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Validation of a Passive Air Sampling Device for Measuring Ambient VOCs at Subzero Temperatures

by

R. Vincent J. Gagner

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Masters of Science

in

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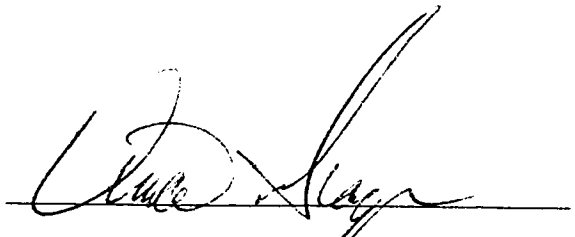

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled, Validation of a Passive Air Sampling Device for Measuring Ambient VOCs at Subzero Temperatures submitted by R. Vincent J. Gagner in partial fulfillment of the requirements for the degree of Masters of Science in Public Health Sciences.

Dr. Steve E. Hrudey

Dr. Warren B. Kindzierski

Dr. X-Chris Le

Dr. David J. Wilson

Date. April 15, 1996

To Jennifer.

We made it!

Abstract

The OVM-3500 passive sampler has been in prevalent use since the mid 1970's. It was originally designed for workplace exposure monitoring, but recent evaluations have proven the method useful in some domestic air sampling applications. This thesis builds on validation studies performed by the manufacturer of the sampler, 3M, and several independent researchers.

In this study, exposure measures included 24 hour sample durations, at ambient concentrations and at temperatures ranging from room to well below freezing. Validations were based on comparisons of readings taken by the passive sampler against reference methods during exposure chamber trials, stationary field co-locations, and personal sampling tests.

Assessments demonstrated that the passive sampler was capable of measuring benzene and toluene within acceptable margins of error. It was also concluded that temperature variations between 25°C and -15°C had no effect on the badge performance. Finally, the use of the passive sampler in a pilot study demonstrated its potential usefulness in the ongoing Alberta Oilsands Community Exposure and Health Effects Assessment Program.

Acknowledgments

This research was made possible by sponsorship of the Eco-Research Chair at University of Alberta. Special mention goes to Alberta Health and the Alberta Oilsands Community Exposure and Health Effects Assessment Program for their direct financial and technical support, and to Alberta Environmental Protection for providing access to laboratory and field resources.

I would especially like to thank Dr. Steve Hrudey, Dr. Warren Kindzierski, Dr. Chris Le, Dr. David Wilson, and Prof. Laird Wilson for making their pool of knowledge and experience available to the study critique and evaluation.

Ray Brassard and his staff were an invaluable source of technical support and practical wisdom in the laboratory. Thanks also to Peter Lea for his assistance in the design and construction of the glasswork for the project.

Acknowledgments to both Larry Serbin and Daryl Bilan of Envirotest Laboratories for ensuring optimum measurements of badge analytes. Generous insight into the sampling and analysis protocol also came from Rein Otson and Phil Fellin who essentially pioneered applications of the OVM-3500 in environmental monitoring.

Support for the study was also granted by Robert Weber of 3M who kindly donated a case of OVM-3500 samplers. In addition, shared knowledge and experience was provided by 3M and the Occupational Hygiene group at Novacor.

All of my colleagues in the Eco-Research Student Group contributed positively to my overall academic experience at the University. Two group members, namely Simon Thomas and Trevor Hilderman, were very generous with providing advice and support to this research.

Lastly, a large part of the energy dedicated to this study came from my immediate and extended families. Dedication of this thesis to my wife was made in reflection of my respect for Jennifer as a scholar and a friend. Immediate and extended family back East also deserve a warm thank-you for their continued interest in what has seemed to be a never ending story.

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List of Abbreviations and Symbols

ADD	Average Daily Dose
ASHRAE	American Society for Heating, Refrigerating, and Air-conditioning Engineers
ATSDR	Agency for Toxic Substances and Disease Registry
CAS	Chemical Abstracts Service
CEPA	Canadian Environmental Protection Act
d6	deuterium attached at benzene's 6 binding sites instead of hydrogen
d8	deuterium attached to toluene's 8 binding sites instead of hydrogen
DQO	Data Quality Objective
EPA	Environmental Protection Agency (US)
FID	Flame Ionization Detector
GC	Gas Chromatography
HP	Hewlett Packard
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
Kow	Octanol-water partition coefficient
LADD	Lifetime Average Daily Dose
LOD	Limit Of Detection
LOQ	Limit Of Quantitation
MD	Multi-Detector
MRL	Minimum Risk Level
MS	Mass Spectrometry
NAPS	National Air Pollution Surveillance program
NIOSH	National Institute for Occupational Safety and Health
OVM	Organic Vapour Monitor
PID	Photo Ionization Detection
SIM	Selected Ion Monitoring
Sr	Standard error of regression coefficient
TAMS	Toxic Air Monitoring System
TEAM	Total Exposure Assessment Methodology
THE	Total Human Exposure
σ	standard deviation on a normal distribution
TWAE	Time-Weighted Average Exposure
VOC	Volatile Organic Compound

Chapter One: Introduction

1.1 The Parent Study

1.1.1 Background

In the Spring of 1995 Alberta Health embarked on a province-wide *Environmental Health Effects Assessment Program.* Kindzierski et al. (1995) stated that the program is designed to identify linkages between human exposure to environmental contaminants and the incidence or prevalence of adverse health effects in the Alberta population. The principal objectives of the program include:

1) Producing data on contaminants in the ambient environment;

2) Developing accurate data on human exposure to contaminants;

3) Producing data on environmental health indicators (health effects);

4) Analyzing associations between environmental contaminants and observed effects;

5) Identifying health priorities and developing suitable risk management strategies.

Northeastern Alberta is important from an economic perspective because of extensive oilsands deposits. Two oilsands companies have been in operation in the region, Suncor Oil Sands Group Inc. (since 1967) and Syncrude Canada Ltd. (since 1978). Research by the Fort McMurray Regional Air Quality Task Force (1987) identified concerns in the communities of Fort McKay and Fort McMurray about industrial emissions from the oilsands activities. The Air Quality Task Force report, however, concluded that point source emissions were within approved limits established by Alberta Environmental Protection. Recent proposals for expansion at

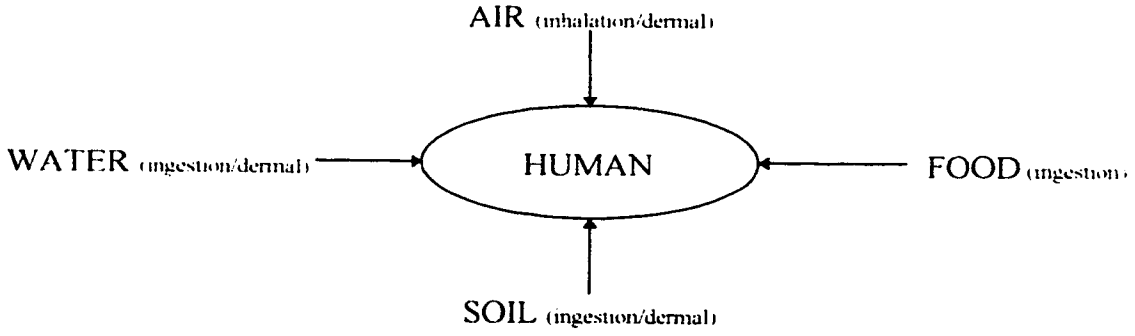
the Syncrude Canada Limited oilsands mining and upgrading operations at Mildred Lake (ERCB, 1994) have peaked the interest of government and other groups in gaining a greater understanding of oilsand emissions and resulting influences on health in the surrounding population. The Alberta Oilsands Community Exposure and Health Effects Assessment Program (1995) was established to accomplish this by following the objectives outlined in the Environmental Health Effects Assessment Program.

CanTox Inc. (1993) modeled emissions, dispersions, and human exposures to 32 chemicals which could be present in ambient air as a result of emissions from the Syncrude Canada Inc. Mildred Lake facility operations. Carter et al. (1993) point out that plume dispersion models, such as those used in the CanTox study, provide valuable insight into the behaviour of environmental contaminants leaving a selected emission source. This information can be effective for generating an impression of overall downwind concentrations, especially when combined with ambient air quality data taken from community-based fixed air monitoring stations. However, the question is posed: does dispersion modeling of point source emissions or stationary monitoring of ambient pollutants provide a good representation of human exposure to the pollutants? Lagrone (1989) emphasized that data from fixed monitoring sites should be interpreted as an indication of outdoor air quality but should not be used for assessing personal exposure. In fact, neither predictive plume dispersion model predictions nor fixed-station monitoring can provide a reliable representation of the variability of personal exposure within an actual study population.

Early work by Wallace and Ott (1982) argued that personal monitoring generates data that is more indicative of the environmental heterogeneity, both indoor and out, that individuals encounter over a typical day. Sampling at the receptor enables researchers to link lifestyle data with exposure data for a more complete understanding of how, when, and where people are exposed to air contaminants. Ott (1990) developed a U.S. Environmental Protection Agency conceptual model of Total Human Exposure (THE). THE, as illustrated in Figure 1.1, defines a three-dimensional surface around the human receptor with exposure occurring when pollutants make direct contact via one or more of the four possible routes of exposure.

Figure 1.1

Conceptual Model of Total Human Exposure



Like the Alberta Health objectives (Kindzierski et al., 1995), Total Human Exposure seeks to gain knowledge of the flow of environmental contaminants from

the source to the receptor. With this understanding, researchers may consider sources of exposure in proportion to each other and focus management strategies accordingly.

1.1.2 Proposed Methodology

The Alberta Oilsands Community Exposure and Health Effects Assessment Program proposes to use passive samplers as the most practical means of evaluating personal exposures to volatile airborne contaminants. Notably, others have successfully used passive samplers in community exposure assessments, including: Seifert and Abraham, 1983; Shields and Weschler, 1987; and, Otson and Fellin, 1994.

Volatile organic compounds (VOCs) are one group of contaminants that have been identified for measurement by Alberta Health in the Alberta Oilsands Community Exposure and Health Effects Assessment Program. Reasons for particular interest in VOCs include:

1. CanTox (1993) linked VOC emissions from the Syncrude Canada Ltd. Mildred Lake Oilsands facility to potential community exposure.
2. VOC emissions may occur from natural sources such as forests (Guenther, Zimmerman and Wildermuth, 1994);
3. Local sources such as gasoline stations and automobile traffic will also emit VOCs (Lioy and Daisey, 1987; Lofgren, 1991);
4. Emissions can also be expected from a variety of indoor sources including building materials, consumer products, and cigarette smoke (Wallace, 1989; Colome, 1994).

The 3M manufactured OVM-3500 passive sampler has been subjected to validation studies (Anders and Mullins, 1981) for 8-hour exposure durations at relatively high VOC concentrations, representing typical workplace exposure

scenarios. From this research, 3M (1989) published air "Sampling Rates" that express the relation between the mass of the VOCs collected by the passive sampler over time and the time-weighted average concentration of VOCs in surrounding air.

More recently, Health Canada and Bovar Consultants (Fellin et al., 1990) validated the OVM-3500 for measuring VOCs at typical levels found inside Canadian homes. Again, passive sampling rates were calculated based on mass collected by the sampler over time at constant exposures to VOCs. The success of this research led to the deployment of over 4,000 samplers in a Canada-wide survey of VOC levels inside 754 homes.(Otson et al., 1994)

The results of these studies appear to support the use of the OVM-3500 as a suitable device for exposure assessment in the oilsands region. However, much of the sampling proposed is to be performed on people and at outdoor temperatures below freezing, and no documented validation of the sampler under such conditions exist.

1.2 Thesis Research

1.2.1 Hypothesis

The ability of the OVM-3500 passive sampler to accurately measure select VOCs under freezing conditions was evaluated through a series of experiments designed to compare the badge with standard sampling methods. Differences between the passive sampler and accepted methods of measurement were evaluated for sampling applications indoors, outdoors, and on people. The study hypothesis was that the passive sampler could perform within acceptable margins of error while measuring exposures to ambient benzene and toluene, over 24 hours, and at temperatures between -15°C and 24°C.

1.2.2 Study Design Overview

This thesis builds on previous OVM-3500 research to determine if the badge is suitable for use under a wide variety of personal, indoor, and outdoor exposure scenarios expected during the Alberta Oilsands Community Exposure and Health Effects Assessment Program. Two volatile organic compounds, benzene and toluene, were selected as the most appropriate VOCs for the validation. Designation of two compounds was necessary to focus the scope of the study. Specific interests in benzene and toluene include: presence of existing literature regarding the passive sampler performance, a recognition of societal concern regarding exposure to these compounds, and the availability of analytical standards and equipment to measure these compounds.

The OVM-3500 passive sampler evaluation was divided into three phases. Each phase was designed to answer an independent question regarding a specific exposure scenario. Conclusions and recommendations generated from the three phase evaluation were applied to a pilot study of two homes in Edmonton, Alberta using the passive sampler to measure indoor, outdoor, and personal exposure to benzene and toluene.

1.2.2.1 Phase I: Laboratory

Phase I included simulation of a 24-hour exposure measurement of constant levels of contaminant under controlled laboratory conditions. "Test atmospheres" were generated in a temperature controlled exposure chamber through the use of permeation tubes. Partially modeled after Tang et al. (1993), and Purdham et al. (1994), the evaluation compared readings from the OVM-3500 against the NIOSH[1] approved method of charcoal tube sampling (NIOSH, 1984).

Correlation was made by assuming 3M sampling rates (3M, 1989) in determination of badge exposure and performing regression analysis between the passive sampler TWAE (time weighted average exposure) readings versus TWAE readings from the NIOSH approved charcoal tube. To define the effect of temperature on the passive sampler, back calculation of OVM-3500 sampling rates was performed using the assumption that the charcoal tubes were 100% accurate.

---

[1] NIOSH: National Institute of Occupational Safety and Health

1.2.2.2 Phase II: Field

The field validation evaluated the passive samplers under actual outdoor environment conditions. Co-location of the passive samplers at the Alberta Environmental Protection 17th Street Air Monitoring Station enabled passive sampler measures to be compared to the NAPS (National Air Pollution Survey) Summa® canister methodology. These canisters were rigorously tested by the U.S. Environmental Protection Agency (McClenny, 1987) and adopted as part of the U.S. Environmental Protection Agency (1989) Compendium Methods for the determination of VOCs in ambient air.

Correlation was made by assuming 3M sampling rates and performing regression analysis between the readings from the passive sampler versus the Summa® canister method. To define the effect of temperature on the sampling rate, back calculation of badge sampling rates was performed on the assumption that the Summa® canisters were 100% accurate.

1.2.2.3 Phase III: Personal

Patterned somewhat after studies by Cohen et al. (1990), Norlinder et al. (1993), and Purdham (1994), passive samplers were placed on a host in series with the NIOSH approved charcoal tube system. It was thought that over the period of a day, a person could be exposed to VOCs in a number of microenvironments. To gain an understanding of passive sampler performance under a range of exposure scenarios,

sets of samples were taken from environments that were expected to show both high and low levels of VOCs.

Correlation was made by assuming 3M sampling rates and performing regression analysis between the readings from the passive sampler versus the charcoal tube method. To define the effect of temperature on the sampling rate, back calculation of badge sampling rates was performed on the assumption that the charcoal tube method was 100% accurate. Qualitative identification of microenvironments and sampling bias were assessed through a review of activity logs completed by the person wearing the samplers.

1.2.2.4 Applications

Two homes in Edmonton were selected for a pilot application of the OVM-3500. Passive samplers were placed on one person per household, in the main indoor living space, and on the front porch. Interpretations of the passive sampler readings were based on the reference comparison evaluations made in Phases I to III. Personal diaries were also maintained by the two study volunteers over the sample duration.

1.2.3 Data Quality Objectives

Taylor (1988) explained that uncertainties in data obtained from a sampling program may be attributed to either the sample itself or the subsequent analysis. Analytical uncertainty was controlled by a quality assurance program in the laboratory, while sample uncertainty was controlled by accounting for all sources of systematic and random error in the sampling protocol. Keith (1991) stated that data quality

objectives (DQO's) function as statements providing the critical definitions of confidence required for drawing conclusions from the project data. The quality of any data set may be represented as a function of five general DQO parameters including accuracy, precision, representation, completeness, and comparability. (Keith, 1988)

1.2.3.1 Accuracy

Accuracy is a measure of closeness to the true value. Passive sampler accuracy was measured through correlation of readings taken by the passive sampler against the reference measurement techniques. Inherent variability of the OVM-3500 measures were assumed similar to the reported charcoal tube accuracy of ± 25% (NIOSH, 1984). Analytical accuracy was not set at a specific value, rather it was a "best practical goal" achieved through routine calibrations, blanks, spikes, and internal deuterated standards.

1.2.3.2 Precision

Precision is a measure of the mutual agreement among individual measurements. Exposure chamber sampling included triplicate passive samplers and duplicate charcoal tube (NIOSH, 1984) samples. Passive samples in the field were obtained in triplicate but there was only one canister (Dann and Wang, 1992) sample per set. Personal badge samples were taken in duplicate and measured against one charcoal tube (NIOSH, 1984) reading. The precision objective was for repeated passive sampler measures to be within ±25% of the mean of repeated sampler measures. Analytical precision was determined by processing triplicate aliquots of the

same sample solution, the objective being to minimize peak chromatographic differences during processing.

1.2.3.3 Representativeness

Representation refers to the ability of the samplers and analytical equipment to provide an "impression" of the environment being sampled. Selected contaminant concentrations for laboratory evaluations were based on ambient air data from locations throughout North America, including Alberta. All sampling methods in this study produced time-weighted average measurements which were ONLY representative of the air making contact with the sampler. Analytical representation was achieved by matching relative retention times to strict peak matching tolerances followed by analysis of the ion species within each peak.

1.2.3.4 Completeness

This is a measure of the amount of valid data obtained from the research compared to the amount expected to be obtained under absolutely correct conditions. Potential sources of bias which deviated sampling from "absolutely correct" were identified and quantified when possible. Analytical completeness was ensured through measures of recovery efficiency and blank contamination on the badges. Complete instrument measures included individual review of automated quantitation of overlapping peaks and/or cases of disproportioned mass spectrum ion abundance.

1.2.3.5 Comparability

Comparability concerns the confidence with which the results of the research can be compared to related studies. Generic sampling durations, badge deployment procedures, and analytical techniques were used to maintain consistency with other studies performed in the past. Common laboratory equipment and reagents were used to ensure that aliquots were processed in a manner similar to past and present studies.

Chapter Two: Literature Review

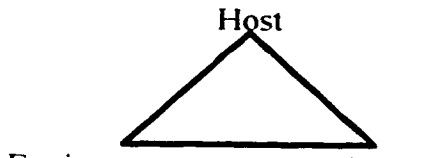
2.1 Concepts of Exposure Assessment

2.1.1 Exposure Scenario

An assessment of human exposure to airborne benzene and toluene requires definition of three parameters: an exposure scenario, a measure of exposure intensity, and a measure of exposure duration. An exposure scenario is created when sources of benzene and toluene are connected to human receptors via an environmental pathway. Theobald Smith pioneered this concept in his 1934 book Parasitism and Disease, where he linked infectious agents, the environment, and a susceptible host together as a model of disease (Duncan, 1988). His writings eventually led to what is now referred to as *The Epidemiological Triad* illustrated below in Figure 2.1. Wayne Ott

Figure 2.1

The Epidemiological Triad



(1990) agreed that there is a connection between human receptors and environmental pollutants that link together like a chain. The five components of this chain include: source, pathway, exposure, dose, and effects.

In Alberta, Environment Canada's National Air Pollution Surveillance (NAPS) program measures concentrations of VOCs in urban areas along environmental pathways downwind from potential sources of pollution (Dann, Wang, 1992). The Alberta Oilsands Community Exposure and Health Effects Assessment Program (1995) is currently being designed to assess exposure at the receptor, interpret findings based on dose, and correlate these results with existing health care data.

2.1.2 Exposure and Dose

Measurements of personal exposure indicate the amount of benzene or toluene coming into physical contact with the receptor; however, the actual dose[1] received by a host is the amount that is made available to human biological processes. The major routes that toxic agents gain access to tissue inside the body are via the gastrointestinal tract (ingestion), lungs (inhalation), and skin (dermal). Conventional measures of dose are expressed as a mass of chemical (e.g. microgram) per mass of human body (e.g. kilogram) per day. OVM-3500 data expresses an averaged concentration of physical exposure over the time that exposure occurred and may be used in calculations of dose via inhalation and/or dermal absorption.

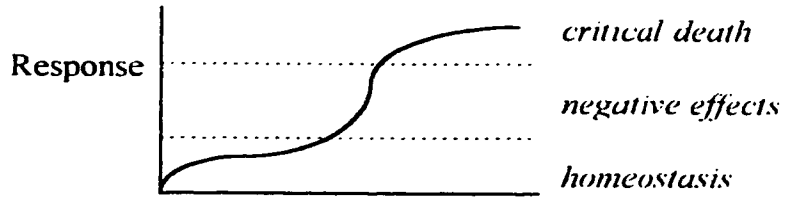
Figure 2.2 is a typical individual dose-response curve. In essence, xenobiotic exposures are translated to dose and finally an effect on the human host. In general, exposure and dose are positively correlated with response. Negative health effects are experienced only when a dose "threshold" is reached where biological defense

[1] At 100% absorption.

systems are unable to cope with the presence of toxicants or their metabolites. The relative toxicity of air contaminants, including benzene and toluene, is indicated

Figure 2.2

Typical Dose-Response Curve



by the shape of their dose-response curve. Measures of potency compare the range of doses over which an increasing response is produced, while efficacy reflects the limit of the dose-response relationship on the response axis. (Amdur et al., 1991a) The dose of airborne benzene and toluene depend on both the duration and intensity (concentration) of the exposure. There are infinite combinations of duration and intensity, but a general rule is that at equal dosage, the acute hazard to the receptor is directly proportionate with intensity and inversely proportionate with duration.

