INVESTIGATION OF NON-METHANE VOLATILE ORGANIC CARBON EMISSIONS FROM INTERIOR MATERIALS USED IN THE INTERCITY BUSES

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ABSTRACT

INVESTIGATION OF NON-METHANE VOLATILE ORGANIC CARBON EMISSIONS FROM INTERIOR MATERIALS USED IN THE INTERCITY BUSES

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The objectives of this study are to determine the non-methane volatile organic carbon emissions from the parts used in the interiors of buses at different temperatures and to analyze the components of these emissions.

The total non-methane volatile organic carbon (NMVOC) concentrations in various sections of a bus were measured in order to determine the indoor air pollution in the bus. Different samples of the materials used in the interior parts of the buses were provided by the manufacturing company and they were tested in the METU Air Pollution Laboratory in order to see what hydrocarbon components make up this total NMVOC concentration.

The results of experiments showed that the leading constituent emitted from the test pieces was toluene. Benzene concentration was very low. This is very important since benzene is a carcinogen and it has very low indoor concentration limits determined by OSHA and NIOSH. When the concentrations of the total NMVOC emitted from various parts are examined, it was seen that the most of the VOC emissions occur from the “floor materials” and “ventilation channel”. After measurements were done in two buses the average indoor total NMVOC concentrations were found as 21.15 ± 5.8 ppmv (as C_3H_8) and 46.04 ± 9.2 ppmv (as C_3H_8) in the first and second bus, respectively.

Suggestions were made to the manufacturing company for some replacement of solvents and adhesives, and measurements were repeated with the newly manufactured parts for the bus. The highest concentrations were observed for toluene in these measurements, too. However, the toluene concentration was at least 40% lower than the initial values. Benzene concentrations were again very low. The average indoor total NMVOC concentrations were found as 10.41 ± 2 ppmv (as C_3H_8) in the measurements done in the bus decorated with new materials. This concentration was about 50% and 25% of the values measured in the first and the second bus at the beginning of the study, respectively.

Keywords: Indoor air pollution, Volatile Organic Carbon emissions, indoor materials.

ÖZ

ŞEHİRLERARSI OTOBÜSLERDE KULLANILAN İÇYAPI MALZEMELERİNDEN KAYNAKLANAN UÇUCU ORGANİK KARBON EMİSYONLARININ ARAŞTIRILMASI

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Bu çalışmanın amacı, otobüslerin iç tasarımında kullanılan parçalardan kaynaklanan metan-dışı uçucu organik karbon emisyonlarının farklı sıcaklıklarda ölçülmesi ve bu emisyonların bileşenlerinin analiz edilmesidir.

Otobüs içerisindeki hava kirliliğini belirlemek amacıyla otobüsün değişik kısımlarında toplam metan-dışı uçucu organik karbon konsantrasyonları ölçülmüştür. Daha sonra ölçülen toplam metan dışı uçucu organik karbon konsantrasyonlarının hangi hidrokarbon bileşiklerinden oluştuğunu görmek için otobüslerin iç

kısımlarında kullanılan ve üretici firmadan sağlanan farklı parçaların örnekleri, ODTÜ Hava Kirliliği Laboratuvarında test edilmiştir.
Deney sonuçları, denenen test parçalarından salınan hidrokarbonlar arasında en önde gelen bileşenin toluen olduğunu göstermiştir. Benzen emisyonu oldukça düşüktür. Bu sonuç çok önemlidir çünkü benzen kansorejen maddeler arasındadır. Benzen için OSHA ve NIOSH tarafından belirlenmiş iç ortam sınır konsantrasyon değerleri çok düşüktür. Toplam metan-dışı uçucu organik karbon konsantrasyonları incelendiğinde en yüksek uçucu organik karbon emisyonunun "taban malzemeleri" ve "havalandırma kanalı"ndan geldiği görülmüştür. İki otobüs içerisinde yapılan ölçümler sonucunda ortalama toplam metan-dışı uçucu organik karbon konsantrasyonları, sırasıyla birinci ve ikinci otobüste 21.15 ± 5.8 ppmv (C_3H_8 cinsinden) ve 46.04 ± 9.2 ppmv (C_3H_8 cinsinden) olarak bulunmuştur.

Üretici firmaya bazı solvent ve yapıştırıcı değişiklikleri önerilmiş ve ölçümler yeni üretilen parçalar ve otobüsle tekrar edilmiştir. Bu ölçümlerde de en yüksek konsantrasyona sahip olan bileşenin toluen olduğu görülmüştür. Ancak, toluen konsantrasyonu ilk ölçümlerdeki değerin en fazla %40 ıdır. Benzen konsantrasyonu yine oldukça düşüktür. Yeni malzemelerle döşenen otobüs içerisinde yapılan ölçümde ortalama toplam metan-dışı uçucu organik karbon konsantarsyonu 10.41 ± 2 ppmv (C_3H_8 cinsinden) olarak bulunmuştur. Bu konsantrasyon çalışmanın başlangıcında birinci otobüste ölçülen değerin %50 si, ikinci otöbüste ölçülen değerin %25 i kadardır.

Anahtar kelimeler: İç ortam havası kirliliği, uçucu organik karbon emisyonu, içortam malzemeleri.

To My Family
And Also To İREMİM

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LIST OF ABBREVIATIONS

^{o}C	Degrees Celcius
cm	Centimeter
FID	Flame Ionization Detector
FM	Floor Material
EPA	USA Environmental Protection Agency
GC	Gas Chromatograph
HC	Hydrocarbon
hPa	HektoPascal
hr	Hour
k_m	Initial release rate (evaporation rate)
L	Liter
m^3	Meter cube
METU	Middle East Technical University
mg	Miligram
min	Minutes
mL	Milliliter
μL	Microliter
NMVOC	Non-methane Volatile Organic Carbon
NR	Natural Rubber
OSHA	Occupational Safety and Health Administration
NIOSH	The National Institute for Occupational Safety and Health
PEL	Permissible Exposure Limit
ppmv	Parts per million by volume
PTFE	Poly Tetrafluoro Ethylene
PUR	Polyurethane
SIS	State Institute of Statistics

STEL	Short-Term Exposure Limit
TWA	Time Weighted Average
USA	United States of America
VOC	Volatile Organic Carbon
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1. General

The air we breathe is being polluted by activities such as driving cars and trucks; burning coal, oil, and other fossil fuels; and manufacturing chemicals. Air pollution can even come from smaller, everyday activities such as dry cleaning, filling the cars with gas, and degreasing and painting operations. These activities add gases and particles to the air we breathe. When these gases and particles accumulate in the air in high enough concentrations, they can harm us and our environment. More people in cities and urban areas mean more cars, trucks, industrial and commercial operations, and generally mean more pollution (Wark et al., 1998).

Air pollution is a problem for all of us. The average adult breathes over 11 m^3 of air every day. Children breathe even more air per kg of body weight and are more susceptible to air pollution. Many air pollutants, such as those that form urban smog and toxic compounds, remain in the environment for long periods of time and are carried by the winds hundreds of miles from their origin. Millions of people live in areas where urban smog, very small particles, and toxic pollutants pose serious health concerns. People exposed to high enough levels of certain air pollutants may experience burning in their eyes, an irritated throat, or breathing difficulties. Long-term exposure to air pollution can cause cancer and long-term damage to the immune, neurological, reproductive, and respiratory systems. In extreme cases, it can even cause death (Wark et al., 1998).

In the context of the current regulatory environment in the United States, air pollution exists in four broad categories (Wark et al., 1998).

1. *Ambient Air Pollution.* This refers to air pollution in the outdoor environment and involves a complex array of sources and pollutants, meteorological transport of the pollutants to a receptor, and a wide range of social, economic, and health effects. The regulatory authority lies within the U.S. Environmental Protection Agency (EPA).

2. *Indoor Air Pollution.* This refers to air pollution in the indoor environment in which people live and sleep. Regulatory responsibility has been a subject of much debate. The U.S. EPA has played an increasingly active role in studying and issuing guidelines, particularly in the areas of radon and passive cigarette smoke. There are, as yet, no federal regulations regarding indoor air pollution.

3. *Occupational (Industrial Hygiene) Air Pollution.* This type of air pollution is associated with exposure to a large range of pollutants (particles, mists, acid vapors, and organic and inorganic gases) in the workplace. The regulatory standards associated with the workplace are under the Occupational Safety and Health Administration (OSHA) and are generally developed by the American Conference of Governmental and Industrial Hygienists (ACGIH) and the National Institute of Occupational Safety and Health (NIOSH).

4. *Personal Exposure.* This final category refers to exposure to dust, fumes, gases, or mists to which an individual exposes oneself. Examples include cigarette/cigar smoking, sniffing of glue, and many other practices which can cause damage to the human body (Wark et al., 1998).

For many industrialized countries, ambient air pollution and efforts to improve the “outdoor air quality” have been under way for the majority of this century. In many locations around the world, significant improvements have taken place. Air quality in many major cities such as London, New York, and Chicago has improved from the conditions present in the first half of the twentieth century. Mechanisms and control programs are in place in the developed countries to continue the improvement of ambient air quality. Considerable effort and energy have been expended to characterize, evaluate, and control air pollution emissions to the atmosphere (Boubel et al., 1994).

In modern societies, a parallel effort has been under way to improve air quality in the industrial occupational setting in manufacturing and other traditional jobs. Also, in many countries today it has been important to consider the quality of air in other locations where we live parts of our lives. Attention is now being refocused on "indoor" air quality (Boubel et al., 1994).

New residences and commercial buildings are designed and built with energy conservation as a major design criterion. New materials have been developed and are being used in construction. Although these modifications have helped save energy, a consequence of some of these modifications has been slower exchange of air with the outside, and therefore an “indoor air pollution” problem.

A second consideration is the change in lifestyle for individuals in industrialized societies. Individuals in industrialized societies mostly have occupations which require them to be indoors for a significant part of the day. Over the past two decades, studies of daily activities have consistently shown for urban populations that, on average, people spend about 90% of their time indoors in their homes, cars, offices, factories, public buildings such as restaurants, malls, and others (Boubel et al., 1994).

Exposure assessment techniques now attempt to include as many as possible of the locations in which individuals now spend time. The concept involves identification of microenvironments which are important for potential exposure. For example, exposure to CO would include time spent in commuting, parking garages, in residences with gas stoves, as well as time spent outdoors. This approach classifies time spent in these microenvironments and the typical concentrations of CO in these locations.

Several factors influence the quality of air indoors: the rate of exchange of air with air from outdoors, the concentration of pollutants in outdoor air, the rate of emissions from sources indoors, the rate of infiltration from soil gases, and the rate of removal in the indoor environment.

The source of indoor air pollutants may be inside the building, or they may be transported into the interior space from the outside. Sources located indoors include building materials, combustion sources, furnishings, and pets. Emissions of organic gases are higher with increased temperature and humidity but usually decrease with age of the structure or furnishings. Construction materials and the composition of furnishings inside the building may give off or outgas pollutants into the interior airspace, e.g., glues or adhesives. Natural gas for cooking and kerosene space heaters release NO and CO; even when operating properly. Molds may grow in the ventilation ducts and be distributed throughout a building (Boubel et al., 1994).

The air exchange rate influences the concentration of indoor pollutants in two ways. At higher air exchange rates, the pollutants inside a structure are removed from the interior. As long as the ambient outside air has lower pollutant concentrations, high exchange rates help lower indoor air pollutant levels. However, if the pollutant concentration outside is elevated, then an increase in the air exchange rate will bring these materials into the building; e.g., an idling vehicle adjacent to an air intake will transfer exhaust fumes into the building. At lower exchange rates, pollutants released from sources inside the building can contribute to higher levels of indoor pollutants.

The concentration of indoor pollutants is a function of removal processes such as dilution, filtration, and destruction. Dilution is a function of the air exchange rate and the ambient air quality. Gases and particulate matter may also be removed from indoor air by deposition on surfaces. Filtration systems are part of many ventilation systems. As air is circulated by the air-conditioning system it passes through a filter which can remove some of the particulate matter. The removal efficiency depends on particle size. In addition, some reactive gases like NO; and SO; are readily adsorbed on interior surfaces of a building or home. Table 1.1 shows the major categories of indoor air pollutants and sources (Boubel et al., 1994).

Table 1.1 Indoor Air Pollutants and Typical Sources (Boubel et al., 1994)

Pollutant	**Source**
Combustion gases—CO, NO	Combustion—furnace, cooking stove, space heater, etc.
Volatile organic compounds (VOCs)	Out gassing of building materials, coatings, wall and floor coverings, and furnishings
Formaldehyde	Out gassing of pressed wood, insulation foam
Pesticides	Household products
Biological agents—molds, spores, dander	Contaminated ventilation systems, pets
Environmental tobacco smoke	Smoking in building
Radon	Infiltration from soil beneath structure
Asbestos	Construction coatings, tile. insulation

As mentioned above indoor air pollution is seen in homes, cars, offices, factories, public buildings and others. Although there are many studies done for indoor air pollution for houses and work places, there are just a few studies about the air pollution in vehicles. Over the past 25 years, these studies have shown that, while traveling inside vehicles during peak-hour traffic, commuters are exposed to concentrations of various pollutants that are substantially higher than the ambient concentrations typical of suburban areas. While the majority of earlier investigations concentrated on CO, more recent studies have focused on in-vehicle concentrations of VOCs. (Jo and Park, 1998; Duffy and Nelson, 1997).

Volatile organic compounds (VOCs) are part of anthropogenic air pollution. VOCs have various effects on human beings: Some are harmless to the human health, some are odorous, and others cause severe diseases like cancer (e.g. benzene). Under the influence of sunlight they are part of photochemical reactions in the atmosphere. Together with nitrogen oxides they are responsible for the formation of ozone (Hartmann et al., 1997).

Most of the studies in the literature are generally focused on the VOC emissions in outdoor air or emissions from engines and coming into indoors. However, there are not many studies on the VOC emission caused from the **plastic materials and the adhesives** used in the construction of the parts used in the interiors of buses, cars and other vehicles, which cause solvent evaporation at different temperatures.

There are many types of materials used in the construction of vehicles. Especially the types of materials used for the interior design of the passenger cars and buses are multi-variant. As an example, in buses fiberglass aided polyester based materials are used in ventilation channels, rubber based materials are used in floor materials and polyurethane based materials are used in torpedo production. Due to the evaporation of solvents from these parts VOC emissions (toluene, decane, undecane, nonane, etc) occur. These emissions cause discomfort and headaches especially in the drivers and passengers in the buses or trucks. As it is known some of these organic materials (BTX compounds- Benzene, toluene, xylene) are harmful and exposing to these materials causes serious health effects.

This problem may be more important for buses, because most of the buses are intercity buses and travel long distances without any stops. Since the drivers are exposed to these emissions almost everyday, these discomforts such as headache and nausea could turn to be chronic.

1.2. Situation in Turkey

The number of cars and buses in Turkey has shown a rapid increase in the last two decades. There are quite a few car and bus manufacturing companies in Turkey.

According to the statistics obtained from SIS, a total of 7,477,043 units of vehicles have been on traffic in Turkey in year 2002, and 952,000 units of this total are heavy vehicles (trucks, buses, etc). The contribution of buses to this number is 120,097 units. The number for motor vehicles in year 2002 is shown in Fig. 1.1 (SIS, 2002).

As explained above, due to the plastic materials and adhesives used in the construction of various parts for the interiors of the vehicles, solvent evaporation and VOC emissions occur. Indoor air pollution problem in vehicles also exists in Turkey and since the customers became more conscious about the products and services they purchase, they make complaints if they are not happy with them.

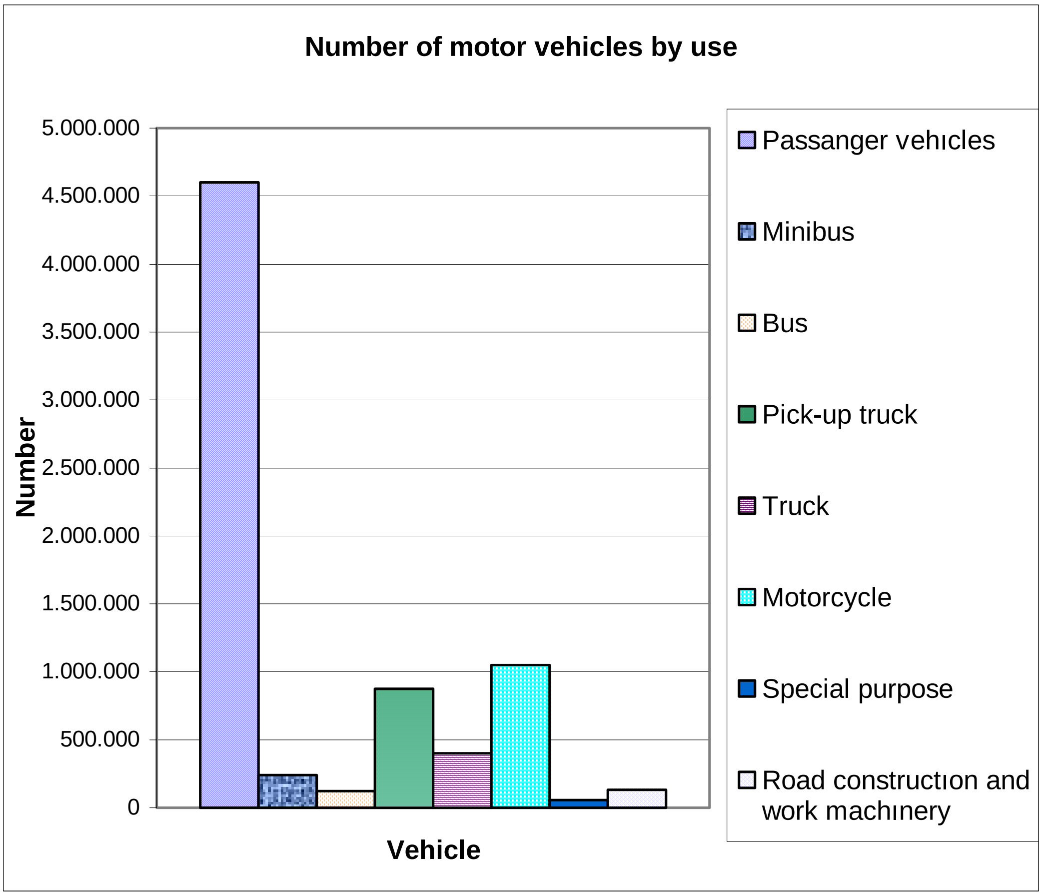

Figure 1.1 Numbers for different uses of motor vehicles in year 2002 (SIS, 2002)

1.3. Objectives and Scope of the Study

There have been some complaints to one of the bus manufacturing company in Turkey from drivers and passengers. The complaint is about having headaches, nausea, and inhaling difficulties after driving new buses or riding in new buses as passengers. In order to resolve this problem the company came to the Middle East Technical University to make some VOC measurements in buses newly manufactured. Therefore, a new research has been started on this subject. When VOC is used in the text, it means the non-methane VOC.

The objectives of this study are, to measure the VOC emissions from the parts used in the interiors of buses at different temperatures and analyze the components of these emissions. This study is handled in four separate phases:

- In Phase I of the study the total non-methane volatile organic carbon (NMVOC) concentration in various parts of the bus is measured. Objective of the Phase I study is to determine the total NMVOC concentration in the bus and to find out in which part of the vehicle the concentration is higher.

- In Phase II of the study the objective is to see what hydrocarbon components make up this total NMVOC concentration and to find out the concentration of each component present in the NMVOC, since some of the components could be carcinogenic organics.

- In Phase III, based on the results obtained from Phase I and Phase II of the study, the objective is to make an interim conclusion and to suggest to the company some replacement of solvents.

- In Phase IV, the objective is to test the NMVOC evaporated from new parts manufactured by using the new solvents.

- In Phase V, the objective is to measure the indoor concentration of the bus built with the new parts and to find out the difference in air quality in the bus.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1. Literature Survey

2.1.1. Studies about indoor air pollution in vehicles

Personal exposure to VOCs and other criteria pollutants including carbon monoxide (CO) and nitrogen oxides (NO_x) have been strongly associated with vehicle use (Wallace, 1987). In fact, over the past 25 years, a number of studies have shown that, while traveling inside vehicles during peak-hour traffic, commuters are exposed to concentrations of various pollutants that are substantially higher than the ambient concentrations typical of suburban areas. While the majority of earlier investigations concentrated on CO, more recent studies have determined in-vehicle concentrations of VOCs, the latter focusing mainly on aromatic hydrocarbons (Duffy and Nelson, 1997).

The vehicle cabin has recently been recognized as an important microenvironment that can lead to personal exposure to many volatile organic compounds (VOCs). Several studies have found that individuals are exposed to elevated levels of 5 to 24 VOCs while commuting as compared to activities in which gasoline is not used (Jo and Park, 1998).

Jo and Park (1998) examined in-vehicle concentrations of selected gasoline derived VOCs. Median in vehicle concentrations of benzene, toluene, ethyl benzene, p-xylene, m-xylene and o-xylene were found as 38.3, 107, 9.2, 7.8, 16.9, and 10.7

μg/m^3, respectively. It was reported that the concentrations of toluene and benzene were significantly higher inside the vehicles than in the roadway air.

2.1.2. Studies about emission characteristics of construction materials

Understanding the emission characteristics of wet materials is important for preventing indoor air pollution problems. Currently, characterization of VOC emissions from wet coating materials is done mainly by experimental approach. The approach uses environmental test chambers to measure VOC emissions under controlled indoor conditions.

