desorber unit to the GC column was kept at 250°C. The GC method began at 45°C, and its temperature was held steady for 2 minutes. Then, it was increased to 65°C with a heating rate of 2 °C/min and kept at this temperature for another 2 minutes. Subsequently, the oven temperature was increased to 200°C to burn out all the residues.



**Figure 3-2: Schematic figure of the sample collecting system**

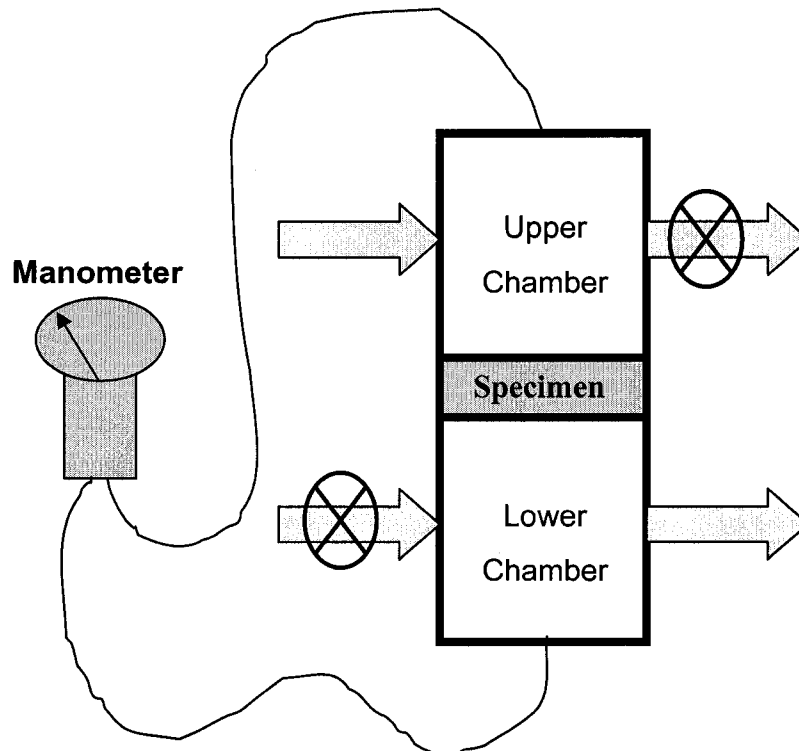
By varying the injection rate, different concentrations were obtained and a calibration curve was plotted with 5 data points (including zero point) for the low concentration zone and 4 data points for the high concentration zone. Calibration curves and a description of their calculations are provided in Appendix B.

## **3.5 Experimental Procedures**

A number of preliminary tests were performed to refine the experimental procedures and to determine the most suitable values for experimental parameters and conditions. Precautions taken before conducting the diffusion measurement included checking for pressure difference across samples and balancing chamber pressures, cleaning the test chambers, checking for air leakage, measuring background contamination, and finally implementing the measurement.

### **3.5.1 Checking for Pressure Difference**

One of the most serious sources of error that may result in misestimation of diffusion coefficients is a pressure difference across the specimen. This pressure difference creates forced diffusion so that the assumption of pure diffusion would no longer be valid. In order to estimate the extent of the pressure difference effect, some changes were made to the experimental set-up as shown in the following diagram so that permeability could be measured.



**Figure 3-3: Diagram of a twin chamber modified to measure permeability**

In this case, the material specimen was placed between the two open ends of the chamber assembly while the outlet port of the upper chamber and the inlet port of the lower chamber were blocked. The entire flow was then directed within the material. According to Darcy's law, if a pressure drop takes place across a porous medium, fluid flows through the porous medium proportional to that pressure gradient (Bird et al., 2002):

$$Q = -\frac{\kappa \cdot A}{\mu} \cdot \nabla P \quad \text{Equation 3-1}$$

where,  $Q$  is the total discharge ( $\text{m}^3/\text{s}$ ),  $\kappa$  is the permeability of the medium ( $\text{m}^2$ ),  $A$  is the cross sectional area to flow ( $\text{m}^2$ ),  $\mu$  is the viscosity of fluid ( $\text{Pa}\cdot\text{s}$ ), and  $\nabla P$  is the pressure gradient vector ( $\text{Pa}/\text{m}$ ).

For a given flow rate of compressed air passing through the specimen, the created drop across the specimen was recorded using a micro manometer (DP-Calc Model 8702).

Solving Equation 3.1 when  $Q$ ,  $A$ ,  $\mu$ , and  $\nabla P$  are known yields permeability of air through the building material as shown below.

**Table 3-2: Obtained data for permeability calculation**

	imposed $Q$ (m <sup>3</sup> /s)	$A$ (m <sup>2</sup> )	$\mu$ (Pa.s) @ 20°C	recorded $\Delta P$ (Pa)	$\Delta x$ (m)	calculated $\kappa$ (m <sup>2</sup> )
Run 1	3.62E-05	0.01327	1.81E-05	136.5	1.18E-02	4.28E-12
Run 2	6.85E-05	0.01327	1.81E-05	268.02	1.18E-02	4.13E-12

From Table 3-2, an average value of 4.20E-12 m<sup>2</sup> for permeability of air,  $\kappa$ , can be assumed in order to estimate the magnitude of the forced diffusion as explained in the following procedure.

Dividing both sides of Equation 3.1 by the cross-sectional area,  $A$ , and multiplying it by the bulk density ( $\rho_b$ ) yields total mass flux,  $J_t$ , the unit of which is kg/m<sup>2</sup>.s.

$$J_t = -\frac{\kappa \cdot \rho_b}{\mu} \cdot \nabla P \quad \text{Equation 3-2}$$

then the partial mass flux of species  $i$  due to advection is:

$$J_i = \varpi_i \cdot J_t = -\frac{\rho_i}{\rho_b} \cdot \frac{\kappa \cdot \rho_b}{\mu} \cdot \nabla P = -\rho_i \cdot \frac{\kappa}{\mu} \cdot \nabla P \quad \text{Equation 3-3}$$

where  $\varpi_i$  is the mass fraction of species  $i$ , and  $\rho_i$  can be replaced with the concentration of species  $i$ ,  $c_i$ .

By replacing appropriate values in Equation 3.3 and assuming a small pressure difference of 0.001 inH<sub>2</sub>O (or 0.25 Pa), which is the accuracy of the measuring device, the contribution of mass flux due to pressure difference is given as:

$$J_i = -C_i \cdot \frac{\kappa}{\mu} \cdot \frac{dP}{dx} = -C_i \cdot \frac{4.2 \times 10^{-12}}{1.81 \times 10^{-5}} \cdot \frac{0.25}{1.18 \times 10^{-2}} \cong -5 \times 10^{-6} \cdot C_i$$

On the other hand, the contribution of pure diffusion can be obtained using Fick's first law (Equation 2.1). Assuming  $10^{-6}$  as the order of magnitude of the diffusion coefficient, diffusion is calculated as:

$$J = -D \frac{dC}{dx} \approx -10^{-6} \times \frac{dC}{1.18 \times 10^{-2}} \approx 10^{-4} dC$$

Also, by assuming that the magnitude order of  $C_i$  is the same as  $dC$ , the error ratio (i.e.,  $J_i/J$ ) created due to the presence of slight pressure differences (0.001 inH<sub>2</sub>O) would be up to 5% in the calculated diffusion coefficient. This pressure difference, which is highly probable due to the sampling system or because of the plumbing system of the setup, has not been considered in many earlier studies. In this study, an attempt was made to eliminate any pressure difference across the specimen (as low as  $0 \pm 0.001$  inH<sub>2</sub>O). This was done by bending the flexible Teflon tube used in the plumbing of the set-up, or reducing the sampling volume to 50 cc/min which is considerably lower than the ventilation rate for each chamber (2.1 l/min).

### 3.5.2 Cleaning the Test Chambers

The following measures were taken to make sure that all contamination was wiped off and the chambers were clean:

- First, the chambers were completely washed with laboratory detergent and distilled water, and then the internal walls of the chambers were rinsed using isopropyl alcohol in a 70% solution.
- Distilled water was used to rinse the chambers again.
- Using clean lint-free cloth and compressed air, the chambers were dried.
- Using compressed air and pure nitrogen, the chambers were purged for two hours before the experiments.

### **3.5.3 Checking for Air Leakage**

Another factor that can reduce the accuracy of measurement is air leakage. Hence, some precautions were taken to assure the tightness of the system such as taping the edges of the specimen using Teflon tape, shutting the open ends of two chambers using three commercial clamps, and measuring the air flow rate into and out of the chamber to verify if there was any difference between them. Also, liquid leak detector was applied on all connections to make sure there was no leakage.

### **3.5.4 Measuring Background Contamination**

As stated earlier, specimens had to be conditioned before testing. Therefore, the whole experimental set-up was assembled, (see Figure 3.1) except the connection of the syringe pump, and then preconditioned first with compressed air and then with nitrogen for two hours. Before running the experiment, the concentration of outlet streams was measured using a sampling tube and recorded as background contamination. If the amount of this contamination was less than the sensibility of the analytical system, there would be no



need to subtract it from the concentration of VOC in the diffusion coefficient measurement.

### **3.5.5 Starting Test**

After completing all the preparation operations outlined above, measurement of the diffusion coefficient was begun by injecting a VOC or a mixture of VOCs into the flow ventilating the upper chamber. Afterwards, samples were taken from both outlets approximately every 30 minutes until equilibrium was reached.

## **3.6 Summary**

In this chapter, a two-chamber experimental set-up was developed to conduct a measurement test to find diffusion coefficients of VOCs as a single compound or of a mixture of VOCs. The experimental set-up was designed to be able to investigate the effect of environmental conditions (temperature and humidity). It was observed that results can be dramatically affected by disregarding pressure differences across the specimen. Special consideration was given to preventing any pressure differences across the specimen. Thus, the following experimental study procedures are:

- Step 1: A twin chamber experimental set-up was assembled to measure the diffusion coefficient of selected VOCs through the given building material.
- Step 2: VOCs to be tested were prepared in desired concentrations. Besides, specimen (ceiling tile) was conditioned before testing.
- Step 3: The analytical instruments (GC/MS) were calibrated for selected VOCs.

- Step 4: Before starting, a number of preliminary precautions were taken to minimize the pressure difference across the specimen, and to avoid possible air leakage. On top of that, the whole experimental set-up was preconditioned, and background contamination was recorded.
- Step 5: The experiment began with measuring the diffusion coefficients of individual compounds followed by testing a mixture of VOCs.
- Step 6: Temperature and relative humidity of the experimental environment were varied to obtain diffusion coefficients at different environmental conditions.

# Chapter 4

## Experimental Results and Data Analysis

### 4.1 Introduction

In the first part of this chapter, the results of diffusion coefficient measurements are presented. In studies to investigate the influence of material properties on VOC emission rates (Little et al., 1994; Yang et al., 2001; Huang & Haghghat, 2002), it was concluded that among the considered parameters (diffusion coefficient, partition coefficient, thickness of solid, and air velocity), only the diffusion coefficient and material thickness have a significant effect (Huang & Haghghat, 2003). However, these studies ignored the impact of temperature, relative humidity, and VOC mixture because of a lack of data. Hence, through a two-factor statistical analysis, a systematic parametric study was conducted in this chapter to provide more details on the impacts of two independent environmental factors (temperature and humidity) on diffusion coefficients and their interaction effects.

### 4.2 Theory of Mass Transfer in Building Materials

Since VOC concentration levels in indoor environments are very low in comparison with the saturated concentration, adsorbed-phase diffusion can be neglected for the purposes of this study, therefore, mass transfer through building materials is assumed to be a gas-phase diffusion (Tiffonnet et al., 2000). Thus, as explained in Chapter 2, a modification

on Fick's first law (Equation 4.1) as used by Meininghaus et al. (1998, 2000) can be used to describe mass transfer within ceiling tile and to measure the effective diffusion coefficient in steady-state conditions.

$$D_{eff} = -\frac{\dot{m} \Delta x}{A \Delta c} = -\frac{Vd}{A} \frac{C_2}{C_2 - C_1} \quad \text{Equation 4-1}$$

where  $D_{eff}$  is the effective diffusion coefficient ( $m^2/s$ ),  $\dot{m}$  the mass flow through the material ( $mg/s$ ),  $A$  the area of specimen ( $m^2$ ),  $V$  the air flow rate ( $m^3/s$ ),  $d$  the material thickness ( $m$ ), and  $C_1$  and  $C_2$  are the VOC concentration at the steady-state condition in the primary (contaminated air supplied) and secondary (clean air supplied) chambers, respectively ( $mg/m^3$ ).

The assumptions made to allow the above method to be used in this study are: 1) the concentration gradient in the material is approximately linear; 2) the diffusion through the boundary layer of air is fast so that respective resistance is negligible; 3) the diffusion coefficients are not dependant on concentration; and finally 4) the mass flow through the material equals the mass flow out of the lower chamber (Meininghaus et al., 1998 & 2000).

### **4.3 Calculation Procedures**

After analyzing the samples from the upper and lower chambers while the experiment was running, the obtained concentration versus time was plotted for each compound. Then, for every pair of concentrations (lower concentration and respective higher concentration), an instant diffusion coefficient was calculated using Equation 4.1. From

then on, the effective diffusion coefficient was averaged out. Appendix C provides the detailed calculations that resulted in the following outcomes.

#### **4.4 Experimental Results and Discussion**

In this section, results are presented in three subsections: the results of the diffusion measurement obtained for each compound individually; the results of the diffusion measurement for a mixture of compounds; and the results of the diffusion measurement when temperature and humidity vary. Results from the present study are then discussed and compared with those in the literature. However, it should be noted that a direct comparison is impossible since the material and VOCs tested in this study are not identical with those tested in the literature. Further, each diffusion coefficient obtained by different investigators implies a different concept; for instance, the diffusion coefficients measured by Kirchner et al. (1999) using the cup method, CLIMPAQ method, and microbalance method take into account the resistance of the boundary layer on both sides of the material. That is, the partitioning between the gas phase and the material phase is included in the calculated effective diffusion coefficient, while other researchers separated these two parameters.

##### **4.4.1 Diffusion Coefficient for a Single Compound**

Diffusion coefficients of five VOCs in ceiling tile were individually measured at a temperature of 23°C in dry conditions. The VOCs were isopropanol, hexane, cyclo hexane, ethyl acetate, and octane. Results are listed in Table 4.1.

**Table 4-1: Diffusion coefficient of single compounds in ceiling tile**

	Isopropanol	Hexane	Cyclo hexane	Ethyl acetate	Octane
Diffusion Coefficient (m <sup>2</sup> /s)	1.86E-06	2.10E-06	2.03E-06	1.79E-06	1.52E-06
Standard Deviation (m <sup>2</sup> /s)	4.48E-07	2.25E-07	6.74E-08	2.924E-07	1.18E-07

The ranking of the investigated compounds with respect to their diffusion coefficients is: hexane  $\approx$  cyclo hexane > isopropanol > ethyl acetate > octane, which means, under same circumstances, ceiling tile is less permeable to octane than ethyl acetate, and so on. With due attention to the overlap of their standard deviation range, hexane and cyclo hexane can be considered to have similar diffusion coefficients.