2.1.3 Measuring Exposure to Airborne Contaminants

Methods of contaminant measurement vary according to agent, accuracy requirements, recommended guidelines, and access to testing equipment (Calgary Health Services, 1993). There are three basic strategies for sampling VOCs from ambient air: grab, time-weighted, and continuous.

A. *Grab* samples are performed over a short period of time (e.g. five minutes) to identify suspect contaminants and to measure short term variations in air quality.

B. *Time-Weighted Measurements* average the concentration of a pollutant over a specified time with the limitation of not being able to identify short term variations.

C. *Continuous Measurements* record a series of grab samples for a specified period of time in an effort to understand both average and variable air quality.

Figure 2.3

Grab vs. Time-Weighted Average (TWA) Samples

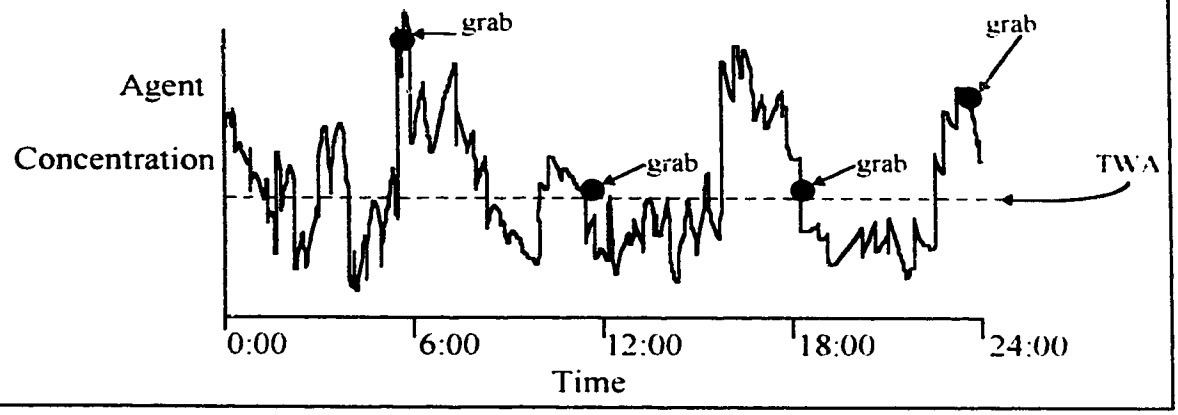


Figure 2.3 (above) illustrates variation of environmental contamination over the period of a day and the limitations of both grab and time-weighted sampling techniques. Furtaw et al. (1991) demonstrated the limitation of TWA measures by placing portable automated gas chromatographs on individuals to measure short averaging-time concentrations of benzene and other VOCs. They concluded that short-term microenvironmental data were needed to accurately assess exposures during highly transient exposure scenarios.

2.1.4 Exposure and Risk

The U.S. EPA (Environmental Protection Agency) developed an equation (1992) stating that exposures over time can be represented by a time-dependent profile of exposure concentration expressed as:

$$E = \int_{t_1}^{t_2} C(t)\ dt \qquad \textbf{(Eq. 2.1)}$$

where E is the magnitude of exposure, C(t) is the exposure concentration as a function of time, and t is time, $t_2 - t_1$ being the exposure duration.

Health Canada (1994) and the U.S. EPA (1992) use time-weighted average exposures to estimate personal dose. For example, the EPA use time-weighted exposure data in an equation to calculate an average daily potential dose or ADD_{pot}.

$$ADD_{pot} = [\ \bar{C} \bullet \bar{IR} \bullet ED\ ] \ / \ [\ BW \bullet AT\ ] \qquad \textbf{(Eq. 2.2)}$$

where, ADD_{pot} is the average daily potential dose, $\bar{C}$ is the time-weighted concentration, $\bar{IR}$ is the inhalation rate, ED is the sum of exposure durations, BW is body weight, and AT is the period of time over which the dose is averaged.

Risk assessments may be made by comparing the ADD_{pot} to published Tolerable Daily Intake values for an estimation of potential threshold effects of VOCs such as toluene. In contrast, the non-threshold carcinogenic risks of benzene may be assessed by converting ADD_{pot} to a lifetime average daily potential dose or $LADD_{pot}$, and using this figure to estimate carcinogenic risk using published carcinogenic potency factors.

2.2 The Contaminants

2.2.1 Volatile Organic Compounds

Hoskins (1995) defined VOCs as, "any organic substance that can release vapour to the atmosphere with the potential of causing effects at low concentrations." Harkov et al. (1987) provided a more narrow definition stating that VOCs are organic substances with vapour pressures greater than or equal to 0.02 psi at ambient temperature. A third, more limited explanation, comes from Keith (1991) who defined volatile compounds as being below the molecular weight of C_{10} hydrocarbons.

VOCs in our environment are described by Health and Welfare Canada (1992) as compounds originating from a variety of sources which can be transported over long distances. Guenther et al.(1994) stated that VOCs exist in all living things and that emissions from several natural sources are present in ambient air. In contrast, Lioy et al. (1990) have reported that VOCs are generally more prevalent indoors with only occasional infiltration from outdoor ambient sources.

Jantunen (1994) reviewed the differences between VOC readings from air monitoring stations versus indoor and transportation microenvironments as well as during certain activities. Based on their findings, Jantunen concluded that ambient air sampling does not provide an assessment of personal exposure and that, "as air pollution regulation begins to shift focus from ambient air to exposure, the resulting control measures may also change significantly from the present."

2.2.2 Benzene

2.2.2.1 Chemical Characteristics

Benzene (CAS Registry Number 71-43-2), is an aromatic hydrocarbon with the chemical formula C_6H_6. At room temperature benzene appears in the form of a colourless liquid with a characteristic sweet odour Parry et al. (1987) explained that the benzene ring is a planar hexagon with 120° angles between each pair of carbon-carbon bonds. Figure 2.4 is an illustration of the compound structure which includes three resonating double bonds indicated as a circle. Table 2.1 is a summary of some physical constants[1] for benzene.

Figure 2.4

The Benzene Molecule

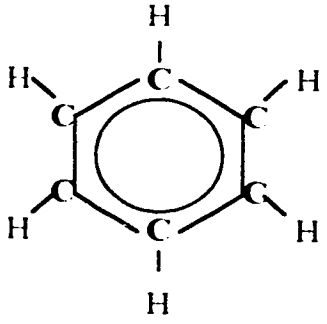


Table 2.1

Physical Constants

Molecular Weight	78.11
Boiling Point (°C)	80.1
Melting Point (°C)	5.5
Density (g/cm^3, 25°C)	0.8736

2.2.2.2 Sources

In a review of a New Jersey TEAM[2] study, Harkov et al. (1987) identified the major source of outdoor benzene as combustion emissions from automobile exhaust.

[1] 1994 CRC Handbook of Chemistry and Physics
[2] TEAM Total Exposure Assessment Methodology

Personal communication with Imperial Oil (Richardson, 1996) revealed that concentrations of benzene in typical unleaded formula gasoline range from 0.01% to 3.5% depending on the ability of the refinery to extract benzene from the product. Field studies conducted by the Windsor Air Quality Committee (1994) showed that, "area sources, particularly from vehicular and fuel combustion, dominate contributions to ground level concentrations of benzene."

Table 2.2 (Hoskins, 1995) is a breakdown of the proportion of outdoor sources of benzene estimated during 1991 in the United Kingdom. All things being equal, the

Table 2.2

Benzene Emissions in the UK in 1991

Source	Tonnes/Year
Gasoline engine exhausts	39 250
Diesel engine exhausts	4 550
Gasoline evaporation from vehicles	3 350
Gasoline refining and distribution	1 350
Combustion of oil, wood, etc.	950
Gas leakage	400
Other industrial processes	350

proportion of benzene sources in the community of Fort McMurray should be similar to data presented in Table 2.2 with the possible exception of potential contributions from industrial activities at Syncrude and Suncor. Forest fires also lead to considerable benzene emissions (ATSDR, 1995) and Fort McMurray has a recent history (Mullen, C., 1995) of forest fires in the region.

Indoor sources of benzene (Lagoudi and Loizidou, 1995) include infiltration of automobile exhaust, vapours or gases from products that contain benzene (e.g. glues, paints, furniture wax, detergents), and tobacco smoke. In a study of ambient air quality, Shields et al. (1995) attributed intermittent levels of indoor benzene to emissions from heated cooking oils. ATSDR (1995) concluded that "about 50% of the entire nationwide [American] exposure to benzene results from smoking tobacco or from exposure to tobacco smoke." Wallace et al. (1987) determined that the average daily intake of benzene due to smoking alone for the average smoker was about 2 mg/day, compared to the average nonsmoker intake of <0.2 mg/day. Wallace (1989) recognized the high proportion of benzene in cigarette smoke but maintained that exposures to benzene are best correlated with personal activity.

2.2.2.3 Environmental Partitioning[1]

The log octanol-water partition co-efficient (K_{ow}) of benzene is 2.13, indicating that benzene will reach concentrations approximately 100 times higher in lipids of biological materials than in water when benzene reaches equilibrium between these two phases. At room temperature, benzene is slightly water soluble (S = 1.77g/L) and highly volatile with a vapour pressure of (P_v) 95 mmHg. The Henry's Law constant (K_w) of benzene is 5.5×10^{-3} atm-m^3/mole at 20°C, indicating that benzene readily partitions from water to air. Reactions caused by photo-oxidation can cleave the benzene ring (Sawyer, 1994); this is the major mechanism of degradation and the

[1] Physical Constants taken from the 1994 CRC Handbook of Chemistry and Physics.

overall half-life of airborne benzene is estimated to range between 0.1 and 21 days (CEPA,1993). At the longer end of this half-life range, there is potential for benzene to travel considerable distances (hundreds of kilometers) from an emission source.

2.2.2.4 Health Effects

Because of the tendency for benzene to migrate through air, the primary route of entry to the human receptor is inhalation and dermal contact. Health risks associated with benzene in community air are focused on chronic inhalation of low concentrations. The potential health effects related to low level, chronic exposure are blood disorders including aplastic anemia and leukemia (ATSDR, 1995).

Chronic animal bioassay studies have required relatively high inhalation exposures to demonstrate a cancer risk for benzene. For example, mice exposed to benzene levels of over 100 000 $\mu g/m^3$ for 112 days demonstrated an increase in lymphomas. (Cronkite, et al., 1989)

The most convincing human epidemiological research comes from Infante (1978) and Rinsky et al. (1981) who analyzed an American cohort study involving 748 white male workers. The cohort was exposed to estimated benzene concentrations between 3,000 to 31,000 $\mu g/m^3$. Retrospective comparison of the exposed group against a normal reference population revealed a statistically significant excess incidence of leukemia up to 10 times higher risk among the benzene exposure cohort. Rinsky et al. (1987) expanded on this study demonstrating a stronger exposure-response relationship in the cohort worker population.

The "MRL" or Minimum Risk Level[1] for benzene effects other than cancer is 5 ppb or 1.57 $\mu g/m^3$ (ATSDR, 1995). The International Agency for Research on Cancer or IARC (1995) classifies benzene as "Carcinogenic to Humans" and has proposed a unit risk factor of 3.7×10^{-6} $(\mu g/m^3)^{-1}$. This corresponds to a potency slope factor of 1.3×10^{-2} $(mg/kg/day)^{-1}$ for a typical 70 kg man. The Integrated Risk Information System (1995a) estimates of cancer risk are provided in Table 2.3.

Table 2.3

IRIS Cancer Risk Estimates for Benzene

Benzene Concentration in Air ($\mu g/m^3$)	Lifetime Risk Level
10	1 in 10 000
1	1 in 100 000
0.1	1 in 1 000 000

2.2.2.5 Previous Studies

In a draft document summarizing VOC levels in Edmonton, Alberta between 1991 and 1993, Cheng et al. (1996) reported a median benzene concentration of 3.4 $\mu g/m^3$ in the downtown core[2] compared with a median industrial area[3] reading of 2.6 $\mu g/m^3$. These data are consistent with the literature outlined in Section 2.2.2.1 where automobile exhaust, typical of a downtown core, is recognized as a primary source of

[1] In deriving the Minimal Risk Level, uncertainty factors are multiplied together with the product then divided into an acceptable bioassay level indicative of no adverse observable effects.
[2] Downtown Edmonton: 10255-104th St.
[3] Industrial Area: 17 St. / 105 Ave.

benzene in outdoor air. Cheng et al. (1996) indicated that VOC levels were consistently higher in the winter months versus the summer. Theories proposed by Cheng et al. include: (1) higher abundance of hydroxy radicals in the summer increases the degradation rate of VOCs; (2) point source [i.e. heating source] emissions of benzene decrease in the summer; and (3) enhanced vertical mixing through increased convection during summer lowers ground level measures of VOCs.

Seasonal variations were also found in research by Singh et al. (1992) who measured VOCs at four American urban centres. During the study period, benzene levels in the wintertime were about three times higher than summer. Overall concentrations of benzene throughout the study ranged from 0.38 to 40 ppb (0.1 to 12.6 $\mu g/m^3$).

The effect of wind direction on ambient VOC levels was highlighted by Kappos, et al. (1994) in a report regarding VOC monitoring around Sarnia, Ontario. Interpretation of the effect of wind direction was clearly demonstrated in the data generated from measures at a park site on the eastern outskirts of the city. At this location, benzene levels showed strong correlation to south-westerly winds (this wind direction put the park directly downwind from "refinery row" which includes over twelve refinery and petrochemical facilities). Consistent with the Sarnia study, Scheff and Wadden (1993) also demonstrated that certain wind trajectories caused higher VOC levels in parts of Chicago that were located downwind from refineries.

The usefulness of centralized outdoor measures, such as those presented in the above studies, was evaluated by Michael et al. (1990). They compared VOC readings from a centralized sampling station in Los Angeles to measures taken from indoor and outdoor environments at individual residences. Their results show that correlation was poor between the three measures and that indoor levels were consistently higher than outdoor. Statistical comparisons of median benzene measures from samples taken from local air monitoring stations and local indoor residence environments were found to be significantly different. The main point conveyed in the study was that conventional exposure measures taken at centralized stations were, at best, an indication of community air quality but not indicative of receptor exposure.

Montgomery and Kalman (1989) measured concentrations of benzene inside and outside of 17 Washington State homes having no history of adverse health effects[1]. The median benzene level for indoor air was reported as 6.2 $\mu g/m^3$ while outdoor levels were slightly lower at 5.1 $\mu g/m^3$. A study by De Bortoli et al. (1986) measured indoor and outdoor benzene concentrations in Northern Italy. Measures of indoor benzene concentrations ranged between 5 to 204 $\mu g/m^3$ while outdoor benzene was again lower at 3 to 67 $\mu g/m^3$. In contrast, Colome et al. (1994) analyzed data obtained during the California Regional Indoor Air Quality Study that was performed over the winter of 1991-1992. The analysis determined that, "median indoor benzene was 2.1 ppb [0.65 $\mu g/m^3$] and the median outdoor was 1.3 ppb [0.41 $\mu g/m^3$]."

[1] Adverse effect in this context refers to the results of a questionnaire which included questions regarding symptomatology associated with chronic exposure to low levels of airborne contaminants.

Lioy (1990) showed that benzene was emitted from a number of different sources and he concluded that personal exposure assessments were required for representative data for human exposure. Wallace (1989) compared 24-hour ambient samples and personal expiratory samples from 700 TEAM study subjects. The results showed a mean personal exposure of 15 $\mu g/m^3$ compared to a mean outdoor concentration of 6 $\mu g/m^3$. Differences between ambient and person measures were even more apparent when considering the maximum personal exposure (measured at 500 $\mu g/m^3$) compared to 90 $\mu g/m^3$ for the outdoor maximum.

Potential sources of personal exposure to benzene include: active and passive smoking, auto-related activities, occupational exposures, consumer products, and miscellaneous combustion sources. Benzene levels cited in the literature discussed here for outdoor, indoor, and personal exposures are summarized in Table 2.4.

Table 2.4

Summary of Reported Benzene Levels

Study	Indoor		Outdoor	
	$\mu g/m^3$	ppb	$\mu g/m^3$	ppb
Edmonton (Cheng)	-	-	2.6 - 3.4	8.3 -10.8
American Range (Singh)	-	-	0.1-12.6	0.4 - 40
Sarnia (Kappos)	-	-	3.4	10.8
LA County (Michael)	6	19	4	13
Washington (Mont./Kal.)	6.2	20	5.1	16
Italy (Bortoli, et al)	5 - 200	16 - 640	3 - 67	9.6 - 214
California (Colome)	0.65	2.1	0.41	1.3
TEAM (Wallace)	**15***	48	6	19

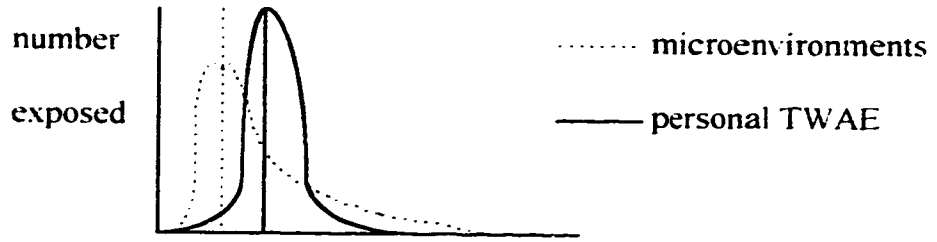
* personal sample, (mean of 700 subjects)

2.2.2.6 Predicted Range of Benzene Exposures

Plausible ranges for personal and ambient benzene exposures in an urban community have been estimated through a **qualitative ad hoc** amalgamation of the literature data. The distribution of personal exposure concentrations is expected to be slightly skewed with a mode of about 10μg/m^3 with outliers measuring from 1μg m^3 to 50μg/m^3. The distribution of all probable microenvironmental concentrations (indoor and outdoor) is a wider and more skewed estimate ranging between 1 and 100 μg/m^3.

Figure 2.5

Distribution of Benzene Exposure



The range of all probable microenvironmental concentrations are indicated in Figure 2.5 as a dotted line, while the range of expected personal time-weighted average exposures (TWAE) are shown as a solid line. The smaller standard deviation of the personal exposures reflects the fact that individuals are exposed to a variety of microenvironments at both high and low levels. It is expected that integrated personal sampling over 24 hours will average out extreme short-term exposures.

2.2.3 Toluene

2.2.3.1 Chemical Characteristics

Toluene (CAS Registry Number 108-88-3), or methyl benzene, is an aromatic hydrocarbon with the chemical formula $C_6H_5CH_3$. At room temperature, toluene appears in the form of a colourless liquid with a distinct pungent odour. Toluene is the simplest alkyl derivative of benzene with the structural appearance of a benzene ring and a methyl group attached to one of the carbon binding sites. Figure 2.6 is an illustration of the compound structure and Table 2.5 is a summary of some physical constants[1] of toluene.

Figure 2.6

The Toluene Molecule

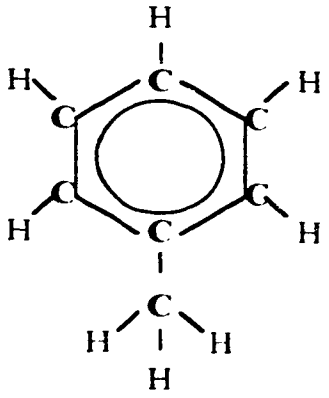


Table 2.5

Physical Constants

Molecular Weight	92.14
Boiling Point (°C)	110.6
Melting Point (°C)	- 95
Density (g/cm^3, 25°C)	0.8669

2.2.3.2 Sources

A review of a New Jersey TEAM study by Harkov et al. (1987) identified the major sources of outdoor toluene as miscellaneous solvent applications and

[1] 1994 CRC Handbook of Chemistry and Physics

combustion emissions from automobile exhaust. Concentrations of toluene in typical unleaded formula gasoline are reported to range from 15 to 28% (Richardson, 1996). After sampling over 1,000 organic solvent products, Inoue et al. (1983) demonstrated that toluene is the most popular solvent being used as a main component in thinners and degreasers. The dominant use of toluene in Canada is in the production of benzene and as a solvent in various industrial processes (CEPA, 1992). As mentioned, toluene is a major component of gasoline and is therefore associated with automobile transportation. Estimates of toluene releases in Canada are summarized in Table 2.6 (CEPA, 1992).

Table 2.6

Estimates of Toluene Emissions in Canada

Source	% of Total
Industrial Processes - Solvents	51
Transportation - Light Duty	32
Transportation - Off Road	4
Transportation - Gasoline Market	3
Forest Fires	4
Other	6

It is expected that the proportion of toluene sources in and around Fort McMurray are somewhat similar to Table 2.6.

Indoor sources of toluene (Lagoudi and Loizidou, 1995; Phalen, 1984) include infiltration of automobile exhaust, vapors or gases from products that contain toluene (e.g. paints, fingernail polish, adhesives, lacquers, cleaners), and tobacco smoke. A study by Pleil (1985) found that overall toluene levels were generally higher in homes with attached garages or indoor storage of volatiles. Pleil (1985) also observed that toluene levels were generally higher in older homes versus new.

Yavick (1994) demonstrated that toluene is the active ingredient in the adhesive vapours associated with "glue sniffing". Stationary monitoring for toluene at a local site or even within a solvent abuser's home would not, in this case, be representative of personal exposure. Given the variety of potential exposure scenarios involving toluene, there is a real need to incorporate personal sampling into the assessment of human exposure to toluene.