Using environmental chambers, previous studies have indicated that the emission process of wet materials appears to have three phases. The first phase represents the period shortly after the material is applied but is still relatively wet. The VOC emissions in this phase are characterized by high emission rates but fast decay. It appears that emissions are related to evaporation at the surface of the material. In the second phase, the material dries as emissions' transition from an evaporation-dominant phase to an internal-diffusion controlled phase occur. In the third phase the material becomes relatively dry. In this phase the VOC off-gassing rate decreases and so does the decay rate. The dominant emission mechanism in this phase is believed to be the internal diffusion of VOCs through the substrate (Yang, 2001).

Previous studies have also found that the emissions of wet materials are likely to depend on environmental conditions (e.g., temperature, air velocity, turbulence, humidity, VOC concentration in air) and also physical properties of the material and the substrate (e.g., diffusivity).

Since the emission behavior of wet materials can be affected by many factors, it would be too expensive to investigate the emissions purely by experiments. A feasible way would be to develop computer models to simulate the emission processes based on limited experimental data. Source models are also useful for analyzing the emission data obtained from test chambers, for extrapolating the test results beyond the test period, for developing simplified methods and procedures for emission testing (Yang, 2001).

Guo et al. (1998, 1999) state that indoor use of solvent based coating materials may cause high amount of VOC concentrations. They defined two methods for estimation of the emission rate of VOCs from solvent-based indoor coating materials based on product formulation. The first method developed a mass transfer model with two key parameters -total vapor pressure and the average molecular weight for TVOC-, which is estimated, based on the VOC contents in the product. Other method is based on first order decay model, in which the parameters are estimated from the properties of both the source and the environment. The proposed methods provide a way to predict the VOC emissions in the indoor environment without having to conduct costly chamber testing. The two proposed methods work for both total VOCs and individual VOCs without conducting costly dynamic chamber testing..

Zhu et al. (1999) developed a method for estimating the VOC emission rates from hydrocarbon solvent based indoor materials which is based on the assumption that the emission rate of individual VOCs is proportional to its molar fraction in the evaporative mixture at the time, its saturated pure vapor pressure and total remaining VOCs in the material.

Emissions can be divided into two stages as ‘high but fast’ and ‘low and slow’. Emissions in the first stage, especially in the initial several hours after application, are largely controlled by evaporation rates of the solvent. However, emissions in the second stage are controlled by diffusion. Emissions can be described by both VB model and VBX model. VB model is used for describing total VOC emissions only while the more advanced VBX model can be used for describing emissions of individual VOCs. However the models are very complex because it requires the knowledge of changes of molar fractions of each individual VOCs in a solvent mixture over evaporation time.

Zhu et al. (2001) used the experimental data, obtained by testing materials under dynamic chamber test conditions to represent characteristics of VOCs and called as measured emission factors. The widely used first order decay model was compared with a power law model in their adequacy to describe measured VOC emissions. Power law model has been used to describe measured VOC emissions from diffusion-controlled sources. After several experiments the power law model was more successful than the first order decay model for describing the emissions of VOCs. It is recommended to use regression analysis to obtain model coefficients because of measurement uncertainties.

2.2. Indoor Air Pollution Standards

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PEL) for the constituents as an 8-hr time-weighted average (TWA) concentration are given at Table 2.1. Computation of the cumulative exposure for an 8-hour work shift is given in Appendix C. Some constituents also have a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. Currently, OSHA had no limit for decane and undecane, so these constituents are not included in Table 2.1.

Table 2.1 OSHA standards and health effects of constituents

Constituent		OSHA Standards		Health Effects
		ppm	mg/m^3	
Ethyl acetate	TWA	400	1400	can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.
	STEL	-	-	
Benzene*	TWA	1	3.2	may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact (human carcinogen)
	STEL	5	15	
Cyclohexane	TWA	300	1050	can affect the body if it is inhaled, is swallowed or comes in contact with the eyes or skin.
	STEL	-	-	
Toluene	TWA	100	375	can affect the body if it is inhaled, if it comes in contact with eyes or skin or if it is swallowed. It may enter the body through the skin.
	STEL	150	500	
Butyl acetate	TWA	150	710	can cause respiratory tract irritation
	STEL	200	950	
Ethyl benzene	TWA	100	435	causes irritation of the eyes nose, throat, and skin
	STEL	125	-	
Styrene	TWA	50	210	may irritate the eyes, nose, throat, and skin. High concentrations may cause a person to become sleepy or to become unconscious
	STEL	100	420	
Nonane	TWA	200	1050	Can cause respiratory diseases
	STEL	-	-	

*The National Institute for Occupational Safety and Health (NIOSH) recommends that benzene be controlled and handled as a potential human carcinogen in the workplace and that exposure be reduced to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 ppm [0.32 milligrams of benzene per cubic meter of air (mg/m^3)] as an 8-hour TWA and 1 ppm (3.2 mg/m^3) as a ceiling in any 15-minute sampling period.

These standards are used in USA and in EU member countries. However, limit values for ethyl acetate, butyl acetate and ethyl benzene are accepted as exposure limits in Turkey in the regulations for the safety and health precautions for the workplaces working with chemical materials.

CHAPTER 3

MATERIALS AND METHOD

3.1. Phase I

In Phase I of the study the total non-methane volatile organic carbon (NMVOC) concentration in various parts of the bus was measured. The objective of the Phase I study was to determine the total NMVOC concentration in various sections of the bus and to find out in which section of the vehicle the concentration of NMVOC's are higher.

3.1.1. Equipment used for Phase I

Bernath Atomic - Model 3006/Total VOC Analyzer was used to measure the total NMVOC concentration in the gas samples withdrawn from the interior of the bus. A picture of the instrument is shown in Fig. 3.1. The analyzer has a FID (Flame Ionization Detector). There is a "data logger" attached to the analyzer. The NMVOC concentration over time can be measured continuously and all concentrations can be stored in the memory of the data logger. Concentrations are measured every second and the average of these concentrations is recorded every minute. After the measurements are over, data collected during the experiment can be downloaded to a computer. The analyzer is calibrated with propane (C_3H_8) and gives the total hydrocarbon concentrations (ppmv) as C_3H_8. The analyzer measures the peaks coming out of the FID. Each peak area is multiplied with a certain factor and a total VOC concentration is calculated. This concentration is converted to C_3H_8 and the result is reported as C_3H_8 concentration. The concentration can be expressed as ppmv of another hydrocarbon, too.

Figure 3.1 A photograph of the total VOC Analyzer

3.1.2. Experimental procedure for Phase I

VOC measurements were done in the indoor environment of the two newly manufactured buses from the same company. Dimensions of a bus were measured approximately as 12 m long, 2.5 m wide and 2 m high. The buses waited in the bus park area for 15-20 days before they were delivered to the customers. The first bus was manufactured and waited in the bus park area for about 15 days. All the doors and windows were kept shut. The second bus has waited in the bus park area about 20 days almost at the same position and conditions. For the total NMVOC measurements the bus length was divided into 5 equal regions as shown in Fig. 3.2.

Out of five regions, the measurements were made in the 1st, 3rd, and the 5th regions. They were called as 1. Region (front), 2. Region (middle) and 3. Region (back) in the figure. During these measurements the windows and doors were kept shut, the bus was in stationary position and air conditioner was not running. All the equipments were taken into the bus in a very short time, the doors were shut immediately and there was about an hour waiting time for the VOC components in the indoor air to reach equilibrium. Then, the measurements were started.

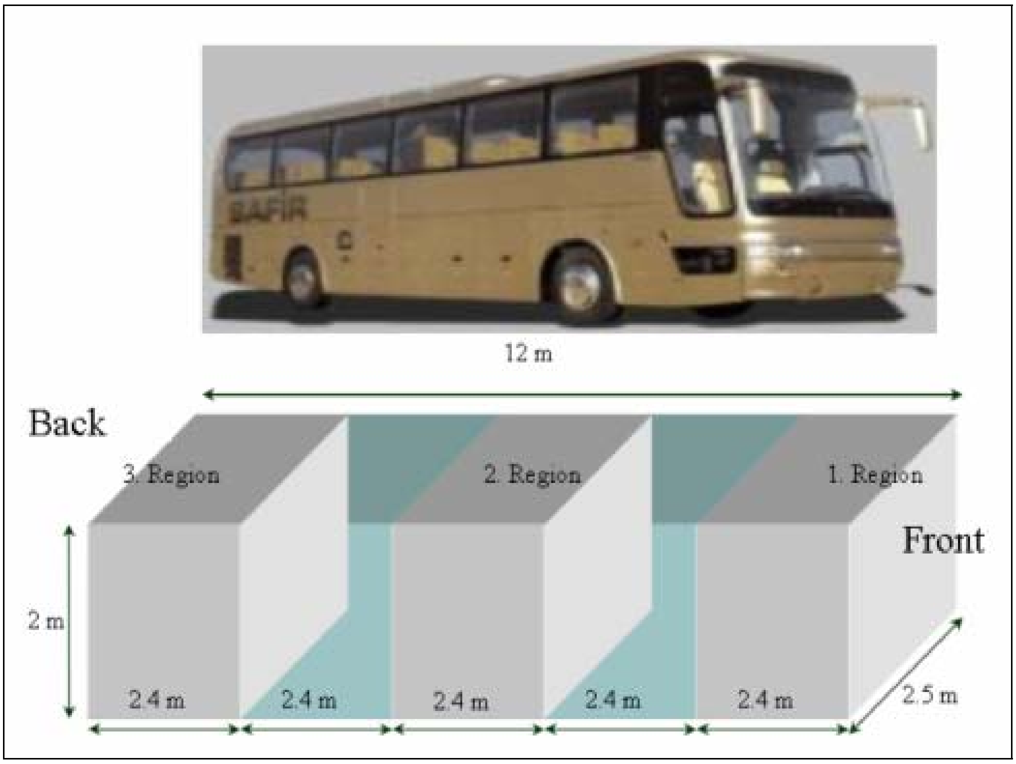

Figure 3.2 Regions of the bus where measurements are made

In each region 18 points were selected as measurement points as seen in the Figs. 3.3 and 3.4. Sampling and measurements were done for 1 minute duration at these points. Data logger which was connected to the VOC Analyzer was set to take data from the analyzer at every second and to record the average to its memory for every minute. The data logger was switched off at the end of each minute. The probe of the analyzer was shifted to the next point and the data logger was switched on again when the measurement started. This procedure was repeated for the whole experimentation period.

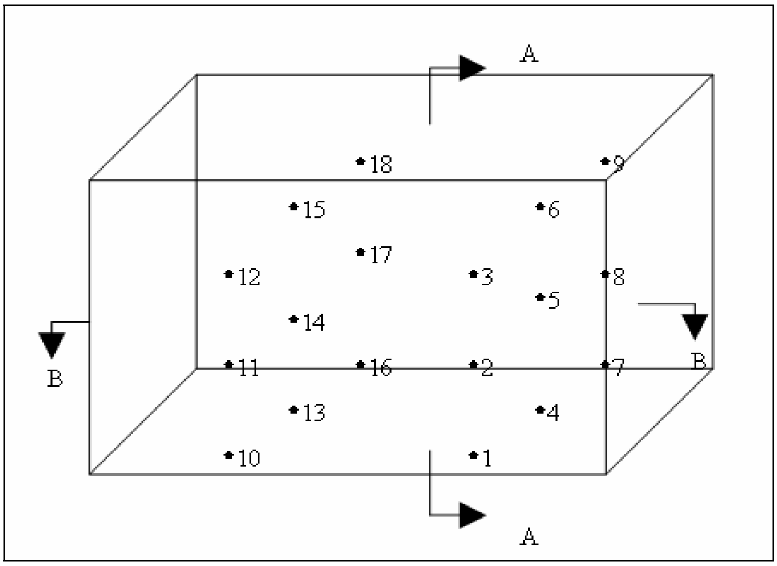

Figure 3.3 Location of sampling points in 1st region

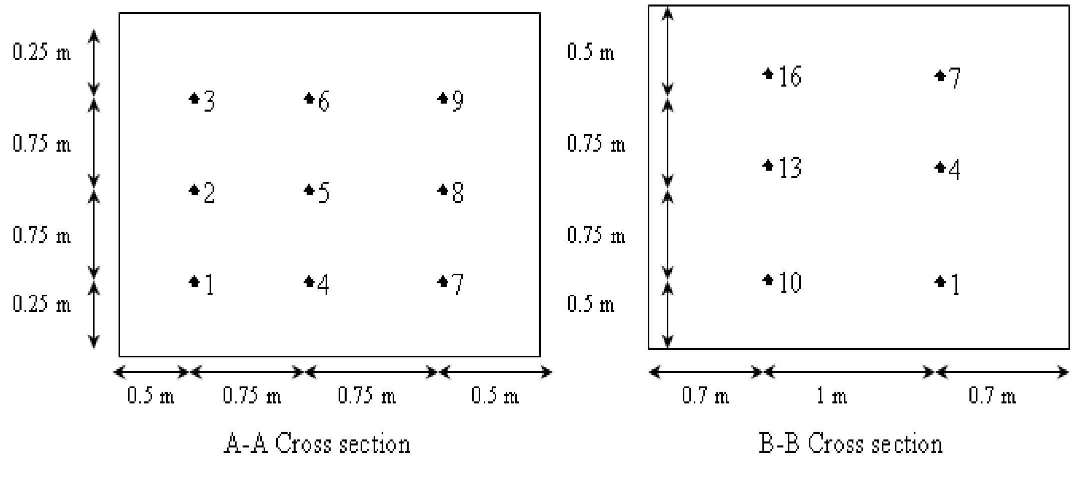

Figure 3.4 Cross sectional view of the first region

3.2. Phase II

At the end of the Phase I study, it was seen that NMVOC concentration in the buses investigated were high. However, it was not possible to see what hydrocarbon components make up this total NMVOC concentration. It is important to know the composition of the VOC components since some of the components could be carcinogenic organics, for example benzene. Different samples of the materials used as interior parts of the buses under investigation were provided by the company and they were tested in the Air Pollution Laboratory of METU Environmental Engineering Department.

3.2.1. Test Pieces

Six different parts were tested in this study. They were:

- Floor material (type 1),
- Floor material (type 2),
- Ventilation channel,
- Window (with adhesive),
- Window holder,
- Door mat

FM (type 1 and type 2): These parts are installed on the floor of the bus. They differ from each other by the material used. In FM (type 1) the material is PVC based and it is produced by a factory of the bus company in Turkey. However, FM (type 2) is a natural rubber (NR)-based material and imported from Germany. The VOC emissions from these pieces come from the adhesive used to stick them to the floor. The adhesive used in Phase II is called "Adhesive A" and the adhesive used in Phases IV is called "Adhesive B".

Ventilation channel: This is the channel which carries the air in the ventilation system of the bus. The material used for manufacturing of ventilation channel is polyester based and it is imported. The ventilation channel is located on the upper part of the bus behind the overhead shelves. The channels are mainly made of fiberglass and adhesives are used to make them stick to their place.

Window (with adhesive): The company places the windows into the window holders and sticks them by using adhesives. The adhesives are polyurethane based and imported from Germany. The VOC emission is mainly due to this adhesive. So the window pieces prepared for emission tests had adhesive applied on the glass.

Window holder: The window on the bus is placed in the window holder. It is the piece around the windows. It has grooves all around where the window fits. The grove is filled with adhesive to make the glass window stick to holder. Window holder materials are polyurethane (PUR) based and produced in Turkey.

Door mat: A typical door mat is placed in vehicles on the stairs at the front and back door. It is made of natural rubber.

3.2.2. Experimental set-up for Phase II

A schematic illustration of the experimental setup is presented in Fig. 3.5. The setup is composed of mainly an oven, a pump, active carbon tubes and a total VOC analyzer. This set-up was used to measure the total VOC concentration, and also to take VOC samples and adsorb them on an activated carbon tube simultaneously during the experiment, which was conducted at constant temperature.

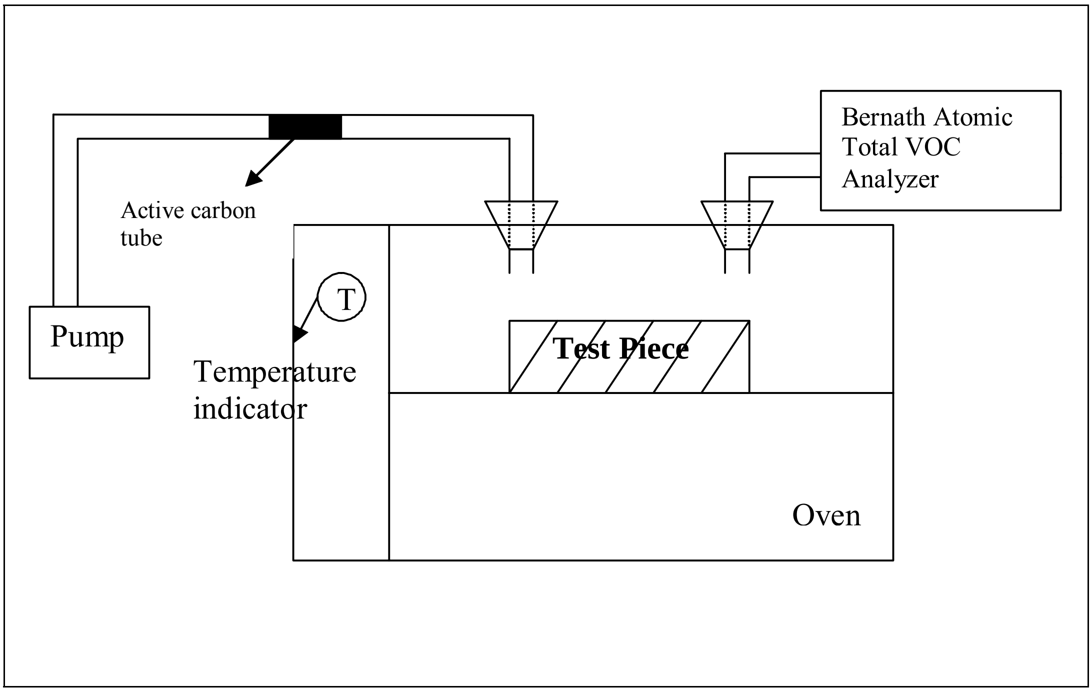

Figure 3.5 Schematic view of the experimental setup

As far as the experimental procedure is concerned, the oven was heated to the desired temperature before the experiment. The test pieces taken from the manufacturing company were placed in the oven. The place was almost the mid-height in the oven. The placement of the test piece in the oven was done very quickly not to affect the oven temperature appreciably. The two holes at the top of the oven were used to take gas samples. Gas sampling was done for the total VOC analyzer and for active carbon tube simultaneously by using 6 mm-ID PTFE tubes. Cork stoppers were used in order to prevent any gas leakage from or into the oven. An Orbo – 32 active carbon tube (Niosh Type) was used to adsorb the hydrocarbons during sampling.

After the test piece was heated up to the oven temperature the tips of the Orbo – 32 tube were broken and it was placed between the sampling port on the oven and the pump. Then the pump which was set to a predetermined flow rate (about 1 – 1.5

L/min), was turned on as well as the total VOC analyzer. Temperature was kept constant.

At the end of the experiment the Orbo – 32 tube was taken out and capped at both ends. It was kept in the refrigerator until analysis. The data collected on the data logger of the total VOC analyzer was transferred to an Excel file on the computer.

3.2.2.1. Equipments used for Phase II

The instrument used for measuring the total NMVOC concentration in the gas phase is again *Bernath Atomic-Model 3006 Total VOC Analyzer*. The description of the instrument was given before in section 3.1.1.

Desaga Pump (Model GS 312) was used to suck gas samples at a constant flow rate. Besides taking samples at a fixed flow rate, this instrument also measures the ambient temperature and pressure, which helps us to calculate the volume of the withdrawn gas sample under normal conditions. The range of the pump is 0-12 L/min and the accuracy is ±0.1 L/min.

An *oven* was used to heat the test pieces to a predetermined temperature and hold that temperature constant during the experiment. A temperature regulator was used to control the oven temperature. The temperature of the oven can be measured with an accuracy of ±2°C. The internal dimensions of the oven are 50 cm x 50 cm x 50 cm.

Orbo –32 Standard Charcoal Tubes were used to sample hydrocarbons. These tubes comply with all NIOSH and OSHA specifications for tube dimensions, adsorbent quality and particle size, divider composition and pore size. Active carbon particles are filled into a glass tube of ~ 4 mm ID. These tubes are used to sample volatile organic carbons. The flow rate range of Orbo tube is 0.1-1 L/min.

Figure 3.6 shows a schematic diagram of the tube. The tube is divided into two adsorbent parts. Section (a) is twice the size of the section (b) and will adsorb the hydrocarbons. Section (b) is a backup section to determine if breakthrough of airbone contaminants occurred on the front portion. The adsorbent parts (a) and (b) are separated from each other by retaining plugs and there is a white quartz wool before part (a). The amount of active carbon in section (a) is approximately 110 mg and the amount in section (b) is approximately 55 mg. The tube is sealed. The tips of the Orbo tube are broken just before sampling and tube is placed between pump and the sampling point.