#### **4.4.2 Relationship between Molecular Weight, Vapor Pressure, and Polarity of VOC and D Measured for a Single Compound**

Figure 4.1 illustrates the relationship between the boiling point of the tested VOCs and the diffusion coefficient of the VOC through the ceiling tile. Although the compound with the highest boiling point (octane) has the least ability to diffuse through the material, and the lightest one (hexane) possesses the highest diffusion coefficient, no definite trend can be concluded from the graph.

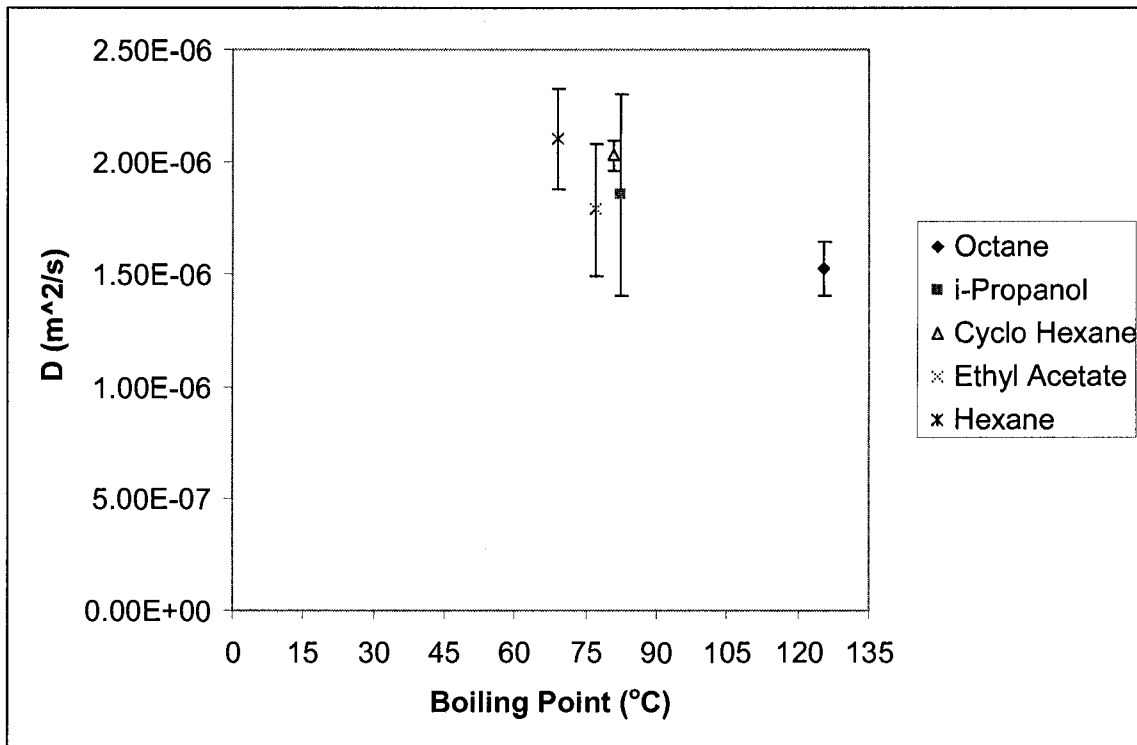


Figure 4-1 : Diffusion Coefficient versus Boiling Point

However, by plotting the determined diffusion coefficients versus vapor pressure (Figure 4.2), it can be inferred that the diffusion coefficients of different VOCs are positively related to the vapor pressure.

Overall, by considering that selected VOCs do not belong to a same functional group, observed relationships between diffusion coefficient and boiling point, and between diffusion coefficient and vapor pressure in this study are in good accordance with findings in the literature (Meininghaus et al., 2002).

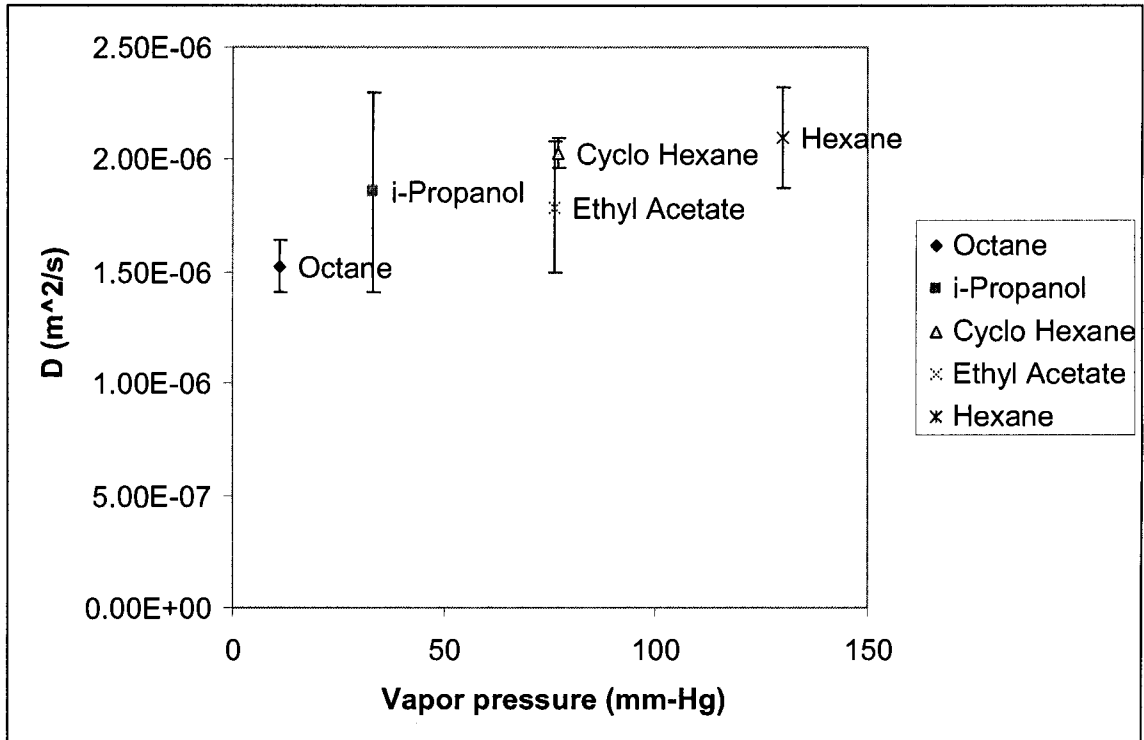


Figure 4-2: Diffusion Coefficient versus Vapor Pressure

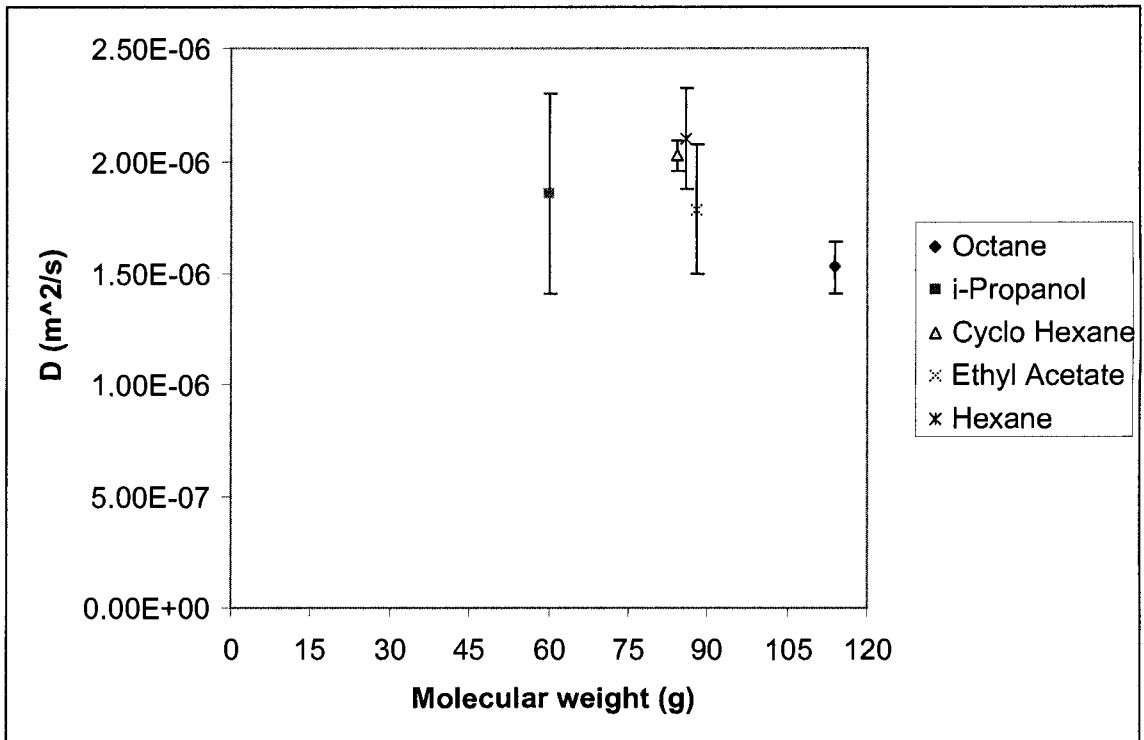


Figure 4-3: Diffusion Coefficient versus Molecular Weight



Additionally, no clear correlation was observed between the diffusion coefficient and molecular weight (Figure 4.3) or between the diffusion coefficient and the polarity of the VOC (Figure 4.4).

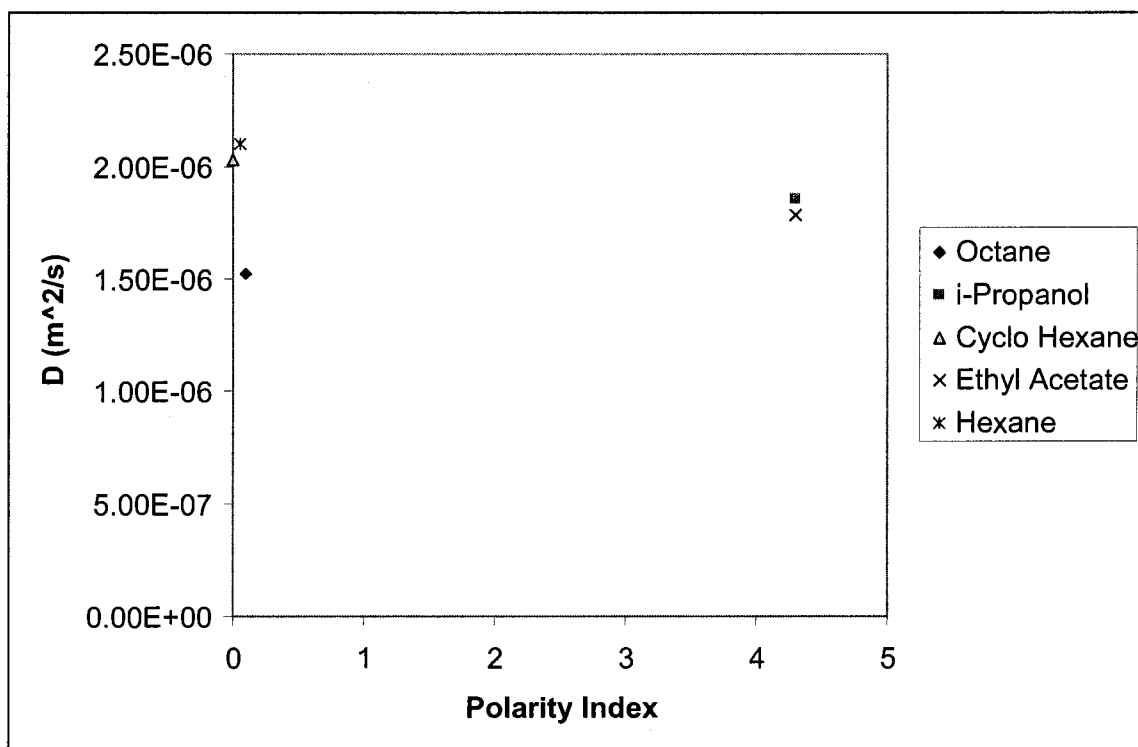


Figure 4-4: Diffusion Coefficient versus Polarity Index

#### 4.4.3 Comparison of Diffusion Coefficients for a Single Compound and a Mixture of Compounds

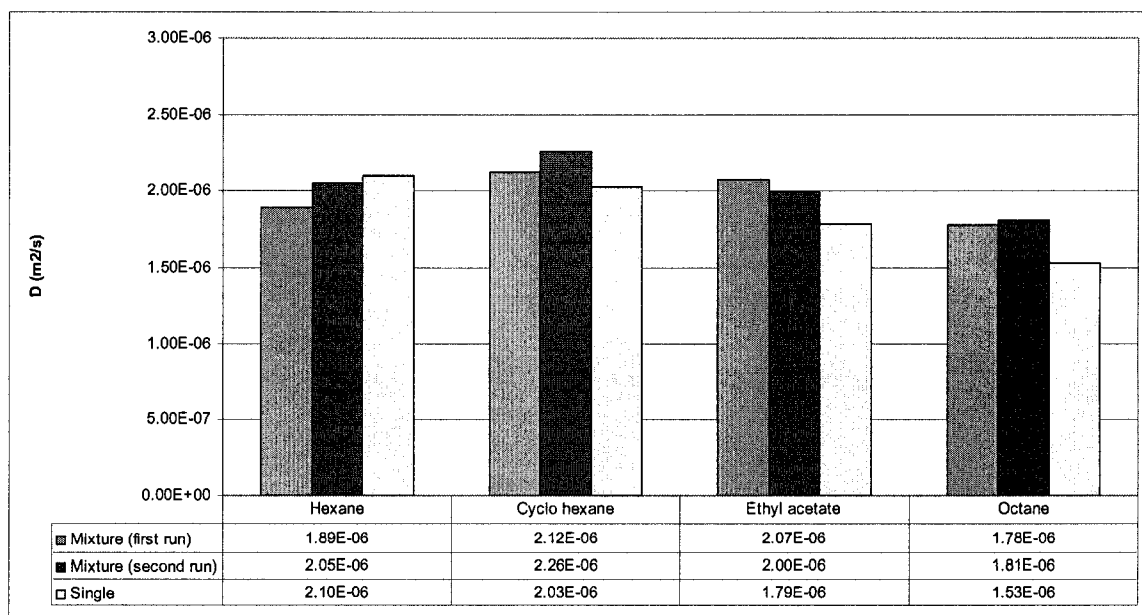
Similarly, diffusion coefficients of VOCs in a mixture were obtained at 23°C in dry conditions, as summarized in Table 4.2. This run was performed twice to assure the repeatability of tests. Note that in the mixture test, all the compounds collected in the sampling tube had to be analyzed simultaneously through a same method developed for GC/MS. Because of this limitation in the GC/MS based program, toluene and isopropanol

failed to comply with the sensitivity requirements of the detection instruments; therefore, they were excluded from the test.