2.2.3.3 Environmental Partitioning[1]

The log octanol-water partition co-efficient (K_{ow}) of toluene is 2.73, indicating that toluene will reach concentrations over 500 times higher in lipids of biological material than in water when toluene reaches equilibrium between these two phases. At room temperature, toluene has limited water solubility (S = 530 mg/L) and a vapour pressure (P_v) of 28.5 mmHg. Consistent with this, toluene readily partitions from water to air with a Henry's Law constant (K_w) of 6.6 x 10^{-3} atm-m^3/mole at 20°C. Photo-oxidation is the major degradation pathway for airborne toluene and the overall

[1] Physical Constants taken from the 1994 CRC Handbook of Chemistry and Physics

half-life of toluene is estimated to range between 4.5 hours to 10 days (CEPA, 1992). At the longer end of this half-life range, there is potential for toluene to travel considerable distances (hundreds of kilometers) from the emission source.

2.2.3.4 Health Effects

Because of the tendency for toluene to migrate to air, the primary routes of entry to the human receptor are dermal and inhalation. The potential adverse health effects of acute exposure to toluene target the central nervous system causing anesthetic or depression effects.

ATSDR (1994) summarized toxicity values for toluene that had been reported in the literature. Health concerns related to acute exposures to high ambient levels of toluene, in order of priority, are immunological and neurological effects. For example, noticeable increases in susceptibility to respiratory infections were reported to be found in mice after 3 hour exposures to 1ppm (26.5 $\mu g/m^3$) of toluene. Furthermore, toluene exposures at 100ppm (2650 $\mu g/m^3$) over 6 hours were found to cause noticeable increases in headaches and dizziness in human subjects. Consistent with neurological effects is the toxicological mechanism of toluene identified by Amdur et al. (1991b) as being similar to that of general anesthetics.

The documented impact of toluene on the central nervous system (CNS) may also be linked to the symptoms of tiredness, headache, and dizziness generally associated with "Sick Building Syndrome" (Stolwijk, 1991). Unfortunately, the distinction of SBS is that sources are rarely identified as the cause of the receptor

response, and concentrations of individual compounds are rarely as high as those used in experimental studies. Interestingly, Kjaergaard et al. (1991) demonstrated that VOCs, including toluene, work together in a synergistic manner to cause irritant and CNS-related health effects typical of SBS symptomatology.

The CEPA (1992) recommended Tolerable Daily Intake for toluene is 1.25 mg/kg/d. Considering CEPA (1994) guidelines, a personal air intake of 23 m^3 for a typical 70 kg person over 24 hours translates into an Average Total Daily Concentration of 3800 $\mu g/m^3$. In comparison, the Integrated Risk Information System (1995b) reference concentration (RfC) for inhalation of toluene is reported as 400 $\mu g/m^3$.

2.2.3.5 Previous Studies

In a draft document summarizing VOC levels in Edmonton between 1991 and 1993, Cheng et al. (1996) reported a median toluene concentration of 7.1 $\mu g\ m^3$ in the downtown core compared with a median industrial area reading of 4.6 $\mu g/m^3$. This is somewhat consistent with the literature outlined in Section 2.2.3.1 where auto exhausts associated with the city core would expectedly increase levels. The lower levels reported at the 17th Street Station seem to disassociate industrial emissions and toluene exposure; however this station is not in the prevailing downwind path from the bulk of industry in Edmonton.

Average concentrations of toluene at six urban sites across Canada measured between 1983 and 1989 (Dann, 1989) ranged from 5.2 to 44 $\mu g/m^3$ with a 24-hour

maxima of 150 $\mu g/m^3$. Although not particularly related to toluene, Dann et al. (1989) identified a consistent trend of total VOC concentration variation based on day of the week. Concentrations seemingly peaked at mid-week, reaching minimum levels by the weekend. This trend is indicative of a decrease in human activities, such as industrial emissions and work-related traffic, during the weekend. The finding shows the associations between VOCs and anthropogenic sources. In contrast to Canadian measures of toluene are American figures found in research by Singh et al. (1992) that range only from 0.1 to 24.5$\mu g/m^3$.

Seasonal variation of toluene reported by Kappos et al. (1994) in the community of Sarnia, Ontario were higher in the winter as compared to the summer. Unlike benzene, toluene concentrations were not positively correlated with wind direction, suggesting that petrochemical industrial emissions may not necessarily contribute to ambient toluene.

Sheff and Wadden (1993) inventoried a number of potential sources of VOCs in the Chicago area, performed predictive plume modeling and compared the results to actual downwind readings. In this case, sources of toluene and downwind exposures were shown to be correlated. For example, it was found that, "due to the large number of printing operations in the central area of the city, the 4-hour mean toluene concentration at the urban site was 9.6 $\mu g/m^3$ whereas the mean concentration at the suburban site was 6.7 $\mu g/m^3$."

As previously outlined, Michael et al. (1990) challenged conventional ambient measures as misrepresentations of actual personal exposures to VOCs. In their report, toluene differences between outdoor and indoor levels were the largest of all VOCs sampled. Toluene level distributions at the 75th percentile were reported as approximately 21 $\mu g/m^3$ for indoor levels, 9 $\mu g/m^3$ for outdoor measures taken at the residence, and 5 $\mu g/m^3$ for outdoor levels taken at the local sampling station. The difference between indoor and outdoor toluene levels was consistent with previous research discussed. However, the difference between centralized and residential outdoor measures introduced strong evidence linking toluene exposure to household sources. In other words, if wide spread regional dispersion of toluene was governing ambient toluene levels, the measures outside the home and at the monitoring station would be expected to be relatively similar.

Montgomery and Kalman (1989) measured concentrations of toluene inside and outside of 17 homes having no history of adverse health effects. The range of indoor toluene concentrations were reported as 4.5 to 360 $\mu g/m^3$ while median outdoor levels were measured at 14.5 $\mu g/m^3$. The large range of toluene concentrations found in this research was indicative of the variability of toluene exposures from one residence to another. In contrast to these results, Colome et al. (1994) reviewed results from an EPA TEAM study (Los Angeles) and observed that indoor toluene concentrations ranged from 1.1 to 36 $\mu g/m^3$ and outdoor toluene levels were somewhat lower at 0.1 to 14.6 $\mu g/m^3$.

De Bortoli et al. (1986) performed a similar study in Northern Italy where samples were taken simultaneously from indoor and outdoor environments at individual residences. The range of toluene concentrations measured indoors was reported as 17 to 380 $\mu g/m^3$ while the outdoor range of toluene was again lower at 3 to 160 $\mu g/m^3$. The mean indoor to outdoor ratio of toluene was calculated to be about 6:1. A summary of toluene concentrations cited in the literature discussed here is provided in Table 2.7.

Table 2.7

Summary of Reported Toluene Levels

Study	Indoor		Outdoor	
	$\mu g/m^3$	ppb	$\mu g/m^3$	ppb
Edmonton (Cheng)	-	-	4.6 - 7.1	17.3 - 26.7
Canadian (Dann, et al)	-	-	5.2 - 44.2	19.6 - 166
American (Singh)	-	-	1.2 - 128.6	4.5 - 484
Sarnia (Kappos, et al)	-	-	24.5	92.14
Chicago (Sheff/Wadden)	-	-	6.7 - 9.6	25.2 - 36.1
LA County (Michael)	21	79	5 - 9	19 - 34
No Symptom (Mont./Kal.)	45	170	14.5	55
Los Angeles (Colome, et al)	1.1 - 36	4.1 - 135	0.1 - 14.6	0.4 - 55
Italy (Bortoli, et al)	17 - 378	64 - 1420	3 - 156	11.3 - 587

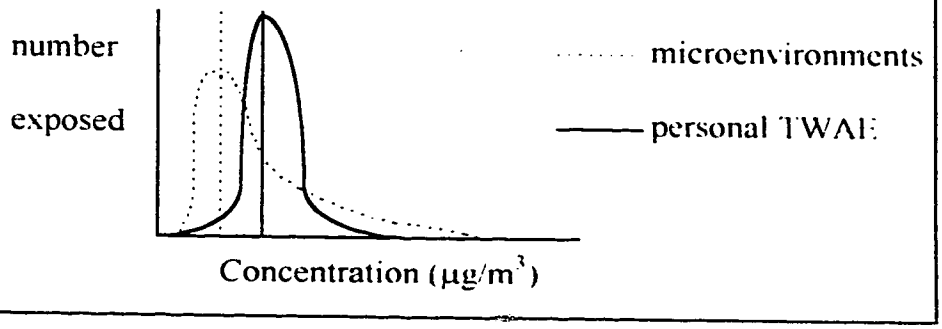
2.2.3.6 Predicted Range of Toluene Exposures

Plausible ranges for personal and ambient toluene exposures in an urban community have been estimated through a **qualitative ad hoc** amalgamation of the

literature data. The distribution of personal exposure concentrations is expected to be slightly skewed with a mode of about 20 μg m^3 having outliers measuring from 1 to 100 $\mu g/m^3$. The distribution of all probable microenvironmental concentrations (indoor and outdoor) is a wider and more skewed estimate ranging between 1 and 200 $\mu g/m^3$.

Figure 2.7

Distribution of Toluene Exposure



The range of all probable microenvironmental concentrations are indicated in Figure 2.7 as a dotted line distribution, while the range of expected personal time-weighted average exposures (TWAE) are shown as a solid line. The smaller standard deviation of the personal exposures reflect the fact that individuals are exposed to a variety of microenvironments at both high and low levels. It is expected that integrated personal sampling over 24 hours will average out extreme short-term exposures.

2.3 Passive Sampling

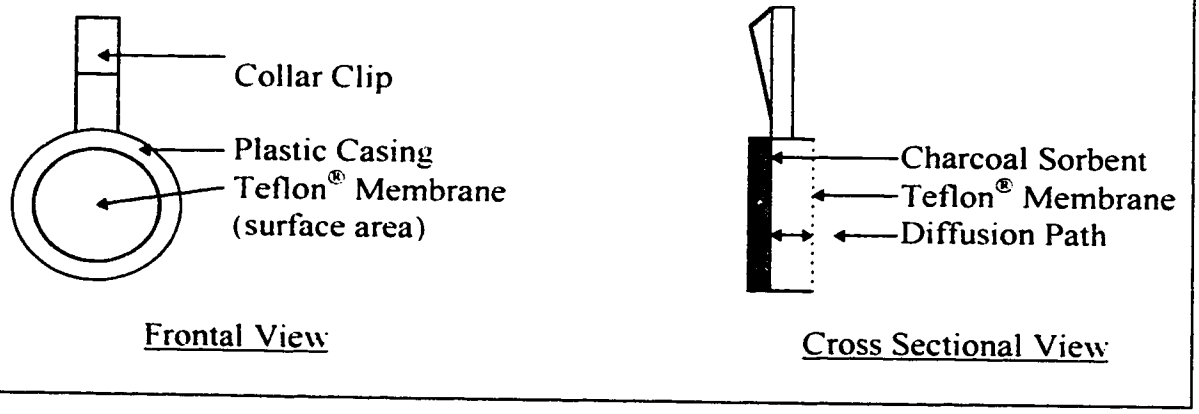
2.3.1 The OVM-3500

The 3M Brand Organic Vapour Monitor #3500 (3M, 1989) is an air sampling badge that can measure exposure to organic compounds either at a receptor or along an environmental pathway. For personal sampling the badge is worn near the breathing zone on a receptor's lapel or shirt collar, while ambient sampling protocol places the badge in open areas with sheltering from the elements if necessary.

The OVM-3500 (Figure 2.8) is made of a metal collar clip attached to a plastic "badge" containing an activated charcoal sorbent pad covered by a Teflon® shield. Contaminants enter the monitor by diffusion across the Teflon® membrane and become trapped by the carbon sorbent. After an allotted period of exposure, the badge is sealed and sent to the laboratory where contaminants are extracted from the

Figure 2.8

Sketch of the OVM-3500



charcoal sorbent with a solvent rinse. The solvent is analyzed to identify and quantify the contaminants collected. The mass of contaminant directly correlates with the average concentration in the air surrounding the badge during the sampling period.

3M have designed the OVM-3500 with a sorbent material, diffusion path, and surface area favorable for workplace ergonomics and standard laboratory analysis[1]. The badges are small, light, quiet, inexpensive, and easy to operate. These attributes have made the badge suitable for applications in domestic environmental sampling studies. Unfortunately, the amount of sample collected at industrial limits over an 8-hour shift is substantially higher than 24-hour samples at normal ambient levels. Consequently, the mass of contaminant provided by an environmental sample is often below the detection limit of conventional laboratory equipment.

Coutant and Scott (1982) found that 24-hour samples of ambient benzene taken by the OVM-3500 could be quantified if analysis included a photoionization detector system. Using mass spectrometry, Shields and Weschler (1987) studied the badge performance at ambient levels and observed that low-level sampling of VOCs remained linear over four week sampling durations. These studies demonstrated that the badge was useful for domestic studies provided that sample durations were between 1 and 30 days, and upgraded analysis was available. Shields and Weschler (1987) also concluded that the chance of contaminants oversaturating the badge within this time frame was remote under normal ambient VOC exposures.

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[1] There is no standard lab practice for badge analysis. The NIOSH Physical and Chemical Analytical Method 1501 for charcoal tube analysis may be adopted. This method recommends gas chromatography with flame ionization detection for analysis of the solvent used to desorb VOCs from charcoal sorbents

2.3.2 Sampling Rate

The theoretical relation between the mass of analyte collected by the charcoal sorbent and the time-weighted average exposure of the badge is based on Fick's First Law of Diffusion (Moore, 1987):

$$\mathbf{F = D \ (d c / d l)} \qquad \textbf{(Eq. 2.3)}$$

where,
F = diffusive flux ($g / cm^2 \ s$)
D = diffusion coefficient (cm^2 / s)
$d c \cong \Delta c$, external concentration (g/cm^3) - concentration at interface (assumed as 0 g/cm^3)
$d l \cong \Delta l$, length of diffusion path (cm)

Equation 2.3 was restated by Shields and Weschler (1987) as:

$$\mathbf{m / (t \ C_a) = D \ (A / l)} \qquad \textbf{(Eq. 2.4)}$$

where,
$m / (t \ C_a)$ = badge sampling rate (cm^3/s)
m = mass of substance that diffuses (μg)
t = sampling interval (s)
C_a = ambient concentration of substance ($\mu g/cm^3$)
D = diffusion coefficient(cm^2/s)
A = cross-sectional area through which diffusion occurs (cm^2: OVM = $7.07 cm^2$)
l = path over which diffusion occurs (cm: OVM = 1cm)

Although sampling rates are best tested under controlled laboratory conditions, theoretical estimates of the diffusion coefficient may be calculated from the Hirschfelder Equation outlined in Appendix 2.1. Using this equation, the diffusion coefficient for benzene and toluene is calculated to be 0.0947 and 0.0827 cm^2/s respectively (3M, 1992). With this, a theoretical sampling rate for benzene and toluene onto the OVM-3500 was calculated using Equation 2.4.

Table 2.8

Theoretical Sample Rates

Compound	Air Sample Rate (mL/min)	Air Sample Rate (L/24hrs)
Benzene	40.2	57.8
Toluene	35.1	50.5

2.3.3 Sources of Sampling Bias

The activated charcoal badge sorbent collects VOCs from the air through chemical and physical adsorption processes. The pore surfaces of the charcoal are non-polar, facilitating the adsorption of organics. Inherent limitations in the badge design such as sampler efficiency, and fluctuations in environmental conditions such as temperature, relative humidity, face velocity, and changing VOC concentrations may affect the adsorption of VOCs onto the carbon.

2.3.3.1 Temperature

The Hirschfelder equation suggests that a decrease in temperature lowers the diffusion coefficient and thus, sampling rate. Accordingly, 3M (1993) stated that a +1% adjustment of calculated TWAE is required for every 6°C below 24°C monitoring conditions. However, Cheremisinoff and Ellerbusch (1978) have pointed out that cold temperatures increase the adsorption efficiency of the carbon. From this observation it is conceivable that the badge sampling rate may be enhanced by lower

temperatures because of increased adsorption efficiency, depending on the relative magnitude of the temperature effects on the diffusion coefficient.

2.3.3.2 Relative Humidity

Adsorption sites on the sorbent pad may become saturated with water at extreme humidity. Compounding this problem is the limited ability of benzene and toluene to diffuse across a water layer. Graham and Ramaratnam (1993) found that the adsorption capacity of carbon diminished significantly as the relative humidity of air exceeded 50%

2.3.3.3 Transient Exposures

Sampling bias due to transient exposure has been shown to be a problem with measurements taken by some passive samplers. For example, Hearl and Manning (1980) observed that TWA readings from an NO_x badge varied when under fluctuating conditions versus steady state. In contrast, Hori and Tanaka (1993) studied an **organic vapour** badge and found that there were no differences between the TWA values taken under transient versus steady state conditions.

2.3.3.4 Sampler Efficiency

Assuming that VOCs readily diffuse into the charcoal sorbent of the 3M badge, it is logical that varied amounts may also diffuse outward. The ability of the badge to retain the adsorbed compounds is the sampling efficiency. The efficiency of a passive dosimeter depends on the adsorption isotherm of the sorbent. Underhill (1984) observed that the adsorption isotherm for activated carbon was consistent with

high sampling efficiency and that retention of adsorbate was maintained until the charcoal binding sites were approximately 90% saturated. This infers that the OVM-3500 efficiency would be reliable to a point of oversaturation.

2.3.3.5 Face Velocity

3M validations (1991) of the OVM-3500 found that the minimum face velocity required to register accurate[1] results was 0.127 meters per second (m/s). Mark, et al. (1990) found that OVM-3500 sampling rates for toluene did not vary more than 10% at face velocities between 1 to 12 m/s. Research by Otson and Fellin (1991) supported this: the authors observed a less than 10% change in sampling rate for both benzene and toluene at velocities between 0.01 to 1.8 m/s. Lastly, a study by Mailahn et al. (1989) successfully incorporated the use of the 3M badge to monitor tracer compounds for measuring ventilation rates in an indoor environment. An estimate of the range of face velocities expected in a typical community are between a minimum indoor velocity of 0.15 m/s (ASHRAE, 1981) and a 2.8 m/s (10 kph) outdoor wind speed.

2.3.4 Previous Validation Studies

2.3.4.1 Occupational Concentrations

In a chronological review of passive sampling, Moore (1987) discovered that applications of the 3M Organic Vapour Monitor began in the early 1970's as one of the first commercially available passive samplers. In the 1980's, research institutions

[1] Accurate refers to the +/- 25% NIOSH guideline

such as NIOSH published validation protocols (Busch, 1981) to help occupational hygienists evaluate badge performance.

3M researchers, Anders and Mullins (1981) compared readings taken by the OVM badge and charcoal tubes at known contaminant levels. Methodology included generation of known contaminant concentrations via syringe delivery into a calibrated dry air stream. The lowest concentrations of benzene and toluene were 3 and 15 mg/m^3 respectively with sample durations ranging between 1 and 8 hours. From this, 3M calculated the sampling rate for benzene and toluene to be 35.5 ± 0.6 and 31.4 ± 0.6 mL/min respectively. These rates have been maintained over 15 years and were published in the 1993 OVM-3500 Sample and Analysis Guide (3M, 1993).

Rose and Perkins (1982) reviewed general concepts of passive sampling and critiqued existing research on different brands of passive samplers, including the 1981 report by Anders and Mullins. The authors commented that although the 3M investigators cited excellent precision and accuracy for the badge, raw data was not provided and conclusions were based on small sample sizes.

Stockton and Underhill (1985) performed field evaluations of the 3M badge in an industrial setting containing benzene, toluene, and xylene. In their study, passive samplers were co-located in the workplace with charcoal tube/pump samplers. Results of the two methods were statistically compared through ANOVA and it was found that the OVM-3500 provided results which did not exhibit a statistically significant difference from the charcoal tubes.

Purdham et al. (1994) compared measures of gasoline vapour taken simultaneously by charcoal tube and OVM badge. Results of comparisons under controlled laboratory exposures were highly correlated ($R^2 = 0.99$) but results from field trials showed greater variability. Testing under a variety of conditions showed that temperature, humidity, and concentration of the gas vapour had no effect on the sampling rate of the OVM-3500.

2.3.4.2 Ambient Concentrations

Coutant and Scott (1982) published an evaluation of the 3M badge at ambient concentrations. Their initial analyses after 24-hour exposures proved futile with standard equipment using gas chromatography-flame ionization detection. By using a photoionization detector the study obtained required detection limits for benzene. Unfortunately, the high sensitivity detection also quantified previously undetected background contamination which led to more complicated sample interpretations.

Geuskens et al. (1990) performed a complete validation of the OVM-3500 for environmental monitoring of styrene. The evaluation included controlled chamber tests in the laboratory and field trials using SKC jumbo charcoal tubes as a reference value. The authors concluded that the OVM-3500 was a useful alternative to active sampling. They recommended however, that the uptake rate of the monitor be verified before any ambient survey because of possible deviations greater than 15% from the value supplied by the manufacturer.

Further evaluation of the 3M badge for use in ambient air was initiated by Health Canada (Otson, 1990) and Bovar Environmental laboratories in Toronto. In their studies, the badge demonstrated to be reliable over a range of VOC concentrations as low as 1 $\mu g/m^3$ at sampling durations of 24 hours. The sampler results not only correlated well with active samplers ($r > 0.95$) but also exceeded the ± 5 to 14% precision of the active sampler with a range of ± 7 to 10%. The findings eventually led to applications of the OVM-3500 in a large research project (Otson et al., 1992) measuring indoor levels of VOCs across Canada.