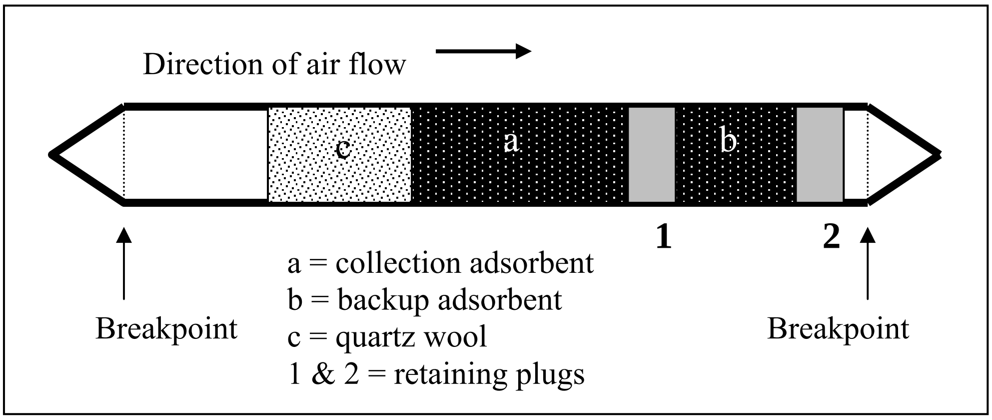

Figure 3.6 Orbo – 32 active carbon tube

Gas Chromatograph (ATI-Unicam with FID) is used in order to measure the concentrations of the constituents in the gas samples. GC is a very well established separation technique for the identification and quantification of volatile materials without decomposing. Analyte volatility is one of the major limiting factors in application of this technique.

The characteristics of GC are:

- Injector Oven:
    - Range: 50 °C to 450 °C in 1 °C steps
    - Capacity: Two injection systems (one split/splitless or one PTV)
    - Accuracy: ±1% over range 100 °C to 300 °C
- Column Oven:
    - Range: 10 °C above ambient to 450 °C in 1 °C steps
    - Accuracy: ±1% over range 100 °C to 300 °C
    - Control: ± 0.05 °C
- Detector Oven:
    - Range: 50 °C to 450 °C in 1 °C steps
    - Accuracy: ±1% over range 100 °C to 300 °C
    - Control: ± 0.02 °C
- Flame Ionization Detector:
    - Operating Temperature: 100 °C to 450 °C
    - Response: typically 1.9×10^{-2} Cg^{-1}
    - Delectability: typically 1×10^{-12} gs^{-1} for toluene
    - Linear Range: 10^{7}

3.2.3. Experimental procedure for Phase II

The test pieces were prepared by the company on the days the tests were made and the pieces provided by the company have been subjected to two types of tests:

1. The "total hydrocarbon concentration" emitted from the parts were measured in an oven at 50 ± 2 °C. During these measurements total hydrocarbon concentration in the oven chamber vs. time was followed by using the total VOC analyzer.

2. Gas samples were sucked from the oven by using a pump at a predetermined suction rate and hydrocarbons were adsorbed on Orbo – 32 tubes. Then, the concentration of each constituent is determined by analyzing the extract of the samples in the GC having a FID.

Each experiment lasted for about 2-3 hours. In phase II, only 50°C was tested in order to see the maximum emissions from the test pieces.

3.2.3.1. Procedure for Analysis of Adsorbed Hydrocarbons

Hydrocarbons in gas samples withdrawn at a constant rate by using the suction pump were adsorbed on the Orbo – 32 tubes. The total amount of sample gas passed over the activated carbon tubes was about 70-100 L. The gas sample was also passed through a silica gel tube after the Orbo – 32 tube to protect the pump. The total volume of the dry gas sucked was accurately determined by Desaga pump as well as the temperature and the pressure of the gas. After adsorbing the hydrocarbons on activated carbon particles in Orbo – 32 tubes, hydrocarbons were extracted in CS_2 by using the ISO standard EN/ISODIS 13528-3, which is explained in detail below.

Extraction:

- First the Orbo tube was cut very carefully from the middle by using a glass cutter, and the front part of the Orbo tube was transferred into a 2 ml vial with discarding the mesh. Then the vial was closed with the lid and it was weighed.
- The foam plug in the middle of the tube was taken out very carefully and discarded (no carbon particles should stay on the foam).
- The back part of the charcoal was transferred into another 2 ml vial. Then the vial was closed with the lid and it was weighed.

- 0.750 ml of CS_2 was injected into each vial containing charcoal samples and the vials with CS_2 were weighed again.
- The Ultrasonic Bath was prepared with ice water and the vials were kept in the ultrasonic bath for at least 10 minutes.
- Then the vials were taken out of the ultrasonic bath and put into the centrifuge for 10 minutes at 4000 rpm.
- After the vials were taken out of the centrifuge, the clear layer (about 0.2 ml) was taken with a syringe and transferred into a glass pipette. The pipettes were sealed in the flame and labeled.

GC Analysis:

The extract was analyzed by a Gas Chromatograph having a FID and a glass capillary column having the following specifications. The conditions for analysis are stated below:

The column specifications:
Length: 25 m
Type : Bonded phase
Material : Fused silica
Phase : BP-1 (non-polar)
Film Thickness : 5 micron
ID : 0.32 mm
OD: 0.43 mm

The Operating Conditions:
Minimum Temperature: 60 ^{o}C
Maximum Continuous Temperature: 280 ^{o}C
Conditioning Temperature: 280 ^{o}C
Carrier Gas: H_2

Column Temperature Programming: 32 °C for 5 minute
12 °C /minute to 180 °C
180 °C for 10 minute
Detector Temperature: 250 °C
Injector Temperature: 240 °C

1 μL of the sample taken from the glass pipette was injected into the GC. The sensitivity of the analysis was 1 $\mu g/m^3$ per 100 L of the sample volume. In Gas Chromatograph, hydrogen was used as carrier gas and air was used for ignition and as combustion air for FID. The injections from the same sample were repeated 2-3 times. The front and back parts of the Orbo tube were analyzed one after another. If the back part contains some hydrocarbons, this experiment was discarded and repeated with another test piece by adjusting the sampling time.

The solvents and the adhesives used in the construction of the interior parts of buses in the company are patented and confidential materials. Therefore, the exact constituents of the solvents and adhesive are not known. However, the company stated the most potential compounds that might be in the solvents and these chemicals were investigated in this study. Analyzed constituents are;

▪ Ethyl acetate	$C_4H_8O_2$
▪ Benzene	C_6H_6
▪ Cyclohexane	C_6H_{12}
▪ Toluene	C_7H_8
▪ Butyl acetate	$C_6H_{12}O_2$
▪ Ethyl benzene	C_8H_{10}
▪ Styrene	C_8H_8
▪ Nonane	C_9H_{20}
▪ Decane	$C_{10}H_{22}$
▪ Undecane	$C_{11}H_{24}$

The chemical and physical properties and also the GC calibration curves for these constituents are given in Appendix A with a sample chromatogram output. Also recovery experiments were done for the chemicals and the procedure and results of recovery experiments are given in Appendix D.

3.3. Phase IV

After the company has prepared the same test pieces with substitute adhesives, measurements were repeated with these newly manufactured pieces. In this phase the total NMVOC evaporated from the pieces were tested and analyzed with the same method and equipments explained in Section 3.2. The adhesive used for sticking the floor materials in this phase is named as “Adhesive B” in order to differentiate between the adhesives used in Phase II and Phase IV.

3.4. Phase V

The indoor concentration of hydrocarbons in the bus built with the new pieces by using “Adhesive B” was measured by the same method and equipments explained in Section 3.1.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Experimental Results (Phase I)

As it was stated in the previous chapter indoor measurements of total NMVOC concentrations were conducted in two newly manufactured buses. These buses were identical buses except the waiting time in the bus park area after manufacturing. The results of measurements for the first and the second bus are given below.

1st BUS:

Results of the measurements recorded on the data logger of the total VOC analyzer are given in Table 4.1. Fig. 4.1 shows the total VOC concentrations at various sampling points in the first bus in each region. The indoor temperature of the first bus during the measurements was 25 ^{o}C. All the windows and doors were kept shut during the measurement. This bus has waited in the bus park area for about 15 days after manufacturing.

Table 4.1 Total VOC concentrations in the 1st bus

1. Region		**2. Region**		**3. Region**	
Sampling pt	**Conc. (ppmv)**	**Sampling pt**	**Conc. (ppmv)**	**Sampling pt**	**Conc. (ppmv)**
1	13.6	1	14	1	29.4
2	18.1	2	12	2	24.8
3	20.3	3	14	3	24.9
4	21	4	20	4	25.3
5	20.3	5	15	5	25.7
6	18.2	6	15	6	27.2
7	17.9	7	16	7	26.2
8	18.6	8	20	8	27.2
9	16.3	9	12	9	28.8
10	16.5	10	24	10	29.3
11	16.4	11	20	11	29.3
12	15.3	12	16	12	29
13	15.8	13	20	13	29.5
14	16	14	20	14	30
15	14.4	15	20	15	30.7
16	14.9	16	22	16	31.3
17	16.6	17	22	17	31.2
18	18	18	22	18	30.1
Average	**17.12 ± 2.1**		**18.0 ± 3.7**		**28.33 ± 2.2**

Average concentration for the bus = 21.15 ± 5.8 ppmv (as C_3H_8)

As can be seen from the results of the measurements, the average total VOC concentrations were found as 17.2 ± 2.1, 18.0 ± 3.7, and 28.33 ± 2.2 ppmv in the first, second and third region of the bus, respectively. The concentration in the third region was found to be the highest.

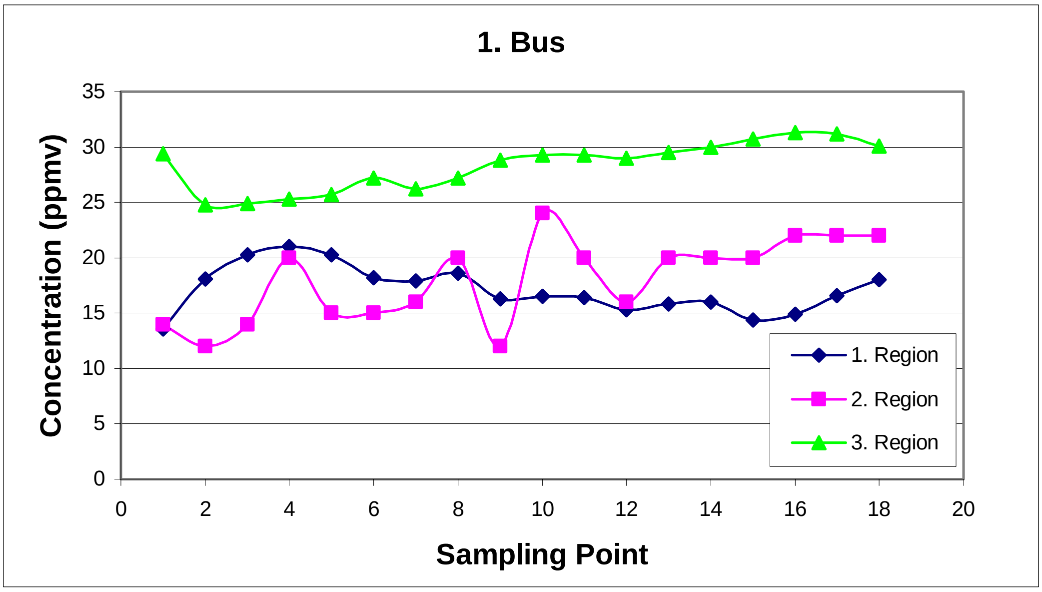

Figure 4.1 Total VOC concentrations in various regions of the first bus

<u>2nd BUS:</u>

Results of the measurements recorded on the data logger of the total VOC analyzer are given in Table 4.2. Fig. 4.2 shows the total VOC concentrations at various sampling points in the second bus. The indoor temperature of the second bus was 28 °C during the measurements. Again all the windows and doors were kept shut during the measurements. This bus has waited in the bus park area for about 20 days after manufacturing.

Table 4.2 Total VOC concentrations in the 2nd bus

1. Region		**2. Region**		**3. Region**	
Sampling Pt	**Concentration (ppmv)**	**Sampling pt**	**Concentration (ppmv)**	**Sampling pt**	**Concentration (ppmv)**
1	46	1	58.6	1	52.5
2	46.6	2	58	2	50
3	45	3	45.6	3	50.3
4	49.8	4	49.2	4	42.6
5	51	5	49.4	5	46.1
6	53.1	6	70	6	44
7	55.8	7	43.3	7	29.4
8	56.2	8	48.5	8	35
9	55.2	9	49.5	9	34.3
10	54.1	10	53.5	10	25.5
11	58.1	11	54	11	26.5
12	58.9	12	52.9	12	28.3
13	42.5	13	55.1	13	33.6
14	41.3	14	47.2	14	31.5
15	43.5	15	50.6	15	34
16	40	16	43.6	16	38.2
17	40	17	45.4	17	37.4
18	48	18	48.4	18	39.2
Average	**49.17 ± 6.4**		**51.27 ± 6.5**		**37.69 ± 8.3**

Average concentration for the bus = 46.04 ± 9.2 ppmv (as C_3H_8)

As can be seen from the results of measurements, the average total VOC concentrations were found as 49.17 ± 6.4, 51.27 ± 6.5 and 37.69 ± 8.3 ppmv in the first, second and third region of the bus, respectively. For the second bus, the concentrations are about twice as much as in the first bus and, especially in this bus the concentrations of the total VOC in the first and second region (that means the driver region) are the highest.

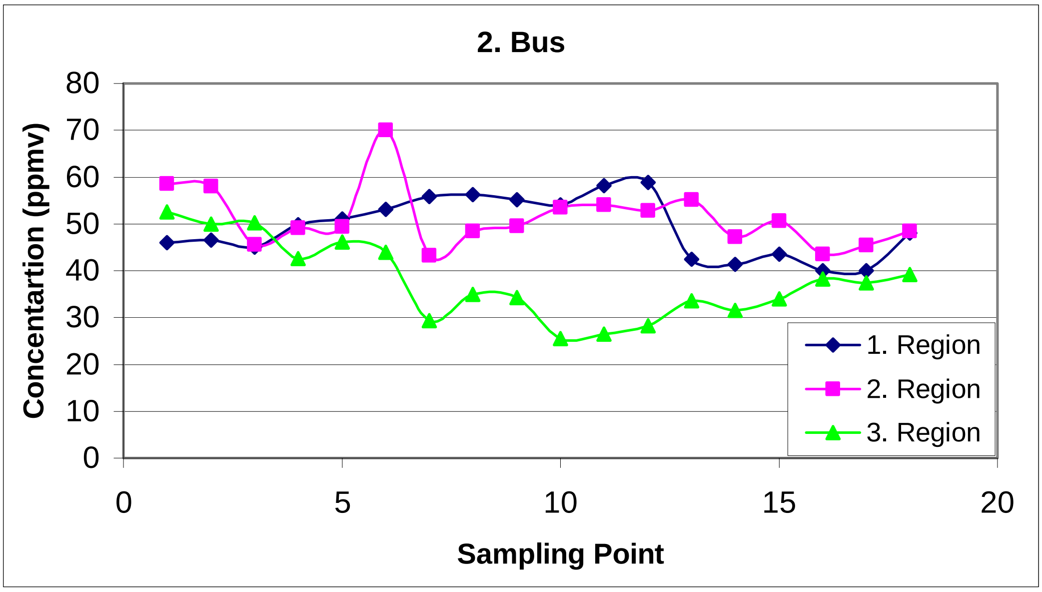

Figure 4.2 Total VOC concentrations in various regions of the second bus

The reason for the total VOC concentration in the second bus to be higher than the first bus is probably the longer waiting time of the second bus in the bus park area. As it was mentioned before, the buses that exit the production line are waited in the bus park area for 15-20 days before they are delivered to the customers. Therefore, we can say that the main reason for the difference in total VOC concentrations in the buses is mainly the difference in waiting times of the buses in the company park area. The second reason may be exposure time to the sun light and having higher temperature in the bus overall.

The results of the Phase I of the study have shown that the plastic materials that are used for the indoors of vehicles and the solvents that are used in adhesives for the manufacture of these materials evaporate by time and cause indoor air pollution in vehicles. Therefore, it is seen that the adhesive materials used in production of indoor materials are very effective in creating indoor air pollution. Also, it can be said that the VOC emissions in the vehicle increase by increasing temperature. This is an expected result, because the evaporation and diffusion rate increase with increasing temperature.

4.2. Experimental Results (Phase II)

In order to determine the concentrations of the VOC components emitted from various parts, different test pieces of the materials used in the buses were prepared by the company on the morning that test will be done. For example, a sample of the part to be tested was taken and a certain amount of “Adhesive A” was spread on the part at a certain thickness in the workshop of the company. This part was taken from the company and brought to the laboratory within an hour and was tested in our laboratories. Similar procedure was applied to the other parts used in the manufacture of the buses except the door mat and window holder on which adhesive was not applied.

Six different types of parts were tested in this study. These parts were listed and explained in Section 3.2.1.

The experiments were conducted in this Phase at 50°C in order to find out the maximum emission rate of the VOCs and to get the most of the components in the emission mixture from the test piece. This was the reason to choose 50 °C as the temperature of experimentation for Phase II. This phase was considered as the initial experimentation phase. No other temperature was tried in this phase. Even 50°C is a quite high temperature for an indoor environment.

Results of the total VOC measurements and GC analysis for each test piece are given in the following sections. Also the equivalent exposures (E(m)) for 8-hr TWA and 15 min STEL values calculated by the formula given by OSHA, are given for each test piece in this section. The value of E(m) should not exceed unity ‘1’. The formula for the calculation of equivalent exposure E(m) is given in Appendix C (8-hr TWA limits were used for the constituents that does not have a STEL value).

4.2.1. Floor Material (Type 1) + Adhesive A

The results of the total VOC concentrations released from the floor material (Type 1) + "Adhesive A" are given in Fig. 4.3. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperature of 50 ± 2 °C. The temperature was held constant at 50 °C in order to obtain the maximum release of the components present in the adhesives and the material.

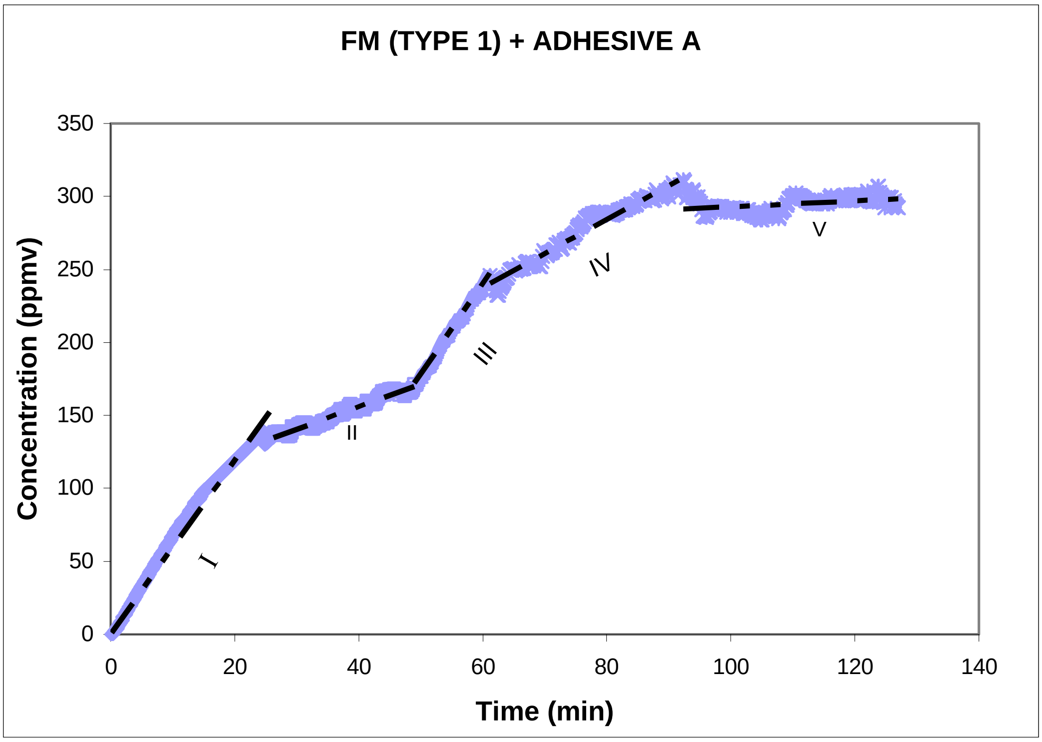

Figure 4.3 Concentration vs. time graph for Floor Material (Type 1) + Adhesive A

As can be seen from Fig. 4.3, the piece from floor material-type 1 starts to release the volatiles first with a release rate of 5.22 ppmv/min. At this step, the more volatile components from the material as ethyl acetate, benzene or cyclohexane are expected to be released. The rate of release at the second step is 1.5 ppmv/min, which is slower than the first step because the slope of the curve in this step is less than the first step. In the second step the medium vapor pressure components as toluene, butyl acetate and ethyl benzene are expected to be released. In the steps III and IV release of hydrocarbons continue depending on the vapor pressure of the components and finally at the last step the concentration reaches to a steady value at 300 ppmv.

The experimental conditions at which the released hydrocarbons from the floor material (Type 1) + Adhesive A adsorbed on the active carbon particles in Orbo – 32 tubes are given in Table 4.3 and the results obtained by analyzing the extracts with GC are given in Table 4.4.

Table 4.3 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from floor material (Type 1) + Adhesive A

Part Name	**Floor Material (Type 1) + Adhesive A**
Temperature	50 ± 2 °C
Duration	45 min
Rate of Sampling	1.7 L/min
Volume of Sample	75 L
Ambient Temperature	27 °C
Ambient Pressure	903 hPa

Table 4.4 Detailed measurement results obtained from floor material (Type 1) + Adhesive A

Constituents	**Concentration (mg/Nm^3)**
Ethyl acetate	1.43 ± 0.01
Benzene	0.01 ± 0.00
Cyclohexane	0.15 ± 0.05
Toluene	292.62 ± 5.00
Butyl acetate	0.00 ± 0.00
Ethyl benzene	0.14 ± 0.01
Styrene	3.79 ± 0.50
Nonane	0.47 ± 0.07
Decane	9.00 ± 0.80
Undecane	2.53 ± 0.50

As can be seen from the results of the GC analysis in Table 4.4, the highest concentration of hydrocarbon is seen for *toluene* as 292.62 mg/Nm^3. Then comes *decane* with a concentration of 9 mg/Nm^3. The smallest concentrations belong to *styrene*, *undecane* and *ethyl acetate*. This result shows us that the adhesive used in making the floor material stick to the floor of the bus is solvent-based and most probably toluene was the major component of the solvent.