**Table 4-2: Diffusion coefficient of compounds in mixture**

		Hexane	Cyclo hexane	Ethyl acetate	Octane
First run	Diffusion Coefficient (m <sup>2</sup> /s)	1.89E-06	2.12E-06	2.07E-06	1.78E-06
	Standard Deviation (m <sup>2</sup> /s)	1.29E-07	1.52E-07	2.44E-07	7.77E-08
Second run	Diffusion Coefficient (m <sup>2</sup> /s)	2.05E-06	2.26E-06	2.00E-06	1.81E-06
	Standard Deviation (m <sup>2</sup> /s)	6.36E-08	1.49E-07	4.64E-07	5.28E-08
Mean	Diffusion Coefficient (m <sup>2</sup> /s)	1.97E-06	2.19E-06	2.03E-06	1.79E-06

Obtained diffusion coefficients were then compared with the results of the diffusion coefficient of respective VOCs in the test as an individual compound (Figure 4.5).



**Figure 4-5: Comparison of Diffusion Coefficients for a Single Compound and a Mixture of Compounds**

Although diffusion coefficients of cyclo hexane, ethyl acetate, and octane in individual tests were slightly lower than those in the mixture test, taking the standard deviations into account, diffusion coefficients for all tested VOCs, in their individual form, were found to be of the same order of magnitude as the determined diffusion coefficients of VOCs in a mixture (Figure 4.5). This outcome agrees well with the previous finding by Jørgensen & Bjørseth (1999) and Meininghaus et al. (2002). As stated earlier, this fact might be interpreted by the abundant amount of adsorption sites compared with the relatively small number of adsorbing VOCs.

#### 4.4.4 Influence of Temperature and Humidity

As described in Chapter 3, in the experimental design for this study, particular attention was paid to systematically investigating the influence of temperature and humidity on diffusion coefficients and to quantifying the effects. The results are summarized in Table 4.3.

**Table 4-3: Diffusion coefficient of VOC at different temperatures and humidity**

		Temperature				
		15 (°C)	23 (°C)	31 (°C)	39 (°C)	
Specific Humidity	0 (g/kg wet air)	Hexane	1.84E-06	1.97E-06	1.50E-06	1.75E-06
		Cyclo hexane	1.88E-06	2.19E-06	1.69E-06	2.04E-06
		Ethyl acetate	1.65E-06	2.03E-06	1.26E-06	1.46E-06
		Octane	1.64E-06	1.79E-06	9.57E-07	1.26E-06
	3.4551 (g/kg wet air)	Hexane	1.72E-06	1.95E-06	1.68E-06	1.59E-06
		Cyclo hexane	1.75E-06	2.15E-06	1.77E-06	1.70E-06
		Ethyl acetate	1.40E-06	2.01E-06	1.53E-06	1.23E-06
		Octane	1.56E-06	1.75E-06	1.09E-06	1.05E-06
	6.9248 (g/kg wet air)	Hexane	1.91E-06	1.84E-06	1.76E-06	1.62E-06
		Cyclo hexane	1.99E-06	1.93E-06	2.03E-06	1.75E-06
		Ethyl acetate	1.72E-06	1.97E-06	1.73E-06	1.28E-06
		Octane	1.32E-06	1.74E-06	1.12E-06	1.04E-06

The statistical analysis of this set of data is described in the next section. It required two independent factors: temperature and humidity content. As a result, instead of relative humidity, specific humidity was chosen as the second independent factor. Chosen values for specific humidity in Table 4.3 correspond to 0%, 20%, and 40% of relative humidity at room temperature (23°C), respectively.

## **4.5 Statistical Data Analysis**

### **4.5.1 Full Factorial Design in Three levels**

A three-level full factorial design is an experimental design with all input factors set at three levels each, and the experiment is carried out at all possible combinations of all the input factors. These levels are called high, low, and center (standard) point, or +1, -1, and

0, respectively (NIST/SEMATECH 2007). In this study, it is of interest to ascertain the relative importance of two main factors: humidity (factor  $A$ ), and temperature (factor  $B$ ), as well as the two-factor interaction ( $A \times B$ ). This requires 12 runs, the results of which are tabulated in Table 4.4 for a single replication of the experiment.

**Table 4-4: Two-factor experiment with 1 replication**

		Factor B				Total	Mean
		Level 1	Level 2	Level 3	Level 4		
Factor A	Level 1	$y_{11}$	$y_{12}$	$y_{13}$	$y_{14}$	$Y_{1j}$	$\bar{y}_{1j}$
	Level 2	$y_{21}$	$y_{22}$	$y_{23}$	$y_{24}$	$Y_{2j}$	$\bar{y}_{2j}$
	Level 3	$y_{31}$	$y_{32}$	$y_{33}$	$y_{34}$	$Y_{3j}$	$\bar{y}_{3j}$
Total		$Y_{i1}$	$Y_{i2}$	$Y_{i3}$	$Y_{i4}$	$Y_{...}$	
Mean		$\bar{y}_{i1}$	$\bar{y}_{i2}$	$\bar{y}_{i3}$	$\bar{y}_{i4}$		$\bar{y}_{...}$

$\bar{y}_{...}$  : mean of all  $ab$  observations  
observations

$Y_{...}$  : sum of all  $ab$  observations

Each observation in Table 4-4 may be written as

$$y_{ij} = \mu_T + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ij}$$

**Equation 4-2**

where  $\mu_T$  = the overall population mean

$\alpha_i$  = the average treatment effect of factor  $A$  at level  $a_i$  ( $\alpha_i = \mu_i - \mu_T$ )

$\beta_j$  = the average treatment effect of factor  $B$  at level  $b_j$  ( $\beta_j = \mu_j - \mu_T$ )

$(\alpha\beta)_{ij}$  = the interaction effect of the  $i$ th level of factor A and the  $j$ th level of factor

$$B ((\alpha\beta)_{ij} = \mu_{ij} - \mu_i - \mu_j + \mu_T)$$

$\varepsilon_{ij}$  = experimental error associated with each score ( $\varepsilon_{ij} = y_{ij} - \mu_{ij}$ )

By splitting the total sum of squares of our obtained data into four components by means of the following identity, the analysis of variance of the two-factor experiment can be performed (Walpole, 2002).

$$\begin{aligned} \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n (y_{ijk} - \bar{y}_{...})^2 &= bn \sum_{j=1}^b (\bar{y}_{i..} - \bar{y}_{...})^2 + an \sum_{j=1}^b (\bar{y}_{.j.} - \bar{y}_{...})^2 + \\ n \sum_{i=1}^a \sum_{j=1}^b (\bar{y}_{ij.} - \bar{y}_{i..} - \bar{y}_{.j.} + \bar{y}_{...})^2 &+ \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n (y_{ijk} - \bar{y}_{ij.})^2 \end{aligned} \quad \text{Equation 4-3}$$

where  $n$  is the number of replications.

Symbolically, the sum-of-squares identity may be written as

$$SST = SSA + SSB + SS(AB) + SSE \quad \text{Equation 4-4}$$

where  $SSA$  and  $SSB$  are the sum of squares for the main effects  $A$  and  $B$  respectively,  $SS(AB)$  is the interaction sum of squares for  $A$  and  $B$ , and  $SSE$  is the error sum of squares.

Dividing each of the sum of squares on the right side of equation 4.4 by their corresponding number of degree of freedom yields mean squares as below:

$$\begin{aligned} S_1^2 &= \frac{SSA}{a-1} & , & & S_2^2 &= \frac{SSB}{b-1} \\ S_3^2 &= \frac{SS(AB)}{(a-1)(b-1)} & , & & S^2 &= \frac{SSE}{ab(n-1)} \end{aligned} \quad \text{Equation 4-5}$$

Since there was only one replication in this survey, there would be no variability due to the difference of output within a group (i.e., experimental error); consequently, the fourth term ( $S^2$ ), which facilitates calculating the  $F$  factor, can not be computed. Instead, the term Standard Omega Squared ( $\omega^2$ ) was employed so as to discuss the parameter effects and their interaction effects (Huang and Haghghat, 2003; Huang, 2003). This value reflects the proportional amount of the total variance that is attributed to the variation among the factor effects (Keppel, 1991), defined as

$$\omega^2 = \frac{SS}{SST} \quad \text{Equation 4-6}$$

By using the following criteria suggested by (Cohen, 1997), one may determine the significance of a factor or factor interaction effect:

A “small” effect is a factor that produces an  $\omega^2$  of 0.01.

A “medium” effect is a factor that produces an  $\omega^2$  of 0.06.

A “large” effect is a factor that produces an  $\omega^2$  of 0.15 or greater.

#### 4.5.2 Analysis of Variance

For one replication, analysis of variance for hexane, cyclo hexane, ethyl acetate, and octane was performed, and the associated  $\omega^2$  was computed for each VOC. In this part, the detailed calculation for the values in Table 4.4 is presented for hexane.

If  $Y_i$  denotes the sum of the observations for the  $i$ th level of factor  $A$  and  $Y_j$  denotes the sum of the observations for the  $j$ th level of factor  $B$ , then

$$\begin{aligned}
Y_{i1} &= 1.84\text{E} - 06 + 1.97\text{E} - 06 + 1.50\text{E} - 06 + 1.75\text{E} - 06 = 7.06\text{E} - 06 & \bar{y}_{i1} &= 1.76\text{E} - 06 \\
Y_{i2} &= 1.72\text{E} - 06 + 1.95\text{E} - 06 + 1.68\text{E} - 06 + 1.59\text{E} - 06 = 6.94\text{E} - 06 & \bar{y}_{i2} &= 1.73\text{E} - 06 \\
Y_{i3} &= 1.91\text{E} - 06 + 1.84\text{E} - 06 + 1.76\text{E} - 06 + 1.62\text{E} - 06 = 7.13\text{E} - 06 & \bar{y}_{i3} &= 1.78\text{E} - 06
\end{aligned}$$

$$\begin{aligned}
Y_{1j} &= 1.84\text{E} - 06 + 1.72\text{E} - 06 + 1.91\text{E} - 06 = 5.47\text{E} - 06 & \bar{y}_{1j} &= 2.74\text{E} - 06 \\
Y_{2j} &= 1.97\text{E} - 06 + 1.95\text{E} - 06 + 1.84\text{E} - 06 = 5.76\text{E} - 06 & \bar{y}_{2j} &= 2.88\text{E} - 06 \\
Y_{3j} &= 1.50\text{E} - 06 + 1.68\text{E} - 06 + 1.76\text{E} - 06 = 4.93\text{E} - 06 & \bar{y}_{3j} &= 2.47\text{E} - 06 \\
Y_{4j} &= 1.75\text{E} - 06 + 1.59\text{E} - 06 + 1.62\text{E} - 06 = 4.96\text{E} - 06 & \bar{y}_{4j} &= 2.48\text{E} - 06
\end{aligned}$$

where  $\bar{y}_{i.}$  is the mean of the observations for the  $i$ th level of factor  $A$ , and  $\bar{y}_{.j}$  is the mean of the observations for the  $j$ th level of factor  $B$ .

The mean of all  $a \times b \times n$  observations is calculated as:

$$\begin{aligned}
\bar{y}_{...} &= 1.84\text{E} - 06 + 1.97\text{E} - 06 + 1.50\text{E} - 06 + 1.75\text{E} - 06 + 1.72\text{E} - 06 + 1.95\text{E} - 06 + 1.68\text{E} - 06 \\
&\quad + 1.59\text{E} - 06 + 1.91\text{E} - 06 + 1.84\text{E} - 06 + 1.76\text{E} - 06 + 1.62\text{E} - 06 = 1.76\text{E} - 06
\end{aligned}$$

Then the sum of squares for the main effects  $A$  would be:

$$SSA = bn \sum_{j=1}^a (\bar{y}_{i.} - \bar{y}_{...})^2 = 4 \times 1 \times ((1.76\text{E} - 06 - 1.76\text{E} - 06)^2 + \dots) = 4.85\text{E} - 15$$

and  $SSB$  and  $SS(AB)$  will be calculated as below:

$$SSB = an \sum_{j=1}^b (\bar{y}_{.j} - \bar{y}_{...})^2 = 3 \times 1 \times ((1.82\text{E} - 06 - 1.76\text{E} - 06)^2 + \dots) = 1.65\text{E} - 13$$

$$\begin{aligned}
SS(AB) &= n \sum_{i=1}^a \sum_{j=1}^b (\bar{y}_{ij} - \bar{y}_{i.} - \bar{y}_{.j} + \bar{y}_{...})^2 = \\
&\quad 1 \times ((1.83\text{E} - 06 - 1.76\text{E} - 06 - 1.82\text{E} - 06 + 1.76\text{E} - 06)^2 + \dots) = 7.48\text{E} - 14
\end{aligned}$$



Dividing each sum of squares by the total sum of squares yields the relevant Omega Squared:

$$\text{for main effect } A: \quad \omega^2 = \frac{4.85E-15}{4.85E-15 + 1.65E-13 + 7.48E-14} = 0.02$$

$$\text{for main effect } B: \quad \omega^2 = \frac{1.65E-13}{4.85E-15 + 1.65E-13 + 7.48E-14} = 0.675$$

$$\text{for interaction } AB: \quad \omega^2 = \frac{7.48E-14}{4.85E-15 + 1.65E-13 + 7.48E-14} = 0.305$$

The results are summarized in Table 4.5. The obtained  $\omega^2$  is discussed in the next section. To better understand the trends, the results are presented in the form of a graph.

Figures 4.6 to 4.9 demonstrate how diffusion coefficients of tested VOCs, at a constant temperature, vary with changes in relative humidity (each corresponds to a specific temperature). Except for Figure 4.8, a slight reduction in diffusion coefficients can be observed in these graphs when humidity varies from 0% to 40% of RH. Also, the ranking of the diffusion coefficients for different VOCs remains more or less unchanged when humidity changes. VOCs with different levels of polarity were suspected to show different diffusive behavior when humidity content increases. This hypothesis, however, is not authenticated with our observations in this study.

**Table 4-5: Summary of the two-factor analysis of variance**

VOC	Source of variation	Sum of squares	Degree of freedom	Mean squares	Omega Squared
Hexane	Main effect A (Humidity)	4.85E-15	2	2.43E-15	0.020
	Main effect B (Temperature)	1.65E-13	3	5.51E-14	0.675
	Two factor interaction AB	7.48E-14	2*3	1.25E-14	0.305
	Total	2.45E-13	11		1.000
Cyclo hexane	Main effect A (Humidity)	2.58E-14	2	1.29E-14	0.075
	Main effect B (Temperature)	1.41E-13	3	4.71E-14	0.412
	Two factor interaction AB	1.76E-13	2*3	2.93E-14	0.513
	Total	3.43E-13	11		1.000
Ethyl acetate	Main effect A (Humidity)	3.63E-14	2	1.81E-14	0.038
	Main effect B (Temperature)	7.42E-13	3	2.47E-13	0.787
	Two factor interaction AB	1.65E-13	2*3	2.74E-14	0.175
	Total	9.43E-13	11		1.000
Octane	Main effect A (Humidity)	2.23E-14	2	1.12E-14	0.020
	Main effect B (Temperature)	1.01E-12	3	3.37E-13	0.908
	Two factor interaction AB	8.01E-14	2*3	1.34E-14	0.072
	Total	1.11E-12	11		1.000

As Figures 4.10 to 4.12 illustrate, diffusion coefficient seems to be more sensitive to the temperature changes rather than humidity changes. This can also be inferred from  $\omega^2$  values (Table 4.5) since these values for main effect *B* (temperature) are the greatest.