Validation of the OVM-3500 sampling rates has been performed with the use of an advanced exposure chamber design referred to as TAGS (Fellin, 1989) or Test Atmosphere Generating System. Unlike the 1981 3M exposure chamber tests, this evaluation included 24-hour exposures at ambient concentrations and was based on over 90 samples. The exposure chamber experiments found that the OVM-3500 air sampling rate for benzene was 38.6 ± 3.2 mL/min and 33.5 ± 3.6 mL/min for toluene (Fellin, 1990). These rate estimates were based on the assumption that the permeation tubes, used to generate known VOC concentrations, were accurate. An interesting observation in the research was that there was no significant change in the OVM-3500 sampling rate for samples taken at 24°C versus samples taken at 10°C. The sensitivity of the mass spectrometry (selected ion monitoring mode) detection identified variable background readings on the badge (Personal communication, Otson, 1995). Moreover, disclosure of these findings to 3M apparently succeeded in improving

quality control conditions at 3M during manufacturing in an effort to minimize the sample background contamination.

2.3.5 3M Recommended Sampling Procedures

The manufacturer's recommended method for handling and storage of the OVM-3500 badge is transcribed onto Table 2.9.

Table 2.9

1. The monitor and closure cap are packaged in an aluminum can. The original shipping carton can be used to send exposed monitors to a laboratory for analysis.
2. Remove the plastic can lid. Open the can by pulling up on the ring tab.
3. Remove the monitor from the can.
4. Before monitoring, record the following information in your data log or on a plastic can lid: monitor serial number, sampling date, employee or area ID, temperature and relative humidity, compounds to be analyzed.
5. Record start time on back label of the monitor. Move to Step 6 IMMEDIATELY.
6. Attach monitor to employee as near to the breathing zone as possible. DO NOT REMOVE WHITE FILM AND PLASTIC RING.
7. After sampling period has ended, remove plastic ring and white film. Move to Step 8 IMMEDIATELY.
8. Snap closure cap firmly onto monitor body. Be sure the two port plugs are firmly seated. SAMPLING IS NOW TERMINATED.
9. Record END TIME on back label of the monitor and on your data log.
10. Return monitor to can and seal with plastic lid provided. Send to laboratory for analysis. KEEP MONITORS IN AREA FREE OF ORGANICS.

2.4 Reference Methods

2.4.1 Pump-Charcoal Tube

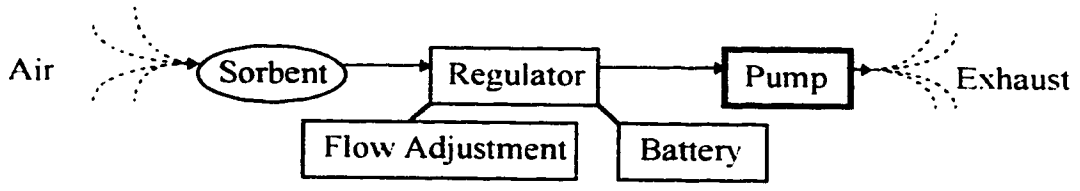
2.4.1.1 Methodology

The pump-tube method has been a long-standing recognized sampling practice in both occupational and environmental health disciplines. In fact, NIOSH (1984) has standardized this approach for sampling in the workplace for over twenty years. Early work by Wallace and Ott (1982) pointed out that the U.S. Environmental Protection Agency used this technology in many of their TEAM studies, including the first which took place prior to 1981.

The design of the method is simple. A consistent and controlled vacuum is generated through the use of a pump which pulls measured amounts of air through a sorbent. A revised schematic from Parmeggiani (1983) is provided in Figure 2.9.

Figure 2.9

Schematic of Active Sampling



The assumption is that the sorbent effectively "cleans" the air being pulled through the system. Given a known volume of air drawn by the pump, a known mass of contaminant collected on the sorbent, and a sample duration, a simple calculation

produces a time-weighted average concentration expressed through Equation 2.5.

$$TWA = [M / SR \times t] / 10^{6} \quad \textbf{(Eq. 2.5)}$$

where,
TWA = Time-weighted average exposure concentration ($\mu g.m^{3}$)
M = Mass of analyte collected (μg)
SR = Air sampling rate (mL/min)
t = time (min)

NIOSH Method #1501 (1984) prescribes active sampling with solid sorbent tubes for the collection of benzene and toluene. The recommended flow rate for active sampling is ≤ 200 mL/minute and the sorbent medium required for collection is granular coconut shell charcoal with 100mg front and 50mg back sections. An evaluation of the pump/tube method for measuring benzene and toluene at **occupational levels** was also provided by NIOSH (1984). Protocol for analysis included a carbon disulfide rinse and solvent analysis by gas chromatography-flame ionization detection. The reported bias for sampling benzene was 0.8% while toluene bias was somewhat higher at 3.8%; the reported precisions (S_r) for benzene and toluene were 0.059 and 0.052 respectively.

2.4.1.2 Applications in the Study

A Du Pont Alpha-1 (Amatek Inc., Largo, Florida) air sampling pump and SKC 226-01 (SKC Inc., Eighty-four, Pennsylvania) certified coconut charcoal sorbent tube were the reference tools used for comparison against the OVM-3500 passive sampler. The Alpha-1 pump is an advanced electronically programmable air sampler. Sampler flow rate capacity ranged between 5 to 5,000mL/min with company documented

validations stating ± 5% accuracy. A feature of the pump was the feedback control system which monitors flow through the pump mechanism and automatically adjusts pump speed. This control system ensured constant flow rate regardless of load variation or other factors such as physical blockage that would otherwise impair flow.

In accordance with the NIOSH Method 1501 (1984), the pump was calibrated to a flow rate of approximately 200 mL/min. Calibration of pump flow was performed with a 100 mL bubble flow meter and stop watch. To minimize bias resulting from pump adjustments, all physical modifications of pump settings were followed by a 30 minute run of the pump prior to calibration. The flow rates were based on the average time taken to displace 100 mL from the bubble flow meter over five attempts; in addition, all measurements were corrected to standard temperature and pressure. Calculations were based on the equation:

$$MF = [60 (V / t)] \bullet [(P - P_v) / 760] \bullet [298 / (273 + T)] \qquad \textbf{(Eq. 2.6)}$$

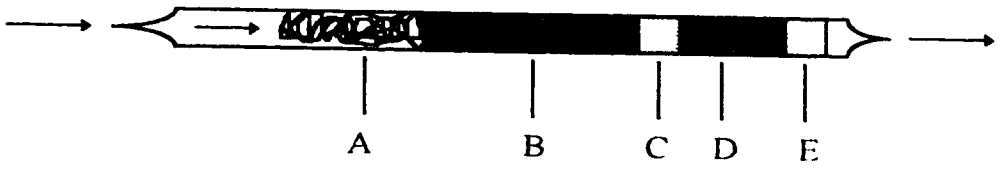
where,
MF = Mass flow (mL/min)
V = Volume displaced in the bubble flow meter
t = Time to displace V (s)
P = Atmospheric pressure (mmHg)
P_v = Vapour pressure of water (mmHg) at T
T = temperature of gas

The SKC 226-01 charcoal tube measured 70 mm long and 6 mm in diameter and was composed of five separate sections, as illustrated in Figure 2.10. Section A was glass wool placed at the front of the tube as an inert yet passive barrier to contain the sorbent material in Section B. Section B held 100 mg of charcoal that was

analyzed by gas chromatography and reported as a mass of contaminant for use in equation 2.5. The air passed through Section C, a small piece of plastic mesh, and

Figure 2.10

Diagram of SKC-226-01



then through Section D. This "back" or "breakthrough" part of the tube contained 50 mg of activated charcoal was also analyzed to ensure that the front charcoal section had not become overloaded. Section E was another small piece of plastic mesh, which like the glass wool, functioned to keep the sorbent in place.

2.4.1.3 NIOSH Method 1501 Sampling Procedures

The NIOSH recommended method for handling and storage of the charcoal tubes is transcribed onto Table 2.10.

Table 2.10

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 30 L for benzene and 8 L for toluene.
4. Cap the samplers with plastic (not rubber) caps and pack for shipment.

2.4.2 Summa® Canister

2.4.2.1 Methodology

The use of stainless steel canisters has evolved into one of the primary methods of sampling VOCs from ambient air. McClenny and Paur (1987) found that custom made containers were used in the early 1970's for whole air collection of VOCs. Today, canisters are available commercially with applications in ambient air studies such as Gholson et al. (1989) and Samaras and Dombro (1991); and also in widespread federal air monitoring networks such as the EPA's Toxic Air Monitoring System or TAMS (Evans, 1992).

Summa® canisters are spherical stainless steel containers with a specially electropolished[1] interior surface to prevent decomposition of collected organic compounds (Keith, 1991). A schematic of a typical ambient air monitoring station Summa® canister system is provided in Figure 2.11; the configuration includes a timer, intake manifold, pump, flow controller, and solenoid valve.

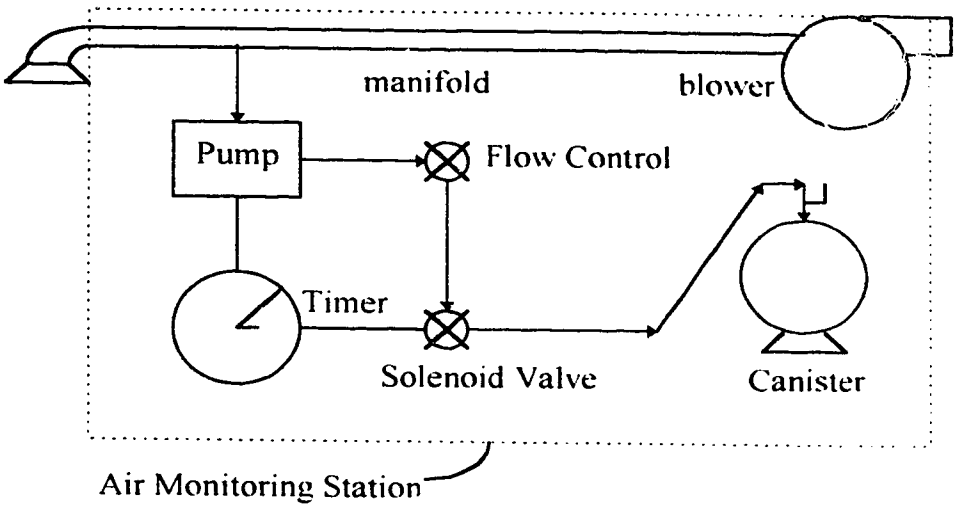
The U.S. EPA (1988) recognizes two canister configurations, subatmospheric and pressurized, in their compendium methods for ambient air quality monitoring. The first method uses subatmospheric canisters that initially sample at an internal pressure of 0.05 mmHg with air drawn inward by the pressure differential. The flow rate is accurately controlled through a critical orifice until internal pressures reach about 700 mmHg. The second method, as shown in Figure 2.11, is a pressurized

[1] Summa® canisters have an internal coating of pure chrome-nickel oxide.

sampling system which is used for longer-term or higher volume samples. This arrangement involves the use of a pump and flow control to reach final canister pressures of about 1100 mmHg.

Figure 2.11

Air Monitoring Station Configuration



2.4.2.2 Applications in the Study

The 17th Street Air Monitoring Station[1] was selected as the site for outdoor co-location of the OVM-3500. The site has a mobile trailer unit located in an open field with oil refineries, chemical plants, and various manufacturers located within a two kilometer radius. Air is brought into the station via glass manifold where lines from nine separate air monitoring instruments feed. The parameters monitored at the station include: coefficient of haze, hydrogen sulfide, sulfur dioxide, carbon

[1] 17th St. / 105 Ave., Edmonton, Alberta

monoxide, total hydrocarbons, ground level ozone, nitrous oxides, VOCs, and high volume particulate.

Volatile organic compound samples are collected over a twenty-four hour sampling period (midnight to midnight) every six days. Detailed method documentation for the 17th Street station is described in Cheng et al. (1996). In summary, integrated ambient air samples were collected in a pressurized type 6 L Summa® canister at a sample flow of 15 mL/min. Upon initiation of the sample, canister pressure and station temperature were recorded, and the electronic timer was set. At the end of the sampling period, time of day, elapsed time, canister pressure, and range of station temperatures were recorded.

The Summa® canister samples from the 17th Street Station collected in this study were delivered to the River Road Environmental Technology Centre in Ottawa for analysis. Dann and Wang (1992) describe the analytical method as gas chromatography with flame ionization and mass spectrometry detection using a cryogenic preconcentration technique. Typical method detection limits were 0.1 $\mu g/m^3$ for the analysis with precision ranging from 10 to 15%. Relative accuracy of the method was estimated to be ± 5% based on EPA (1988) TO-14 method of direct injection of VOC standards.

Chapter Three: The Experiments

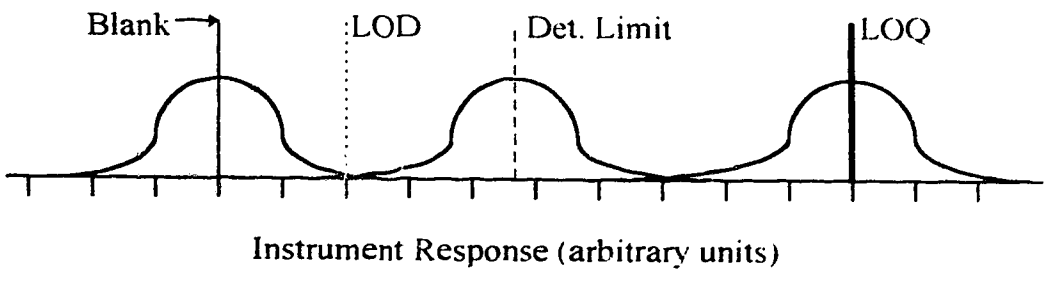
3.1 Sample Analysis

3.1.1 Analytical Equipment Selection

Unlike the codified Summa® canister analyses, there were no previously established or recognized methods for analyzing samples taken by the OVM-3500 or SKC 226-01 charcoal tube at ambient levels. Accordingly, detection and integration capabilities of available analytical equipment dictated the mass of benzene and toluene that had to be collected by each sampler in order to attain confident results.

Figure 3.1 illustrates the concept of confidence in analyte interpretation. Kennedy et al. (1995) stated that the *minimum limit of detection* or LOD is the lowest concentration injected that can be determined to be statistically different from a blank at 95% confidence (2 standard deviations from blank mean). A *reliable detection limit* signal is a peak integration at 4.66 times the standard deviation (4.66σ) of the blank response; at this level, the chance of the peak being a false positive is ≤1%. The *limit of quantitation* is an analytical signal that is 10σ of the blank distribution and is the level considered reliable for quantitative comparisons.

Figure 3.1
Illustration of Analytical Confidence



Estimates of the amount of benzene and toluene expected to be collected by the badge were made by combining the OVM-3500 sample rate (3M, 1993) with predicted VOC levels outlined in Sections 2.2.2.6 and 2.2.3.6. Sampling rates (3M, 1993) were converted to daily sample rates of 51.12 and 45.22 liters per 24 hours for benzene and toluene respectfully. Back calculations were performed to determine the mass of VOC to be injected onto analytical equipment. For example 1 $\mu g/m^3$ of airborne benzene sampled at 51.12 L/day equates to 51 ng collected on the sampler. 2mL of CS_2 solvent is added to the sampler to desorb the 51 ng of benzene, of which 10µL is injected onto the analytical equipment which would carry 0.26 ng of benzene. Table 3.1 provides an impression of the range of sensitivity required for analysis.

Table 3.1

Analyte Mass and Injection Concentration

Ambient Levels (µg/m3)	Collected Contaminant (ng)	GC Injection (ng/10µL)
Benzene		
1	50	0.26
10	510	2.56
100	5110	25.6
Toluene		
1	50	0.23
10	450	2.25
200	9040	45.2

The most practical analytical equipment for measuring VOCs at these levels was determined to be either gas chromatography (GC) with flame ionization (FID) and photoionization detection (PID), or GC-mass spectrometer (MS) with selected ion

monitoring (SIM). Ogle et al. (1993) reviewed results obtained with different detectors for volatile organic compound analysis and found that flame ionization detectors could measure some organics to 1 ng and that photoionization detection may, in some cases, measure down to 2 pg. Ogle et al. (1993) determined that the outstanding disadvantage of the GC-FID-PID system was its lack of specificity for detecting a given compound within a heterogeneous sample matrix. Given the potential inconsistency of air in Fort McMurray, there would be a clear disadvantage in using analytical systems that had trouble distinguishing compounds.

Mass spectrometer detection working in selected ion monitoring mode was the preferred choice for analyzing the badge samples. Ogle et al. (1993) commented that GC-MS (SIM) could distinguish between co-eluting compounds. Although the sensitivity of the system is purported by Ogle et al. (1993) to decrease with the number of ions monitored, the narrow scope of this research was not seen to be a risk to the sensitivity of the instrument. In addition, Health Canada and Bovar Environmental had been using GC-MS (SIM) in all of their ongoing applications of the OVM-3500 (Otson, 1995). Consequently, mirroring these methods was judged as an opportunity to enable results from both studies to be compared in common interest.

3.1.2 3M Recommended Analytical Procedures

Table 3.2 is a transcription of the recommended analytical technique provided by 3M (1993) for samples taken at **occupational** concentrations. Note that 3M recommends a maximum storage time of 4 weeks after sampling.

Table 3.2

1. Ensure that codes on resealable package match the sampler.
2. Ensure cap has been firmly attached to sampler.
3. Ensure closure plugs on the cap have not dislodged.
4. Open the center port and add 1.5 mL of carbon disulfide.
5. Reseal both ports and let monitor stand for 1/2 hour with occasional agitation.
6. Reopen both ports.
7. Insert decanting spout in rim port and transfer liquid to a sampler vial used with the automatic sampler on the gas chromatography unit.
8. Perform gas chromatography analysis to determine mass of contaminant desorbed from the sample medium.
9. The corrected weight of the contaminant is obtained by subtracting the weight measured on the blank.

3M also provided a general discussion for determining recovery coefficient of the badge by adding a known weight of contaminant onto the dosimeter and measuring the weight of the contaminant extracted with the CS_2. In this study, the recovery coefficient was expressed as a percent recovery and calculated by dividing the recovered weight by the known weight imparted onto the badge. The reported recoveries by 3M for the VOCs of interests were 1.02 (102%) for benzene and 1.05 (105%) for toluene. 3M also made clear however, that desorption efficiencies should be determined by each individual laboratory.

3.1.3 Quality Assurance and Control

In preliminary quality assurance trials, residual benzene was found in Anachemia Scientific analytical grade carbon disulfide. A higher grade desorbing

solution was prepared by acid washing the CS_2 with concentrated acid[1] solutions. This procedure was reviewed with the laboratory (Serbin, 1995) and it was agreed that the nitric acid would combine with the majority of the residual benzene in CS_2 to become nitrobenzene - effectively removing this residual contamination.

Internal deuterated benzene (benzene d6) and toluene (toluene d8) standards were also added to the CS_2 at concentrations of 3 µg/mL. This concentration was lowered to 1 µg/mL after the first set of analyses because of an unwanted addition of residual benzene from the deuterated benzene solution. These solutions were used for desorption of all samples, spikes, desorption efficiency tests and calibration solutions.

After standards and acids were adjusted, the CS_2 desorbing solution was analyzed in triplicate to determine benzene and toluene background levels. Although the acid washed CS_2 did not show detectable amounts of benzene or toluene, the desorbing solution did show levels of approximately 0.05 µg/mL benzene from undeuterated benzene in the deuterated benzene d6. Toluene was not detected in the desorbing solution to a level of 0.01 µg/mL. All resulting analyses were internally corrected for this background before proceeding with any calculations.

Background contamination on the charcoal sorbent in the passive badge and charcoal tube was evaluated along with a determination of sampler desorption efficiency. Each sampler was tested under various conditions and independent judgments were made regarding each compound sampled. All work orders for

[1] Approximately 25mL of concentrated nitric/sulfuric acid per liter of carbon disulfide

Enviro•Test data are included in Appendix 3.1 and Table 3.3 is provided as a summary of the following discussion.

Table 3.3

Blanks and Desorption Efficiencies

Parameter	Averaged Blank (ng)	Desorption Efficiency (%) ~5µg/m^3	~20µg/m^3	~40µg/m^3
Benzene (badge)	40	90	100	102
Toluene (badge)	200	85	95	100
Benzene (tube)	70	120	105	102
Toluene (tube)	30	95	107	107

3.1.3.1 Badge Blanks

Analytical results for 6 blank badges are presented in Enviro•Test work order #E510634 (Appendix 3.1). Blank badges were disassembled at the lab, charcoal sorbents placed in vials with 2.0 mL of CS_2, shaken for 30 minutes and analyzed by GC-MS(SIM). Assuming zero for non-detect values, the mean solvent corrected benzene background for the 6 badges was 60 ng while the mean solvent corrected toluene background was 340 ng.

An additional six samples were submitted to the laboratory, all of which had been exposed to "zero air" in the exposure chamber over 24 hours. The results of the blank chamber runs are reported in Enviro•Test work order #H2515 (Appendix 3.1) as sample numbers, LO02338C, LO02525C, LO02347C, LO02329C, LO02528 and

LO02328C. The mean benzene value for these six sample results was 43 ng while the mean toluene value was 205 ng. It was decided that the chamber badges were more reflective of the net contribution of badge contamination, thus benzene and toluene backgrounds were taken as 40 ng and 200 ng respectively for the study

3.1.3.2 Badge Desorption Efficiency

As stated, 3M (1993) reported that the OVM-3500 desorption efficiency was 1.02 for benzene and 1.05 for toluene. This study recognized that one general sampler efficiency number would not be representative when extracting extremely low levels of VOC adsorbate because residuals remaining on the activated charcoal would be proportionately higher. As a result, desorption efficiencies were determined at loadings of 17 600, 2 540, and 250 ng of benzene and toluene. These spikes were injected directly onto charcoal sorbent pads that had been removed from the badge. The pads were then rinsed with CS_2, analyzed and evaluated based on conformity with the spiked amount.