In addition to the emissions from the adhesive used in the floor material, there may be some diffusion of hydrocarbons from the floor material itself. In order to test this issue, the floor material itself without any adhesive was tested in the oven at the same temperature. The peak value of total NMVOC measured from this test was 1 ppmv which is far below the value obtained from the measurement of floor material with adhesive. Therefore, it can be concluded that the VOC emission from the piece floor material (Type 1) is caused from the “Adhesive A” used to stick the material to the floor.

4.2.2. Floor Material (Type 2) + Adhesive A

The change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperature of 50 ± 2 °C for the floor material (Type 2) + Adhesive A are given in Fig. 4.4.

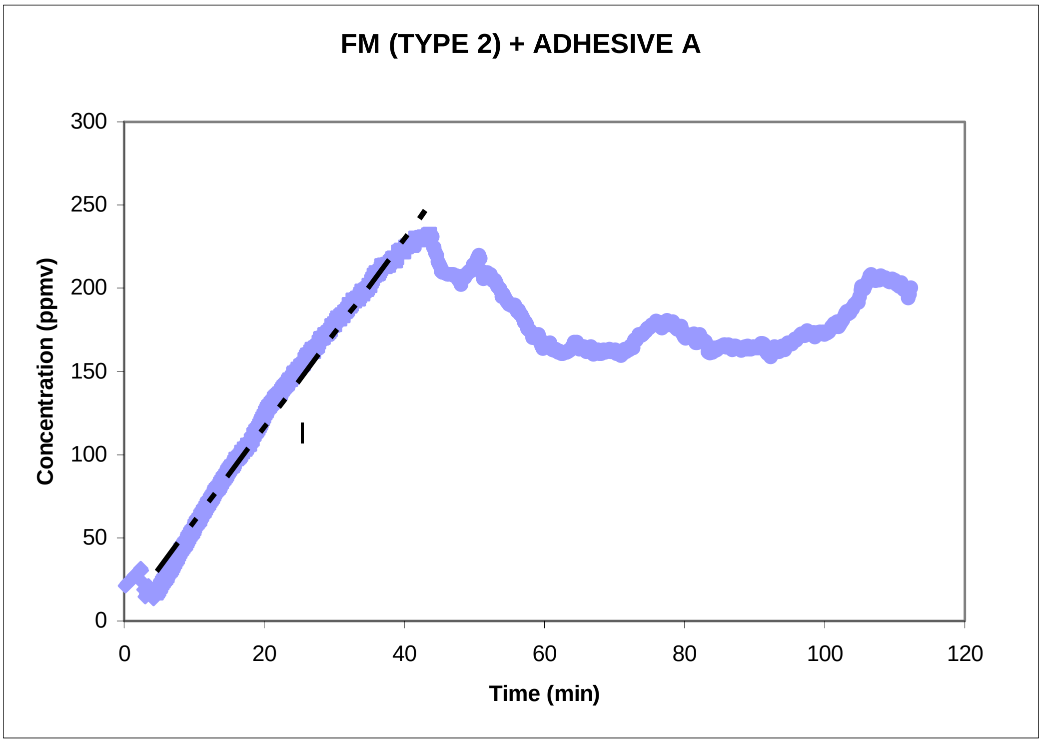

Figure 4.4 Concentration vs. time graph for Floor Material (Type 2) + Adhesive A

As can be seen from Fig. 4.4, the piece from the FM (Type 2) takes some time (about 4.5 min) to heat to the oven temperature and then the volatiles start to release. First an emission with a release rate of 4.86 ppmv/min occurred and then the release rate slows down. FM (Type 2) is quite different from FM (Type 1) because FM (Type 1) is PVC based and FM (Type 2) is natural-rubber based material. The steady state is reached here in about 60 minutes and the concentration was about 175 ppmv.

The experimental conditions at which the released hydrocarbons from the floor material (type 2) + Adhesive A adsorbed on the active carbon particles in Orbo – 32 tube are given in Table 4.5 and the results obtained by analyzing the extracts with GC are given in Table 4.6.

Table 4.5 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from floor material (Type 2) + Adhesive A

Part Name	**Floor Material – Type 2 + Adhesive A**
Temperature	50 ± 2 °C
Duration	60 min
Rate of Sampling	1.7 L/min
Volume of Sample	106 L
Ambient Temperature	27 °C
Ambient Pressure	905 hPa

Table 4.6 Detailed measurement results obtained from floor material (Type2) + Adhesive A

Constituents	**Concentration (mg/Nm^3)**
Ethyl acetate	0.19 ± 0.01
Benzene	0.00 ± 0.00
Cyclohexane	0.00 ± 0.00
Toluene	182.32 ± 5.00
Butyl acetate	0.31 ± 0.05
Ethyl benzene	0.12 ± 0.02
Styrene	0.00 ± 0.00
Nonane	0.13 ± 0.01
Decane	0.05 ± 0.01
Undecane	0.02 ± 0.01

As can be seen from the results of the GC analysis in Table 4.6, the highest concentration of hydrocarbon is seen again for *toluene* as 182.32 mg/Nm^3. Then comes *ethyl acetate* and *butyl acetate* with very low concentrations. This result shows us that the adhesive used in making the floor material stick to the floor of the bus is solvent-based and it seems that toluene is the major component of the solvent. Also, there may be some diffusion of hydrocarbons from the floor material itself.

In order to test this issue, the floor material itself without any adhesive was tested in the oven at the same temperature. The peak value of total NMVOC measured from this test was 1 ppmv which is far below the value obtained from the measurement of floor material with adhesive. So it can be said that the VOC emission from the piece floor material (Type 2) is caused from the adhesive used to stick the material to the floor.

4.2.3. Ventilation Channel

The results of the total VOC concentrations released from the ventilation channel are given in Fig. 4.5. This figure shows the change of total VOC concentration (as C_3H_8) from the ventilation channel with respect to time in the oven at constant temperature of 50 ± 2 °C.

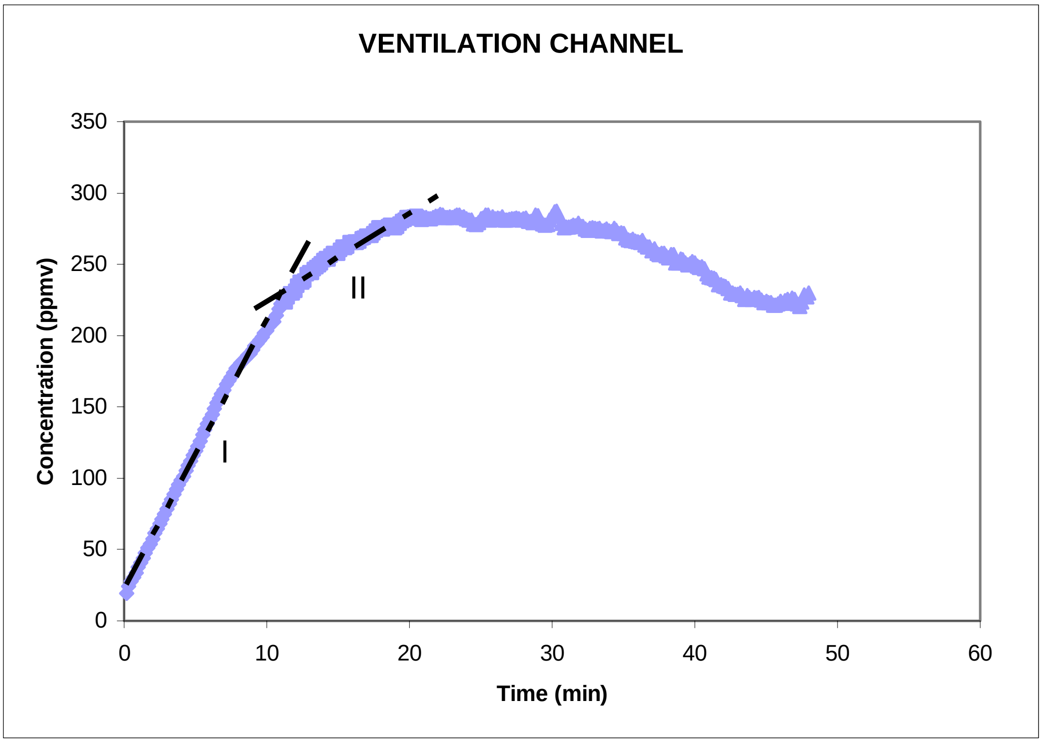

Figure 4.5 Concentration vs. time graph for ventilation channel

As can be seen from the figure, the rate of release of volatiles is initially 18.8 ppmv/min. Possibly the more volatile components were released at this step. Then the release rate slows down to 6.18 ppmv/min and becomes steady at around 280 ppmv. Finally the overall VOC concentration starts to decrease probably because the mechanism of release of volatiles shifts from "evaporation" to "diffusion" controlled phase.

The experimental conditions for adsorbing the hydrocarbons released from the piece of "ventilation channel" + Adhesive A provided by the company and adsorbed on the active carbon particles in Orbo – 32 tube are given in Table 4.7 and the results obtained by analyzing the extracts with GC are given in Table 4.8.

Table 4.7 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from ventilation channel + Adhesive A

Part Name	**Ventilation Channel + Adhesive A**
Temperature	50 ± 2 °C
Duration	41 min
Rate of Sampling	1.7 L/min
Volume of Sample	72.6 L
Ambient Temperature	27 °C
Ambient Pressure	905 hPa

Table 4.8 Detailed measurement results obtained from ventilation channel + Adhesive A

Constituents	**Concentration (mg/Nm^3)**
Ethyl acetate	0.20 ± 0.01
Benzene	0.00 ± 0.00
Cyclohexane	0.19 ± 0.01
Toluene	167.37 ± 7.00
Butyl acetate	7.46 ± 0.80
Ethyl benzene	7.84 ± 0.70
Styrene	105.23 ± 6.00
Nonane	2.37 ± 0.20
Decane	0.00 ± 0.00
Undecane	0.13 ± 0.01

As can be seen from the results of the GC analysis in Table 4.8, the highest concentration of hydrocarbon is seen again for *toluene* as 167.37 mg/Nm^3. Then comes *styrene* with a concentration of 105.23 mg/Nm^3. *Ethyl benzene*, *butyl acetate* and *nonane* also exists with smaller concentrations than styrene. This result shows us that the adhesive used in making the ventilation channel stick to its place in the bus was solvent-based and contains toluene as solvent. Again, there may be some diffusion of hydrocarbons from the ventilation channel itself. In order to test this issue, the ventilation channel itself without any adhesive was tested in the oven at the same temperature. The total NMVOC measured from this test was near zero which is far from the value obtained from the measurement of ventilation channel with adhesive. It can be said that the VOC emission from the piece of ventilation channel is caused from the adhesive.

4.2.4. Window (+ adhesive A)

The results of the total VOC concentrations from window piece with adhesive are given in Fig. 4.6. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperature of 50 ± 2 °C.

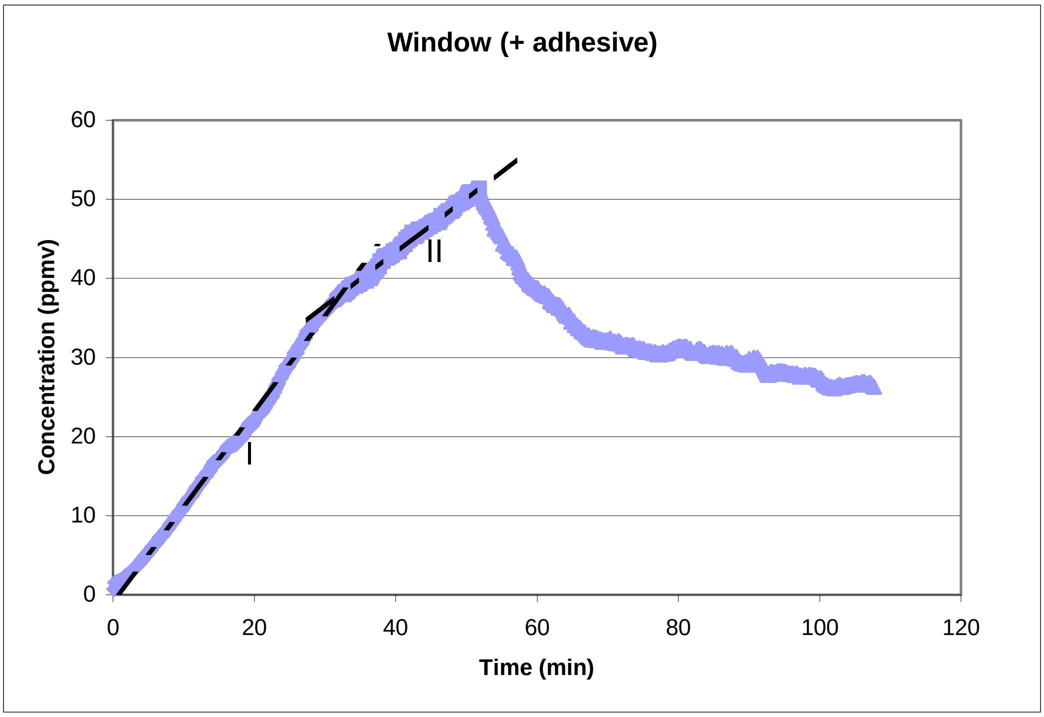

Figure 4.6 Concentration vs. time graph for window piece + adhesive A

Two steps of VOC release can be observed from figure. At the beginning the rate of volatalization was fast (1.18 ppmv/min) which is due to release of more volatile compounds. The mechanism was mainly evaporation. Then the release rate decreases to 0.7 ppmv/min and the cumulative VOC started to decrease after 50 minutes. The reason may be the slow down of the emission of VOCs from the adhesive placed on the window piece. If the heating had continued for a long time (more then 2 hrs), possibly the emissions would reach to a plateau and only the diffusion mechanism would be important for the release of volatiles.

The experimental conditions for adsorbing hydrocarbons released from the window piece on activated carbon particles in Orbo – 32 tube are given in Table 4.9 and the results obtained by analyzing the extracts with GC are given in Table 4.10.

Table 4.9 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from window piece + adhesive A

Part Name	Window (+ adhesive A)
Temperature	50 ± 2 °C
Duration	60 min
Rate of Sampling	1.7 L/min
Volume of Sample	106 L
Ambient Temperature	28 °C
Ambient Pressure	901 hPa

Table 4.10 Concentration of constituents obtained from window piece + adhesive A

Constituents	**Concentration (mg/Nm^3)**
Ethyl acetate	0.18 ± 0.01
Benzene	0.00 ± 0.00
Cyclohexane	0.01 ± 0.00
Toluene	63.68 ± 0.90
Butyl acetate	0.00 ± 0.00
Ethyl benzene	0.69 ± 0.30
Styrene	0.00 ± 0.00
Nonane	0.46 ± 0.08
Decane	0.08 ± 0.01
Undecane	0.00 ± 0.00

As can be seen from the results of the GC analysis in Table 4.10, the highest concentration of hydrocarbon is found for *toluene* as 63.68 mg/Nm^3. Then comes *ethyl benzene*, *ethyl acetate* and *nonane* with very small concentrations compared to toluene. This result shows us that the adhesive used to stick the window to the window holder contains most probably toluene, and it is released mostly due to high vapor pressure of toluene as compared to other constituents. Most probably toluene was used as solvent.

Emission from the window piece with no adhesive is zero, simply because window glass will not emit anything due to its structure.

4.2.5. Window Holder

The results of the total VOC concentrations released from window holder given in Fig. 4.7. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperature of 50 ± 2 °C.

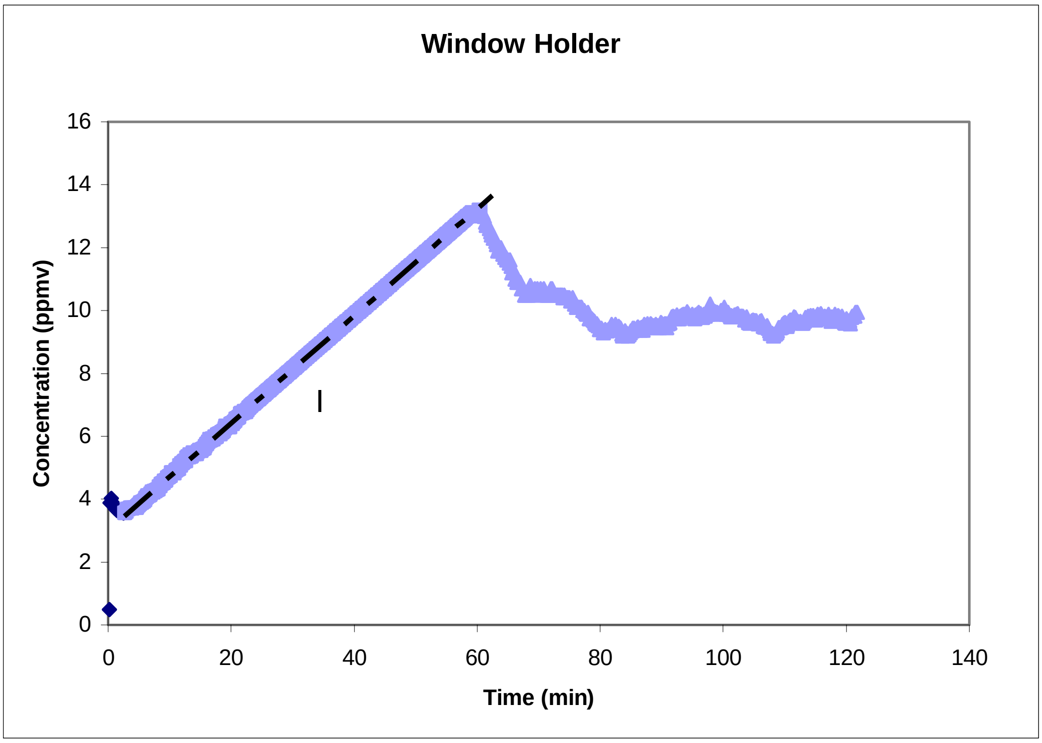

Figure 4.7 Concentration vs. time graph for window holder

As can be seen from the figure, the piece takes some time (about 2.5 min) to heat to the oven temperature and then the volatiles start to be released with a very slow rate (0.17 ppmv/min) as compared to floor materials or ventilation channel. Then, a decrease on the overall VOC concentration was observed and finally a steady value was obtained at around 10 ppmv.

The experimental conditions at which the released hydrocarbons from the "window holder" piece adsorbed on the active carbon particles in Orbo – 32 tube are given in Table 4.11 and the results obtained by analyzing the extracts with GC are given in Table 4.12.

Table 4.11 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from window holder

Part Name	Window Holder
Temperature	50 ± 2 °C
Duration	60 min
Rate of Sampling	1.7 L/min
Volume of Sample	106 L
Ambient Temperature	27 °C
Ambient Pressure	903 hPa

Table 4.12 Concentration of constituents obtained from window holder

Constituents	Concentration (mg/Nm^3)
Ethyl acetate	8.94 ± 0.80
Benzene	0.00 ± 0.00
Cyclohexane	0.00 ± 0.00
Toluene	0.97 ± 0.06
Butyl acetate	0.00 ± 0.00
Ethyl benzene	0.00 ± 0.00
Styrene	8.55 ± 1.20
Nonane	0.35 ± 0.02
Decane	10.53 ± 1.30
Undecane	2.20 ± 0.40

As can be seen from the results of the GC analysis in Table 4.12, the largest concentration of hydrocarbon is seen for *ethyl acetate*, *styrene* and *decane* at about 9-10 mg/Nm^3 which were quite low concentrations as compared to other materials given before. Then comes *undecane* and *toluene* with very small concentrations. This result shows us that the window holder does not contain solvent-based adhesive or any other organics which can evaporate or diffuse easily.

4.2.6. Door Mat

The results of the total VOC concentrations released from "door mat" and measured with the total VOC analyzer are given in Fig. 4.8. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperature of 50 ± 2 °C.