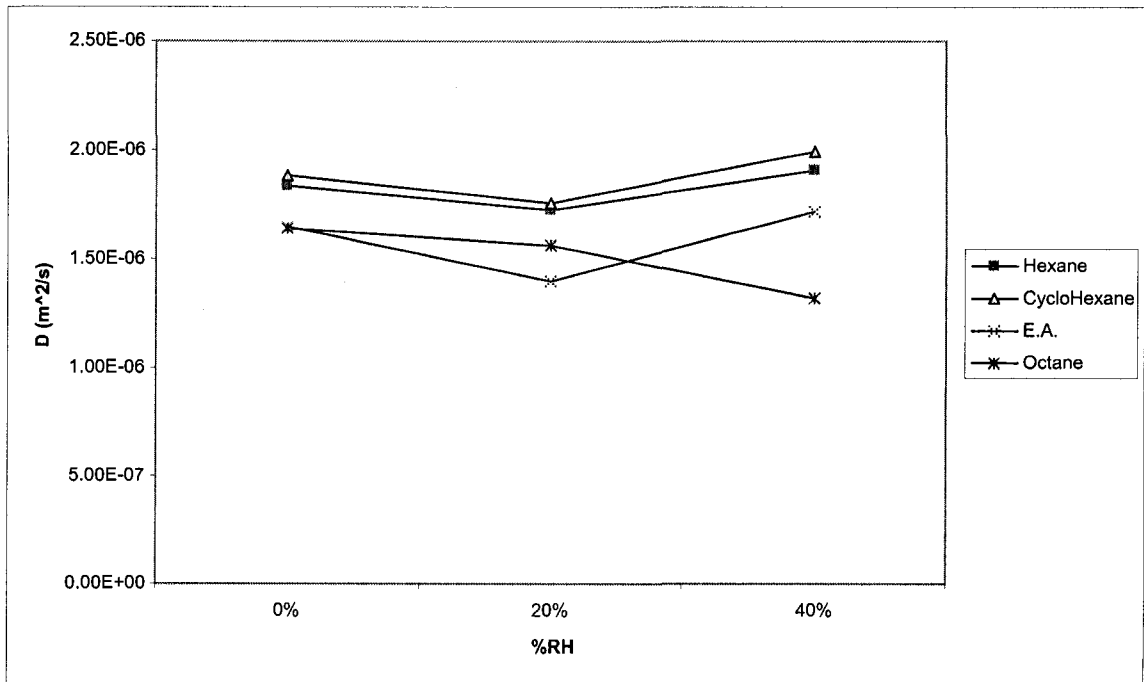


Figure 4-6: Diffusion Coefficient vs. RH at T=15°C

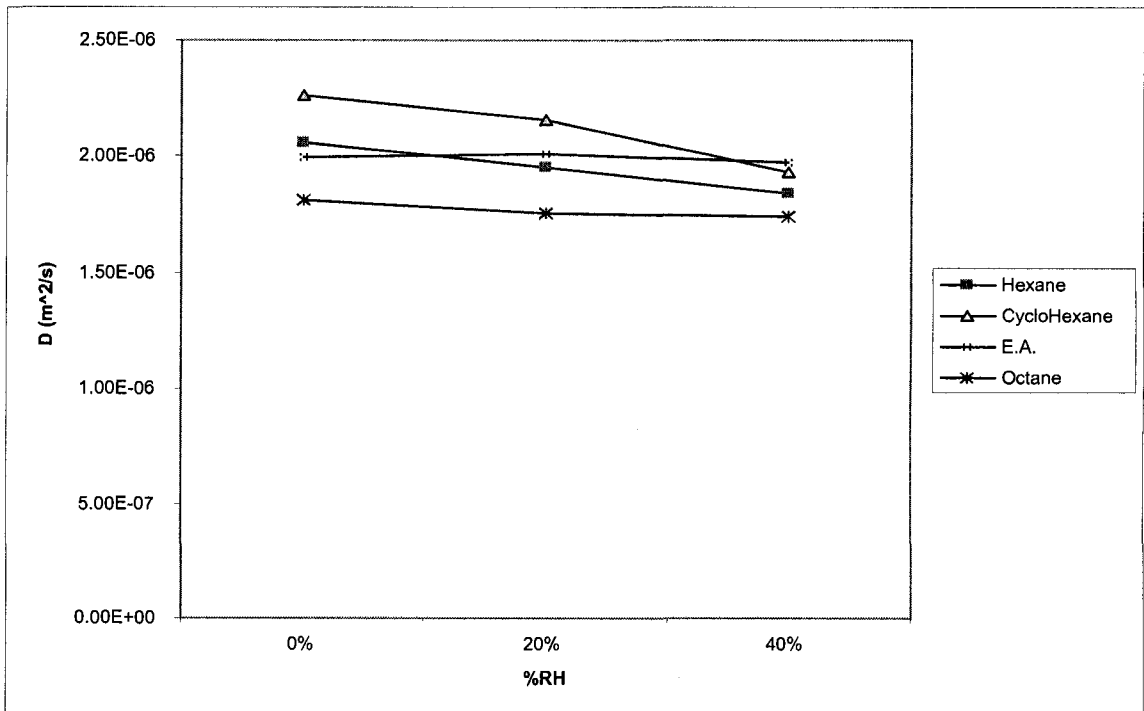


Figure 4-7: Diffusion Coefficient vs. RH at T=23°C

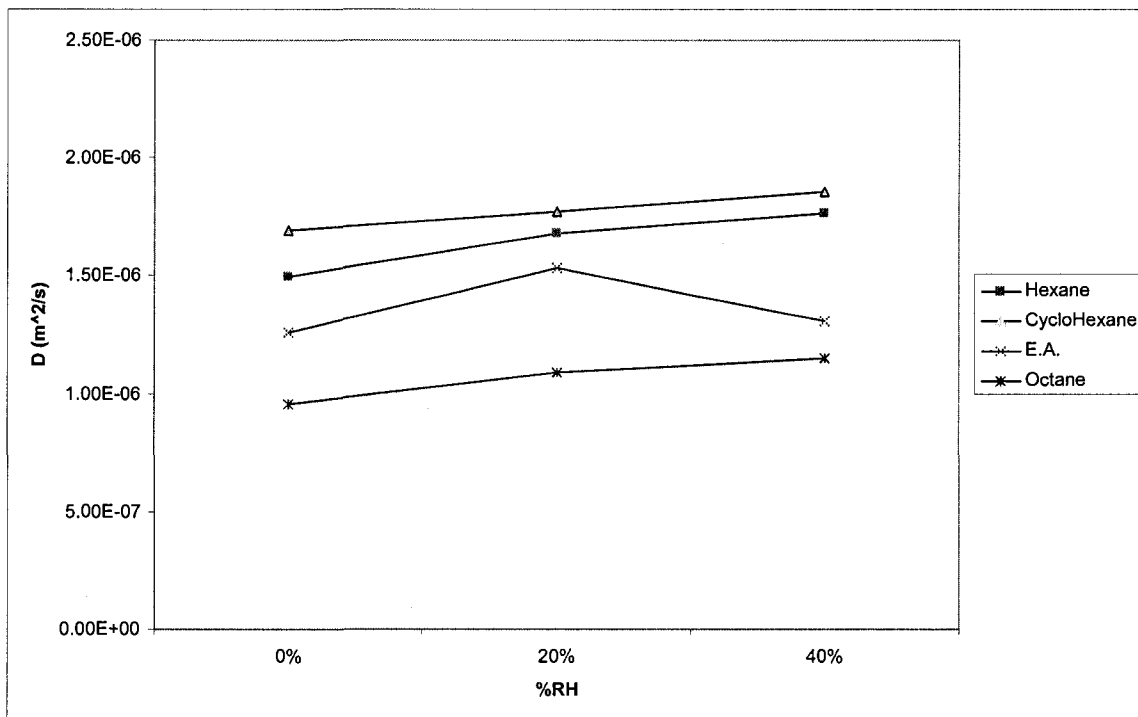


Figure 4-8: Diffusion Coefficient vs. RH at T=31°C

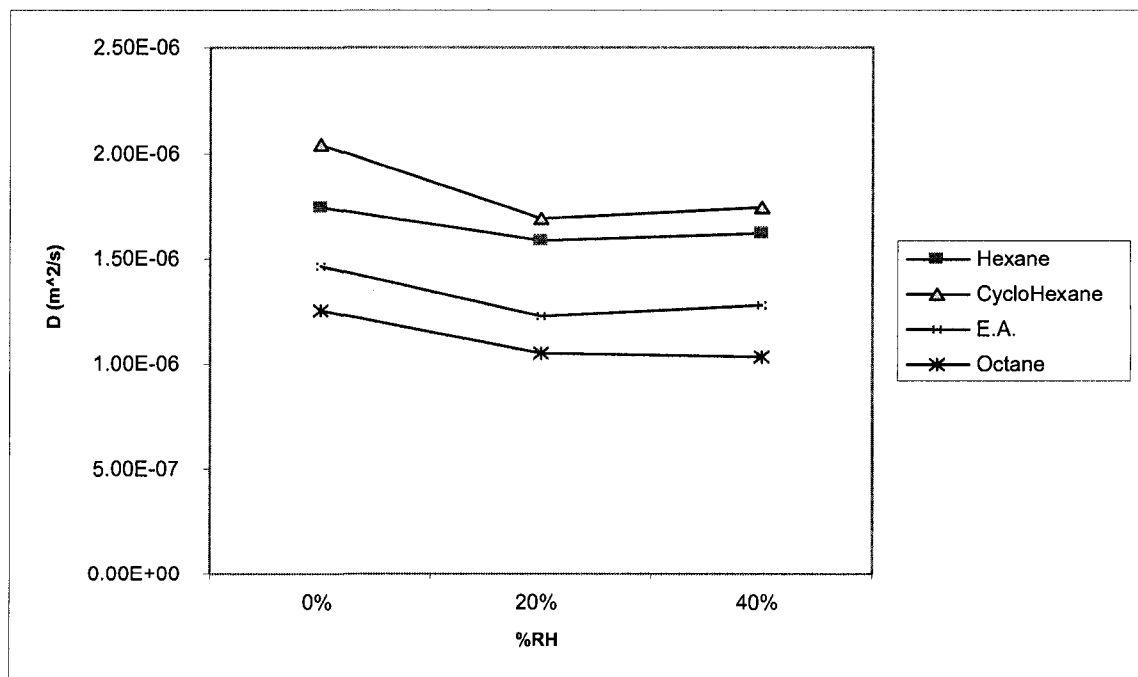


Figure 4-9: Diffusion Coefficient vs. RH at T=39°C

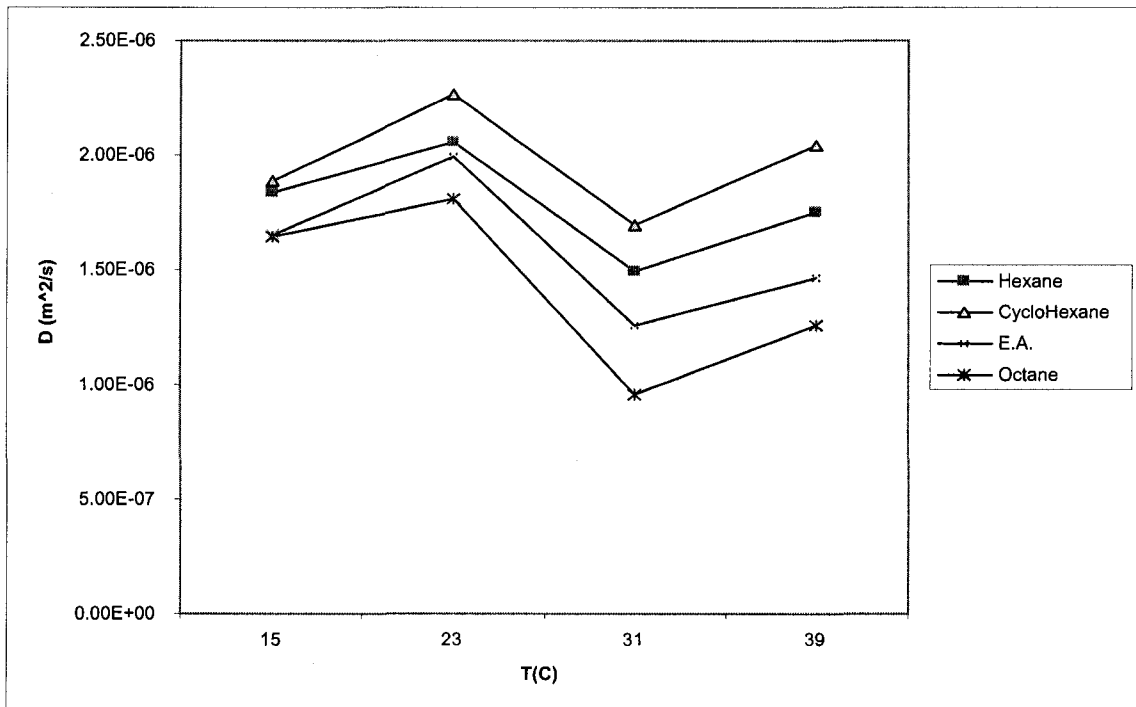


Figure 4-10: Diffusion Coefficient vs. Temperature at RH=0%

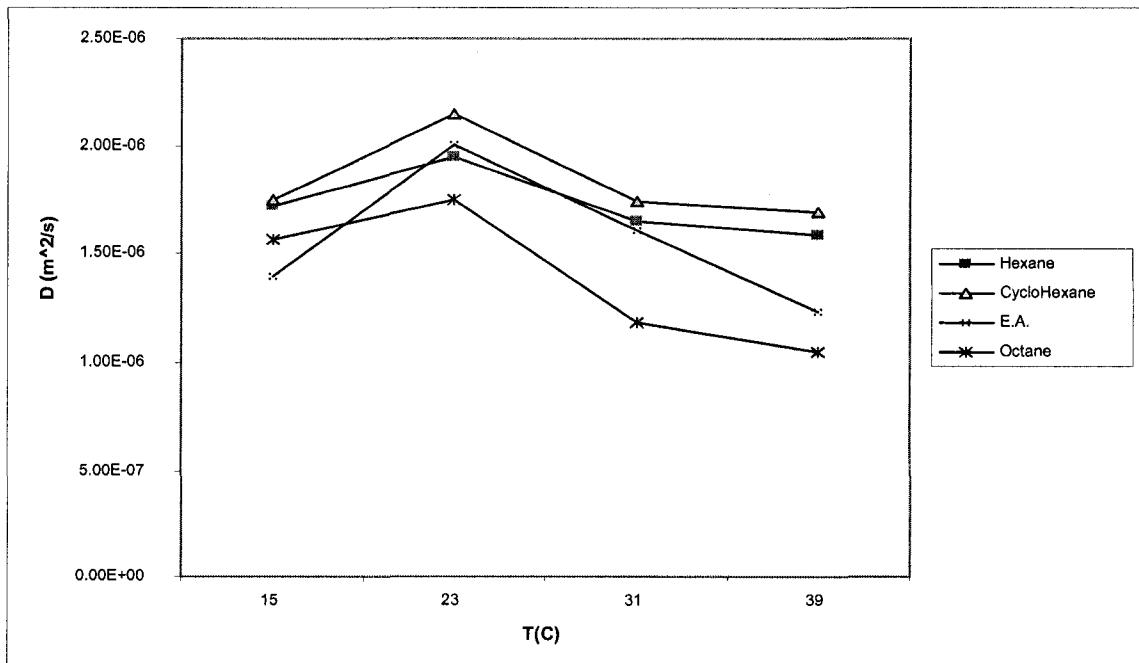


Figure 4-11: Diffusion Coefficient vs. Temperature at RH=20%

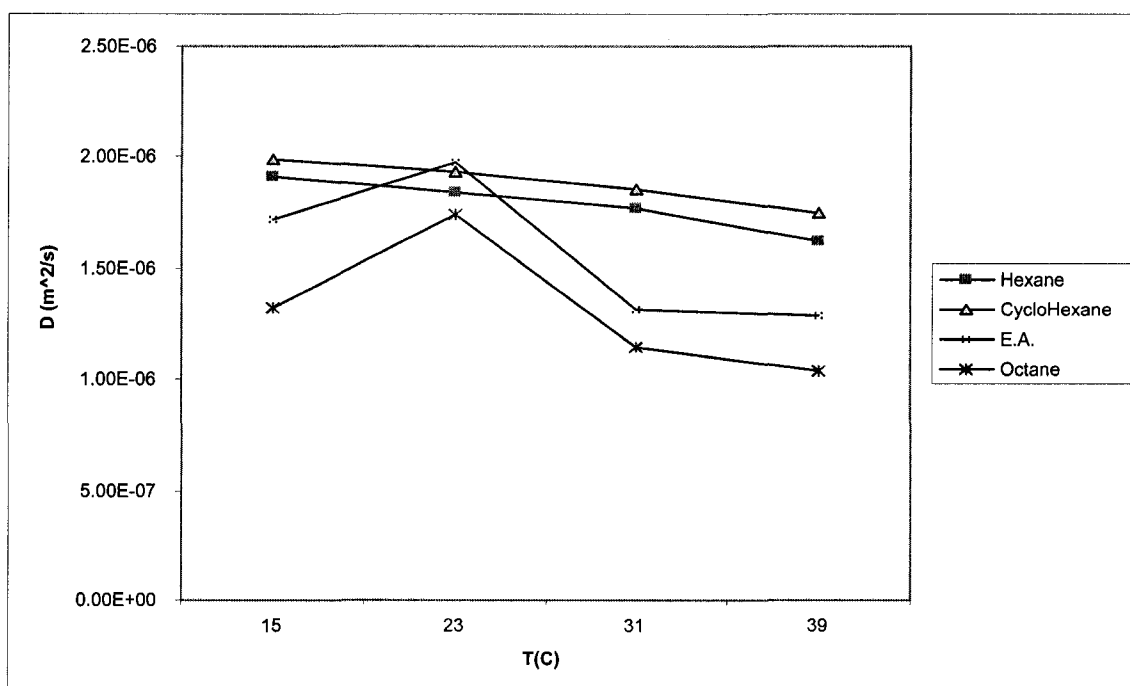


Figure 4-12: Diffusion Coefficient vs. Temperature at RH=40%

#### **4.6 Further Discussion and Uncertainty Analysis**

Using the outcome of the statistical analysis in Table 4.5, a comparison of Omega Squared values shows that the diffusion coefficients of all tested VOCs in mixture test (hexane, cyclo hexane, ethyl acetate, and octane) are affected by temperature (main effect B) rather than by the other factor, humidity, or their interaction ( $A \times B$ ). Moreover, the statistical results show that neither the humidity nor the interaction has such a limited impact that can be disregarded entirely (all their  $\omega^2$  are greater than 0.01).

As noted earlier, deviations associated with experimental error were ignored because of one-time replications. This condition may lower the level of certainty in our justification, and even further, this justification may alter in some cases as the experiment undergoes more replications. Therefore, more investigation with supplementary experimental

replications is required. In any case, the significance of the Temperature factor was observed to be greater than that of the Humidity factor and greater than the interaction of the two.

As illustrated in Figures 4.10 to 4.12, there is an upward trend in diffusion coefficients as temperature increases from 15°C to 23°C. However, for some VOCs, the trend is so slight that it falls within the range of standard deviation for the measured diffusion coefficients, and this may toughen making any solid conclusion. Moreover, an unexpected drop in diffusion coefficients occurs as temperature increases further to 31 and 39°C. This might be because of less affinity of sampling tube for adsorbing VOCs at higher temperatures compared to the room temperature, in which the calibration of GC/MS was carried out.

Humidity was reported as a factor reducing the diffusion coefficient of VOC as water content increases (Bouilly et al., 2006). Here, except for the experimental results obtained at 31°C, the other data measured at 15, 23, and 39°C are in agreement with that statement. However, the amount of change is very small as their  $\omega^2$  values show. This reduction in diffusion coefficients may be explainable by the blockage of microscopic material pores, which fill with water molecules; that is, these pores no longer contribute or contribute differently to diffusion transports of gases in the material. In another study (Won, 2004), however, relative humidity was found to have no effect on emissions of two non-polar groups of compounds, namely alkanes and alkyl benzenes. This also is in accord with the results of our study in which the diffusion coefficients of two compounds from alkanes group, hexane and octane, were observed to be the least influenced by the humidity

changes. The omega squared of main effect *A* (humidity) for these two VOCs had a value of  $\omega^2 = 0.20$  (see Table 4.5), and was the smallest compared to the other  $\omega^2$  values.

In the same study (Won & Shaw, 2004), diffusion coefficients of alkanes and alkyl benzenes were described as an increasing function of temperature:

$$D = (b_1 + b_2 \cdot MW)(b_3 + b_4 \cdot T)(b_5 + b_6 \cdot C_0) \quad \text{Equation 4-7}$$

where *D* is the diffusion coefficient ( $\mu\text{m}^2/\text{h}$ ), *MW* is molecular weight, *T* is air temperature ( $^{\circ}\text{C}$ ), *C*<sub>0</sub> is the initial concentration of a chemical in a paint sample (g/L), and *b*<sub>1</sub>, *b*<sub>2</sub>, *b*<sub>3</sub>, *b*<sub>4</sub>, *b*<sub>5</sub>, and *b*<sub>6</sub>, are correlation constants.

According to the correlation 4.7, increasing the temperature from 15 $^{\circ}\text{C}$  to 23 $^{\circ}\text{C}$  (the first and second level of temperature factor in our experimental design might lead to magnifying the diffusion coefficient of both alkanes and alkyl benzenes. Comparably, the diffusion coefficients obtained in our study showed a similar increasing trend as temperature increased from 15 $^{\circ}\text{C}$  to 23 $^{\circ}\text{C}$ , which agrees well with the other outcomes in the literature (Zhang et al., 2007; Won & Shaw, 2004; Haghghat et al., 2002). However, the amount of this increase was not found to be of the same order of magnitude as literature. This may be interpreted by different characteristics of VOCs as well as building materials used by different researchers. Nevertheless, the study described in this chapter contributed to the database of VOCs properties and their diffusion coefficients under typical environmental condition for representative building material.



# Chapter 5

## Conclusions and Recommendations

### 5.1 Summary

The present study was intended to help understanding of the interactions among VOCs, building materials, and IAQ under different environmental conditions. The main objective was to develop an experimental method which enables us to measure the diffusion coefficient of different VOCs, with different physical/chemical properties, within building materials. The method used also allowed us to investigate the impact of environmental parameters, temperature and humidity, on effective diffusion coefficients. Both objectives have been achieved in this study.