Similar evaluations were processed for spikes of 725, and 290 ng of benzene and 4,520 and 1,810 ng of toluene that were injected onto the sorbent pads while still inside the badge. Results are presented in Appendix 3.1, in work order #E510634. For the purposes of this research, badge loadings of 17 600 ng of either VOC were not expected to be of practical use for interpretation of badge results. The 250 and 290 ng spikes were considered for low level benzene exposures; 92.2% and 97.5% recovery was achieved at 250 ng but only 69% was retrieved at 290 ng. From this it was

assumed that the 69% recovery, from the spiked badge, was an outlier and a conservative assumption for low level benzene recovery was 90%. The 250 ng injections of toluene averaged 84.6% recovery and was assumed as 85% recovery.

The 725 ng spikes of benzene that were performed by the lab were considered to be representative of "mid-level" benzene exposures. The average percent recovery of the 2 samples inoculated at this level was reported as 100% and was assumed as such in this study. An oversight in the QA/QC design caused "mid level" toluene levels to be missed and were therefore assumed as an approximate value between the high level and low level spike recoveries. From this logic, the mid level toluene desorption efficiency was assumed to be 95%.

The mean of the two benzene desorption efficiencies at 2,540 ng injections was reported at 103.7%, however the 3M desorption efficiency of 102% was considered to be a maximum value indicative of analyte loadings at workplace levels. Therefore, 102% was designated as the desorption efficiency for high level benzene exposures. Toluene, on the other hand, had a mean desorption efficiency of 97% which was also compared to the 3M figure of 105%. From this it was decided that 100% would be an appropriate assumption for toluene desorption efficiency at high ambient exposures.

3.1.3.3 Tube Blanks

Analytical results for blank tubes are presented in Appendix 3.1 of Enviro•Test work order #E510634. Two blank charcoal tubes were analyzed during

the QA/QC analyses. The solvent corrected level of benzene reported to be found on the tubes ranged from 40 ng to 110 ng with a reported mean of 70 ng. Considering not only the variation between these two numbers but also the high level of benzene in the CS_2 during this preliminary study, confidence in this figure was low. However, it was decided to use 70 ng as the blank value for all tube corrections and that subsequent interpretations would factor in this uncertainty. Conversely, variable toluene contamination in the CS_2 solvent was not a problem and charcoal tube contaminant levels were measured at 20 ng and 40 ng. Although these results were below confident detection limits, a 30 ng toluene background was assumed.

3.1.3.4 Tube Desorption Efficiencies

Loadings of 17 600, 2 540, and 250 ng of benzene and toluene were injected onto charcoal tube sorbents that had been removed from the glass tubing. In addition, 750 ng of benzene and 4,520ng of toluene were injected directly onto charcoal sorbents that remained inside the tubes. All charcoal was rinsed with 2mL of CS_2 and analyzed via GC-MS(SIM). Results are presented in Appendix 3.1 in Enviro•Test work order #E510634.

For the purposes of this research, tube loadings of 17,600 ng of either VOC were expected to be higher than would be of practical use for interpretations. The 250 ng injections were considered for low level benzene exposures. 147% and 97.3% recoveries were achieved at 250 ng and although variability was high, the assumed desorption efficiency for low level benzene was set at 120%. The 250 ng injections of

toluene averaged at 94.3% recovery and thus the assumed toluene recovery was rounded up to 95%.

The 725 ng spikes of benzene that were performed by the lab were considered to be representative of "mid-level" benzene exposures. The mean desorption efficiency of 9 samples inoculated at this level was reported as 103.9% and was rounded to 105% for the study. Two tubes were spiked with 420 ng of toluene by the lab (work order #E511215) and produced a mean desorption efficiency of 107.8%. From this, it was determined that 107% would be assumed for the "mid level" toluene exposure badge interpretations.

The two benzene and toluene desorption efficiencies reported at 2,540 ng injections were 98% and 94.5% for benzene and 87.9% and 94.3% for toluene. In addition to these figures, lab report #E601028 (Appendix 3.1) documented desorption efficiencies for benzene at 106%, 110%, and 108% and for toluene at 115%, 117%, and 117%. Although spike levels were not reported by the laboratory, a comparison of peak areas indicated that spikes were indicative of high benzene and toluene exposures. The mean of the recovery efficiencies for benzene was 103%, and 102% was assumed as an appropriate representation of the results. The mean recovery efficiencies for toluene was 106%; considering that 107% was determined for the mid level exposure levels, it was decided that 107% would be an appropriate figure for the high l[illegible] interpretations as well.

3.1.4 Sample Analysis

After being stored for up to two weeks at -15°C, batches of samples were brought into Enviro•Test Laboratories, 9936-67 Avenue, Edmonton. Upon delivery, a chain of custody form was documented to confirm that the samples had been relinquished. Samples were then stored for no more than one week and processed as per the following procedures developed by Serbin (1995).

OVM-3500 charcoal sorbent pads, and front and back charcoal sections from the SKC 226-01 charcoal tubes were removed from their casing and placed in separate 4 mL glass vials. 2.0 mL of the acid modified carbon disulfide desorption solution were added and the vials were shaken for a minimum of thirty minutes with a Thermolyne Maxi-Mix 3, Type 65A00. The solvent was then drained from the sampling matrix and injected (10μL) onto a gas chromatogram. The GC carrier gas was extra dry high purity helium and the GC column was a 30 meter, HP-INNO-WAX (Hewlett Packard, Edmonton), with a diameter of 0.32 mm and a film thickness of 0.5 μm. Detection of the analytes was through mass spectrometry (HP 5890-5970 MSD with multiplier 5972) operating in selected ion mode monitoring for deuterated and undeuterated benzene and toluene.

The deuterated compounds acted as sample specific and analyte specific internal standards but did not interfere with the GC/MS analysis. The ions monitored were the benzene quantitation 51 ion[2], benzene deuterated 54 ion, toluene quantitation

[2]The benzene 78 ion was the most abundant but too close to CS_2 76 ion

92 ion, and toluene deuterated 100 ion. Calibration solutions were prepared at levels of 0.1, 1.0, and 10 µg/mL for each analyte in CS_2 desorbing solution. Each set of calibration solutions was analyzed before and after each set of samples at a frequency of fifteen analyses or less.

Separate detection limits were determined for the QA/QC sample submission (#E510634) and the remaining four sets of samples submitted to the lab. The first submission of samples was processed on newly purchased laboratory equipment that had not yet been tuned to the needs of the study, and the CS_2 solvent rinse was higher in benzene contamination for the first run versus the remaining four. For both calculations of detection limits, low level solutions of the analytes were prepared in deuterated CS_2 at levels close to instrument noise.

Detection limits for the initial set of samples (#E510634):

Benzene MDL at 2σ = 100ng	Toluene MDL at 2σ = 20ng
Benzene RDL at 4.66σ = 210ng	Toluene RDL at 4.66σ = 30ng
Benzene LOQ at 10σ = 450ng	Toluene LOQ at 10σ = 70ng

Detection limits for the remaining samples (#E511529):

Benzene MDL at 2σ = 8ng	Toluene MDL at 2σ = 14ng
Benzene RDL at 4.66σ = 19ng	Toluene RDL at 4.66σ = 33ng
Benzene LOQ at 10σ = 41ng	Toluene LOQ at 10σ = 70ng

The laboratory recalculated the second set of detection limits after they had made appropriate changes such as replacing a standard DB column with a wax column for increased resolution between chromatogram peak. All reports other than the initial work order assumed a conservative limit of quantitation of 100ng for both benzene and toluene.

3.2 Phase One: Exposure Chamber

3.2.1 Purpose

The first evaluations of the OVM-3500 were conducted in an exposure chamber under controlled laboratory conditions with two variable parameters: temperature and contaminant concentration. Other factors such as face velocity, transient exposure, humidity, pressure, and interaction with other VOCs were either eliminated or kept constant. There were two objectives to Phase 1:

1. Evaluate the effect of temperature on the sampling rate of the OVM-3500; and
2. Compare OVM-3500 and SKC 226-01 charcoal tube results.

3.2.2 Apparatus

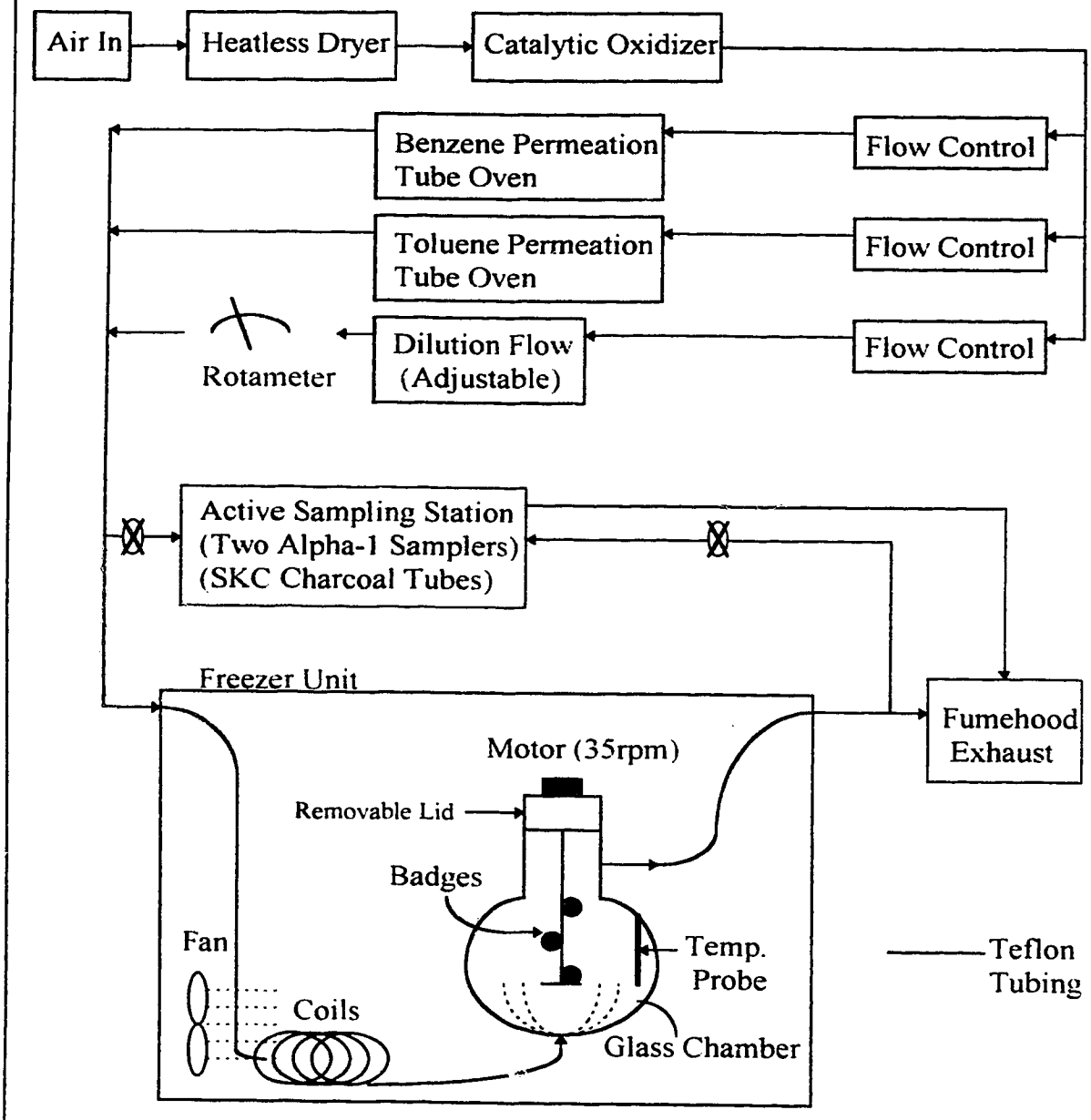
There were four main sections to the exposure chamber design: generation of clean, dry air; introduction of known amounts of VOCs; an active pump sampling station; and the badge exposure chamber. Figure 3.2 illustrates how each component was linked by Teflon® tubing and how the system could be configured to control gas flows to the chamber or to the reference method.

3.2.2.1 Clean Dry Air

Test trials of the exposure chamber system demonstrated that normal humidity from room air caused condensation problems in the chamber during tests at temperatures below freezing. Some methods considered for removal of excess water from a gas stream were adsorption onto surfaces, adsorption by chemical binding, condensation by cooling, and condensation by compression. Silica gel media was

Figure 3.2

Exposure Chamber Schematic



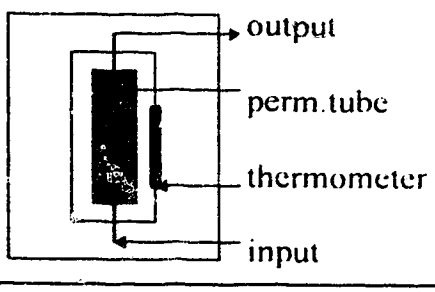
initially used to remove moisture from the air, however condensation persisted at temperatures less than -5°C. The final configuration included a compression-type Pure Gas Heatless Dryer (CFM Air Equipment, Calgary, Alberta) made available to the study by Alberta Environmental Protection. The dryer was used for subzero conditions and was bypassed for experiments at room temperature. Raw data for relative humidity are presented in Appendix 3.2; relative humidity at -15°C, -5°C, and 24°C was measured as 50%, 30%, and 20% respectively.

Removal of organic vapours from the air flow included an Alberta Environmental Protection modified Bendix® (ABB Process Analytics, Sarnia, Ontario) nickel oxide bed catalytic oxidizer. It was set to a temperature of 400°C to ensure removal of benzene and toluene present in the ambient feed air.

3.2.2.2 Contaminant Generation

Permeation tubes (VICI Metronics, Santa Clara, California) and modified Bendix® (ABB, Sarnia) ovens were used to create levels of benzene and toluene. The tubes (Figure 3.3) were constructed of Teflon® and contained a defined quantity of gas, compressed to liquidity, and sealed. When the seal was broken, the gas dissolved in the tubing walls and permeated out at a rate governed by oven temperatures set to within ± 0.05°C. The vapour mixed with the clean dry dilution air and was carried to the chamber.

Figure 3.3



A more complete overview of permeation tubes and their applications may be found in Lucero (1971). Phalen (1984) explained that the permeation rate for the vapour generating tubes could be expressed as:

$$Q = (D) \bullet (S) \bullet (A) \bullet ((P_i - P_o) / t) \qquad \textbf{(Eq. 3.1)}$$

where,
Q = rate of permeation
S = solubility coefficient of the vapour
A = surface area for permeation
P_o = pressure outside the tube
D = vapour diffusion coefficient
t = thickness of the tube
P_i = pressure in the tube

Given the rate of permeation (ng/min), the concentration of gas reaching the exposure chamber was calculated using ideal gas law relationships:

$$C = \frac{Q\ [T/273]\ [760/P]}{F} \qquad \textbf{(Eq. 3.2)}$$

where,
C = concentration of the gas ($\mu g/m^3$)
Q = permeation rate (ng/min)
T = temperature (°K)
P = pressure of the system (mmHg)
F = flow of dilution gas (L/min)

The practical operating dilution range of the permeation tube oven system was set between 500 and 7,000 mL/min (Brassard, 1995). The selected permeation rates were based on these flow rate limitations and the desired concentrations outlined in Sections 2.2.2.6 and 2.2.3.6. The selected permeation rate for benzene was 17.6 ng/min ± 10% at 30°C, and for toluene, 23.7 ng/min ± 10% at 50°C. Table 3.4 indicates the three approximate flow rates and resulting chamber concentrations.

Table 3.4

Flow Rate and Chamber Concentration at STP

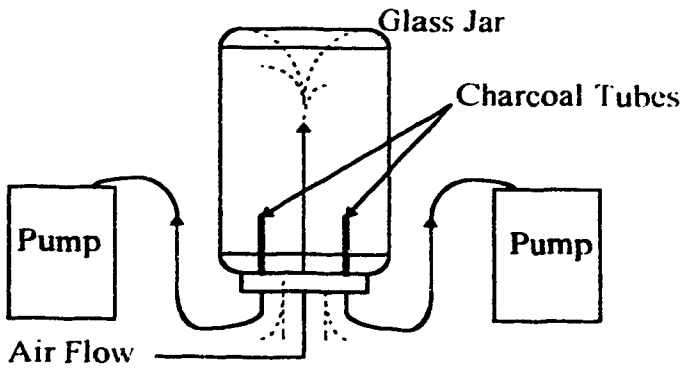
Compound	Permeation (ng/min)	Dilution (mL/min)	Chamber ($\mu g/m^3$)
Benzene	17	7000	2.4
	17	1000	17.0
	17	500	34.0
Toluene	23	7000	3.3
	23	1000	23.0
	23	500	46.0

3.2.2.3 Active Sampling Station

Although the permeation tubes were certified according to National Institute of Standards and Technology specifications (Appendix 3.3), the reference method was the SKC 226-01 charcoal tube. The intention was for the permeation tubes to generate VOCs to approximate levels followed by a measurement by the SKC tubes at the active sampling station. The station was comprised of a one liter glass jar mounted about 20 cm above counter height on a retort stand.

Figure 3.4

Active Sampling Station



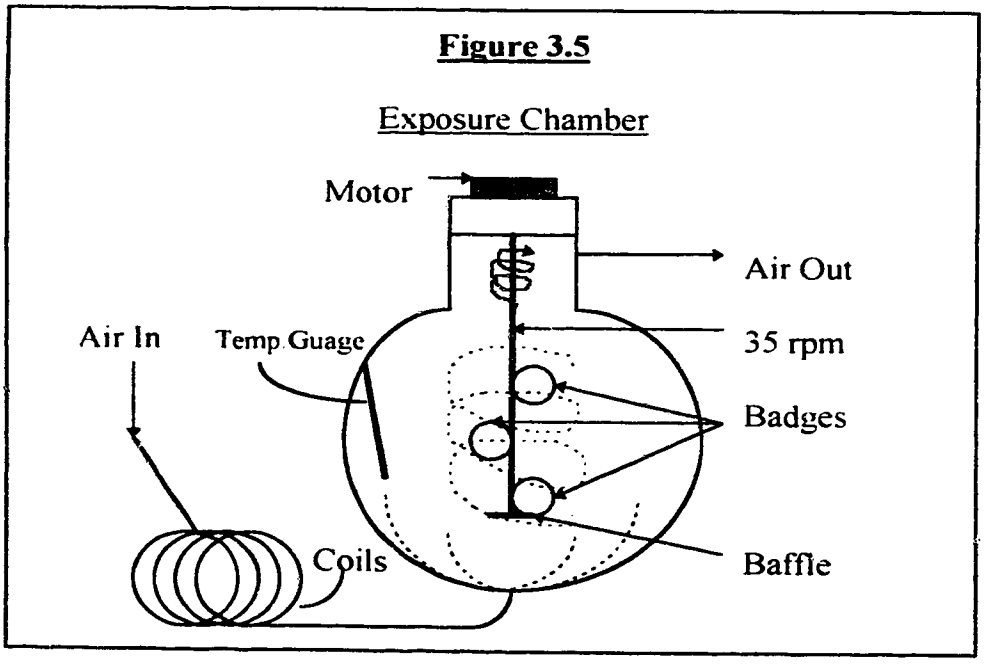
Five, one-quarter inch holes were made in the downward facing lid of the jar to facilitate insertion of the charcoal tubes and Teflon® tubing that carried gas from the ovens. Minimum flows of 500 mL/min into the jar were greater than the combined 400 mL/min flow rates being removed via the pumps, hence the need for the other holes in the cap to vent the jar of excess gas.

3.2.2.4 The Chamber

Air from the permeation ovens could also by-pass the active sampling station to be sent to the exposure chamber. Designed by Vince Gagner and assembled by Peter Lea of Technical Services at the University of Alberta, the chamber (Figure 3.5) was a 4L spherical shaped glass flask with a removable top seal and temperature probe

Figure 3.5

Exposure Chamber



fitting. The unit was housed in a 10 ft^3 freezer modified with a retrofit thermostat control to ensure a dead-band of ±0.5°C from mean temperatures. The air was delivered to the chamber via 1/4 inch Teflon tubing; approximately three meters of the

tubing was coiled in the bottom of the freezer to ensure that a temperature equilibrium was achieved between the freezer and chamber air.

Unlike other chamber designs (e.g. TAGS), this system was not engineered to create a laminar flow of air[1]; on the contrary, this simple chamber promoted random turbulence. The air entered the chamber from the bottom where it was somewhat baffled by the square [illegible] attached to the stainless steel rotation rod. The rotation of the badges that were attached to the rod was intended to create eddies throughout the chamber and promote a thorough mixing of the air passing through. The rotating rod also turned the badges to ensure a minimum face velocity of about 10 cm/sec. The increased pressure due to the influx of dilution flow air was negligible (Appendix 3.4).

Kumarathasan et al. (1995) measured steady state xylene in a 27.5 L chamber after 45 minutes with flow rates of 3.5 L/min. This was equivalent to 4.9 full exchanges of the chamber and this approach was used prior to all testing performed in the Phase I evaluation of the OVM-3500.

3.2.3 Quality Assurance and Control

Rearrangement of flows brought air to the active sampling station from the "back" end of the system, i.e. after the air had passed through the chamber. This allowed samples to be taken to test if flow concentrations entering the exposure chamber were the same as those exiting. It was thought that if there were no significant discrepancies between the two readings, the air reaching the badges in the exposure chamber was congruent with the air sampled by the reference method at the

[1] Laminar flow is reached when the Reynolds Number is less than 2000

active sampling station. Table 3.5 lists the averaged results of the two pump charcoal tube samples taken simultaneously at the pump sampling station. Appendix 3.5 provides raw data for each individual pump under each sampling scenario, including pump flow rates, analyte masses reported, and the blank and desorption efficiency adjustments according to Table 3.3.