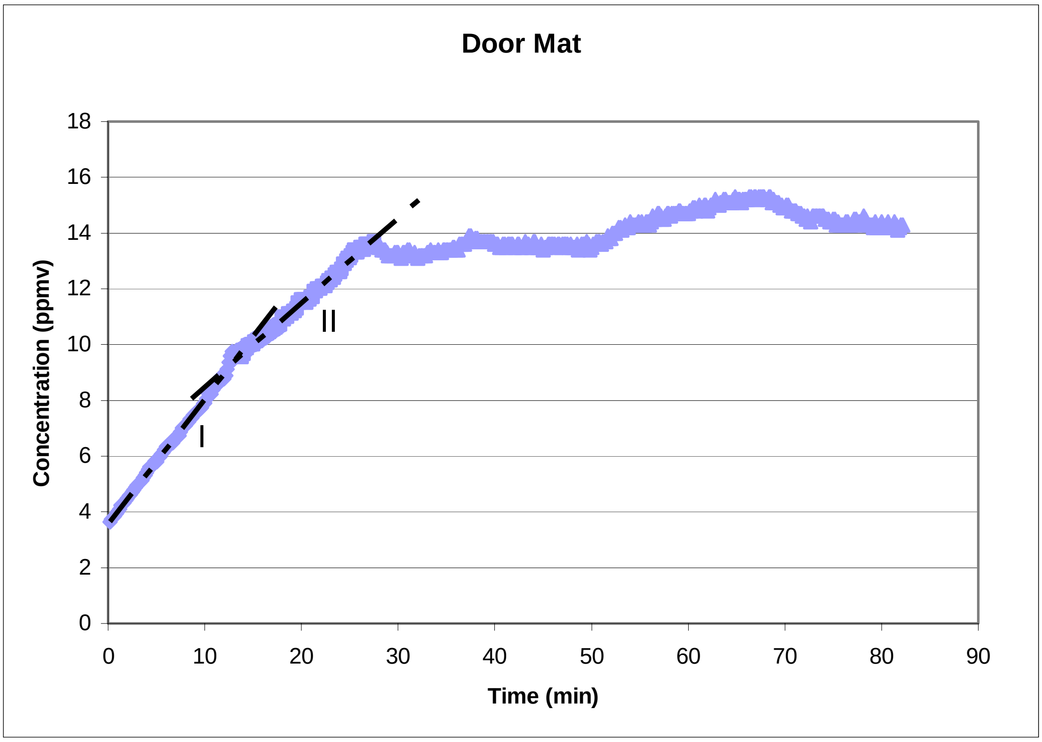

Figure 4.8 Concentration vs. time graph for door mat

The first step is a release of organics at a rate of 0.45 ppmv/min. This is the initial release rate. This rate is fast due to evaporation mechanism. Then the release rate decreases to 0.3 ppmv/min. The concentration finally reaches to a steady value at around 14 ppmv, after 25 minutes. After the steady state is reached, the release rate of organics become very slow and even the diffusion rate is very minimal.

The conditions at which the gas sample is taken from the released hydrocarbons from the door mat and adsorbed on the active carbon particles in Orbo – 32 tube are given in Table 4.13 and the results obtained by analyzing the extracts with GC are given in Table 4.14.

Table 4.13 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from door mat

Part Name	**Door Mat**
Temperature	50 ± 2 °C
Duration	60 min
Rate of Sampling	1.7 L/min
Volume of Sample	107 L
Ambient Temperature	28 °C
Ambient Pressure	901 hPa

Table 4.14 Concentration of constituents obtained from door mat

Constituents	**Concentration (mg/Nm^3)**
Ethyl acetate	0.16 ± 0.02
Benzene	0.00 ± 0.00
Cyclohexane	0.00 ± 0.00
Toluene	10.88 ± 8.00
Butyl acetate	0.08 ± 0.01
Ethyl benzene	0.10 ± 0.01
Styrene	0.03 ± 0.00
Nonane	0.63 ± 0.03
Decane	0.60 ± 0.03
Undecane	0.00 ± 0.00

As can be seen from the results of the GC analysis in Table 4.14, the highest concentration of hydrocarbon is seen for *toluene* as 10.88 mg/Nm^3 which is far below the concentration obtained for toluene in other pieces investigated before.

Then comes *decane* and *nonane* with very small concentrations. This result shows us that the door mat does not contain solvent-based adhesive or any other organics which can evaporate or diffuse easily. However, some finishing material on the door mat may volatilize and give some hydrocarbon emissions at a test temperature of 50 ± 2°C

4.2.7. Summary of Results (Phase II)

A summary of the results obtained by analyzing the extracts of samples with GC for each test piece are given altogether in Table 4.15.

Table 4.15 Concentration of constituents obtained from GC analysis

	Concentration (mg/Nm^3)					
Constituents	**F. M. Type 1 + Adh. A**	**F. M. Type 2 + Adh. A**	**Ventilation Channel + Adh. A**	**Window + Adh. A**	**Window Holder**	**Door mat**
Ethyl acetate	1.43	0.19	0.20	0.18	8.94	0.16
Benzene	0.01	0	0	0	0	0
Cyclohexane	0.15	0	0.19	0.01	0	0
Toluene	292.62	182.32	167.37	63.68	0.97	10.88
Butyl acetate	0	0.31	7.46	0	0	0.08
Ethyl benzene	0.14	0.12	7.84	0.69	0	0.10
Styrene	3.79	0	105.23	0	8.55	0.03
Nonane	0.47	0.13	2.37	0.46	0.35	0.63
Decane	9.01	0.05	0	0.08	10.53	0.60
Undecane	2.53	0.02	0.13	0	2.20	0
E(m) 8-hr TWA	0.8	0.5	0.73	0.17	0.03	0.03
E(m) STEL	0.60	0.37	0.61	0.13	0.03	0.02

In Table 4.15, it is seen that high amounts of *toluene*, *decane*, *styrene*, *ethyl acetate* and *undecane* concentrations are measured in the emissions from floor material

(Type 1). For floor material (Type2), which is the alternative for floor material (Type1), these concentrations are very low (except *toluene* – but, it is less than the emission observed from FM (Type 1)). As mentioned before, the first one of the floor material is PVC – based and the second one is natural rubber-based. As a result it can be said that floor material (Type2) is a better selection as compared to floor material (Type1), as far as the hydrocarbon emissions are concerned.

When the emissions from different pieces are compared, it can be easily seen that the *toluene* emission is high in almost all the parts except window and window holder pieces. *Benzene* emissions are near or equal to zero for all pieces, which is good. *Decane* and *undecane* concentrations are high for floor material (Type1) and window holder, and *styrene* concentration is very high in ventilation channel as compared to the other pieces. It is seen from the table that there is not a considerable amount of VOC emission from the pieces of window holder and door mat. This is an expected situation, since the total VOC emissions also show that the emissions from these pieces are very low.

The equivalent exposure values as 8-hr TWA and 15-min STEL for all pieces were less than 1, which is good for the health of people. However, attention must be paid on the floor materials and ventilation channel, since their TWA values are higher than 0.7 and 0.5, respectively. Also low concentration for *benzene* for all pieces is good news because benzene is a human carcinogen and nobody wants it to be present in the indoor air.

When the total VOC concentrations are examined it is seen that the most VOC emissions occur from the “floor materials” and “ventilation channel”, and the detailed analysis by GC confirmed these results. The initial release rate (k_m) of each test piece, which is mainly due to evaporation mechanism, is given in Table 4.16.

Table 4.16 Initial evaporation rates of VOCs from test pieces

Test Piece	**k_m (ppmv/min)**
F. M.-Type 1	5.22
F. M.-Type 2	4.86
Ventilation Channel	6.18
Window	1.18
Window Holder	0.17
Door Mat	0.45

From Table 4.16 it is seen that the highest evaporation rate belongs to the ventilation channel and then to the floor materials. Therefore, it can be said that the solvents used in adhesives of the ventilation channel and floor materials are more likely to evaporate in the bus. This is very important because floor materials cover all the floor area of the bus, and the ventilation channels extend all along the bus. When some volatile emissions occur from these parts, it will change the air quality in the bus. This could be the main reason for the complaints received by the bus manufacturing company.

The studies investigated in Chapter 2 are all applicable to the work done in this study. However, as it was mentioned at Chapter 3 the compositions of the solvents used in this study were not exactly known, and if they were known exactly the models and methods could be used and the emission rates and the concentrations of individual VOCs could be found without making GC analysis which is expensive and time consuming.

4.3. Results (Phase III)

This phase of the study was not experimental, but it served as the collection and evaluation of the results obtained in Phase I and II. The interim conclusion reached in this phase was that the adhesives used in preparing the parts were solvent-based and cause indoor pollution in buses due to evaporation of the solvents. It was recommended to the company that the use of these constituents found in Phase II in the preparation or manufacture of various parts for the bus must be decreased or new alternatives that require less of these constituents should be developed.

4.4. Experimental Results (Phase IV)

After the company has used “substitute adhesives” instead of the adhesive used before, the measurements done in Phase I and Phase II of this study were repeated in order to monitor the changes occurred at NMVOC concentrations emitted from the new pieces. For measuring the total NMVOC concentrations from the pieces, this time three different temperatures (25 °C, 40 °C and 50 °C) were used in order to see the effect of temperature on the NMVOC emission. Simultaneous with the total VOC measurement, hydrocarbon emissions were also collected on Orbo – 32 tubes for further GC analysis.

Five different pieces were tested in this phase:

- Floor material (Type 1),
- Floor material (Type 2),
- Window (with adhesive),
- Window holder,
- Door mat

Total VOC measurements and detailed analysis with GC were carried out for all these pieces at three different temperatures mentioned above. Only pieces from ventilation channel were not included in this study, because the company could not provide them due to the change of old vendor. Results of the total VOC measurements and GC analysis are given in the following sections.

4.4.1. Floor Material (Type 1) + Adhesive B

The results of the total VOC concentrations released from the floor material (Type 1) + Adhesive B are given in Fig. 4.9. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperatures of 25 ± 2 °C, 40 ± 2 °C and 50 ± 2 °C.

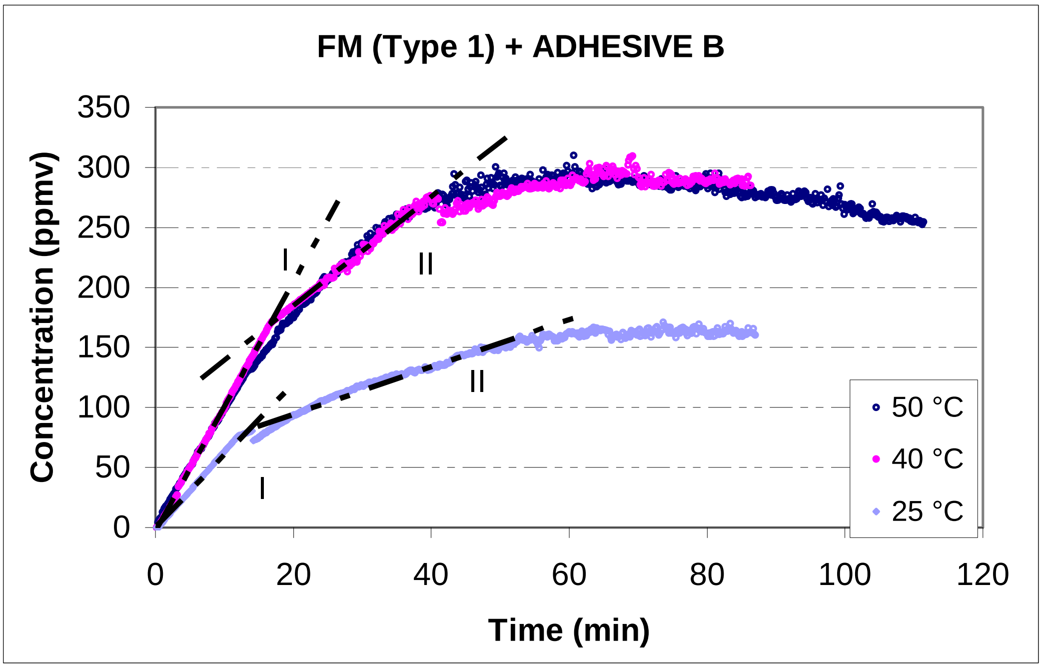

Figure 4.9 Concentration vs. time graph for floor material (Type1) + Adhesive B

As can be seen from Fig. 4.13, the release of VOCs from the floor material (type 1) at 50 °C and 40 °C is almost the same. The piece starts to release the volatiles first with a release rate of 10.4 ppmv/min for both temperatures. The more volatile components from the material as ethyl acetate, benzene or cyclohexane are expected to be released at this step. The release rate at the second step is 4.5 ppmv/min. In the second step the medium vapor pressure components as toluene, butyl acetate and ethyl benzene are expected to be released. Finally the total VOC concentration reached to a maximum value at 300 ppmv and than started to decrease.

For the floor material (Type1), the release rate of VOCs at 25 °C, is slower than at temperatures 50 °C and 40 °C. Total VOCs are released with a rate of 6 ppmv/min initially and then followed by a release rate of 2 ppmv/min before total VOC concentration reached a steady value at 165 ppmv. Of course to have an indoor temperature of 25°C in the bus is more common than having 40°C or 50°C, since most of the buses have air-conditioning system today. The release rates of volatiles at temperatures of 40°C and 50°C were investigated only to see the effect of temperature on the increase of concentration of hydrocarbons in the bus.

The experimental conditions for adsorbing hydrocarbons released from the floor material (Type1) + Adhesive B on activated carbon particles in Orbo – 32 tube at 25 ± 2 °C, 40 ± 2 °C, 50 ± 2 °C are given in Table 4.17 and the results obtained by analyzing the extracts with GC are given in Table 4.18.

Table 4.17 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from floor material (Type 1) + Adhesive B

Part Name	**Floor Material (Type 1) + Adhesive B**		
Temperature	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Duration	116 min	60 min	60 min
Rate of Sampling	0.4 L/min	0.4 L/min	0.4 L/min
Volume of Sample	47 L	26 L	28.1 L
Ambient Temperature	20.9 °C	25.5 °C	26.1 °C
Ambient Pressure	902 hPa	902 hPa	905 hPa

Table 4.18 Concentration of constituents obtained from floor material (Type1) + Adhesive B

	Concentration (mg/Nm^3)		
Constituents	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Ethyl acetate	0.00 ± 0.00	39.83 ± 5.00	13.44 ± 3.00
Benzene	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Cyclohexane	2.30 ± 0.03	1.37 ± 0.30	0.00 ± 0.00
Toluene	229.91 ± 10.00	162.17 ± 5.00	68.69 ± 6.00
Butyl acetate	0.00 ± 0.00	1.84 ± 0.05	0.82 ± 0.01
Ethyl benzene	0.67 ± 0.90	1.02 ± 0.02	0.20 ± 0.02
Styrene	0.00 ± 0.00	0.37 ± 0.08	0.71 ± 0.03
Nonane	0.00 ± 0.00	4.96 ± 0.80	2.89 ± 0.08
Decane	8.81 ± 1.00	9.83 ± 1.30	4.43 ± 0.07
Undecane	9.10 ± 1.10	40.28 ± 2.30	23.45 ± 2.50

The total VOC measurements for 50°C and 40°C were almost the same, so it was expected to obtain similar results from GC analysis. As can be seen from the results of the GC analysis in Table 4.18, this is the case for most of the constituents except *ethyl acetate* and *undecane*, which were higher at 40°C. At 25°C the constituent were in lower concentrations than obtained from the test at 50°C and 40°C. This is an expected result since the total VOC concentrations obtained at 25°C were lower than total VOC concentrations obtained at 50°C and 40°C.

It is seen from the results of the GC analysis in Table 4.18, the highest concentration of hydrocarbon is seen for *toluene* at all temperatures. Then comes un*decane* and *ethyl acetate*. The smallest concentrations belong to *benzene*, *decane* and *nonane*.

4.4.2. Floor Material (Type 2) + Adhesive B

The results of the total VOC concentrations released from the floor material (Type2) + Adhesive B are given in Fig. 4.10. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperatures of 25 ± 2 °C, 40 ± 2 °C and 50 ± 2 °C.

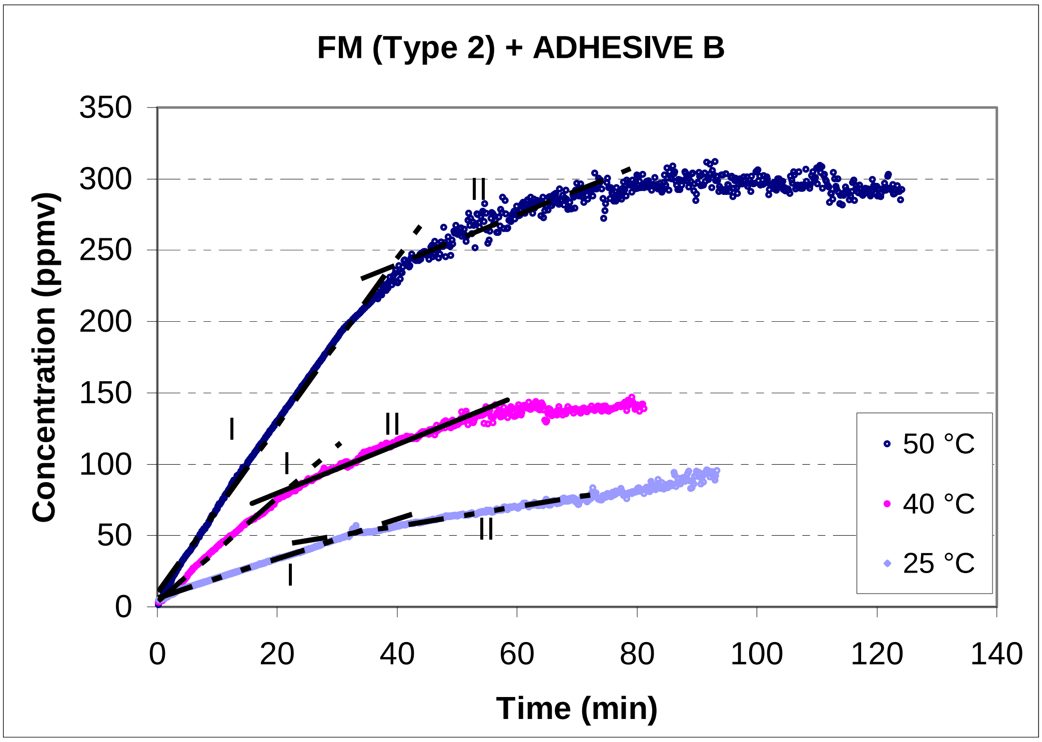

Figure 4.10 Concentration vs. time graph for floor material (Type2) + Adhesive B

As can be seen from Fig. 4.14, the release patterns of VOCs from the floor material (Type2) at 50°C and 40°C and 25°C are similar but the release rates decrease with decreasing temperature. For the test done at 50°C, total VOCs were started to be released with a rate of 5.9 ppmv/min, then at the second step the release rate decreased to 1.7 ppmv/min, and finally a steady value of 300 ppmv was obtained. The test piece at 40°C was started to release VOCs at a rate of 3.6 ppmv/min, which is lower than the initial release rate at 50°C as expected. The second step had a release rate of 1.7 ppmv/min and finally total VOC concentrations reached to a steady value at 140 ppmv. For the test done at 25°C, first a release rate of 1.38 ppmv/min observed followed by a release rate of 0.67 ppmv/min. release rates slow down as the temperature goes lower and the release of volatiles shift from the evaporation mechanism to the diffusion mechanism. From the figure it is clearly seen that the total VOC concentrations and release rates decrease with decreasing temperature.

The experimental conditions for adsorbing hydrocarbons released from the floor material (Type2) + Adhesive B on activated carbon in Orbo – 32 tube at 50 ± 2 °C, 40 ± 2 °C and 25 ± 2 °C are given in Table 4.19 and the results obtained by analyzing the extracts with GC are given in Table 4.20.

Table 4.19 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from floor material (Type2) + Adhesive B

Part Name	**Floor Material (Type 2) + Adhesive B**		
Temperature	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Duration	127 min	52 min	52 min
Rate of Sampling	0.4 L/min	0.4 L/min	0.4 L/min
Volume of Sample	65.2 L	23.8 L	28 L
Ambient Temperature	21.5 °C	25.9 °C	26 °C
Ambient Pressure	902 hPa	902 hPa	905 hPa

Table 4.20 Concentration of constituents obtained from floor material (Type2) + Adhesive B

	Concentration (mg/Nm^3)		
Constituents	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Ethyl acetate	40.12 ± 3.00	24.76 ± 3.00	10.76 ± 1.00
Benzene	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Cyclohexane	0.00 ± 0.00	0.46 ± 0.05	0.00 ± 0.00
Toluene	282.20 ± 12.00	117.87 ± 11.00	83.27 ± 2.00
Butyl acetate	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Ethyl benzene	0.00 ± 0.00	0.19 ± 0.02	0.00 ± 0.00
Styrene	0.00 ± 0.00	0.37 ± 0.03	0.00 ± 0.00
Nonane	0.00 ± 0.00	0.07 ± 0.01	0.00 ± 0.00
Decane	0.24 ± 0.50	0.07 ± 0.01	0.23 ± 0.02
Undecane	0.00 ± 0.00	4.25 ± 0.80	2.01 ± 0.04

As can be seen from the results of the GC analysis in Table 4.20, the highest concentration of hydrocarbon is seen for *toluene* at all temperatures. The values for toluene concentrations at 50°C, 40°C and 25°C were 282.2 mg/Nm^3, 117.87 mg/Nm^3 and 83.27 mg/Nm^3, respectively. Then comes *ethyl acetate* and *undecane* with lower concentrations than toluene. It was observed that the total VOC concentration decreases with decreasing temperature as it was expected. The concentrations of individual constituents decrease with decreasing temperature as well.

4.4.3. Window (+ Adhesive B)

The results of the total VOC concentrations released from window piece with Adhesive B are given in Fig. 4.11. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperatures of 25 ± 2 °C, 40 ± 2 °C and 50 ± 2 °C.