Five VOCs, namely octane, isopropanol, cyclo hexane, ethyl acetate, and hexane, were studied by using the twin chamber method; their diffusion coefficients in ceiling tile were experimentally measured in two different forms: as individual VOCs, and as VOCs in a mixture. By using Fick's law and monitoring the concentration gradient at steady conditions, diffusion coefficients were calculated and linked to physicochemical properties of VOCs. During the measurements, temperature (factor *B*) was set at 4 levels: 15, 23, 31 and 39°C and the specific humidity (factor *A*) varied in three levels: 0, 3.4551, and 6.9248 g/kg wet air which represents a relative humidity of 0%, 20%, and 40% at 23 °C, respectively. In all, 12 runs were performed for all combinations of levels for the two

factors, and based on obtained data, a systematic parametric study was conducted to quantify the importance of investigated factors in measured diffusion coefficients. The statistical procedure of such factorial design was presented with results interpreted. Additionally, the magnitude of the measurement error caused by pressure differences between the two chambers was estimated and analyzed.

## **5.2 Conclusion**

The conclusions of the investigations in this study are as follows:

- Diffusion coefficients obtained for the five tested VOCs rank as follows: hexane  $\approx$  cyclo hexane > isopropanol > ethyl acetate > octane. That is, under same circumstances, ceiling tile is less permeable to octane than ethyl acetate. Also, hexane and cyclo hexane showed the highest diffusivity among the tested VOCs.
- It was found that among different physical/chemical properties, the diffusion coefficient is positively related to vapor pressure. That is, diffusion coefficients of different VOCs are proportional to increases in vapor pressure, which is consistent with results reported in previous studies.
- No significant difference was observed between the diffusion coefficient of a single VOC compound and that of a mixture of VOCs. Therefore, it may be recommended to carry out experiments with a VOC mixture. In this way, more information can be provided through one single experiment.
- Study results indicated that temperature and humidity (in the range of a typical indoor environment) had a minor effect on the measured diffusion coefficient.

Specifically, according to their obtained Omega Squared, the effect of temperature as a factor was determined to be greater than that of humidity as a influencing factor.

- The ranking of VOC diffusivity (see above) remained relatively valid under changes in environmental conditions. In particular, VOCs with different characteristics of polarity showed behaviors similar to those seen with humidity variations.
- By employing Darcy's law, it was showed theoretically that the presence of even a minor pressure difference (0.001 inH<sub>2</sub>O) may cause dramatic error, up to 5%, in calculations of diffusion coefficients. For that reason, appropriate precautions must be taken before performing the test to balance pressure across the specimen.

### **5.3 Limitations of the Present Study**

Among the VOCs to be tested in a preliminary list, some were excluded because they did not meet the sensitivity requirements of the detection instruments in the method developed for GC/MS. In addition, not all VOCs can be tested using an Air-Toxics sampling tube. This kind of sampling tube is recommended for use with dry carrier gas. The presence of humidity during sampling affects the obtained data analyzed by MS. Consequently, this study was limited to a fairly low range of humidity variations (RH of 0% to 40% at 23 °C) which is the typical range in indoor environment. Besides, measurements were limited to the relatively low temperatures close to the temperature of environment at which the GC/MS system was calibrated. Otherwise, it could be the risk of data misevaluation.

## **5.4 Recommendations for Future Studies**

- More experimental replications are needed to improve the reliability of data obtained from the factorial design used.
- There are many more building materials typically used indoors and volatile organic compounds frequently found indoors than the ones examined in this study. In order to establish a database that provides valuable information for researchers, manufacturers, and consumers, further research should look at all these building materials and VOCs.
- The experimental method developed in the present study measured the effective diffusion coefficients comprising internal diffusion coefficients within materials and partitioning between gas phase and material phase. More investigation is needed to explore these processes separately so as to have a better understanding of the influence of environmental parameters on each phenomenon.
- The relationship between the structural properties of building materials (e.g., porosity) and emission parameters (e.g., diffusion coefficient) still raises questions. Further studies should address the nature of this relationship.
- More research concerning the influence of temperature as well as humidity is required, particularly when VOCs characteristics is involved.
- Another interesting avenue for investigation is the impact of gas phase concentration on the measurement of diffusion coefficients in parallel with adsorption properties (Huang et al. 2006).

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# Appendix A

## VOCs solution preparation (procedure for calculations)

Inj. Rate (ul/min):	C(gr/ml)	Flow Rate (Lit/min)	VOC Concentration (mg/m <sup>3</sup> )
1	0.099855	2.219	45

to make 25ml of solution with a concentration of 45(mg/m<sup>3</sup>) for each VOC:

1 ml	0.099855 gr
25 ml	X=2.496375 gr

VOC:	Boiling Point	Density (gr/ml):	Amount of each VOC to be used (x/Density):
Octane	125.52	0.703	3.551031294 ml
Toluene	110.6	0.867	2.87932526 ml
i-Propanol	82.3	0.785	3.180095541 ml
Cyclo Hexane	80.74	0.779	3.204589217 ml
Ethyl Acetate	77.1	0.897	2.783026756 ml
Hexane	69	0.661	3.776664145 ml
Methanol	64.7	0.7918	3.152784794 ml
		<b>SUM:</b>	<b>22.52751701 ml</b>