Table 3.5

Concentrations($\mu g/m^3$), Front and Back

Sample	Zero Air	1000mL/min dil.	500mL/min dil.
Benzene Front	non-detect	6.3	35.5
Benzene Back	non-detect	4.4	34.4
Comparison	acceptable	not acceptable	acceptable
Toluene Front	2.1	9.8	39.5
Toluene Back	non-detect	9.5	39.6
Comparison	not acceptable	acceptable	acceptable

The above table is constructed to compare measures taken from the front and back ends of the exposure chamber system. Results are separated into three different concentrations, beginning with zero air comparisons. The relatively large discrepancy in the benzene readings found during the second run at 1000 mL/min dilution led to a design change in the system. Initially a three meter industrial-grade copper coil was used for cooling the air entering the chamber and it was felt that adsorption from tubing contamination could have caused the loss of benzene from front to back. The tubing was replaced with Teflon® and the outcome of this modification verified by the results in the final column of the Table 3.5 where comparisons between front and back

measures of VOCs are very similar. Based on this data, it was assumed that the active samplers received concentrations of VOCs equivalent to the air circulated through to the chamber.

3.2.4 Phase I Procedures

OVM-3500 Chamber Samples

1. Dilution flows were calibrated to STP according to desired concentrations of benzene and toluene and recorded in laboratory log.

2. Exposure chamber system was configured to bypass active sampling station to deliver gas flows directly to the exposure chamber.

3. Flow rates exiting chamber were checked to ensure flows were within 10% of the front end dilution flows.

4. Time, based on flow rate, was allowed for 5 full exchanges of air in the 4L chamber to bring the internal air concentration to equilibrium.

5. Three OVM-3500 badges were prepared for sampling. Time and date were recorded in the log and written on the badge.

6. After the seal on the chamber was removed the monitors were attached to the stainless steel rod with the front of the badge facing with the direction of rotation

7. The chamber was resealed and the rotation of the stainless steel rod was initiated

8. The following was then recorded in the log book: date, time of sample initiation, sampler numbers, and temperature of chamber with dead-band.

9. After the 24hr. exposure, the rod rotation was stopped and the badges were removed from the chamber.

10. Sample termination time was recorded on the back of the badge; badges were then capped and placed in their original aluminum cans. The cans were then capped and the seal wrapped with Teflon® tape.

11. All samples were stored at -15°C until delivery to the analytical laboratory.

12. Dilution flow rate was measured at the end of each sampling period to ensure consistency with initial readings.

13. The flow rate of the air exiting the chamber was also checked to ensure that it was within 10% of dilution flow.

Active Sampling Station

1. Provided that dilution flows were within ±10% of initial readings, the system was reconfigured to feed gas from the permeation ovens to the active sampling station.

2. Based on flow rate, 5 full exchanges of the 1L active sampling chamber were passed through to bring the concentrations to equilibrium.

3. Flow rates were then calibrated on the two Alpha-1 pumps to approximately 200mL/min at STP; five bubble flow meter readings were taken and recorded in the laboratory log. Both pumps were then set to standby.

4. Two SKC tubes and Du Pont pumps were prepared for sampling.

5. The two charcoal tube ends were inserted into two of the five holes in the cap of the glass jar.

6. Time was recorded [illegible] samplers were initiated.

7. After a 4-hour sampling duration, pumps were placed on standby and the tubes were removed.

8. Both tubes were capped, with sample number recorded in the log book and directly on the tube with masking tape.

9. All samples were stored at -15°C until delivered to the analytical laboratory.

10. Du Pont pump sampling rates were measured and averaged with initial flow rates for the determination of volume of air sampled over the 4-hour duration.

11. Dilution flow rates were then check to determine if flows were within ±10% of the original chamber flow rate.

3.2.5 Observations

All results obtained from Enviro•Test Laboratories (Appendix 3.1) were reported in µg/badge with corrections for background benzene and toluene in the CS_2, but not for badge background or desorption efficiency. Appendix 3.6 provides raw data with blank and desorption efficiency corrections for the SKC charcoal tubes according to Table 3.3. Appendix 3.7 lists raw data for the OVM-3500 with blank and desorption efficiency corrections also in accordance with Table 3.3.

There were two data sets, run #7a and run #9b, that were excluded from the data used for interpretation of correlations between active and passive samplers. The integrity of run #7a was seen as questionable due to the large difference (1.6 vs. 7.2 $\mu g/m^3$) between the two charcoal tube benzene readings and it was decided that a rerun under identical conditions (run #7b) was warranted. Run #9b was performed for similar reasons as #7b, however after the experiment was completed it was determined that run #9a had acceptable results and that the reported differences were caused by an inaccurate transfer of data onto the spreadsheet. The decision was made to stay with the original data set from run #9a even though data from #9b was also very acceptable for the purposes of the experiment.

3.2.5.1 Objective One

The first objective of the Phase I exposure chamber study was to evaluate the effect of temperature on the sampling rate of the OVM-3500. Equation 2.5 was used to relate badge TWAE to the air sampling rate and analyte mass collected. By rearranging this equation, the air sampling rate was calculated using the measured

mass of contaminant (ng) collected by the badge over the sampling duration (24 hrs) and a known ambient air contaminant concentration ($\mu g/m^3$) measured by the reference method. The rearranged form of the equation:

$$SR = M / TWA \qquad \textbf{(Eq. 3.3)}$$

where,
SR = sampling rate (L/24hrs)
M = mass of contaminant collected (ng) over a 24 hour duration
TWA = ambient contaminant concentration ($\mu g/m^3$)

Tables 3.6 and 3.7 provide summaries of the data collected during all tests in the Phase I exposure chamber trials. For the purposes of meeting the first objective, the time-weighted average concentrations generated by the SKC 226-01 charcoal tube were assumed as 100% accurate. Sampling rates for the OVM-3500 were calculated by using the mass of contaminant collected by the badge sorbent pad and a time-weighted average value from measures taken by the two pumps that ran simultaneously in the active sampling station.

Figures 3.6 and 3.7 illustrate the data from the tables. Previously determined sampling rates for the OVM-3500 are indicated on the graphs as benchmarks. The referenced air sampling rates were taken from empirical tests by 3M and Bovar and theoretical calculations listed in Table 2.9 of this report. Data has been stratified into high, mid, and low level concentrations of the contaminants, and into three temperature groups of 24°C, -5°C, and -15°C.

Table 3.6

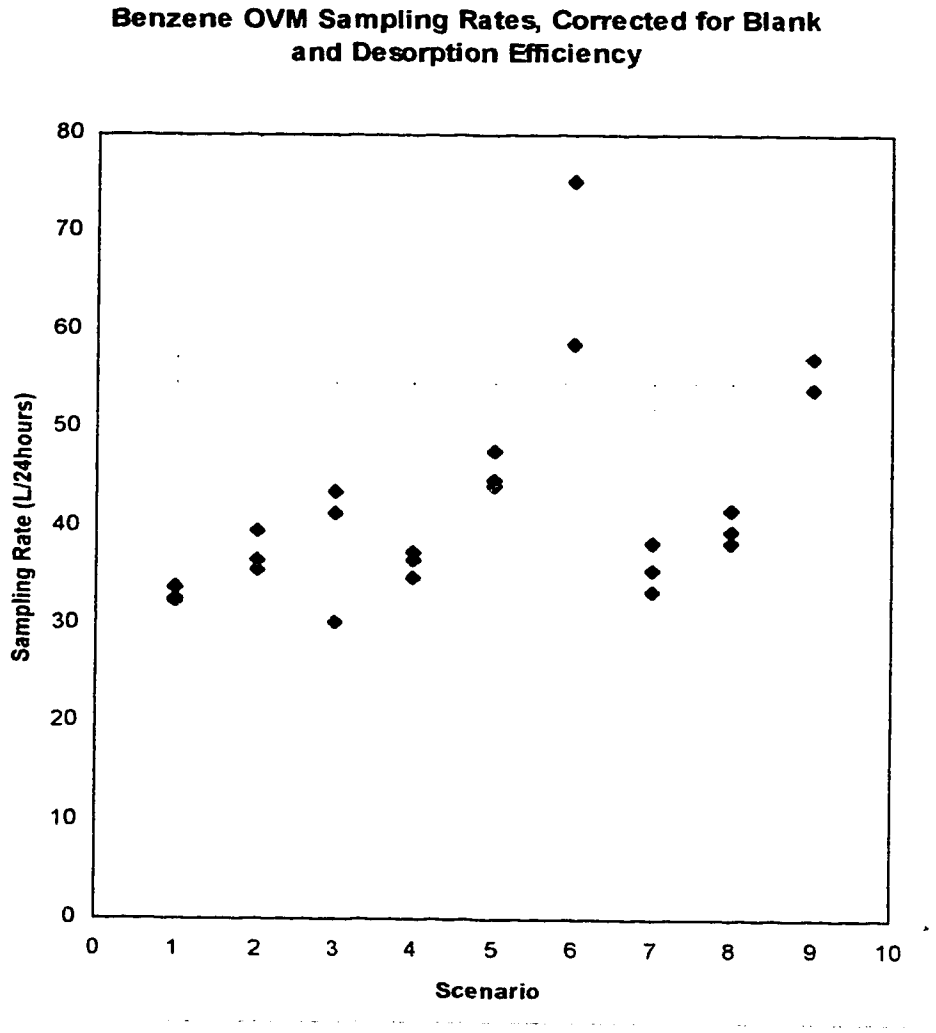
Phase I OVM-3500 Sampling Rates for BENZENE

Temp. (°C)	Pump 1	Pump 2	TWAE (µg/m3)	Badge (ng)	Rate (L/day)	Average (L/day)
24	39.4	40.1	39.8	1294	32.6	32.9
			39.8	1284	32.3	
			39.8	1343	33.7	
25	21.8	17.6	19.7	700	35.5	37.2
			19.7	720	36.6	
			19.7	780	39.6	
24	6.2	5.6	5.9	244	41.4	38.3
			5.9	178	30.2	
			5.9	256	43.4	
-5	40.2	42.1	41.2	1500	36.5	36.2
			41.2	1431	34.7	
			41.2	1539	37.4	
-5	17.2	16.4	16.8	750	44.6	45.4
			16.8	800	47.6	
			16.8	740	44.1	
-5	3.4	3.7	3.6	267	75.2	64.1
			3.6	211	58.6	
			3.6	211	58.6	
-15	33.8	33.7	33.8	1196	35.4	35.7
			33.8	1294	38.3	
			33.8	1127	33.3	
-15	17.9	17.1	17.5	730	41.7	39.4
			17.5	670	38.3	
			17.5	690	39.4	
-15	3.6	3.4	3.5	200	57.1	55.1
			3.5	189	54.0	
			3.5	189	54.0	

Benzene Sampling Rates: $\bar{x} = 42.7$, $\sigma = 10.6$ @ 0.05, (2-tailed)

Figure 3.6

Phase I Graphical Representation of Sampling Rates for BENZENE



Scenario 1: 24°C, 39.8 µg/m^3
Scenario 2: 25°C, 19.7 µg/m^3
Scenario 3: 24°C, 5.9 µg/m^3
Scenario 4: -5°C, 41.2 µg/m^3
Scenario 5: -5°C, 16.8 µg/m^3
Scenario 6: -5°C, 3.6 µg/m^3
Scenario 7: -15°C, 33.8 µg/m^3
Scenario 8: -15°C, 17.5 µg/m^3
Scenario 9: -15°C, 3.5 µg/m^3

Legend

..... 3M Rate
- - - - - - - - - Bovar Rate
- . - . - . - . - Theoretical Rate

Table 3.7

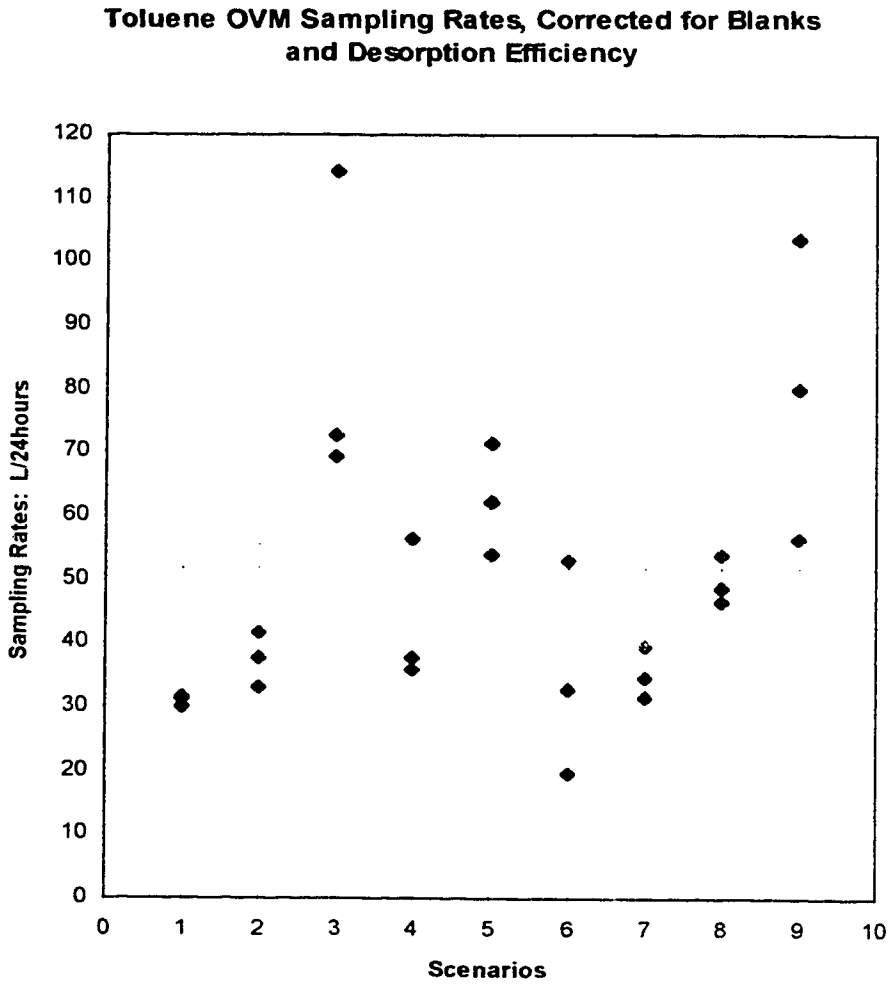
Phase I OVM-3500 Sampling Rates for TOLUENE

Temp. (°C)	Pump 1	Pump 2	TWAE ($\mu g/m^3$)	Badge (ng)	Rate(L/day)	Average (L/day)
24	48.9	47.4	48.1	1450	30.1	30.9
			48.1	1500	31.1	
			48.1	1520	31.5	
25	23.5	23.1	23.3	768	33.0	37.3
			23.3	874	37.5	
			23.3	968	41.6	
24	3.3	3.5	3.4	388	114.1	85.3
			3.4	235	69.1	
			3.4	247	72.7	
-5	47.6	47.4	47.5	2320	48.8	37.5
			47.5	1470	31.0	
			47.5	1550	32.6	
-5	19.2	18.1	18.6	1042	56.0	56.4
			18.6	1200	64.5	
			18.6	905	48.7	
-5	2.4	2.6	2.5	188	75.2	50.3
			2.5	71	28.4	
			2.5	118	47.2	
-15	38.2	39	38.6	1330	34.5	35.2
			38.6	1530	39.6	
			38.6	1220	31.6	
-15	18.9	18.7	18.8	1011	53.8	49.7
			18.8	874	46.5	
			18.8	916	48.7	
-15	2.6	2.4	2.5	141	56.4	80.0
			2.5	200	80.0	
			2.5	259	103.6	

Toluene Sampling Rates: $\bar{x} = 51.4$, $\sigma = 22.45$ @ 0.05, (2-tailed)

Figure 3.7

Phase I Graphical Representation of Sampling Rates for TOLUENE



Scenario 1: 24°C, 48.1 µg/m^3
Scenario 2: 25°C, 23.3 µg/m^3
Scenario 3: 24°C, 3.4 µg/m^3
Scenario 4: -5°C, 47.5 µg/m^3
Scenario 5: -5°C, 18.6 µg/m^3
Scenario 6: -5°C, 2.5 µg/m^3
Scenario 7: -15°C, 38.6 µg/m^3
Scenario 8: -15°C, 18.8 µg/m^3
Scenario 9: -15°C, 2.5 µg/m^3

Legend

3M Rate
Bovar Rate
Theoretical Rate

3.2.5.2 Objective Two

The second objective of the Phase I exposure chamber study was to compare the SKC 226-01 charcoal tube TWAE values against the TWAE values of the OVM-3500 badge. The air sampling rate of the pump/charcoal tube method was determined by pre- and post- calibrations, while 3M (1993) sampling rates[1] were taken from the manufacturer literature. The first evaluations to meet objective two assumed that neither the reference method nor the badge were capable of producing 100% accurate impressions of exposure. TWAE range for each method were set at ± 25% and comparisons are presented on Tables 3.8 and 3.9. Calculations were based on Equation 3.3 with badge TWAEs determined by factoring the mass of analyte collected with the 3M published air sampling rates. Reference method results were considered to be an average of the two simultaneously sampled SKC tube readings. Acceptable correlation between the tube and badge was achieved when the two ±25% ranges overlapped: any of the measures that did not meet this criteria are **highlighted**.

The second evaluation for objective two was a simple linear regression analysis under the assumption that the mean of the two pump samples was 100% accurate. Figure 3.8 illustrates six correlations; one at each of the three experimental temperatures of 24°C, -5°C, and -15°C for both benzene and toluene. Each relationship was statistically analyzed based on the assumption of a normal distribution and nine data points at three different concentrations.

[1] Interpretations do NOT corrected for temperature

Table 3.8

SKC Tube vs. OVM-3500 Badge at ± 25% Accuracy (BENZENE)

SKC Tube TWAE $\mu g/m^3$ (-25% to +25%)	**OVM-3500 TWAE** $\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)	$\mu g\ m^3$ (-25% to +25%)
Temp.: 24°C			
5.9 (4.4 to 7.4)	5.0 (3.8 to 6.3)	**3.5 (2.6 to 4.3)**	4.8 (3.6 to 6.0)
19.7 (14.8 to 24.6)	15.3 (11.4 to 19.1)	14.1 (10.6 to 17.6)	13.7 (10.3 to 17.1)
39.8 (29.9 to 49.8)	26.3 (19.7 to 32.8)	25.1 (18.8 to 31.4)	25.3 (19.0 to 31.6)
Temp.: -5°C			
3.6 (2.7 to 4.5)	4.1 (3.1 to 5.2)	4.1 (3.1 to 5.2)	5.2 (3.9 to 6.5)
16.8 (12.6 to 21.0)	14.5 (10.9 to 18.1)	15.7 (11.7 to 19.6)	14.7 (11.0 to 18.34)
41.2 (30.9 to 51.5)	30.1 (22.6 to 37.6)	28.1 (21.0 to 35.0)	29.3 (22.0 to 36.7)
Temp.: -15°C			
3.5 (2.6 to 4.4)	3.7 (2.8 to 4.6)	3.7 (2.8 to 4.6)	3.9 (2.9 to 4.9)
17.5 (13.1 to 21.9)	13.5 (10.1 to 16.9)	13.1 (9.8 to 16.38)	14.3 (10.7 to 17.9)
33.8 (25.4 to 42.3)	22.1 (16.5 to 27.6)	25.3 (19.1 to 31.6)	23.4 (17.6 to 29.2)

Above: **highlighting** indicates unsuccessful correlation at ±25%.

Table 3.9

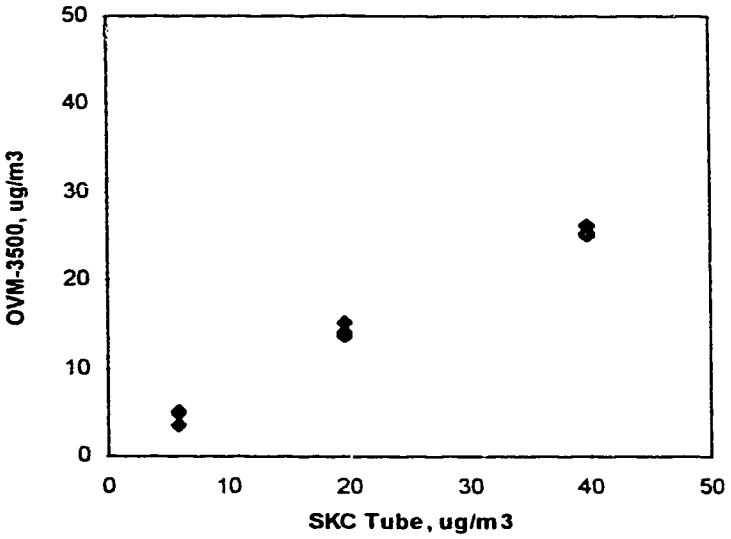
SKC Tube vs. OVM-3500 Badge at ± 25% Accuracy (TOLUENE)

SKC Tube TWAE $\mu g/m^3$ (-25% to +25%)	**OVM-3500 TWAE** $\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)
Temp.: 24°			
3.4 (2.6 to 4.3)	4.8 (3.6 to 6.0)	4.6 (3.5 to 5.8)	**7.6 (5.7 to 9.5)**
23.3 (17.5 to 29.1)	18.9 (14.2 to 23.7)	17.1 (12.8 to 21.4)	15.0 (11.3 to 18.8)
48.1 (36.1 to 60.1)	29.7 (22.3 to 37.2)	29.3 (22.0 to 36.7)	**28.4 (21.3 to 35.5)**
Temp.: -5°			
2.5 (1.9 to 3.1)	2.3 (1.7 to 2.9)	**1.4 (1.0 to 1.7)**	3.7 (2.8 to 4.6)
18.6 (14.0 to 23.3)	17.7 (13.3 to 22.1)	23.5 (17.6 to 29.3)	20.4 (15.3 to 25.5)
47.5 (35.6 to 59.4)	30.3 (22.7 to 37.9)	28.8 (21.6 to 35.9)	45.4 (34.0 to 56.7)
Temp.: -15°			
2.5 (1.9 to 3.1)	**5.1 (3.8 to 6.3)**	3.9 (2.9 to 4.9)	2.8 (2.1 to 3.5)
18.8 (14.1 to 23.5)	17.9 (13.4 to 22.4)	17.1 (12.8 to 21.4)	19.8 (14.8 to 24.7)
38.6 (29.0 to 48.3)	23.9 (17.9 to 29.8)	29.9 (22.5 to 37.4)	26.0 (19.5 to 32.5)

Above: **highlighting** indicates unsuccessful correlation at ±25%.