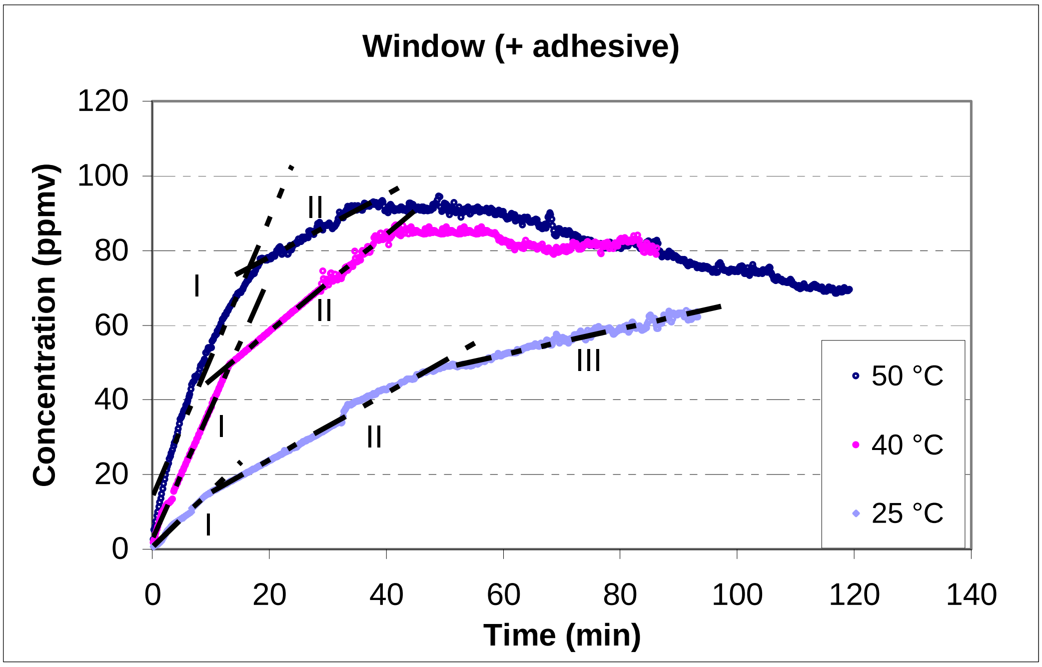

Figure 4.11 Concentration vs. time graph for window piece with Adhesive B

As can be seen from Fig. 4.15, the release patterns of VOCs from the window piece at 50°C, 40°C and 25°C are similar but the release rates decrease with decreasing temperature as in the case for floor material (Type 2). For the test done at 50°C, total VOCs were released with a rate of 3.5 ppmv/min at first step, then at the second step the release rate decreased to 0.8 ppmv/min. Maximum total VOC concentration reached was 90 ppmv. The decrease in the total VOC concentration at the end possibly means that the VOC release from the window material will end after some time. The test piece at 40°C was released VOCs at a rate of 3.5 ppmv/min initially and then at second step had a release rate of 1.3 ppmv/min and finally total VOC concentrations reached to a steady value at 84 ppmv. For the test done at 25°C, first a release rate of 1.5 ppmv/min observed followed by a release rate of 0.88 ppmv/min. At the third and last step it is seen that VOCs are still being released and this is possibly because the solvents on the test piece didn't evaporate completely at that time because of low temperature.

The experimental conditions for adsorbing hydrocarbons released from the window piece with adhesive on activated carbon in Orbo – 32 tube at 25 ± 2 °C, 40 ± 2 °C and 50 ± 2 °C are given in Table 4.21 and the results obtained by analyzing the extracts with GC are given in Table 4.22.

Table 4.21 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from window piece + Adhesive B

Part Name	**Window (+ adhesive B)**		
Temperature	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Duration	119 min	60 min	60 min
Rate of Sampling	0.4 L/min	0.4 L/min	0.4 L/min
Volume of Sample	64.6 L	27.5 L	27.1 L
Ambient Temperature	21.4 °C	26.4 °C	26.2 °C
Ambient Pressure	903 hPa	903 hPa	904 hPa

Table 4.22 Concentration of constituents obtained from window piece + Adhesive B

	Concentration (mg/Nm^3)		
Constituents	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Ethyl acetate	2.20 ± 0.60	0.28 ± 0.40	0.00 ± 0.00
Benzene	0.66 ± 0.50	0.00 ± 0.00	0.00 ± 0.00
Cyclohexane	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Toluene	20.08 ± 3.00	0.67 ± 0.60	0.21 ± 0.03
Butyl acetate	0.00 ± 0.00	0.51 ± 0.03	0.00 ± 0.00
Ethyl benzene	0.00 ± 0.00	0.18 ± 0.02	0.26 ± 0.04
Styrene	0.00 ± 0.00	0.57 ± 0.03	0.00 ± 0.00
Nonane	0.94 ± 0.80	3.70 ± 0.80	1.83 ± 0.40
Decane	6.42 ± 0.90	8.63 ± 1.00	4.16 ± 0.80
Undecane	9.93 ± 1.00	14.59 ± 1.10	5.73 ± 1.00

As can be seen from the results of the GC analysis in Table 4.22, the largest concentration of hydrocarbon is seen for *toluene* at 50°C as 20.08 mg/Nm^3. Then comes *undecane* and *decane* with lower concentrations than toluene. For the tests done at 40°C and 25°C, *toluene* concentration is very low, however, *decane* and *undecane* had the highest concentrations.

4.4.4. Window Holder

The results of the total VOC concentrations released from window holder piece are given in Fig. 4.12. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperatures of 25 ± 2 °C, 40 ± 2 °C and 50 ± 2 °C.

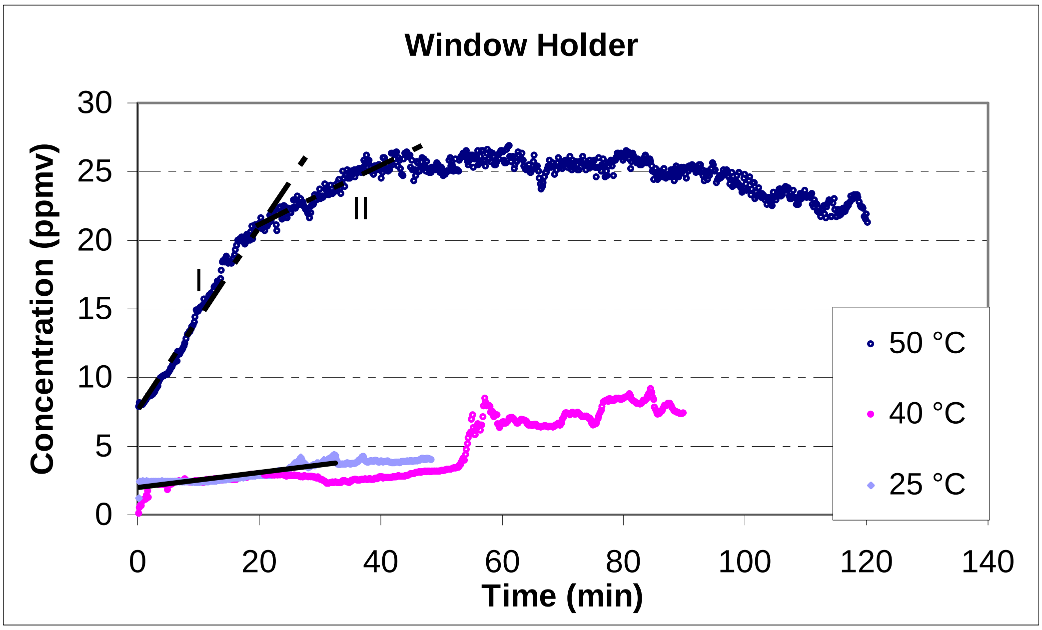

Figure 4.12 Concentration vs. time graph for window holder

As can be seen from Fig. 4.16, for the test done at 50°C initially total VOCs were released with a rate of 0.66 ppmv/min at first step, and then with a release rate of 0.21 ppmv/min at the second step. Total VOC concentration reached to a steady value of 25 ppmv before it started to decrease which is possibly meant that most of the VOCs on the test piece released. The test pieces at 40°C and 25°C were started to release VOCs with a very low rate (0.05 ppmv/min) and the releases were still continued at the end of the experiment.

The experimental conditions for adsorbing hydrocarbons released from the window holder piece on activated carbon in Orbo – 32 tube at 50 ± 2 °C, 40 ± 2 °C and 25 ± 2 °C are given in Table 4.23 and the results obtained by analyzing the extracts with GC are given in Table 4.24.

Table 4.23 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from window holder

Part Name	**Window Holder**		
Temperature	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Duration	120 min	60 min	60 min
Rate of Sampling	0.5 L/min	0.4 L/min	0.4 L/min
Volume of Sample	65.3 L	26.7 L	28.6 L
Ambient Temperature	21.3 °C	26.5 °C	26.9 °C
Ambient Pressure	904 hPa	901 hPa	903 hPa

Table 4.24 Concentration of constituents obtained from window holder

	Concentration (mg/Nm^3)		
Constituents	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Ethyl acetate	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Benzene	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
Cyclohexane	0.00 ± 0.00	0.06 ± 0.00	0.00 ± 0.00
Toluene	14.72 ± 0.90	0.78 ± 0.08	0.52 ± 0.00
Butyl acetate	1.85 ± 0.40	0.15 ± 0.03	0.07 ± 0.00
Ethyl benzene	0.08 ± 0.01	0.00 ± 0.00	0.01 ± 0.00
Styrene	0.00 ± 0.00	0.06 ± 0.00	0.00 ± 0.00
Nonane	0.00 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
Decane	0.20 ± 0.04	0.05 ± 0.00	0.05 ± 0.00
Undecane	0.35 ± 0.04	0.17 ± 0.03	0.14 ± 0.02

As can be seen from the results of the GC analysis in Table 4.24, the largest concentration of hydrocarbon is seen for *toluene* at 50°C as 14.72 mg/Nm^3. Then comes *butyl acetate* with 1.85 mg/Nm^3. For the tests done at 40°C and 25°C the concentrations of all of the constituents were almost zero, except *toluene*.

4.4.5. Door Mat

The results of the total VOC concentrations released from door mat piece are given in Fig. 4.13. This figure shows the change of total VOC concentration (as C_3H_8) with respect to time in the oven at constant temperatures of 25 ± 2 °C, 40 ± 2 °C and 50 ± 2 °C.

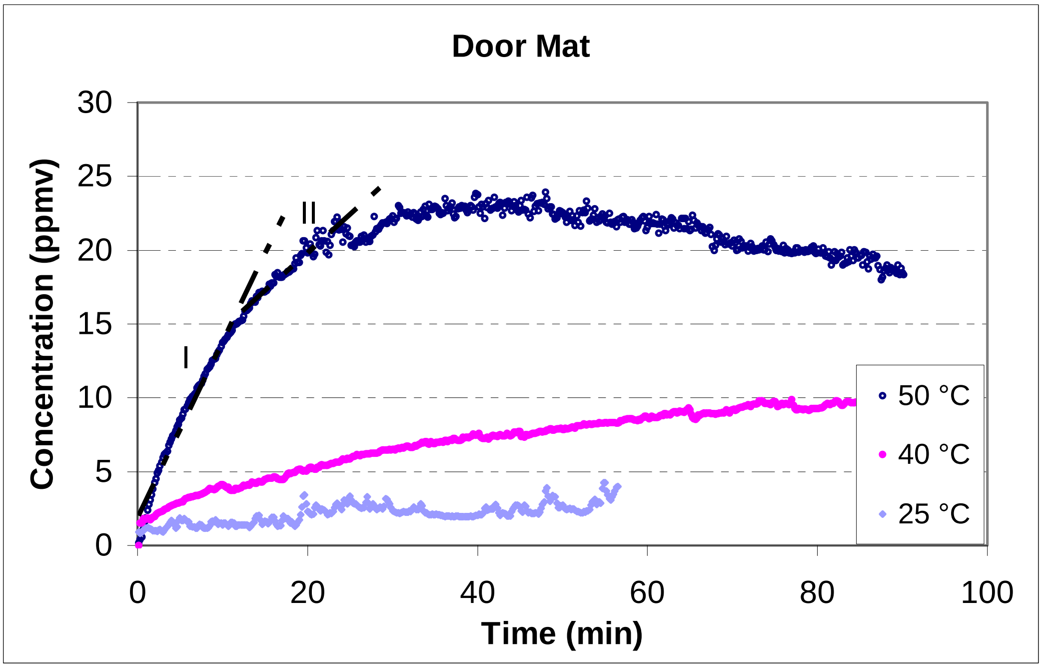

Figure 4.13 Concentration vs. time graph for door mat

As can be seen from Fig. 4.13, for the test done at 50°C initially total VOCs were released with a rate of 1.2 ppmv/min, and then with a release rate of 0.5 ppmv/min at the second step. Total VOC concentration reached to a maximum value of 23 ppmv before it started to decrease which is possibly meant that most of the VOCs on the test piece are released. The test pieces at 40°C and 25°C were started to release VOCs with very low release rates (0.08 ppmv/min for 40°C and 0.03 ppmv/min for 25°C) and the releases were still continued at the end of the experiment.

The experimental conditions for adsorbing hydrocarbons released from the door mat piece on activated carbon in Orbo – 32 tube at 50 ± 2 °C, 40 ± 2 °C and 25 ± 2 °C are given in Table 4.25 and the results obtained by analyzing the extracts with GC are given in Table 4.26.

Table 4.25 Experimental conditions for sampling hydrocarbons with Orbo – 32 tubes from door mat

Part Name	**Door Mat**		
Temperature	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Duration	90 min	60 min	60 min
Rate of Sampling	0.5 L/min	0.4 L/min	0.4 L/min
Volume of Sample	47.1 L	27.7 L	29.6 L
Ambient Temperature	22.8 °C	27.2 °C	27.7 °C
Ambient Pressure	907 hPa	896 hPa	902 hPa

Table 4.26 Concentration of constituents obtained from door mat

	Concentration (mg/Nm^3)		
Constituents	**50 ± 2 °C**	**40 ± 2 °C**	**25 ± 2 °C**
Ethyl acetate	0.71 ± 0.60	0.21 ± 0.30	0.43 ± 0.40
Benzene	0.18 ± 0.30	0.00 ± 0.00	0.00 ± 0.00
Cyclohexane	0.03 ± 0.00	0.16 ± 0.30	0.30 ± 0.40
Toluene	18.03 ± 1.20	2.79 ± 0.60	3.46 ± 0.80
Butyl acetate	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Ethyl benzene	0.04 ± 0.00	0.07 ± 0.00	0.08 ± 0.01
Styrene	0.00 ± 0.00	0.02 ± 0.00	0.13 ± 0.01
Nonane	0.00 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
Decane	0.06 ± 0.00	0.19 ± 0.30	0.16 ± 0.03
Undecane	0.06 ± 0.00	0.14 ± 0.20	0.46 ± 0.05

As can be seen from the results of the GC analysis in Table 4.26, the largest concentration of hydrocarbon were seen for *toluene* at all temperatures, as 18.03 mg/Nm^3, 2.79 mg/Nm^3 and 3.46 mg/Nm^3 for 50°C, 40°C and 25°C, respectively. All the other constituents existed at very low or zero concentrations, except *toluene*.

4.4.6. Summary of Results (Phase IV)

A summary of the results obtained by analyzing the extracts of samples with GC for each test piece at 25°C, 40°C and 50°C are given altogether in Tables 4.27 to 4.29.

As it is seen from the Table 4.27 *toluene* is the compound emitted at the highest concentration from all parts. Considerable amount of *decane and undecane* emission has occurred from floor material type 1 and window parts. The other compounds are either not emitted or emitted at very low concentrations. Again it was seen that the *benzene* concentration is very low, and this is very good since *benzene* is a carcinogen and it has very low exposure limits determined by NIOSH and OSHA. All the exposure equivalents were less than unity 1, which was required by OSHA.

Table 4.27 Concentration of constituents obtained from GC analysis at 50 °C

	Concentration (mg/Nm^3)				
Constituents	**F. M. Type 1 + Adh. B**	**F. M. Type 2 + Adh. B**	**Window + Adh. B**	**Window Holder**	**Door mat**
Ethyl acetate	0	40.12	2.20	0	0.71
Benzene	0	0	0.66	0	0.18
Cyclohexane	2.30	0	0	0	0.03
Toluene	229.91	282.20	20.08	14.72	18.03
Butyl acetate	0	0	0	1.85	0
Ethyl benzene	0.67	0	0	0.08	0.04
Styrene	0	0	0	0	0
Nonane	0	0	0.94	0	0
Decane	8.81	0.24	6.42	0.20	0.06
Undecane	9.10	0	9.93	0.35	0.06
E(m) 8-hr TWA	0.62	0.78	0.26	0.04	0.11
E(m) STEL	0.46	0.60	0.09	0.03	0.05

Table 4.28 Concentration of constituents obtained from GC analysis at 40 °C

	Concentration (mg/Nm^3)				
Constituents	**F. M. Type 1 + Adh. B**	**F. M. Type 2 + Adh. B**	**Window + Adh. B**	**Window Holder**	**Door mat**
Ethyl acetate	39.83	24.76	0.28	0	0.21
Benzene	0	0	0	0.01	0
Cyclohexane	1.37	0.46	0	0.06	0.16
Toluene	162.17	117.87	0.67	0.78	2.79
Butyl acetate	1.84	0	0.51	0.15	0
Ethyl benzene	1.02	0.19	0.18	0	0.07
Styrene	0.37	0.37	0.57	0.06	0.02
Nonane	4.96	0.07	3.70	0.02	0.02
Decane	9.83	0.07	8.63	0.05	0.19
Undecane	40.28	4.25	14.59	0.17	0.14
E(m) 8-hr TWA	0.47	0.33	0	0	0
E(m) STEL	0.36	0.26	0	0	0

From Table 4.28 it is seen that there is not a considerable VOC emission from parts called window holder and door mat, and these results are very well correlated with the total VOC measurements which were very low for these parts, too. *Ethyl acetate* and *toluene* emissions were high from floor materials type 1 and type 2, but the amounts emitted from type 1 were higher. Considerable amounts of *decane* and *undecane* were emitted from floor material type 1 while *benzene* emission was very low or zero for all pieces. Some amount of *decane* and *undecane* emission observed from window part but the other constituents were not considerable. The exposure equivalents were also less than unity 1, as given at Table 4.28.

Table 4.29 Concentration of constituents obtained from GC analysis at 25 °C

	Concentration (mg/Nm^3)				
Constituents	**F. M. Type 1 + Adh. B**	**F. M. Type 2 + Adh. B**	**Window + Adh. B**	**Window Holder**	**Door mat**
Ethyl acetate	13.44	10.76	0	0.07	0.43
Benzene	0	0	0	0	0
Cyclohexane	0	0	0	0	0.30
Toluene	68.69	83.27	0.21	0.52	3.46
Butyl acetate	0.82	0	0	0.07	0
Ethyl benzene	0.20	0	0.26	0.01	0.08
Styrene	0.71	0	0	0	0.13
Nonane	2.89	0	1.83	0.01	0.02
Decane	4.43	0.23	4.16	0.05	0.16
Undecane	23.45	2.01	5.73	0.14	0.46
E(m) 8-hr TWA	0.20	0.23	0	0	0
E(m) STEL	0.15	0.17	0	0	0

For the measurements done at 25°C, very low values of emissions occurred from the parts window holder and door mat. Again the highest emissions occurred from the floor materials type 1 and type 2. As in the other measurements (50°C, 40°C) *toluene* is the compound emitted at highest concentration. *Ethyl acetate, decane* and *undecane* emissions are also observed for floor material type 1. Exposure equivalents were also very low as can be seen from Table 4.29 (on the order of 0.1 to 0.01).

When the total VOC and GC analyses at different temperatures (25°C, 40°C and 50°C) were compared, it was seen that the emission concentrations decrease with the decreasing temperature. *Toluen* was the leading constituent in almost all the samples. *Benzene* emission was very low in all pieces at each temperature which is good news for human health. The initial release rate (k_m) of each test piece, which is due to evaporation mechanism, is given in Table 4.30. The highest initial release rate is obtained at 50 °C and the mechanism of release is mainly evaporation. The initial release rates of organics for FM (Type 1) and (Type 2) and window piece was more than window holder and door mat.

In Phase IV studies, the ventilation channel could not be tested, because the vendor of this material was changed.

Table 4.30 Evaporation rates of test pieces at different temperatures

Test Piece	**k_m (ppmv/min)**		
	50 °C	**40 °C**	**25 °C**
F. M.-Type 1 + Adhesive B	10.4	10.4	6
F. M.-Type 2 + Adhesive B	5.9	3.6	1.38
Window + Adhesive B	3.5	3.5	1.5
Window Holder	0.66	0.05	0.05
Door Mat	1.2	0.08	0.03

From Table 4.30 it is seen that the highest evaporation rate belongs to floor materials. It is also seen that emission rates decreases with decreasing temperatures.

4.5. Experimental Results (Phase V)

Total VOC measurements in a newly manufactured bus, which was produced by using new parts with “substitute adhesive” were conducted. The results of the measurements recorded by data logger are given in Table 4.31 and the following Figures 4.18-4.20 show the VOC concentrations at various sampling points in the vehicle. The indoor temperature of the bus was 35 °C during the measurement.