Sampling Time (min): 360 Required Syringe Volume (ul): 360

# Appendix B

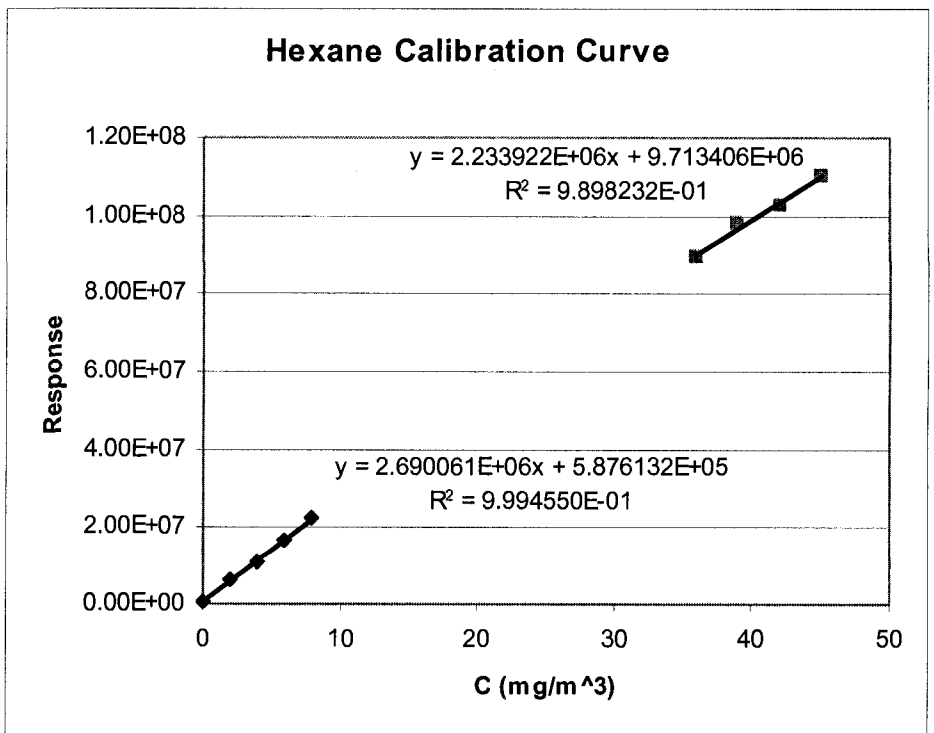
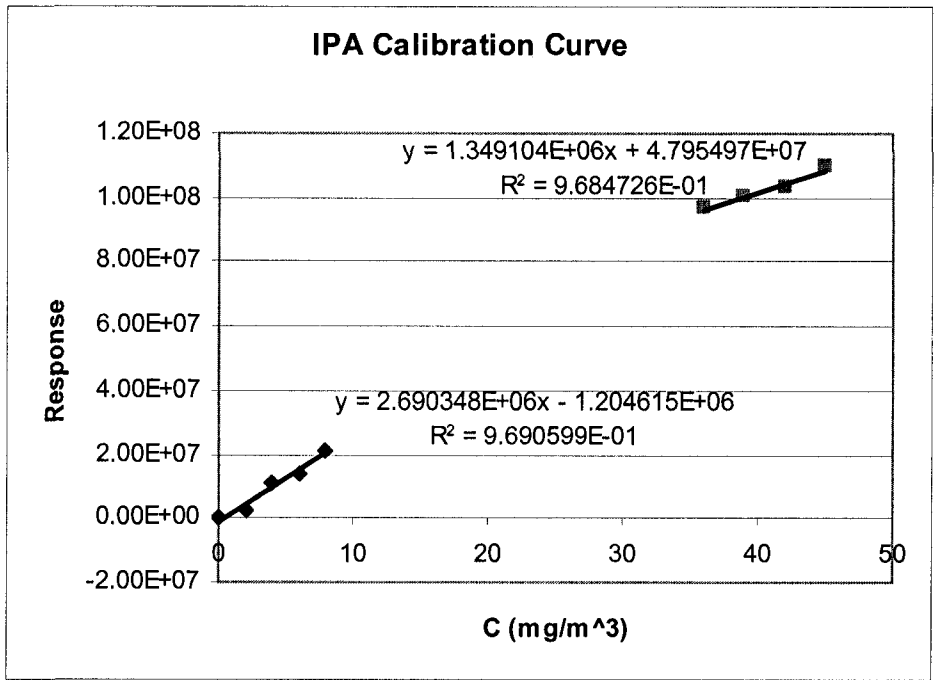
## GC/MS Calibration for tested VOCs

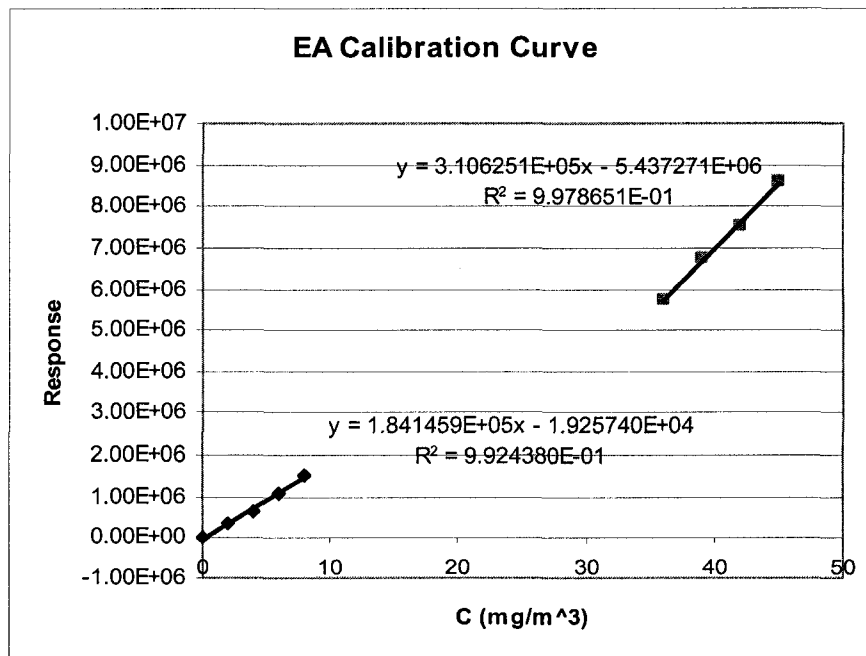
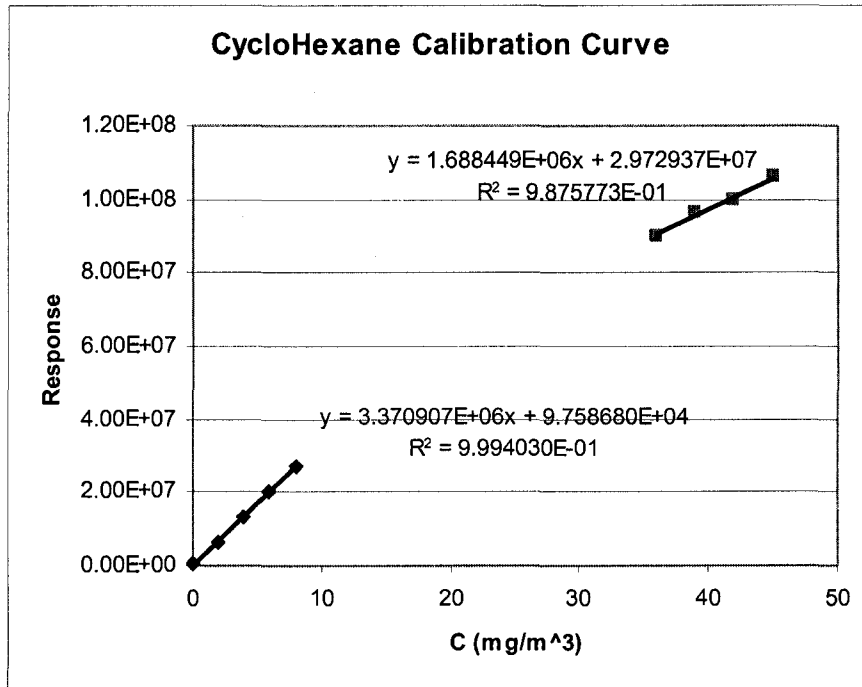
	Concentration (mg/m <sup>3</sup> )							Concentration (mg/m <sup>3</sup> )			
	0	2	4	6	8	36	39	42	45		
IPA	0	2135927	10808895	13735239	21103824	97130848	1E+08	1.03E+08	1.1E+08		
Hexane	650756	6111669	11011532	16716257	22249072	89624160	98006920	1.03E+08	1.1E+08		
CycloHexane	398580	6629255	13255562	20400804	27221878	90287784	96370408	99738344	1.06E+08		
EA	16928	358272	633129	1081557	1496744	5732995	6731700	7536510	8570976		
Octane	143925	576461	892638	1361682	1841779	7042787	7941165	8652284	9733356		
Toluene	3094191	11946480	16474963	24397758	31951478	82334088	77992400	76916736	87327568		

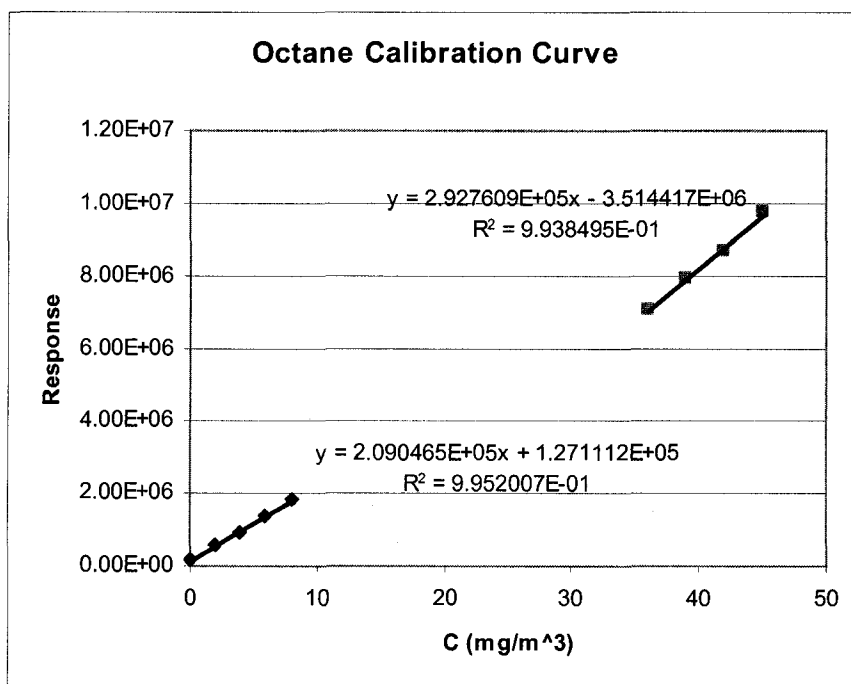
Response of GC/MS apparatus to different level of injected VOC

	IPA		Hexane		CycloHexane		E.A.		Octane	
	Intercept:	Slope:	Intercept:	Slope:	Intercept:	Slope:	Intercept:	Slope:	Intercept:	Slope:
Higher Conc.	-6.70E+06	2.34E+06	9.71E+06	2.23E+06	2.97E+07	1.69E+06	-5.44E+06	3.11E+05	-3.51E+06	2.93E+05
Higher Conc.	-1.36E+06	2.28E+06	5.88E+05	2.69E+06	9.76E+04	3.37E+06	-1.93E+04	1.84E+05	1.27E+05	2.09E+05

Obtained calibration curves parameters







# Appendix C

## Experimental data of single test

	Time	IPA		Hexane		Time		CycloHexane		Time		E.A.		Time		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC	HC	LC	HC	LC	HC	LC	HC	LC
GC/MS Response	0:45	8.9E+07	0	1:30	9.2E+07	7206606	0:00	0	0	0:00	0	0	0	0:00	0	0	0
	1:30	9.4E+07	1575085	2:00	9.2E+07	6477189	0:30	8.7E+07	7516204	1:30	5542567	283536	0:30	6844972	454499		
	2:30	9.5E+07	3129276	2:40	8.7E+07	6457160	1:15	8.5E+07	7387374	2:50	17753	350636	1:40	6806187	515378		
	3:35	9.1E+07	3865329	3:10	9.1E+07	7863214	3:00	8.5E+07	7231629	5:20	5842748	390800	2:35	6850523	482192		
						3:35	8.7E+07	7114426	5:25	5870528	397419	3:05	6959552	503428			
Concentration (mg/m <sup>3</sup> )	0:45	30.4443	1.0067	1:30	36.8101	2.46054	0:00	-17.6075	-0.02895	0:00	17.5043	0.10458	0:00	12.0044	-0.60805		
	1:30	33.807	1.53322	2:00	36.8313	2.18938	0:30	34.18	2.20078	1:30	35.3476	1.64431	0:30	35.3852	1.5661		
	2:30	35.0519	2.05275	2:40	34.7194	2.18194	1:15	32.9031	2.16256	2:50	17.5614	2.0087	1:40	35.2527	1.85732		
	3:35	31.9172	2.2988	3:10	36.1756	2.70462	3:00	32.9048	2.11636	5:20	36.3139	2.22681	2:35	35.4041	1.69857		
						3:35	34.0976	2.08159	5:25	36.4034	2.26275	3:05	35.7765	1.80016			

	IPA	Hexane	CycloHexane	E.A.	Octane
D (m <sup>2</sup> /s)	1.02E-06	2.13E-06	4.90E-08	1.79E-07	-1.43E-06
	1.41E-06	1.88E-06	2.05E-06	1.45E-06	1.38E-06
	1.85E-06	1.99E-06	2.09E-06		1.65E-06
	2.31E-06	2.40E-06	2.04E-06	1.94E-06	1.50E-06
Mean	1.86E-06	±4.48E-07	2.10E-06	±2.25E-07	2.03E-06
			±6.74E-08	1.79E-06	±2.92E-07
				1.57E-06	±1.18E-07

**Experimental data of mixture test obtained @ RH=0% and T=15°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	0:45	91310232	7224034	91676992	8551044	5334236	284121	8283168	689571
	Sample2	1:30	84386120	5990416	86263488	7113671	5539455	268274	7597306	557332
	Sample3	2:15	83004000	5648334	84496632	6616885	4316091	262288	7534840	527712
	Sample4	3:10	80124640	5415599	82097624	6261968	4869889	289288	7079513	519003
	Sample5	3:55	81893376	5412334	84029696	6366314	4222465	305735	7245773	529117
	Sample6	4:20	81779504	5908094	84593336	6622599	4061405	330833	7409390	538505
Concentration (mg/m <sup>3</sup> )	Sample1	0:45	3.65E+01	2.47E+00	3.67E+01	2.51E+00	3.47E+01	1.65E+00	4.03E+01	2.69E+00
	Sample2	1:30	3.34E+01	2.01E+00	3.35E+01	2.08E+00	3.53E+01	1.56E+00	3.80E+01	2.06E+00
	Sample3	2:15	3.28E+01	1.88E+00	3.24E+01	1.93E+00	3.14E+01	1.53E+00	3.77E+01	1.92E+00
	Sample4	3:10	3.15E+01	1.79E+00	3.10E+01	1.83E+00	3.32E+01	1.68E+00	3.62E+01	1.87E+00
	Sample5	3:55	3.23E+01	1.79E+00	3.22E+01	1.86E+00	3.11E+01	1.76E+00	3.68E+01	1.92E+00
	Sample6	4:20	3.23E+01	1.98E+00	3.25E+01	1.94E+00	3.06E+01	1.90E+00	3.73E+01	1.97E+00

Run 1 (0%-15C)

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
□ (m <sup>2</sup> /s)	Sample1	0:45	2.15E-06	2.18E-06	1.48E-06	2.13E-06			
	Sample2	1:30	1.9E-06	1.97E-06	1.37E-06	1.7E-06			
	Sample3	2:15	1.81E-06	1.88E-06	1.52E-06	1.59E-06			
	Sample4	3:10	1.79E-06	1.86E-06	1.58E-06	1.62E-06			
	Sample5	3:55	1.75E-06	1.82E-06	1.79E-06	1.64E-06			
	Sample6	4:20	1.94E-06	1.88E-06	1.97E-06	1.66E-06			
Mean	1.84E-06	±8E-08	1.88E-06	±5.35225E-08	1.65E-06	±2.34E-07	1.64E-06	±4.2E-08	