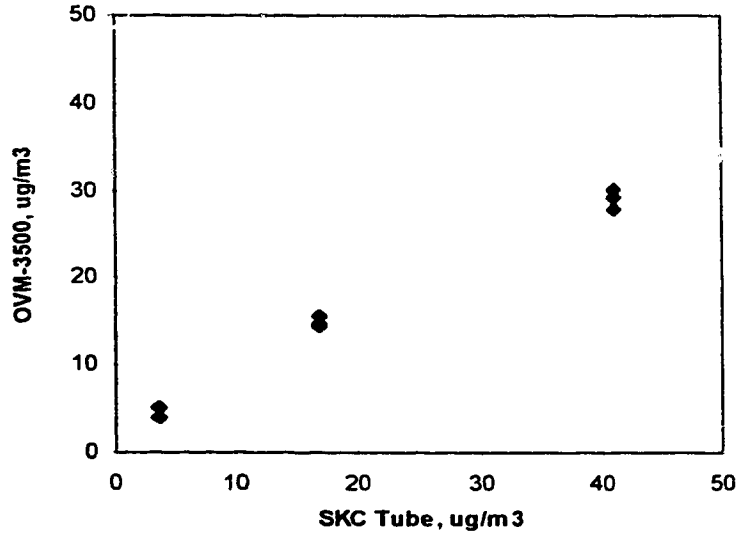
Figure 3.8

1. Benzene Measures at 24 ℃



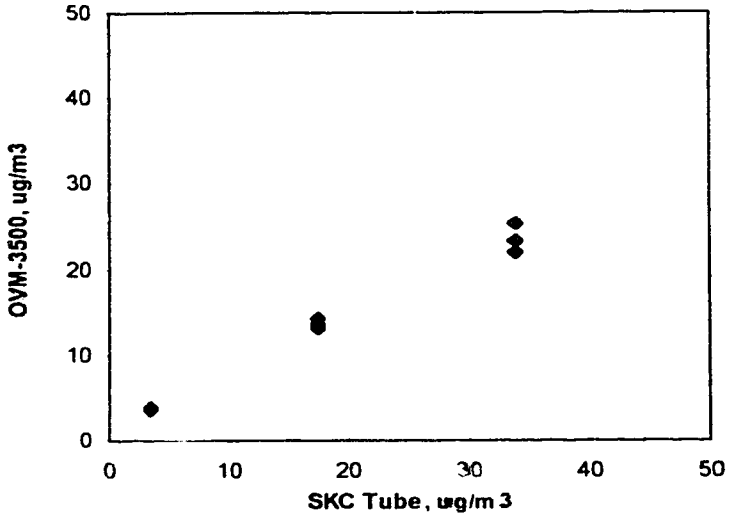
Regression: y = 1.28 + 0.62x, slopes at 95% confidence are 0.677 and 0.563.

2. Benzene Measures at -5 ℃



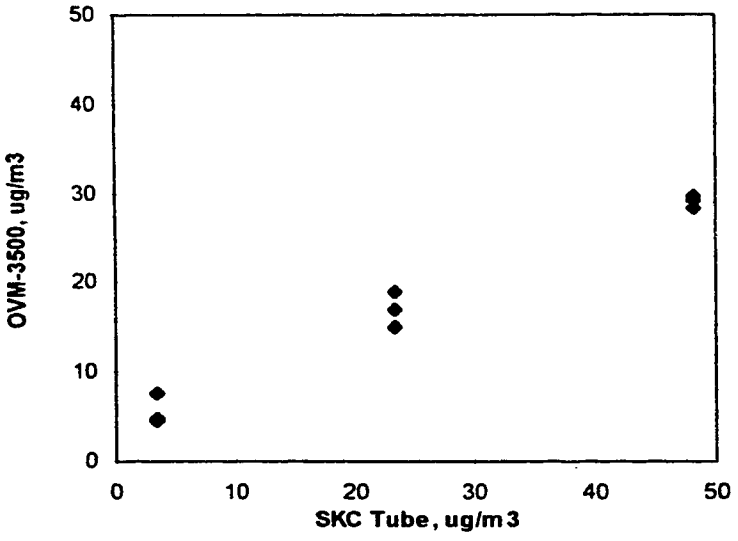
Regression: y = 2.91 + 0.65x, slopes at 95% confidence are 0.711 and 0.589.

3. Benzene Measures at -15 ℃



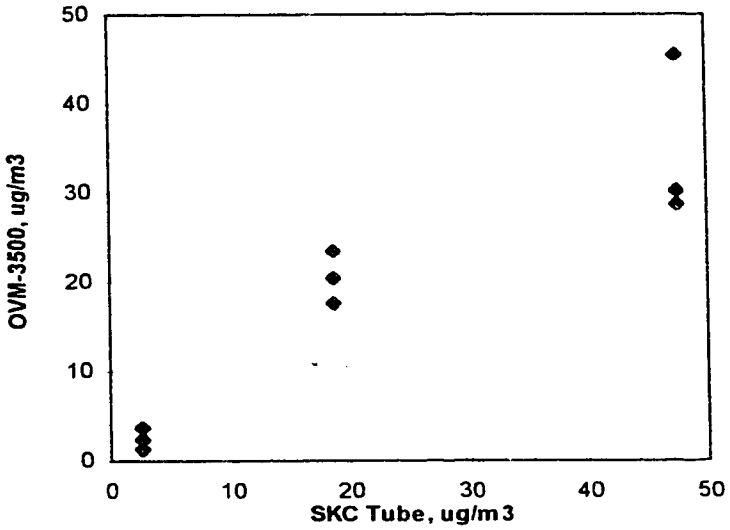
Regression: y = 1.74 + 0.65x, slopes at 95% confidence are 0.714 and 0.586.

4. Toluene Measures at 24 ℃



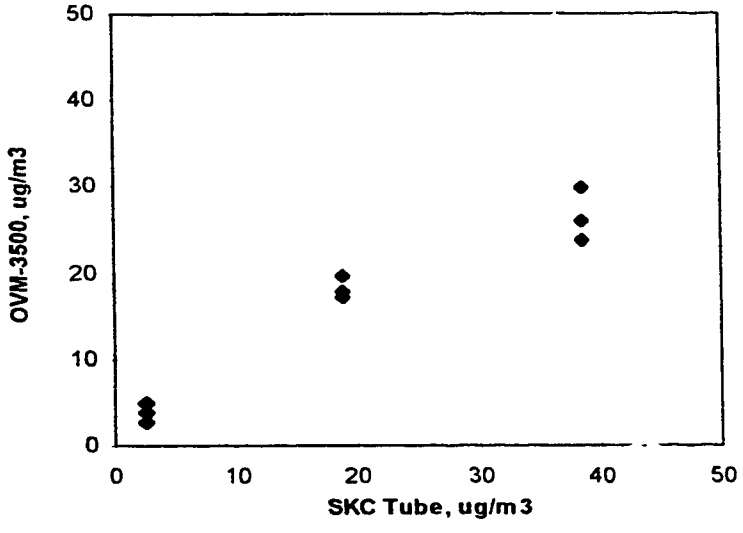
Regression: y = 4.22 + 0.52x, slopes at 95% confidence are 0.584 and 0.456.

5. Toluene Measures at - 5 ℃



Regression: y = 3.43 + 0.69x, slopes at 95% confidence are 0.953 and 0.427.

6. Toluene Measures at - 15 ℃



Regression: y = 3.86 + 0.62x, slopes at 95% confidence are 0.776 and 0.464.

3.3 Phase Two: Field Co-location

3.3.1 Purpose

The second set of evaluations for the OVM-3500 included 24-hour samples from an outdoor environment where variables were not controlled but measured. Temperature, relative humidity, wind speed and direction were all logged, while reference sampling was performed via Summa® canisters.

The objectives of the Phase II field co-location study were:

1. Evaluate OVM-3500 sample rate based on canister TWAEs; and,
2. Evaluate the badge against the canister while assuming 3M sampling rates.

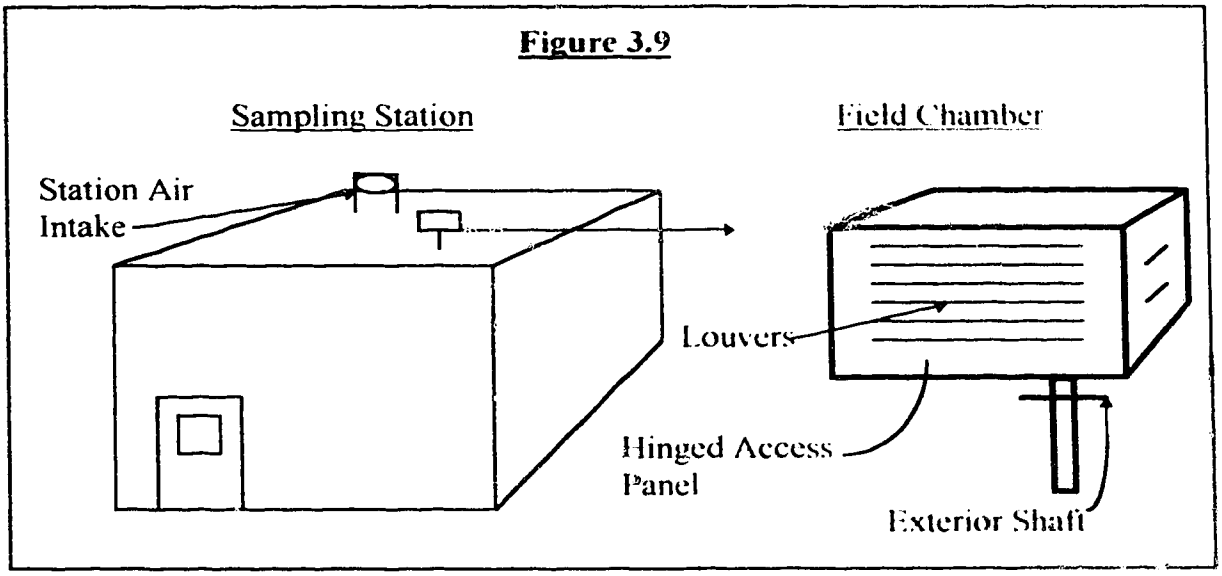
3.3.2 Apparatus

Sampling in the field required that the badges received adequate exposure to circulating air while remaining protected from environmental elements. It was thought that placement of the samplers under a protective structure or within a permeable box would satisfy this requirement. For example, Alberta Environmental Protection uses two liter, sheltered but permeable, exposure boxes made of galvanized steel for collecting passive samples. One such unit was located on the top of their 17th Street monitoring station where VOCs were monitored with Summa® canisters on a six day rotation.

At the station, sampling for benzene and toluene was performed over 24 hours from midnight to midnight. Sampling dates selected for co-location of samplers included: October 24th, November 5th and 17th, and December 5th, 1995 with

temperatures ranging from -30 to 10°C. During sampling, the canister was located inside the station collecting air fed via a main manifold line linked to an air intake on the roof of the station. Figure 3.9 illustrates a schematic of the sampling station, air intake, and badge chamber. The box was located far enough away from the station air intake to ensure no cross contamination of either sampling system but close enough to allow comparisons to be made between readings.

Figure 3.9



3.3.3 Quality Assurance and Control

To provide an indication of sampler precision in the field, three samples were simultaneously taken for each of the sampling periods. The first of four sampling sets was placed inside the chamber while the final three were located on the exterior shaft under the chamber. This change in protocol was made after concerns were raised about the adequacy of ventilation inside the box. Placing the badges under the

chamber ensured adequate ventilation of each badge but meant that careful observation of the weather had to be maintained. For example, sampling that was originally scheduled for November 29th was changed to December 5th due to blizzard-like conditions which could have threatened the integrity of the badge.

Field blanks were taken for the first three sample sets but not for the fourth. Upon receipt of results from the initial tests, it was observed that the background toluene and benzene on the unexposed badge was actually higher than the sample itself. In fact, in one instance it was observed that the background toluene on the OVM-3500 was a factor of four higher than all field samples. Given the possibility that background contamination on the badges may have desorbed to the air at such low levels, it was determined that the 24-hour zero air blank values from the exposure chamber runs (Table 3.3) were more representative. Notably, desorption efficiencies provided for low level toluene and benzene on Table 3.3 were also used for adjustment of reported badge analyte mass.

3.3.4 Phase II Procedures

1. Prior to sampling, a personal timer (Timex stop watch) was calibrated with the timing device at the station.
2. Arrival at the station was planned for 10 minutes prior to 12:00 midnight on the selected sampling days. Visual and olfactory inspections were made at the station prior to each run and all outstanding observations were recorded in a log.
3. At 12:00 midnight, the badges were removed from the aluminum cans and labeled with time and date.

4. Chamber access panel was opened and monitors were attached to the galvanized steel rod inside the box or to the steel rod outside the box as prescribed.

5. The access panel was closed and all pertinent information was recorded in the field log book: date, time of sample initiation, and sampler numbers.

6. Return to the station was planned for 10 minutes prior to 12:00 midnight the following evening. Visual and olfactory inspections were again made at the station and inconsistencies were logged.

7. At the end of the sampling duration, badges were removed and sample termination time was recorded on the back of the badge.

8. The Teflon® coating was removed and the plastic cap was snapped onto the badges. Badges were then placed in the aluminum can, capped, and wrapped with Teflon® tape.

9. Samples were stored in a cooler at temperatures of less than -5°C during transport from the station to the -15°C freezer unit where samples were stored until delivered to the laboratory.

3.3.5 Observations

All results obtained from analyses of the Summa® canisters were reported as TWAE ($\mu g/m^3$) directly from Daniel Wang (1996) at Environment Canada. Appendix 3.1 provides raw badge data reported by Enviro•Test while blank and desorption efficiency corrections are provided in Appendix 3.8.

3.3.5.1 Objective One

The first objective of the Phase II field co-location study was to evaluate the air sampling rate of the OVM-3500 based on TWAE values from the canisters. Table 3.10 provides a summary of the data collected during the tests in the Phase II field trials. For the purposes of meeting the first objective, the time-weighted average concentration of the Summa® canisters were assumed as 100% accurate. Once again

using Equation 3.3, sampling rates for the OVM-3500 were back calculated using the mass of contaminant collected by the badge and the canister TWAE. Figures 3.10 and 3.11 illustrate the data from Table 3.10. Empirical air sampling rates from 3M and Bovar are shown with the theoretical sampling rate as benchmarks.

Table 3.10

OVM-3500 Sampling Rates Based on Canister Measures

		BENZENE			TOLUENE	
Date	TWAE	Badge	Rate	TWAE	Badge	Rate
	($\mu g/m^3$)	(ng)	(L/day)	($\mu g/m^3$)	(ng)	(L/day)
24-Oct	1.96	111	56.6	6.16	n/d	n/d
24-Oct	1.96	n/d	-	6.16	59	9.58
24-Oct	1.96	n/d	-	6.16	n/d	n/d
05-Nov	2.76	200	72.5	4.28	353	82.5
05-Nov	2.76	144	52.2	4.28	259	60.5
05-Nov	2.76	233	84.4	4.28	353	82.5
17-Nov	2.11	111	52.6	3.44	235	68.3
17-Nov	2.11	133	63.0	3.44	224	65.1
17-Nov	2.11	133	63.0	3.44	329	95.6
05-Dec	3.64	178	48.9	8.05	459	57.0
05-Dec	3.64	211	58.0	8.05	435	54.0
05-Dec	3.64	189	51.9	8.05	424	52.7

Average Temperature Range

-24°C to 5°C

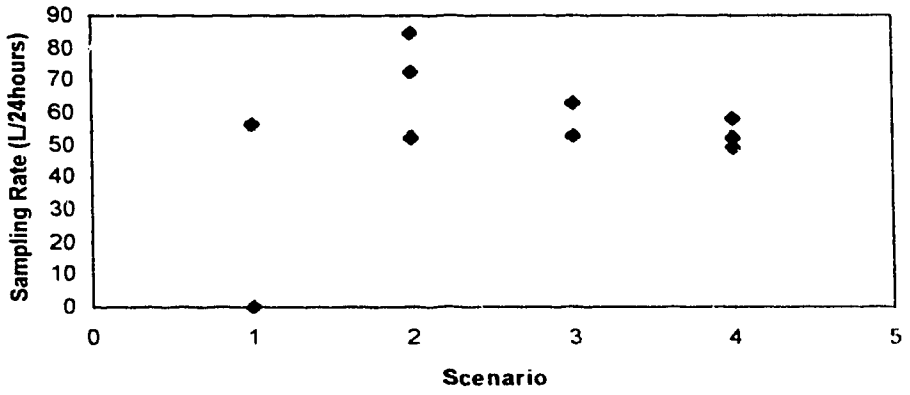
Benzene Sampling Rates (not including first set):

$\bar{x} = 60.7$, $\sigma = 11.6$ @0.05, (2-tailed)

Toluene Sampling Rates (not including first set):

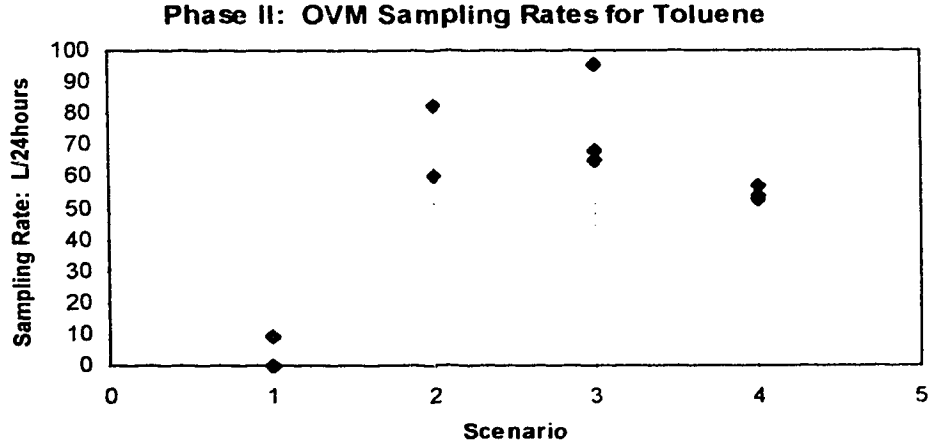
$\bar{x} = 68.7$, $\sigma = 14.97$ @0.05, (2-tailed)

Figure 3.10



Scenario 1: 1.96 µg/m^3	Sampling Rate
Scenario 2: 2.76 µg/m^3	3M
Scenario 3: 2.11 µg/m^3	Bovar
Scenario 4: 3.64 µg/m^3	Theory

Figure 3.11



Scenario 1: 6.16 µg/m^3	Sampling Rate
Scenario 2: 4.28 µg/m^3	3M
Scenario 3: 3.44 µg/m^3	Bovar
Scenario 4: 8.05 µg/m^3	Theory

3.3.5.2 Objective Two

The second objective of the Phase II field co-location was a comparison of TWAE values from the Summa® canisters to the TWAE values from the OVM-3500. All results for the 3M badges were based on the 3M (1993) sampling rates for benzene and toluene with no adjustment for temperature. There were two separate evaluations to satisfy objective two: the first was a comparison based on ±25% variance around the results of both sampling methods. Tables 3.11 and 3.12 present these ranges of accuracy with acceptable correlation satisfied when measures overlap. Any data sets that do not meet this criteria are **highlighted**. Note that the first set of three samples was taken inside the field chamber and was disregarded due to the sampling bias from potential lack of air circulation.

The second evaluation was a linear regression analysis of the TWAE values measured by each method. Results from the first sample set of three were NOT included in this evaluation; thus the interpretation was specifically based on samples located under a protective overhead with direct exposure to the outdoor air. Each relationship between canister and badge were statistically analyzed based on the assumption of a normal distribution of the 9 data points. Figure 3.12 illustrates the data and states the regression correlations for benzene and toluene.