Table 4.31 Measurement results of the new bus

1. Region		**2. Region**		**3. Region**	
Sampling pt	**Conc. (ppmv)**	**Sampling pt**	**Conc. (ppmv)**	**Sampling pt**	**Conc. (ppmv)**
1	6.2	1	10.3	1	11.5
2	6.3	2	9.8	2	12
3	6.5	3	10.5	3	11.7
4	7	4	10.8	4	12.3
5	7.3	5	11	5	12
6	7.5	6	10.7	6	11
7	8.5	7	10.3	7	11.5
8	8	8	11	8	11
9	8,2	9	11.8	9	11.5
10	8.5	10	11.5	10	11.8
11	8.3	11	12	11	12
12	8.5	12	12.5	12	12.2
13	8.8	13	12.9	13	12
14	8.5	14	12.7	14	11.8
15	8.9	15	12.8	15	11.5
16	9.1	16	13	16	11
17	8.7	17	13.5	17	11.2
18	8	18	13.2	18	10.8
Average	**7.93 ± 0.92**		**11.68 ± 1.17**		**11.6 ± 0.45**

Average concentration for the bus = 10.41 ± 2 ppmv (as C_3H_8)

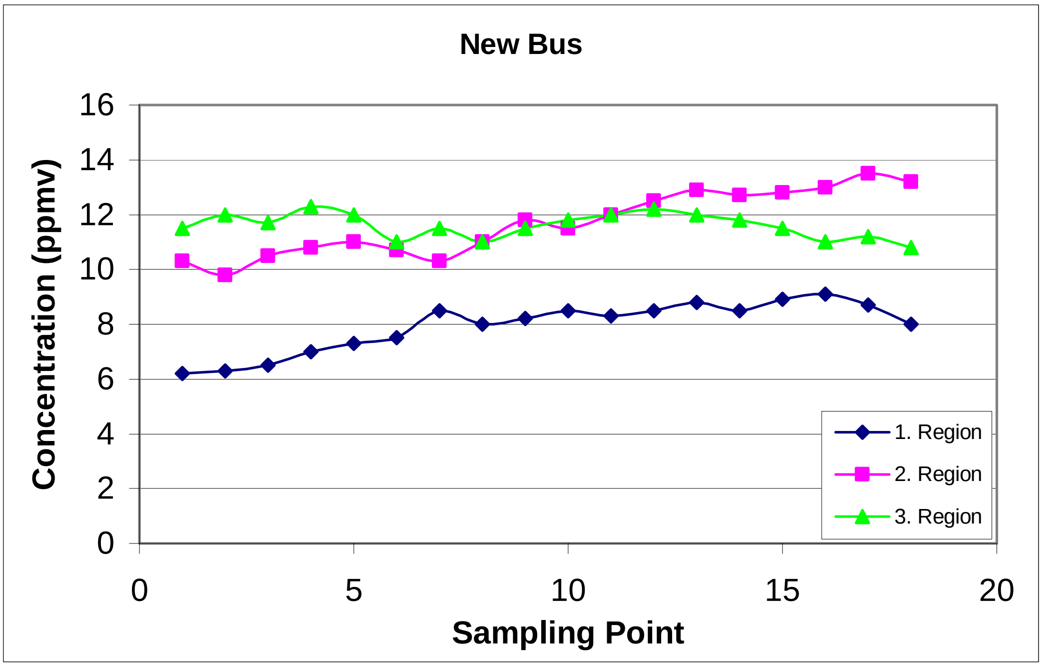

Figure 4.14 Total VOC concentrations in various regions of the new bus

When the measurements of Phase I and Phase IV are compared and reconsidered it is seen that the vehicle average of the two new manufactured buses in Phase I were 21.15 ppmv (as C_3H_8) and 46.04 ppmv (as C_3H_8) for indoor temperatures of 25°C and 28°C, respectively. For the new bus with the new parts used in manufacturing, the total VOC average for indoor air temperature of 35°C was measured as 10.41 ppmv (as C_3H_8). Therefore, it can be said that the replacements done for the parts used in manufacturing caused a significant decrease in the total VOC average in the newly manufactured bus. Temperature is also very effective in release of the volatiles from the parts in the bus. This concentration is 50% of the first bus and 25% of the second bus measured in Phase I. This result shows that using substitute adhesives improved the indoor air quality in the bus considerably.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In Phase I of the study it was found that the adhesives used for the manufacture of the parts used in the interiors of buses evaporate by time and cause indoor air pollution.

Most of the VOC emissions occurred from the *floor materials* and *ventilation channel*, and *toluene* emission was high from almost all the parts, while *benzene* emission was found to be very low. The equivalent exposure values as 8-hr TWA and 15-min STEL for all pieces were less than 1. However, attention must be paid to floor materials and ventilation channel, which have TWA values higher than 0.7 and 0.5 respectively. Also low concentration for *benzene* for all pieces was good news because benzene is a carcinogen and nobody wants it to be present in the indoor air. Based on these findings it was recommended to the company that the use of these constituents must be decreased in manufacturing the parts or new alternatives that require less of these constituents should be developed.

In new parts manufactured with a substitute adhesive, *toluene* was again the leading constituent observed in GC analysis. However, the concentration was much lower than the previous case. *Benzene* emissions were still very low. When the constituents were compared with the OSHA standards individually and totally as exposure equivalent, they were all under the specified limits.

When the total VOC measurement results in Phase I and Phase IV are compared, it was seen that the vehicle average of the two new manufactured buses in Phase I were

21.15 ppmv (as C_3H_8) and 46.04 ppmv (as C_3H_8) for indoor temperatures of 25°C and 28°C, respectively. For the new bus with the new parts used in manufacturing, the average total VOC concentration for indoor air temperature of 35°C was measured as 10.41 ppmv (as C_3H_8). Therefore, it can be said that the replacement of adhesives used in manufacturing of the parts tested caused a significant decrease (between %50 and %75) in the total VOC emission in the newly manufactured buses. Also, no complaints reached to the manufacturing company from the drivers or passengers for the newly manufactured buses after the new solvents or adhesives were started to be used.

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APPENDIX A

PROPERTIES AND GC CALIBRATIONS OF CONSTITUENTS

The boiling points and retention times of the constituents used were given in Table A.1. The GC calibration curves and properties of the standards were given in the order of boiling points are listed in the following pages.

Table A.1 Properties of standards used

Standard	Abbreviation	B. P. (°C)	Company & Catalog No.	Retention Time (min)
Ethyl Acetate	EAc	77	Fluka 45763	5:32
Benzene	B	80-81	Fluka 12540	7:08
Cyclohexane	CHx	80-81	Fluka 28918	7:31
Toluene	T	110-112	Fluka 89680	10:11
Butyl Acetate	BAc	126-127	Fluka 45860	11:08
Ethyl Benzene	EB	135-137	Fluka 03079	12:22
Styrene	S	145	Fluka 85959	13:03
Nonane	N	148-150	Fluka 74252	13:17
Decane	D	171-174	Fluka 30550	15:06
Undecane	UD	195-196	Fluka 94000	16:43

Two mixtures were prepared for calibration calculations. For each mixture a 2 mL vial was used. In the first mixture 0.1 mL of each of benzene, toluene, butyl acetate, ethyl benzene and decane were added into 1 mL of CS_2. In the second mixture the same procedure was repeated by using cyclohexane, undecane, nonane, styrene and ethyl acetate again in a 2 mL vial. Then, 1 μL of the first calibration mixture was injected into GC and injections were repeated for 2-3 times. The same procedure for GC analysis was repeated for the second calibration mixture. From the chromatogram the concentrations of each component were calculated.

Ethyl Acetate ($C_4H_8O_2$)

Properties

Code:	Fluka 45763
Assay:	99.8 %
M. W.:	88.11 g/mole
B. P.:	77 °C
Density:	0.90 kg/L

GC Calibration

Retention time: 5:32 min

Table A.1 Peak areas obtained from GC for given concentrations of ethyl acetate

Conc. (mg/l)	Area (mV.sec)
54,25	33875,54
26,91	11564,93
13,56	6559,37
5,43	2907,00
1,81	817,67

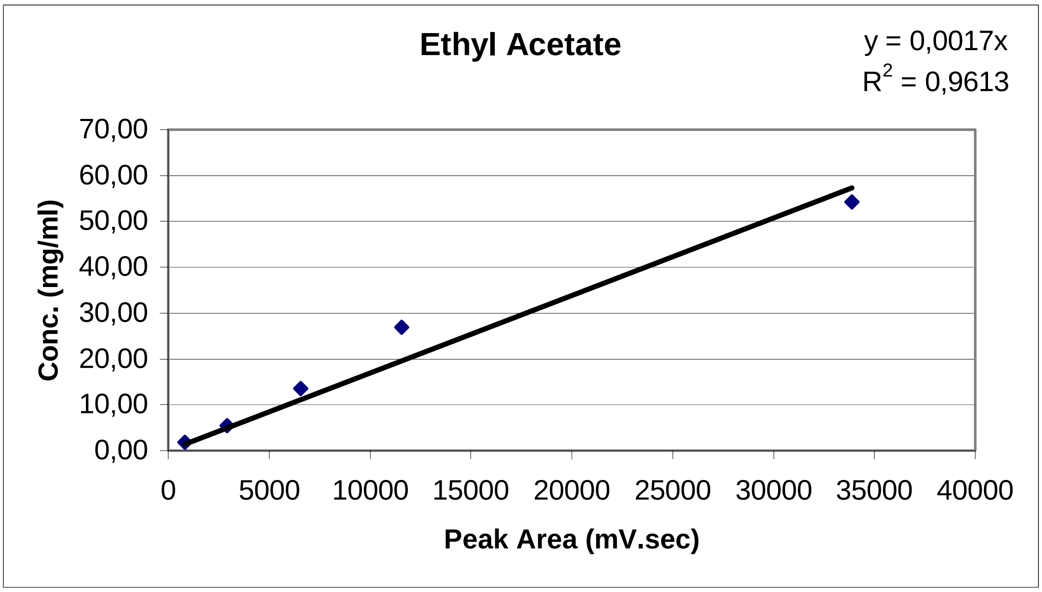

Figure A.1 Calibration Curve for Ethyl Acetate

Benzene (C_6H_6)

Properties

Code:	Fluka 12540
Assay:	99.9 %
M. W.:	78.12 g/mole
B. P.:	80-81 °C
Density:	0.879 kg/L

GC Calibration

Retention time: 7:08 min

Table A.2 Peak areas obtained from GC for given concentrations of benzene

Conc. (mg/l)	Area (mV.sec)
38,95	64402,74
19,48	30712,88
9,74	13030,93
7,79	11339,32
6,49	8645,417
3,90	5109,768

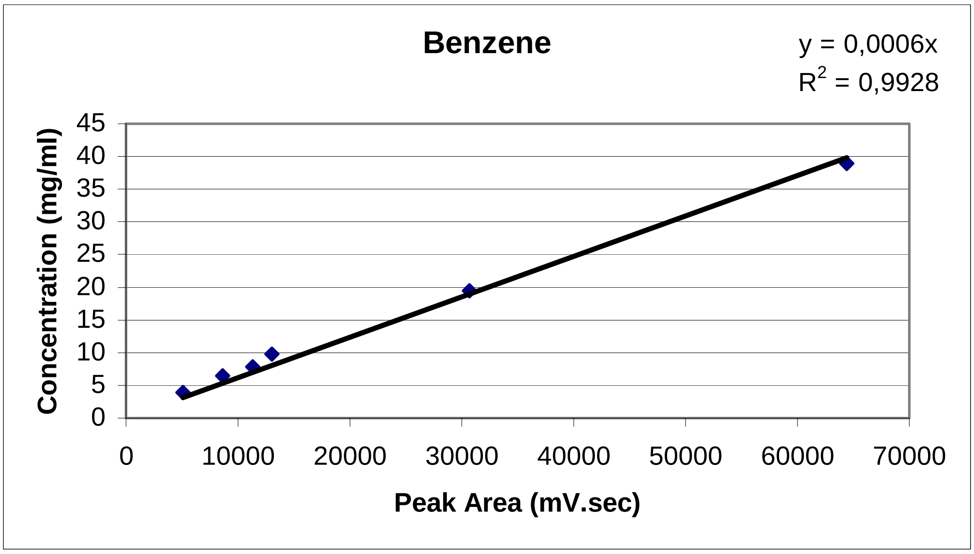

Figure A.2 Calibration Curve for Benzene

Cyclohexane (C_6H_{12})

Properties

Code:	Fluka 28918
Assay:	99.5 %
M. W.:	84.16 g/mole
B. P.:	80-81 °C
Density:	0.778 kg/L

GC Calibration

Retention time: 7:31 min

Table A.3 Peak areas obtained from GC for given concentrations of cyclohexane

Conc. (mg/l)	Area (mV.sec)
47,90	70884,89
23,76	30185,39
11,98	16368,35
4,79	7636,27
1,60	2295,9

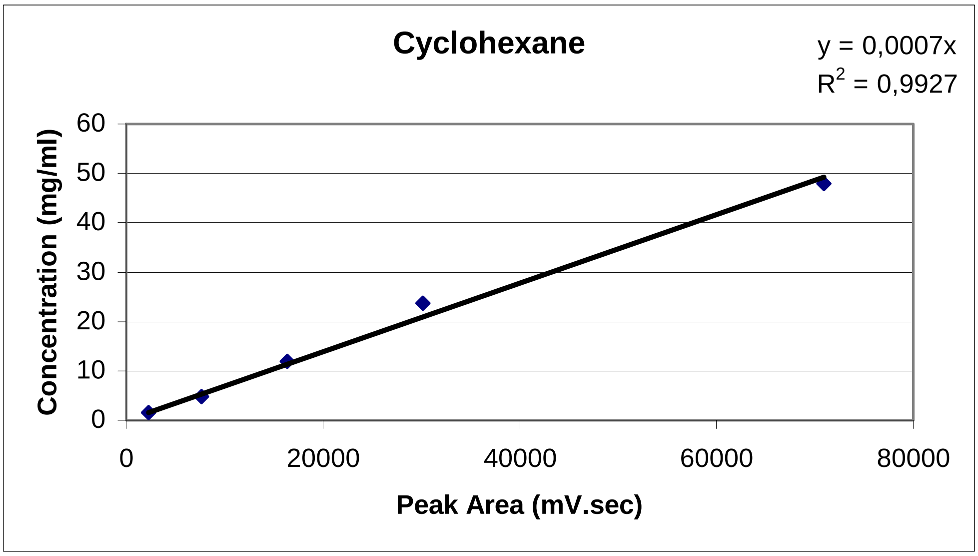

Figure A.3 Calibration Curve for Cyclohexane

Toluene (C_7H_8)

Properties

Code:	Fluka 89680
Assay:	99.9 %
M. W.:	92.14 g/mole
B. P.:	110-112 °C
Density:	0.867 kg/L

GC Calibration

Retention time: 10:11 min

Table A.4 Peak areas obtained from GC for given concentrations of toluene

Conc. (mg/l)	Area (mV.sec)
7,76	25037,19
6,47	20599,13
3,88	11861,54

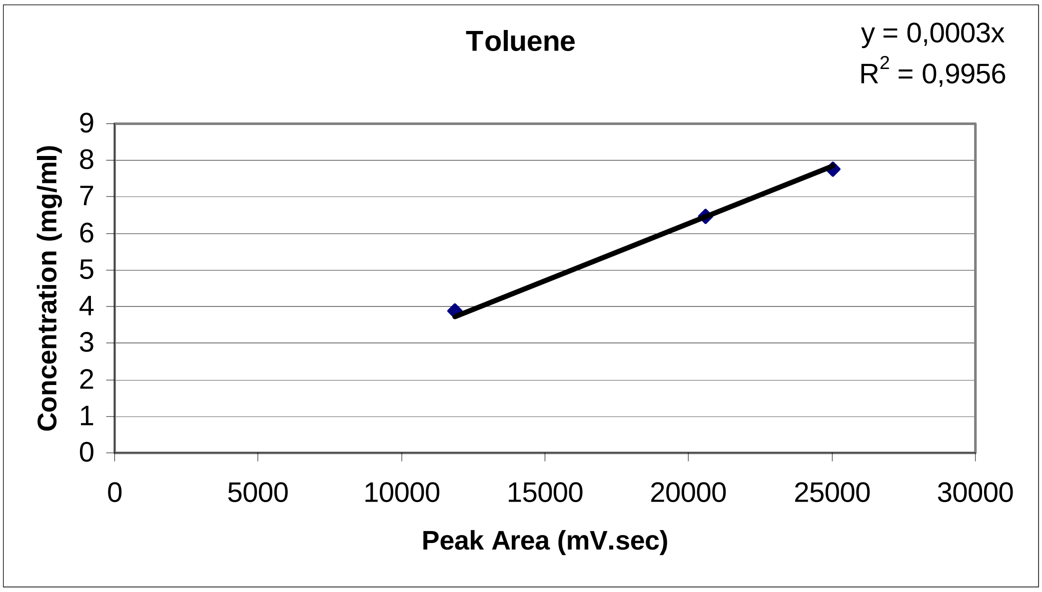

Figure A.4 Calibration Curve for Toluene

Butyl acetate ($C_6H_{12}O_2$)

Properties

Code:	Fluka 45860
Assay:	99.0 %
M. W.:	116.16 g/mole
B. P.:	126-127 °C
Density:	0.881 kg/L

GC Calibration

Retention time: 11:08 min

Table A.5 Peak areas obtained from GC for given concentrations of butyl acetate

Conc. (mg/l)	Area (mV.sec)
7,91	14236,42
6,59	12272,97
3,96	7454,463

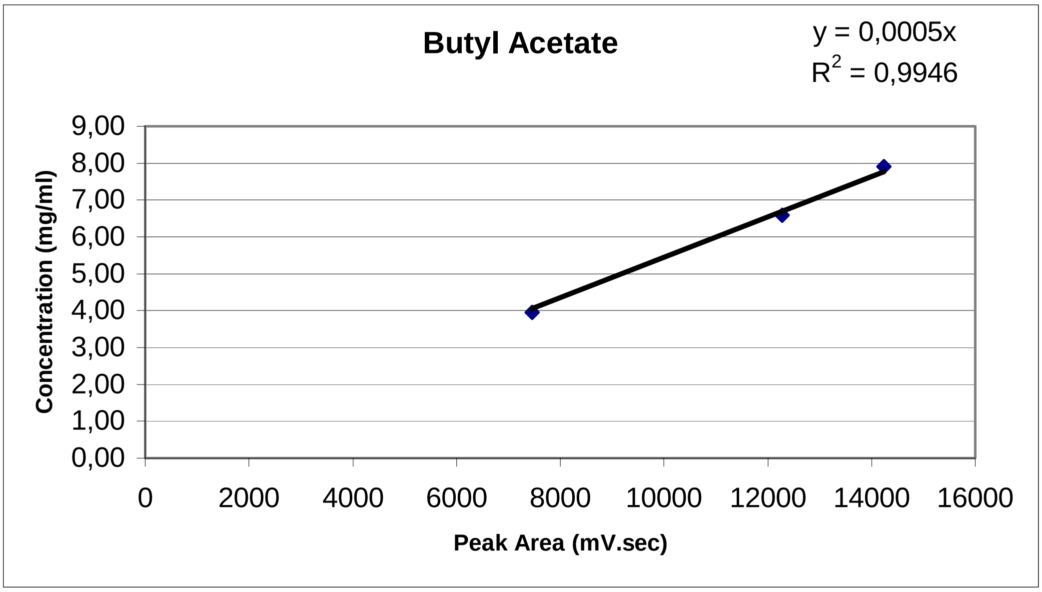

Figure A.5 Calibration Curve for Butyl acetate

Ethyl benzene (C_8H_{10})

Properties

Code:	Fluka 03079
Assay:	99.5 %
M. W.:	106.17 g/mole
B. P.:	135-137 °C
Density:	0.867 kg/L

GC Calibration

Retention time: 12:22 min

Table A.6 Peak areas obtained from GC for given concentrations of ethyl benzene

Conc. (mg/l)	Area (mV.sec)
7,77	30548,00
6,48	27311,6
3,89	16104,24

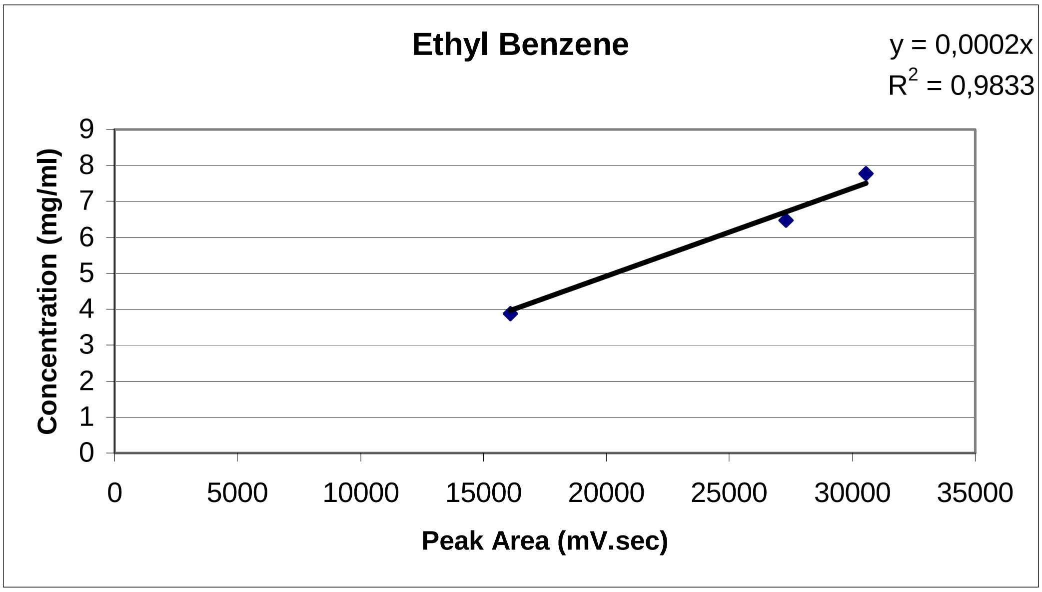

Figure A.6 Calibration Curve for Ethyl benzene

Styrene (C_8H_8)

Properties

Code: Fluka 85959
Assay: 99.5 %
M. W.: 104.15 g/mole
B. P.: 145.2 °C
Density: 0.906 kg/L