**Experimental data of mixture test obtained @ RH=29% and T=15°C**

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
GC/MS Response	Sample1	82678376	5270561	86222648	6172238	4619866	256312	7692433	519578
	Sample2	82162616	5308800	86299128	6147307	5335960	269326	7624253	523828
	Sample3	81607056	5343605	84084920	6313131	3421614	251262	7371474	520665
	Sample4	80983184	5412963	83905064	6253695	3943645	211840	7353379	519454
	Sample5	80445664	5305444	83710480	6240672	4529310	218175	7411918	515928
Concentration (mg/m <sup>3</sup> )	Sample1	3.27E+01	1.74E+00	3.35E+01	1.80E+00	3.24E+01	1.50E+00	3.83E+01	1.88E+00
	Sample2	3.24E+01	1.76E+00	3.35E+01	1.79E+00	3.47E+01	1.57E+00	3.80E+01	1.90E+00
	Sample3	3.22E+01	1.77E+00	3.22E+01	1.84E+00	2.85E+01	1.47E+00	3.72E+01	1.88E+00
	Sample4	3.19E+01	1.79E+00	3.21E+01	1.83E+00	3.02E+01	1.25E+00	3.71E+01	1.88E+00
	Sample5	3.17E+01	1.75E+00	3.20E+01	1.82E+00	3.21E+01	1.29E+00	3.73E+01	1.86E+00

D (m <sup>2</sup> /s)	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
Sample1	1:00	1.67E-06	1.69E-06	1.69E-06	1.69E-06	1.44E-06		1.53E-06	
Sample2	2:00	1.7E-06	1.68E-06	1.68E-06	1.68E-06	1.41E-06		1.56E-06	
Sample3	3:50	1.73E-06	1.81E-06	1.81E-06	1.81E-06	1.61E-06		1.59E-06	
Sample4	4:05	1.77E-06	1.79E-06	1.79E-06	1.79E-06	1.29E-06		1.58E-06	
Sample5	4:55	1.74E-06	1.8E-06	1.8E-06	1.8E-06	1.24E-06		1.56E-06	
Mean	1.72E-06	±3.76E-08	1.75E-06	±6.14175E-08	1.40E-06	±1.45E-07		1.56E-06	±2.12E-08

**Experimental data of mixture test obtained @ RH=58% and T=15°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	1:10	76725688	4824043	80286464	5277629	4249651	239842	7458639	483023
	Sample2	2:15	78265336	5105541	81121504	5490563	4336052	255622	7081767	444328
	Sample3	3:05	74722328	7063863	77977680	9580882	3902688	396436	6930507	531528
	Sample4	3:30	74601672	4734431	77919032	5510189	4008180	253463	6900719	414860
	Sample5	4:10	76897712	5449129	79567832	5440332	4157804	262041	7145937	421766
	Sample6	4:40	75487128	4583514	78101272	5046142	3927069	272566	6993024	421270
Concentration (mg/m <sup>3</sup> )	Sample1	1:10	3.00E+01	1.57E+00	2.99E+01	1.54E+00	3.12E+01	1.41E+00	3.75E+01	1.70E+00
	Sample2	2:15	3.07E+01	1.68E+00	3.04E+01	1.60E+00	3.15E+01	1.49E+00	3.62E+01	1.52E+00
	Sample3	3:05	2.91E+01	2.41E+00	2.86E+01	2.81E+00	3.01E+01	2.26E+00	3.57E+01	1.93E+00
	Sample4	3:30	2.90E+01	1.54E+00	2.85E+01	1.61E+00	3.04E+01	1.48E+00	3.56E+01	1.38E+00
	Sample5	4:10	3.01E+01	1.81E+00	2.95E+01	1.58E+00	3.09E+01	1.53E+00	3.64E+01	1.41E+00
	Sample6	4:40	2.94E+01	1.49E+00	2.86E+01	1.47E+00	3.01E+01	1.58E+00	3.59E+01	1.41E+00

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
D (m <sup>2</sup> /s)	Sample1	1:10	1.65E-06	1.61E-06	1.4E-06	1.41E-06	1.41E-06	1.41E-06	1.41E-06
	Sample2	2:15	1.72E-06	1.65E-06	1.48E-06	1.3E-06	1.3E-06	1.3E-06	1.3E-06
	Sample3	3:05	2.68E-06	3.25E-06	2.41E-06	1.7E-06	1.7E-06	1.7E-06	1.7E-06
	Sample4	3:30	1.67E-06	1.77E-06	1.52E-06	1.2E-06	1.2E-06	1.2E-06	1.2E-06
	Sample5	4:10	1.9E-06	1.69E-06	1.55E-06	1.2E-06	1.2E-06	1.2E-06	1.2E-06
	Sample6	4:40	1.58E-06	1.61E-06	1.65E-06	1.21E-06	1.21E-06	1.21E-06	1.21E-06
Mean	1.91E-06	±4.47E-07	1.99E-06	±7.03772E-07	1.72E-06	±3.91E-07	1.32E-06	±2.18E-07	±2.18E-07

**Experimental data of mixture test obtained @ RH=0% and T=23°C (first run)**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	2:20	73167512	5253488	87117168	7969455	7352136	419419	9214892	650152
	Sample2	2:45	72716952	5363073	87192360	8088444	7528423	483241	9405904	663036
	Sample3	3:15	70932080	4684529	86662648	7084058	6773342	503612	8900611	604106
Concentration (mg/m <sup>3</sup> )	Sample1	2:20	2.84E+01	1.73E+00	3.40E+01	2.34E+00	4.12E+01	2.38E+00	4.35E+01	2.50E+00
	Sample2	2:45	2.82E+01	1.78E+00	3.40E+01	2.37E+00	4.17E+01	2.73E+00	4.41E+01	2.56E+00
	Sample3	3:15	2.74E+01	1.52E+00	3.37E+01	2.07E+00	3.93E+01	2.84E+00	4.24E+01	2.28E+00

(m <sup>2</sup> )	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
Sample1	2:20	1.93E-06	2.19E-06	1.83E-06	1.81E-06	1.83E-06	1.81E-06	1.83E-06	1.81E-06
Sample2	2:45	2E-06	2.23E-06	2.08E-06	1.83E-06	2.08E-06	1.83E-06	1.83E-06	1.83E-06
Sample3	3:15	1.75E-06	1.95E-06	2.31E-06	1.69E-06	2.31E-06	1.69E-06	1.69E-06	1.69E-06
Mean	1.89E-06	±1.29E-07	2.12E-06	±1.52E-07	2.07E-06	±2.44E-07	1.78E-06	±7.77E-08	1.78E-06

**Experimental data of mixture test obtained @ RH=0% and T=23°C (second run)**

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
GC/MS Response	Sample1	0	0	0	0	0	0	0	0
	Sample2	93800512	6928121	92502608	8571867	6573014	343900	8378717	599895
	Sample3	95109056	7228280	95015256	8980229	7108875	327201	8497616	622119
	Sample4	94595160	7218665	93989472	9028844	6498306	449896	8555878	607107
	Sample5	96261304	7375480	95023136	9462569	7216654	523370	8561498	627491
	Sample6	95285744	7276525	94762032	9327464	6126818	484067	8360646	624800
	Sample7	95469528	7032299	95179816	8857005	6340625	322565	8468392	606566
	Sample8	97122200	7749049	96556552	10721201	7230278	586342	8630246	644274
Concentration (mg/m <sup>3</sup> )	Sample1	-4.35E+00	-2.18E-01	-1.76E+01	-2.89E-02	1.75E+01	1.05E-01	1.20E+01	-6.08E-01
	Sample2	3.76E+01	2.36E+00	3.72E+01	2.51E+00	3.87E+01	1.97E+00	4.06E+01	2.26E+00
	Sample3	3.82E+01	2.47E+00	3.87E+01	2.64E+00	4.04E+01	1.88E+00	4.10E+01	2.37E+00
	Sample4	3.80E+01	2.47E+00	3.81E+01	2.65E+00	3.84E+01	2.55E+00	4.12E+01	2.30E+00
	Sample5	3.87E+01	2.52E+00	3.87E+01	2.78E+00	4.07E+01	2.95E+00	4.12E+01	2.39E+00
	Sample6	3.83E+01	2.49E+00	3.85E+01	2.74E+00	3.72E+01	2.73E+00	4.06E+01	2.38E+00
	Sample7	3.84E+01	2.40E+00	3.88E+01	2.60E+00	3.79E+01	1.86E+00	4.09E+01	2.29E+00
	Sample8	3.91E+01	2.66E+00	3.96E+01	3.15E+00	4.08E+01	3.29E+00	4.15E+01	2.47E+00

Run 2 (0%-23C)

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
D (m <sup>2</sup> /s)	Sample1	1.57E-06		4.9E-08		1.79E-07		-1.4E-06	
	Sample2	1.99E-06		2.16E-06		1.6E-06		1.75E-06	
	Sample3	2.05E-06		2.17E-06		1.45E-06		1.82E-06	
	Sample4	2.06E-06		2.22E-06		2.11E-06		1.75E-06	
	Sample5	2.07E-06		2.3E-06		2.32E-06		1.83E-06	
	Sample6	2.06E-06		2.27E-06		2.36E-06		1.85E-06	
	Sample7	1.98E-06		2.14E-06		1.53E-06		1.76E-06	
	Sample8	2.17E-06		2.57E-06		2.61E-06		1.89E-06	
Mean	2.05E-06	+6.36E-08	2.26E-06	±1.49433E-07	2.00E-06	±4.64E-07	1.81E-06	±5.28E-08	

**Experimental data of mixture test obtained @ RH=20% and T=23°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	0:45	92322160	7503543	92597072	8757173	6657200	420215	8346799	695596
	Sample2	1:30	91394344	2253687	92164464	5600695	6508810	777	8198648	777
	Sample3	2:15	91401216	6707129	92316288	8100895	6448345	391522	8256067	602769
	Sample4	3:05	92628032	7016307	93185672	9713685	5953311	387835	8339189	589926
	Sample5	3:50	93453128	6356041	93177408	7654498	6669476	434279	8525381	592453
	Sample6	4:40	90033792	6742558	89639752	9116347	6191763	458465	8216807	591417
	Sample7	4:55	89681176	6403275	91025696	7749402	5714679	411255	8084640	602387
Concentration (mg/m <sup>3</sup> )	Sample1	0:45	3.70E+01	2.57E+00	3.72E+01	2.57E+00	3.89E+01	2.39E+00	4.05E+01	2.72E+00
	Sample2	1:30	3.66E+01	6.19E-01	3.70E+01	1.63E+00	3.85E+01	#VALUE!	4.00E+01	#VALUE!
	Sample3	2:15	3.66E+01	2.27E+00	3.71E+01	2.37E+00	3.83E+01	2.23E+00	4.02E+01	2.28E+00
	Sample4	3:05	3.71E+01	2.39E+00	3.76E+01	2.85E+00	3.67E+01	2.21E+00	4.05E+01	2.21E+00
	Sample5	3:50	3.75E+01	2.14E+00	3.76E+01	2.24E+00	3.90E+01	2.46E+00	4.11E+01	2.23E+00
	Sample6	4:40	3.60E+01	2.29E+00	3.55E+01	2.68E+00	3.74E+01	2.59E+00	4.01E+01	2.22E+00
	Sample7	4:55	3.58E+01	2.16E+00	3.63E+01	2.27E+00	3.59E+01	2.34E+00	3.96E+01	2.27E+00

Run 1 (20%-23C)

	Time	Hexane		CycloHexane		E.A.		Octane	
		Hexane	Hexane	CycloHexane	CycloHexane	E.A.	E.A.	Octane	Octane
D (M <sup>2</sup> /s)	Sample1	0:45	2.22E-06		2.2E-06		1.94E-06		2.14E-06
	Sample2	1:30	5.12E-07		1.37E-06		#VALUE!		#VALUE!
	Sample3	2:15	1.97E-06		2.03E-06		1.84E-06		1.78E-06
	Sample4	3:05	2.05E-06		2.44E-06		1.91E-06		1.72E-06
	Sample5	3:50	1.8E-06		1.89E-06		2.01E-06		1.7E-06
	Sample6	4:40	2.02E-06		2.42E-06		2.21E-06		1.74E-06
	Sample7	4:55	1.91E-06		1.98E-06		2.07E-06		1.81E-06
Mean		1.95E-06	±9.69E-08	2.15E-06	±2.60435E-07	2.01E-06	±1.45E-07	1.75E-06	±4.47E-08

**Experimental data of mixture test obtained @ RH=40% and T=23°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	0:45	85914608	6055149	88340464	7212917	5817797	375950	7994827	611075
	Sample2	1:30	84072312	5807333	87044536	6969736	5695640	381851	8068112	581235
	Sample3	2:15	82790928	5662565	86328144	6779192	5211768	373304	7946568	575639
	Sample4	3:00	79229304	6072312	83003616	6891690	5158058	389037	7643534	583857
	Sample5	3:45	84150960	5843985	87886248	6939900	5446808	391638	8101843	595833
	Sample6	4:35	83773664	5762836	86996520	8462463	5096790	463649	8098959	583522
	Sample7	5:00	81980424	5458795	85412968	6460824	5058747	331709	8010135	581362
	Sample8	5:05	82234544	5303428	86727632	6233923	5456842	300809	8186368	576767
Concentration (mg/m <sup>3</sup> )	Sample1	0:45	34.11095	2.0324951	34.712979	2.1108058	36.233608	2.1461645	39.312777	2.3151012
	Sample2	1:30	33.286259	1.9403723	33.945453	2.0386647	35.840346	2.1782098	39.563101	2.1723578
	Sample3	2:15	32.712656	1.8865564	33.521163	1.9821387	34.282609	2.1317955	39.147936	2.1455887
	Sample4	3:00	31.118319	2.0388753	31.55218	2.0155119	34.1097	2.2172332	38.112846	2.1849005
	Sample5	3:45	33.321465	1.9539973	34.443965	2.0298137	35.039277	2.2313579	39.678318	2.2421892
	Sample6	4:35	33.152571	1.923831	33.917015	2.4814912	33.912459	2.6224119	39.668467	2.183298
	Sample7	5:00	32.349839	1.8108072	32.979141	1.8876929	33.789987	1.9059148	39.365065	2.1729653
	Sample8	5:05	32.463595	1.7530513	33.757763	1.8203813	35.07158	1.7381131	39.967035	2.1509846

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
D (m <sup>2</sup> /s)	Sample1	0:45	1.88E-06	1.92E-06	1.87E-06	1.86E-06	1.86E-06	1.86E-06	1.86E-06
	Sample2	1:30	1.84E-06	1.9E-06	1.92E-06	1.92E-06	1.73E-06	1.73E-06	1.73E-06
	Sample3	2:15	1.82E-06	1.87E-06	1.87E-06	1.97E-06	1.72E-06	1.72E-06	1.72E-06
	Sample4	3:00	2.08E-06	2.03E-06	2.07E-06	2.07E-06	1.81E-06	1.81E-06	1.81E-06
	Sample5	3:45	1.85E-06	1.86E-06	2.02E-06	2.02E-06	1.78E-06	1.78E-06	1.78E-06
	Sample6	4:35	1.83E-06	2.35E-06	2.49E-06	2.49E-06	1.73E-06	1.73E-06	1.73E-06
	Sample7	5:00	1.76E-06	1.8E-06	1.78E-06	1.78E-06	1.74E-06	1.74E-06	1.74E-06
	Sample8	5:05	1.7E-06	1.69E-06	1.55E-06	1.55E-06	1.69E-06	1.69E-06	1.69E-06
Mean		1.84E-06	±1.2E-07	1.93E-06	±2.09699E-07	1.97E-06	±2.89E-07	1.74E-06	±3.9E-08