GC Calibration

Retention time: 13:03 min

Table A.7 Peak areas obtained from GC for given concentrations of styrene

Conc. (mg/l)	Area (mV.sec)
49,60	87152,07
24,60	38865,31
12,40	20367,64
4,96	10280,38
1,65	3220,325

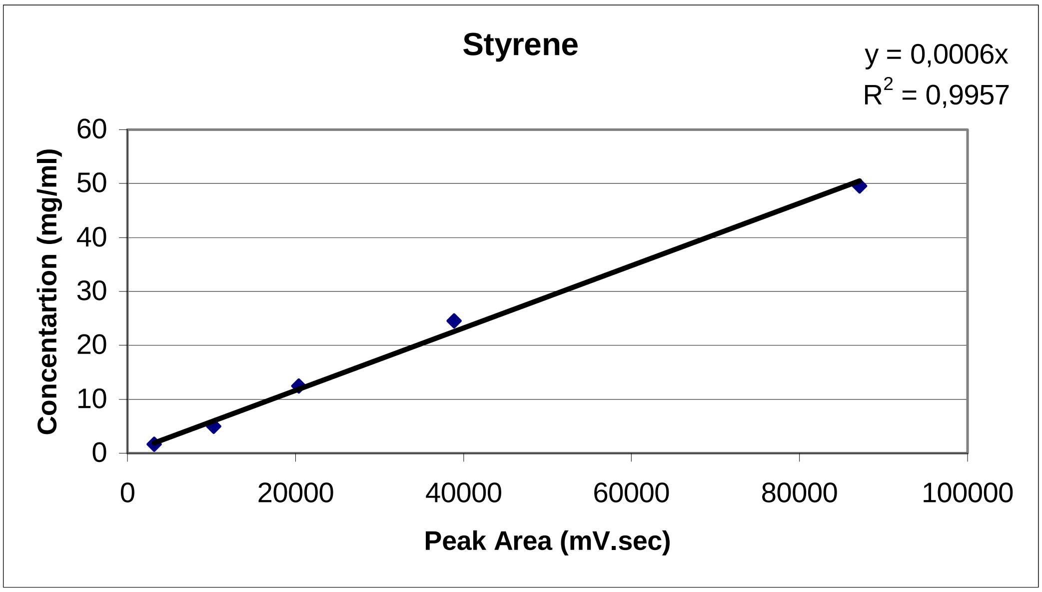

Figure A.7 Calibration Curve for Styrene

Nonane (C_9H_{20})

Properties

Code:	Fluka 74252
Assay:	99. %
M. W.:	128.26 g/mole
B. P.:	148-150 °C
Density:	0.718 kg/L

GC Calibration

Retention time: 13:17 min

Table A.8 Peak areas obtained from GC for given concentrations of nonane

Conc. (mg/l)	Area (mV.sec)
6,49	23265,03
5,41	21443
3,25	11946,58

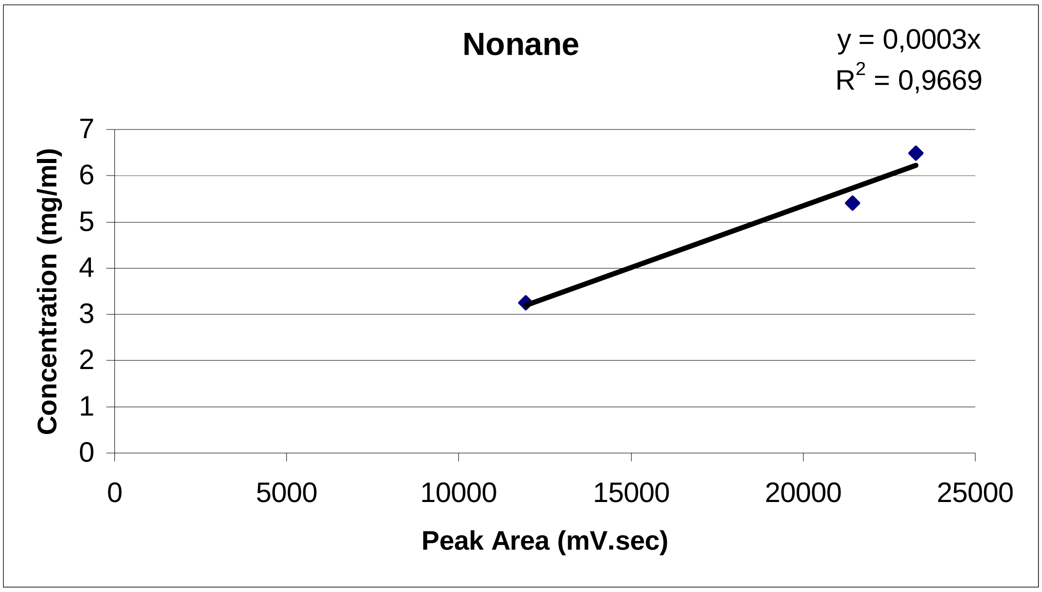

Figure A.8 Calibration Curve for Nonane

Decane ($C_{10}H_{22}$)

Properties

Code: Fluka 30550
Assay: 98 %
M. W.: 142.29 g/mole
B. P.: 171-174 °C
Density: 0.73 kg/L

GC Calibration

Retention time: 15:06 min

Table A.9 Peak areas obtained from GC for given concentrations of decane

Conc. (mg/l)	Area (mV.sec)
6,51	24860,17
5,43	24128
3,26	12670,39

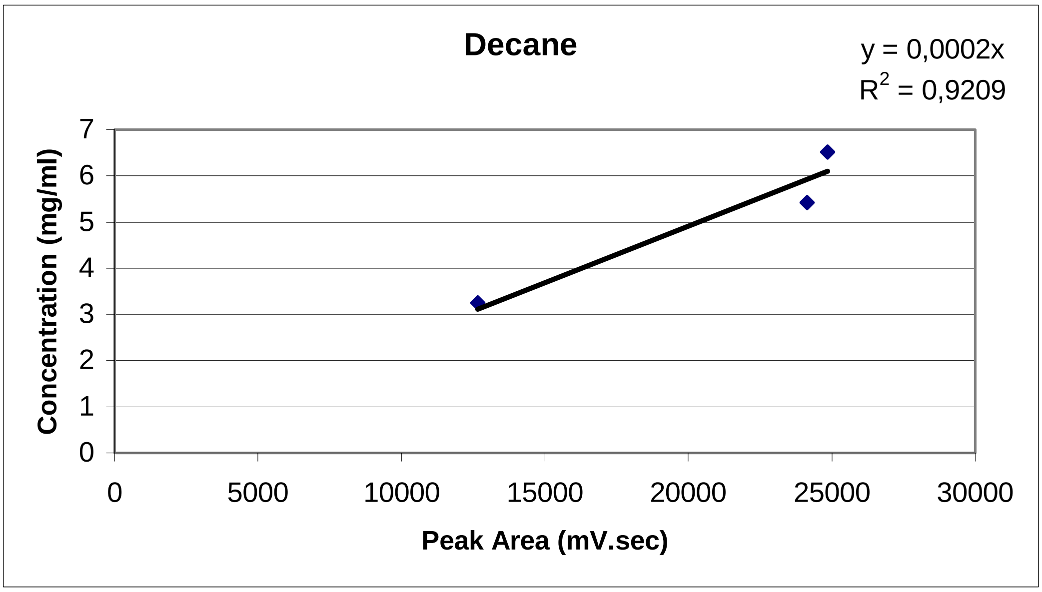

Figure A.9 Calibration Curve for Decane

Undecane ($C_{11}H_{24}$)

Properties

Code:	Fluka 94000
Assay:	99.8 %
M. W.:	156.31 g/mole
B. P.:	195-196 °C
Density:	0.74 kg/L

GC Calibration

Retention time: 16:43 min

Table A.10 Peak areas obtained from GC for given concentrations of undecane

Conc. (mg/l)	Area (mV.sec)
46,70	74546,23
23,16	30425,55
11,68	15322,32
4,67	8037,285
1,56	2794,285

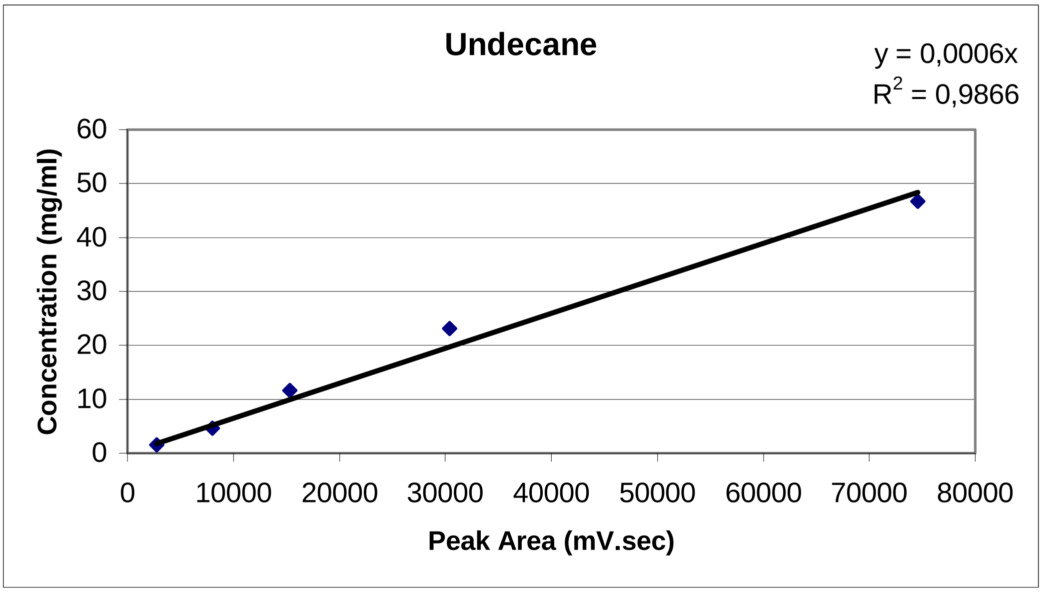

Figure A.10 Calibration Curve for Undecane

A sample chromatogram output is shown in Figure A.11. The chromatogram is the output of one of the test mixtures used for GC calibration. As it can be seen from the figure the mixture is composed of benzene, toluene, butyl acetate, ethyl benzene, nonane and decane.

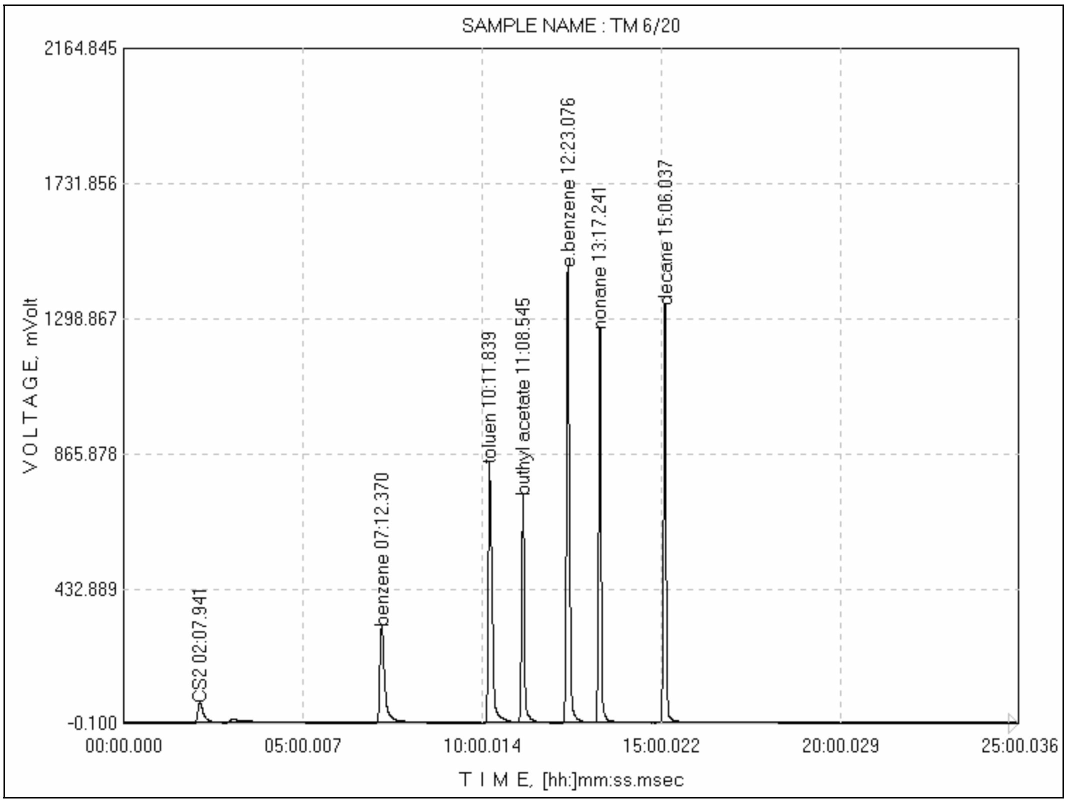

Figure A.11 A sample for chromatogram output

APPENDIX B

CALCULATION OF CONCENTRATIONS OF CONSTITUENTS

Calculation method:

Step 1:

The peak area obtained from the gas chromatogram for the constituent is multiplied by the calibration constant of that constituent, which was shown in Appendix A, to find the concentration of the constituent in the extraction of active carbon in CS_2.

$C_{ext} = P.A. * C_{cons}$

where;
C_{ext}: Concentration of constituent in the extraction,
P.A.: Peak area obtained from GC for the constituent
C_{cons}: Calibration constant of constituent

Step 2:

After finding the concentration of the constituent in the extraction, the weight of the constituent adsorbed by active carbon is calculated by multiplying the concentration with the volume of CS_2 used in extraction.

$W_{cons} = C_{ext} * V_{CS2}$

where;

V_{CS2}: Volume of CS_2 used in extraction of active carbon

W_{cons}: Weight of constituent in the extraction

Step 3:

From the known values of the gas temperature, volume and pressure (obtained from DESEGA pump) the volume of sampling gas under normal conditions is calculated.

$$V_N = \frac{P_G * V_G * T_N}{T_G * P_N}$$

where;

V_N : Volume of sampling gas under normal conditions,

V_G : Actual volume of sampling gas,

P_G : Actual pressure of sampling gas,

P_N : Normal pressure (1013 hPa),

T_G : Actual temperature of sampling gas,

T_N : Normal temperature (273 K),

Step 4:

The concentration of the constituent in the emitted gas is found by dividing the weight of constituent to the normal volume of emitted gas.

$$C_{Cons} = \frac{W_{Cons}}{V_N}$$

where

C_{Cons}: Concentration of constituent in the emitted gas from the sample part.

Step 5:

The concentration of constituent is corrected by the recovery factor of constituent (given in Appendix D).

$$C_{ConsC} = \frac{W_{Cons}}{R_{cons}}$$

where

C_{ConsC}: Corrected concentration of constituent.

R_{cons}: Recovery factor of constituent

Example:

Calculation for toluene concentration emitted from floor material-type 1 at 40 °C is given below in order to clarify the method described above.

Step 1:

The peak area obtained from the gas chromatogram for toluene is multiplied by the calibration constant of toluene to find the concentration of toluene in the extraction of active carbon in CS_2.

P.A. of toluene = 10789.5 mV sec

Calibration constant of toluene = 3×10^{-4} mg ml^{-1} mV^{-1} sec^{-1} (App. A)

$C_{ext\text{-}tol} = P.A._{tol} * C_{tol}$

$C_{ext\text{-}tol} = 10789.5$ mV sec $* 3 \times 10^{-4}$ mg ml^{-1} mV^{-1} sec^{-1}

$C_{ext\text{-}tol} = 3.24$ mg/ml

Step 2:

After finding the concentration of toluene in the extraction, the weight of toluene adsorbed by active carbon is calculated by multiplying the concentration with the volume of CS_2 used in extraction.

$W_{tol} = Cext_{\text{-}tol} * V_{CS2}$

$W_{tol} = 3.24$ mg/ml $* 0.74$ ml

$W_{tol} = 2.392$ mg

Step 3:

From the known values of the gas temperature, volume and pressure (obtained from DESEGA pump) the volume of sampling gas under normal conditions is calculated.

$$V_N = \frac{P_G * V_G * T_N}{T_G * P_N}$$

$$V_N = \frac{902\,\text{hPa} * 26\,\text{L} * 273\,\text{K}}{(25.5 + 273)\,\text{K} * 1013\,\text{hPa}}$$

$$V_N = 21.07\ \text{L}$$

Step 4:

The concentration of toluene in the emitted gas is found by dividing the weight of toluene to the normal volume of emitted gas.

$$C_{tol} = \frac{W_{tol}}{V_N}$$

$$C_{tol} = \frac{2.392\,\text{mg}}{21.07\,\text{L}}$$

C_{tol} = 113.52 mg/Nm^3

Step 5:

The concentration of toluene is corrected by the recovery factor of toluene (0.70 from Appendix D)

$$C_{tolC} = \frac{W_{tol}}{R_{tol}}$$

C_{tolC} = 113.52 mg/Nm^3 / 0.70 = 162.17 mg/Nm^3

APPENDIX C

CALCULATION OF EXPOSURE VALUES

The **cumulative exposure** for an 8-hour work shift shall be computed as follows:

$$E = (C(a)T(a) + C(b)\,T(b)\ +...C(n)T(n)) + 8$$

where:

E is the equivalent exposure for the working shift.

C is the concentration during any period of time (T) where the concentration remains constant.

T is the duration in hours of the exposure at the concentration C

The value of E should not exceed the 8-hour TWA specified in Table 3.1.

In order to illustrate how to use the formula, assume that Substance A has an 8-hour time weighted average limit of 100 ppm noted in Table 3.1. Assume that an employee is subject to the following exposure:

Two hours exposure at 150 ppm,
Two hours exposure at 75 ppm,
Four hours exposure at 50 ppm,

Substituting this information in the formula, we have

$$(2 \times 150 + 2 \times 75 + 4 \times 50) + 8 = 81.25 \text{ ppm}$$

Since 81.25 ppm is less than 100 ppm., the 8-hour time weighted average limit, the exposure is acceptable.

In case of a mixture of air contaminants an employer shall compute the **equivalent exposure** as follows:

E(m) = (C(1) / L(1) + C(2) / L(2)) +...(C(n) / L(n))

where:

E(m) is the equivalent exposure for the mixture.

C is the concentration of a particular contaminant.

L is the exposure limit for that substance specified in Table 3.1

The value of E(m) shall not exceed unity (1).

In order to illustrate how to use the formula, consider the following exposures listed in Table C.1:

Table C.1 Exposures and limits for substances

Substance	Actual concentration of 8 hour exposure (ppm)	8 hr. TWA PEL (ppm)
B	500	1000
C	45	200
D	40	200

Substituting in the formula, we have:

Em = 500 / 1,000 + 45 / 200 + 40 / 200

Em = 0.500 + 0.225 + 0.200

Em = 0.925

Since Em is less than unity ‘1’, the exposure combination is within acceptable limits.

APPENDIX D

RECOVERY CALCULATIONS

The recovery calculations were done in order to see if any loss happens during the extraction of samples from the active carbon before GC analysis. The recovery experiments were done according to the following procedure.

- Calibration mixtures as explained in Appendix A (p. 76) were prepared.
- The tips of an Orbo – 32 tube were broken.
- 0.1 mL of the first calibration mixture was taken from the vial with a syringe and injected carefully into an Orbo – 32 tube from the top and the tips were capped immediately.
- Again the same procedure was repeated with the second calibration mixture on another Orbo – 32 tube.
- Then, the Orbo tubes were left at room temperature for some time (at least 1 day) in order to make chemicals evaporate in the tube and be adsorbed by activated carbon particles.
- After the adsorption period was completed, the activated carbons in the Orbo tubes were extracted by using the same extraction procedure given in Section 3.2.3.1.
- GC analyses of the extracted samples were carried out and each sample was injected into GC twice.
- The concentration of each component in the "calibration mixture" was calculated and they are given in Table D.1.
- The concentrations of each component found by "GC analysis" were calculated and these concentrations were the concentration of each component in the extract. These values are given in Table D.1.

- Therefore by comparing the results obtained for each component a recovery factor for the chemicals included in the calibration mixture were calculated. The average of two analysis results was taken as the recovery factor for the constituent. These results are given in table D.2.
- The GC analysis results of each extract obtained during the experiments were corrected by using the average “recovery factor” for each component.

Table D.1 Concentrations of constituents in the calibration mixture (CM) and extract

constituent	Concentration in CM (mg/mL)	Concentration in E1* (mg/mL)	Concentration in E2* (mg/mL)
Ethyl Acetate	149.3	117.5	121.3
Benzene	146.3	122.4	132.8
Cyclohexane	138.0	110.1	110.9
Toluene	147.3	110.3	96.1
Butyl Acetate	147.0	103.5	102.4
Ethyl Benzene	145.7	105.4	98.6
Styrene	149.0	112.1	111.2
Nonane	120.0	81.1	84.5
Decane	119.3	84.1	83.1
Undecane	134.3	94.2	93.8

*E1 = Results of first injection of extract into GC
E2 = Results of second injection of extract into GC

Table D.2 Recovery factors for constituents

constituent	1st Analysis (%)	2nd Analysis (%)	Recovery Factor (%)
Ethyl Acetate	78.70	81.25	79.97
Benzene	87.15	83.66	85.40
Cyclohexane	79.78	80.36	80.07
Toluene	74.88	65.24	70.06
Butyl Acetate	70.41	69.66	70.03
Ethyl Benzene	72.34	67.67	70.00
Styrene	75.23	74.63	74.93
Nonane	67.58	70.42	69.00
Decane	70.49	69.66	70.07