**Experimental data of mixture test obtained @ RH=0% and T=31°C**

	Time	Hexane		CycloHexane		E.A.		Octane			
		HC	LC	HC	LC	HC	LC	HC	LC		
GC/MS Response	Sample1	0:00	415898	112099	145744	583347	145744	21982	0	64485	9314
	Sample2	1:10	63792024	3714948	4332067	70219032	4332067	2867628	161915	5396619	323533
	Sample3	3:00	62065760	3924410	68402816	4676798	2783618	212727	5445085	334388	
	Sample4	3:30	67698832	3985665	73643856	4627468	2239360	151567	5820755	353734	
	Sample5	4:00	61846868	4063160	68823520	4784953	2871040	158902	5327255	359936	
	Sample6	4:20	62689060	2769921	69836136	3731390	2704616	196001	5388258	265177	
Concentration (mg/m <sup>3</sup> )	Sample1	0:00	-4.16E+00	-1.77E-01	1.43E-02	-1.73E+01	1.43E-02	1.76E+01	1.05E-01	1.22E+01	-5.63E-01
	Sample2	1:10	2.42E+01	1.16E+00	2.40E+01	1.26E+00	2.67E+01	2.67E+01	9.84E-01	3.04E+01	9.40E-01
	Sample3	3:00	2.34E+01	1.24E+00	2.29E+01	1.36E+00	2.65E+01	2.65E+01	1.26E+00	3.06E+01	9.92E-01
	Sample4	3:30	2.60E+01	1.26E+00	2.60E+01	1.34E+00	2.47E+01	2.47E+01	9.28E-01	3.19E+01	1.08E+00
	Sample5	4:00	2.33E+01	1.29E+00	2.32E+01	1.39E+00	2.67E+01	2.67E+01	9.67E-01	3.02E+01	1.11E+00
	Sample6	4:20	2.37E+01	8.11E-01	2.38E+01	1.08E+00	2.62E+01	2.62E+01	1.17E+00	3.04E+01	6.60E-01

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
D (m <sup>2</sup> /s)	Sample1	0:00	1.32E-06	-2.5E-08	1.78E-07	1.78E-07	-1.3E-06		
	Sample2	1:10	1.5E-06	1.64E-06	1.14E-06	1.14E-06	9.47E-07		
	Sample3	3:00	1.66E-06	1.87E-06	1.49E-06	1.49E-06	9.95E-07		
	Sample4	3:30	1.52E-06	1.62E-06	1.16E-06	1.16E-06	1.05E-06		
	Sample5	4:00	1.74E-06	1.9E-06	1.12E-06	1.12E-06	1.14E-06		
	Sample6	4:20	1.05E-06	1.41E-06	1.39E-06	1.39E-06	6.6E-07		
Mean	1.50E-06	±2.67E-07	1.69E-06	±2.00934E-07	1.26E-06	±1.69E-07	9.57E-07	±1.81E-07	

**Experimental data of mixture test obtained @ RH=12% and T=31°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	0:50	65143692	4171715	71331968	5064804	2022618	224992	5583435	358839
	Sample2	1:10	66489332	4063993	73285392	4820369	1690932	158461	6127420	341542
	Sample3	1:25	64190944	4074264	70629672	4599840	1845095	239880	5585228	373256
	Sample4	1:40	66800232	4204432	72625080	4822322	2480762	179011	5671403	373658
	Sample5	2:00	65185152	4373451	71049368	49600386	2231722	187582	5627939	350443
Concentration (mg/m <sup>3</sup> )	Sample1	0:50	24.812991	1.3323496	24.639535	1.4735551	24.015732	1.3263907	31.076049	1.1084988
	Sample2	1:10	25.415357	1.2923052	25.796469	1.401042	22.94793	0.9650956	32.934169	1.0257565
	Sample3	1:25	24.3865	1.2961233	24.223593	1.3356207	23.444229	1.4072396	31.082173	1.1774643
	Sample4	1:40	25.55453	1.3445118	25.405393	1.4016213	25.490641	1.0766919	31.376526	1.1793874
	Sample5	2:00	24.83155	1.4073427	24.472162	14.685306	24.688903	1.1232365	31.228064	1.0683355

D (M <sup>2</sup> /s)	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
Sample1	0:50	1.69E-06	1.89E-06	1.74E-06	1.1E-06	1.74E-06	1.1E-06	1.1E-06	1.1E-06
Sample2	1:10	1.59E-06	1.71E-06	1.3E-06	9.56E-07	1.3E-06	9.56E-07	9.56E-07	9.56E-07
Sample3	1:25	1.67E-06	1.73E-06	1.9E-06	1.17E-06	1.9E-06	1.17E-06	1.17E-06	1.17E-06
Sample4	1:40	1.65E-06	1.74E-06	1.31E-06	1.16E-06	1.31E-06	1.16E-06	1.16E-06	1.16E-06
Sample5	1:79E-06	1.79E-06	4.46E-05	1.42E-06	1.05E-06	1.42E-06	1.05E-06	1.05E-06	1.05E-06
Mean	1.68E-06	±7.05E-08	1.77E-06	±8.35329E-08	1.53E-06	±2.69E-07	1.09E-06	±8.8E-08	±8.8E-08



**Experimental data of mixture test obtained @ RH=24% and T=31°C**

	Time	Hexane			CycloHexane			E.A.			Octane		
		HC	LC		HC	LC		HC	LC		HC	LC	
GC/MS Response	Sample1	0:00	159604	186335	140292	98518		37501	13319		23741	16384	
	Sample2	0:35	68963568	4233846	73940376	4803167		3518170	187096		6004369	385799	
	Sample3	1:10	63149232	4993432	69358200	5553308		3113107	241403		5721263	379455	
	Sample4	1:25	66454092	4046270	72255744	4630768		2618239	163865		5736199	367886	
	Sample5	1:40	61971644	3987645	69103448	4354404		3040509	116392		5538230	363089	
	Sample6	1:50	66472564	4413770	72510784	5560097		2445538	237674		5782981	369036	
Concentration (mg/m <sup>3</sup> )	Sample1	0:00	-4.276695	-0.149171	-17.52441	0.002762		17.625015	0.1769054		12.085487	-0.529677	
	Sample2	0:35	26.522932	1.3554461	26.184389	1.3959389		28.830384	1.1205973		32.513857	1.2374653	
	Sample3	1:10	23.920184	1.6378137	23.470552	1.6184728		27.526359	1.4155102		31.546836	1.207118	
	Sample4	1:25	25.399582	1.2857169	25.18665	1.3447957		25.933223	0.9944419		31.597853	1.1517763	
	Sample5	1:40	23.393045	1.2639237	23.319673	1.2628106		27.292643	0.7366409		30.921639	1.1288292	
	Sample6	1:50	25.407851	1.4223309	25.3377	1.6204868		25.377244	1.39526		31.757649	1.1572774	

D (m <sup>2</sup> /s)	Time	Hexane			CycloHexane			E.A.			Octane					
		1.07E-06	1.6E-06	2.18E-06	1.67E-06	2.2E-06	1.61E-06	3.01E-07	1.2E-06	1.61E-06	1.19E-06	1.12E-06	1.13E-06	1.12E-06	1.15E-06	±2.99E-08
Sample1	0:00				-4.7E-10			3.01E-07			-1.2E-06					
Sample2	0:35				1.67E-06			1.2E-06			1.18E-06					
Sample3	1:10				2.2E-06			1.61E-06			1.18E-06					
Sample4	1:25				1.68E-06			1.19E-06			1.12E-06					
Sample5	1:40				1.7E-06			8.25E-07			1.13E-06					
Sample6	1:50				2.03E-06			1.73E-06			1.12E-06					
Mean	1.77E-06	±2.45E-07	±2.45E-07	±2.45E-07	1.86E-06	±2.445E-07		1.31E-06	±3.64E-07		1.15E-06	±2.99E-08				

**Experimental data of mixture test obtained @ RH=0% and T=39°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	1:10	39443764	4588749	48220692	5304066	2649260	244371	4030385	474216
	Sample2	2:00	72973280	5211199	78251616	6787168	3098080	214055	6350646	432721
	Sample3	2:55	65881128	4195433	73176648	4784152	3761128	199082	5858296	405287
	Sample4	3:40	64848932	4442083	72144840	7178446	3469739	293912	5563384	380303
	Sample5	4:05	65324768	4134044	72282808	5191394	3446081	177859	5748031	386434
	Sample6	4:20	64645992	4073083	72545984	4707447	2477349	220444	5697584	385836
Concentration (mg/m <sup>3</sup> )	Sample1	1:10	1.33E+01	1.49E+00	1.10E+01	1.54E+00	2.60E+01	1.43E+00	2.58E+01	1.66E+00
	Sample2	2:00	2.83E+01	1.72E+00	2.87E+01	1.98E+00	2.75E+01	1.27E+00	3.37E+01	1.46E+00
	Sample3	2:55	2.51E+01	1.34E+00	2.57E+01	1.39E+00	2.96E+01	1.19E+00	3.20E+01	1.33E+00
	Sample4	3:40	2.47E+01	1.43E+00	2.51E+01	2.10E+00	2.87E+01	1.70E+00	3.10E+01	1.21E+00
	Sample5	4:05	2.49E+01	1.32E+00	2.52E+01	1.51E+00	2.86E+01	1.07E+00	3.16E+01	1.24E+00
	Sample6	4:20	2.46E+01	1.30E+00	2.54E+01	1.37E+00	2.55E+01	1.30E+00	3.15E+01	1.24E+00

D (m <sup>2</sup> /s)	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
Sample1	1:10	3.74E-06	4.88E-06	1.73E-06	2.05E-06				
Sample2	2:00	1.92E-06	2.2E-06	1.44E-06	1.35E-06				
Sample3	2:55	1.67E-06	1.7E-06	1.24E-06	1.29E-06				
Sample4	3:40	1.83E-06	2.71E-06	1.87E-06	1.21E-06				
Sample5	4:05	1.66E-06	1.9E-06	1.16E-06	1.21E-06				
Sample6	4:20	1.65E-06	1.69E-06	1.6E-06	1.22E-06				
Mean	1.75E-06	±1.21E-07	2.04E-06	±4.29125E-07	1.46E-06	±2.88E-07	1.26E-06	±6.17E-08	

**Experimental data of mixture test obtained @ RH=8% and T=39°C**

	Time	Hexane		CycloHexane		E.A.		Octane		
		HC	LC	HC	LC	HC	LC	HC	LC	
GC/MS Response	Sample1	1:00	58330196	4136742	66338168	4880810	2355195	179558	5222434	372802
	Sample2	2:00	58747732	3487953	64931236	3809205	2309058	188585	5008286	314917
	Sample3	3:55	68695224	3910778	75610952	4632521	2761100	180215	5914710	341331
	Sample4	4:05	67184288	3869451	75226400	4577500	3443425	148168	5905968	358697
	Sample5	4:15	62722384	3737359	4482217		2980554	168562	5437896	345136
Concentration (mg/m <sup>3</sup> )	Sample1	1:00	2.18E+01	1.32E+00	2.17E+01	1.42E+00	2.51E+01	1.08E+00	2.98E+01	1.18E+00
	Sample2	2:00	2.19E+01	1.08E+00	2.08E+01	1.10E+00	2.49E+01	1.13E+00	2.91E+01	8.98E-01
	Sample3	3:55	2.64E+01	1.24E+00	2.72E+01	1.35E+00	2.64E+01	1.08E+00	3.22E+01	1.02E+00
	Sample4	4:05	2.57E+01	1.22E+00	2.69E+01	1.33E+00	2.86E+01	9.09E-01	3.22E+01	1.11E+00
	Sample5	4:15	2.37E+01	1.17E+00	2.47E+01	1.30E+00	2.71E+01	1.02E+00	3.06E+01	1.04E+00

Run 1 (8%-39C)

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
D (m <sup>2</sup> /s)	Sample1	1:00	1.92E-06	2.08E-06	2.08E-06	1.34E-06	1.22E-06	1.22E-06	1.22E-06
	Sample2	2:00	1.54E-06	1.66E-06	1.66E-06	1.41E-06	9.47E-07	9.47E-07	9.47E-07
	Sample3	3:55	1.46E-06	1.55E-06	1.55E-06	1.27E-06	9.77E-07	9.77E-07	9.77E-07
	Sample4	4:05	1.48E-06	1.54E-06	1.54E-06	9.76E-07	1.06E-06	1.06E-06	1.06E-06
	Sample5	4:15	1.54E-06	1.66E-06	1.66E-06	1.16E-06	1.05E-06	1.05E-06	1.05E-06
Mean		1.59E-06	±1.89E-07	1.70E-06	±2.22083E-07	1.23E-06	±1.69E-07	1.05E-06	±1.06E-07

**Experimental data of mixture test obtained @ RH=16% and T=39°C**

	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
GC/MS Response	Sample1	1:00	60209352	3592064	4106821	2037315	167210	5247072	373149
	Sample2	2:00	57113044	3460391	65852852	2879308	144189	5275621	331698
	Sample3	3:40	52375380	3719113	62885036	4615251	2682046	4973396	342313
	Sample4	4:15	54972088	3582837	64179520	4387239	2646193	5162298	334307
	Sample5	4:30	61176472	3226032	71634936	3674266	3076252	5407150	304246
Concentration (mg/m <sup>3</sup> )	Sample1	1:00	2.26E+01	1.12E+00	2.27E+01	1.19E+00	2.41E+01	1.01E+00	2.99E+01
	Sample2	2:00	2.12E+01	1.07E+00	2.14E+01	1.10E+00	2.68E+01	8.88E-01	3.00E+01
	Sample3	3:40	1.91E+01	1.16E+00	1.96E+01	1.34E+00	2.61E+01	1.27E+00	2.90E+01
	Sample4	4:15	2.03E+01	1.11E+00	2.04E+01	1.27E+00	2.60E+01	1.33E+00	2.96E+01
	Sample5	4:30	2.30E+01	9.81E-01	2.48E+01	1.06E+00	2.74E+01	8.69E-01	3.05E+01

D (m <sup>2</sup> /s)	Time	Hexane		CycloHexane		E.A.		Octane	
		HC	LC	HC	LC	HC	LC	HC	LC
Sample1	1:00	1.55E-06		1.64E-06		1.31E-06		1.22E-06	
Sample2	2:00	1.58E-06		1.62E-06		1.02E-06		1E-06	
Sample3	3:40	1.93E-06		2.18E-06		1.52E-06		1.09E-06	
Sample4	4:15	1.73E-06		1.98E-06		1.6E-06		1.03E-06	
Sample5	4:30	1.32E-06		1.33E-06		9.73E-07		8.5E-07	
Mean	1.62E-06	±2.26E-07		1.75E-06	±3.32476E-07	1.28E-06	±2.86E-07	1.04E-06	±1.34E-07