Table 3.11

Phase II: Canisters vs. OVM-3500 Badges at ±25% Accuracy (Benzene)

Summa® TWAE $\mu g/m^3$ (-25% to +25%)	**OVM-3500 TWAE** $\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)
2.0 (1.5 to 2.5)	2.2 (1.6 to 2.7)	**1.0 (0.8 to 1.3)**	**1.0 (0.8 to 1.3)**
2.8 (2.1 to 3.5)	3.9 (2.9 to 4.9)	2.8 (2.1 to 3.5)	4.6 (3.4 to 5.7)
2.1 (1.6 to 2.6)	2.2 (1.6 to 2.7)	2.6 (2.0 to 3.3)	2.6 (2.0 to 3.3)
3.6 (2.7 to 4.6)	3.5 (2.6 to 4.4)	4.1 (3.1 to 5.2)	3.7 (2.8 to 4.6)

Table 3.12

Phase II: Canisters vs. OVM-3500 Badges at ±25% Accuracy (Toluene)

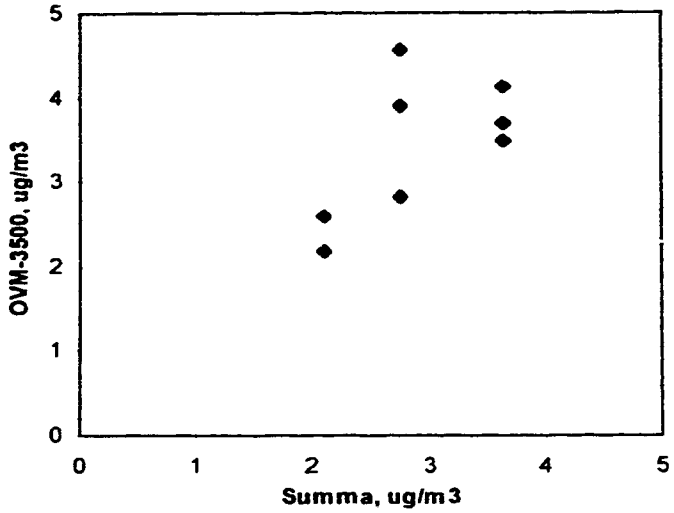
Summa® TWAE $\mu g/m^3$ (-25% to +25%)	**OVM-3500 TWAE** $\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)
2.0 (1.5 to 2.5)	2.2 (1.6 to 2.7)	**1.0 (0.8 to 1.3)**	**1.0 (0.8 to 1.3)**
2.8 (2.1 to 3.5)	3.9 (2.9 to 4.9)	2.8 (2.1 to 3.5)	4.6 (3.4 to 5.7)
2.1 (1.6 to 2.6)	2.2 (1.6 to 2.7)	2.6 (2.0 to 3.3)	2.6 (2.0 to 3.3)
3.6 (2.7 to 4.6)	3.5 (2.6 to 4.4)	4.1 (3.1 to 5.2)	3.7 (2.8 to 4.6)

Above: **highlighting** indicates unsuccessful correlation at ±25%.

Figure 3.12

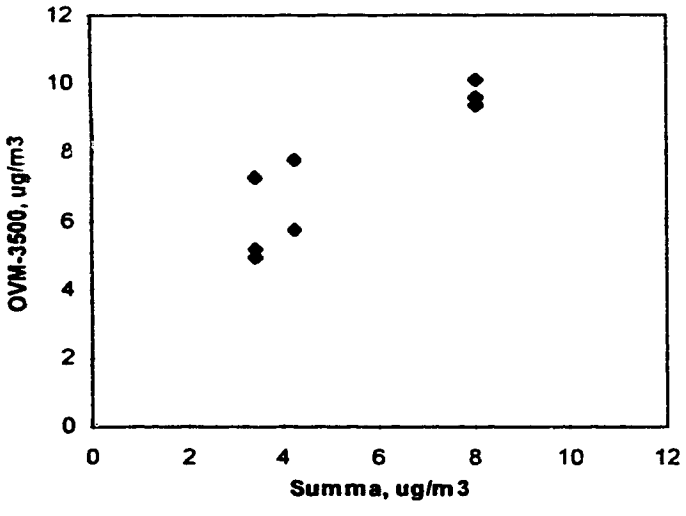
Regression Analysis: Canister vs. Badge

1. Benzene Measures



Regression: y = 1.03 + 0.81x, slopes at 90% confidence are 1.47 and 0.15.

2. Toluene Measures



Regression: y = 3.35 + 0.8x, slopes at 95% confidence are 1.2 and 0.41.

3.4 Phase Three: Personal Sampling

3.4.1 Purpose

The final set of evaluations for the OVM-3500 included six sets of two 24 hour samples taken simultaneously from the breathing zone of a person. The reference values for comparison to the badge were generated through the use of an Alpha-1 Du Pont pump (Amatek Inc., Largo, Florida) and SKC 226-01 charcoal tube (SKC Inc. Eighty-four, Pennsylvania). Unlike the previous phases, Phase III badge exposures were expected to vary considerably over the sampling duration as the receptor was spending time in different microenvironments. An activity diary was maintained to construct an understanding of exposure scenarios.

The objectives of the Phase III personal sampling study were:

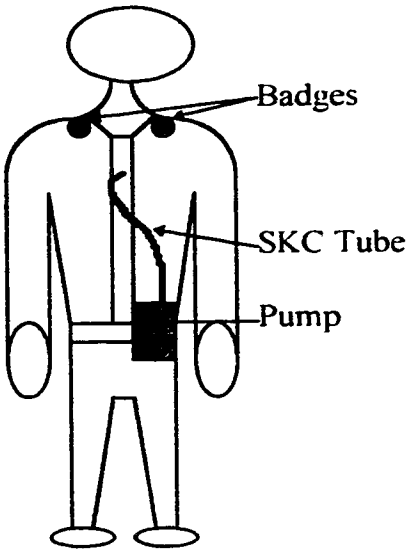
1. Evaluate the OVM-3500 sample rate based on pump/tube TWAEs; and,
2. Evaluate badge TWAE at 3M sample rates against the tube measures.

3.4.2 Apparatus

Sampling on a person required that the badges and tubes were placed on the receptor in the most ergonomically friendly manner without sacrificing sample representativeness of the breathing zone. To accommodate two badges and a tube sampler, the host simply wore a belt and a collared shirt. One badge was attached to each collar with the Alpha-1 clip fastened to the belt and the SKC tube fastened to a button seam on the shirt. Figure 3.13 illustrates the configuration of sampling systems placed on the host.

Figure 3.13

Placement of Personal Monitors on Host



3.4.3 Quality Assurance and Control

Personal sampling for benzene and toluene was performed over 24 hours. During this time, the subject may have been required to reposition the badges and tube clip to ensure that clothing (including coat) did not impair the sampling rate. While sleeping and bathing the badges and tubes remained functioning on a table or vanity until personal sampling was resumed. It was important that the samplers were not separated to a point where exposures varied; however, it was also necessary to keep a minimum distance of about 10 cm between the samplers to minimize bias from shared sampling.

Handling of the badges was increased during personal sampling and care was to be taken to ensure that the Teflon® membrane was not ruptured or contaminated. Furthermore, active pump samples relied on battery power which could be exhausted during the test if the charge was not sufficient. Care was taken to ensure full battery charges at the onset of sampling and periodical inspections of the pump during the sampling period.

Finally, the personal sampling evaluation was intentionally performed in environments that were both positively and negatively conducive to VOC exposures. This approach was meant to encourage a wide range of values for regression analyses representative of the potentially wide range of personal exposures.

3.4.4 Phase II Procedures

1. Flow rates on both pumps were calibrated to approximately 200mL/min at STP and recorded in laboratory log notes.
2. One pump was turned off and the other was place on standby.
3. An SKC tube was prepared for sampling by breaking the tips and inserting into tubing connected to the pump.
4. The pump was then attached to the belt of the host with the charcoal tube clipped to the button seam.
5. Two OVM-3500 badges were opened and the pump "ON" button was immediately pushed.
6. Time and date were recorded on the badges prior to attaching to the host's collars.
7. The following were logged: date, time of sample initiation, and sampler numbers.
8. A daily activity log was maintained from beginning to end of the sampling period.

9. After approximately 12 hours, the first pump was replaced with the second and time of replacement was recorded; note that the SKC tube remained unchanged.

10. After 24 hours, the second pump was placed on standby. The charcoal tube was then removed, capped and labeled.

11. The Teflon badge membrane was also removed to allow the badge to be capped and stored in the sealed aluminum container.

12. All samples were stored at -15°C until shipped for analysis.

13. The flow rates of both pumps were once again measured with a bubble flow meter and this data was combined with initial flow rates to calculate the entire volume of air sampled over the 24 hour period.

3.4.5 Observations

All analytical results received from Envirotest Laboratories are reported as μg/sampler (Appendix 3.1) with corrections for CS_2 background but not for badge background or desorption efficiency. Appendices 3.9 and 3.10 provide raw data with blank and desorption efficiency corrections for the SKC tubes and OVM-3500 badges respectively. Appendix 3.11 provides pertinent meteorological information and daily activity logs maintained over the course of the six sampling trials.

3.4.5.1 Objective One

The first objective of the Phase III personal sampling study was to evaluate the sampling rate of the OVM-3500 based on TWAE values from the tubes. Table 3.13 provides a summary of the data collected during the tests including average daily temperatures. The time-weighted average concentration of the SKC tubes were assumed as 100% accurate and Equation 2.5 was used to back calculate sampling rates

for the badges. Figures 3.14 and 3.15 illustrate the data from Table 3.13. Three benchmark sampling rates were provided including the 3M, Bovar, and theoretically calculated values.

Table 3.13

Personal Sampling OVM-3500 Rates Based on SKC Tubes

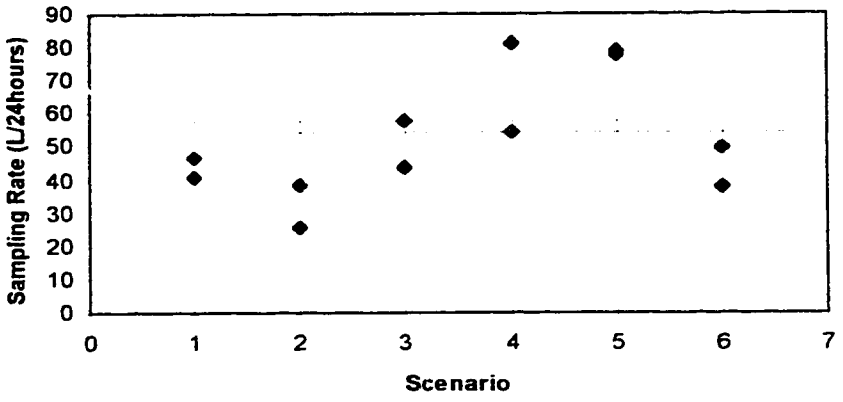
		BENZENE			TOLUENE	
Date/ Temp	Tube TWAE ($\mu g/m^3$)	Badge (ng)	Badge Rate (L/day)	Tube TWAE ($\mu g/m^3$)	Badge (ng)	Badge Rate (L/day)
06-Dec	1.9	78	41.1	12.6	589	46.8
-20.4°C	1.9	89	46.8	12.6	495	39.3
11-Dec	2.6	67	25.8	13.4	526	39.3
-22.3°C	2.6	100	38.5	13.4	526	39.3
13-Dec	4.8	278	57.9	14.4	937	65.1
-19.5°C	4.8	211	44.0	14.4	611	42.4
24-Jan	8.5	460	54.1	101	5160	51.0
-27.6°C	8.5	690	81.2	101	5180	51.2
26-Jan	6.7	520	77.6	11.7	740	63.3
-25°C	6.7	530	79.1	11.7	840	71.8
30-Jan	13.7	680	49.6	25.6	1470	57.4
-21.7°C	13.7	520	38.0	25.6	1460	57.0

Overall Sampling Rates

Benzene: $\bar{x} = 52.8$, $\sigma = 18.0$ @ 0.05, (2-tailed)

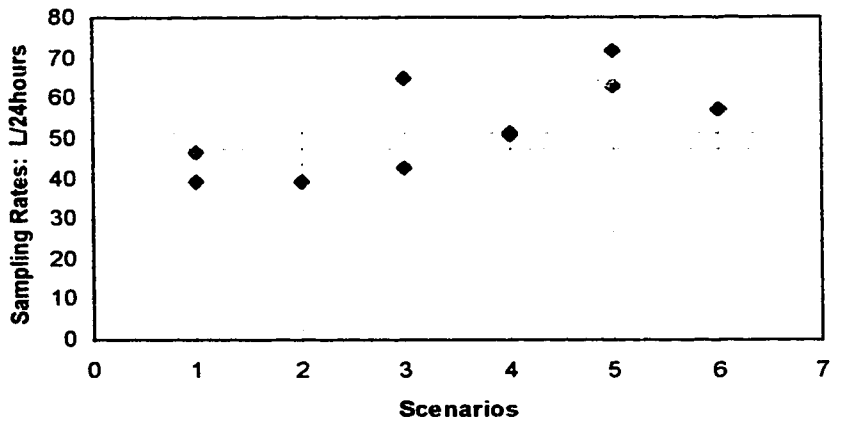
Toluene: $\bar{x} = 52.0$, $\sigma = 11.1$ @ 0.05, (2-tailed)

Figure 3.14



Scenarios (1 to 6): 1.9, 2.6, 4.8, 8.5, 6.7, 13.7 µg/m3
Legend: ..... 3M rate ------Bovar — - - —-Theory

Figure 3.15



Scenarios (1 to 6): 12.6, 13.4, 14.4, 101, 11.7, 25.6 µg/m3
Legend: ..... 3M rate ------Bovar — - - —-Theory

3.4.5.2 Objective Two

The second objective of the Phase III personal sampling study was to compare the tube TWAE values against the TWAE values of the OVM-3500 badge. The air sampling rate of the pump/charcoal tube method was determined by pre and post calibrations, while the 3M (1993) air sampling rates were taken from the manufacturer's literature. The first evaluation assumed that neither the reference method nor the badge were capable of producing 100% accurate impressions of exposure. TWAE ranges for each method were set at ±25% and comparisons were made as per Tables 3.14 and 3.15. Calculations were based on Equation 3.3 with badge TWAEs determined by factoring the mass of analyte collected with the 3M air sampling rates. Reference method results were limited to one tube sample per 24 hour sampling period. Acceptable correlation between the tube and badge was achieved when the two ±25% ranges overlapped; any of the measures that did NOT meet this criteria are **highlighted** on the following tables.

The second evaluation for objective two was a simple linear regression analysis made under the assumption that the mean of the pump sample was 100% accurate. Each relationship between tube and badge was statistically analyzed based on the assumption of a normal distribution of the 12 data points. Figure 3.16 illustrates the data points and states the regression correlations for benzene and toluene.

Table 3.14
Phase III: SKC Tubes vs. OVM-3500 at ±25% Accuracy (Benzene)

SKC Tube TWAE $\mu g/m^3$ (-25% to +25%)	**OVM-3500 TWAE** $\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)
1.9 (1.4 to 2.4)	1.5 (1.1 to 1.9)	1.7 (1.3 to 2.2)
2.6 (2.0 to 3.3)	**1.3 (1.0 to 1.6)**	2.0 (1.5 to 2.5)
4.8 (3.6 to 6.0)	5.4 (4.1 to 6.8)	4.1 (3.1 to 5.2)
8.5 (6.4 to 10.6)	9.0 (6.8 to 11.3)	13.5 (10.1 to 16.9)
6.7 (5.0 to 8.4)	10.2 (7.6 to 12.7)	10.4 (7.8 to 13.0)
13.7 (10.3 to 17.1)	13.3 (10.0 to 16.6)	10.2 (7.6 to 12.7)

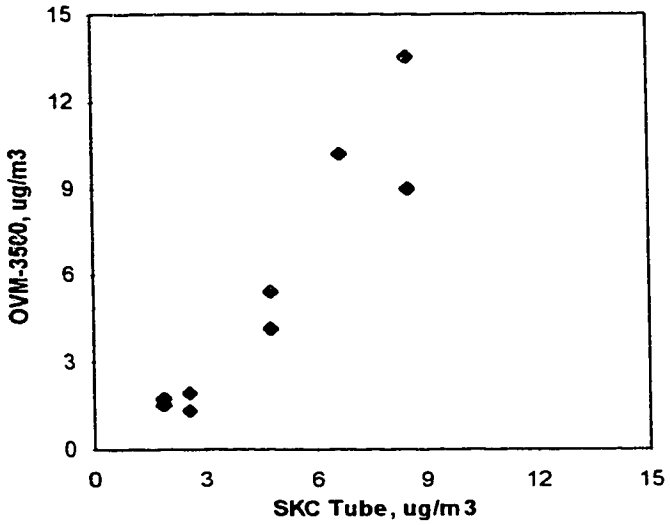
Table 3.15
Phase III: SKC Tubes vs. OVM-3500 at ±25% Accuracy (Toluene)

SKC Tube TWAE $\mu g/m^3$ (-25% to +25%)	**OVM-3500 TWAE** $\mu g/m^3$ (-25% to +25%)	$\mu g/m^3$ (-25% to +25%)
12.6 (9.5 to 15.8)	13.0 (9.8 to 16.3)	11.0 (8.2 to 13.7)
13.4 (10.1 to 16.8)	11.6 (8.7 to 14.5)	11.6 (8.7 to 14.5)
14.4 (10.8 to 18.0)	20.7 (15.5 to 25.9)	13.5 (10.1 to 16.9)
101 (75.8 to 126)	114 (85.6 to 143)	115 (85.9 to 143)
11.7 (8.8 to 14.6)	16.4 (12.3 to 20.5)	18.6 (13.9 to 23.2)
25.6 (19.2 to 32.0)	32.5 (24.4 to 40.6)	32.3 (24.2 to 40.4)

Above: **highlighting** indicates unsuccessful correlation at ±25%.

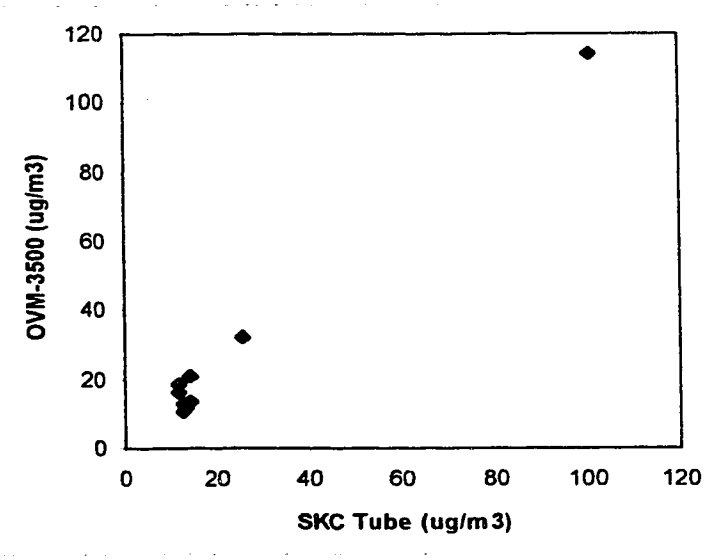
Figure 3.16

1. Personal Benzene Measures



Regression: y = 0.68 + 0.97x, slopes at 95% confidence are 1.38 and 0.57.

2. Personal Toluene Measures



Regression: y = 0.49 + 1.13x, slopes at 95% confidence are 1.2 and 1.06.

3.5 Pilot Study

3.5.1 Purpose

Two Edmonton residents participated in a small pilot study designed to demonstrate the ability of the OVM-3500 badge in assessing exposures to benzene and toluene. During the study, each volunteer wore two badges for 24 hours while badge samples were collected from indoor living areas and the main outdoor entrance. The sampling strategy attempted to construct an understanding of both personal exposure and ambient levels of VOCs in immediate living space. The objective of the pilot study was to generate data for subsequent interpretations based on findings from Phases I through III, and to gain experience with the OVM-3500 for validating its usefulness in a Total Human Exposure based study.

3.5.2 Apparatus

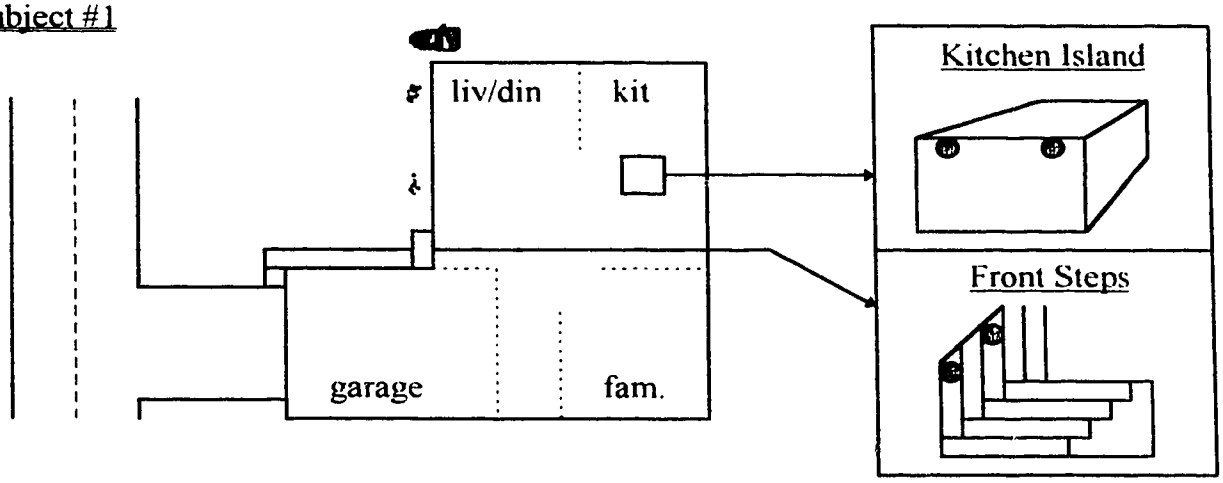
A total of six 24-hour badge samples were deployed at each household; two for personal sampling, two indoors, and two outdoors. Subject #1 was a smoker who lived in a 1990's home built, but not certified, to R-2000 (insulation) standards. The home was located in the south-west corner of the City of Edmonton with no obvious outstanding fugitive emission sources nearby. Subject #2 was a non-smoker who lived in a 1980's home that was well insulated. The building was located in the eastern "bedroom" community of Sherwood Park which may, depending on wind direction, be in the path of emissions from oil refineries in northern Edmonton.

Subjects were originally approached with a formal proposal and written consent form (Appendix 3.12) to ensure full understanding of their responsibilities in the study. Upon approval by the Research Ethics Board, Faculty of Medicine at the University of Alberta, the sampling date was set for Saturday, February 4th, 1996. Crude floor plans and badge locations were constructed and are provided below.

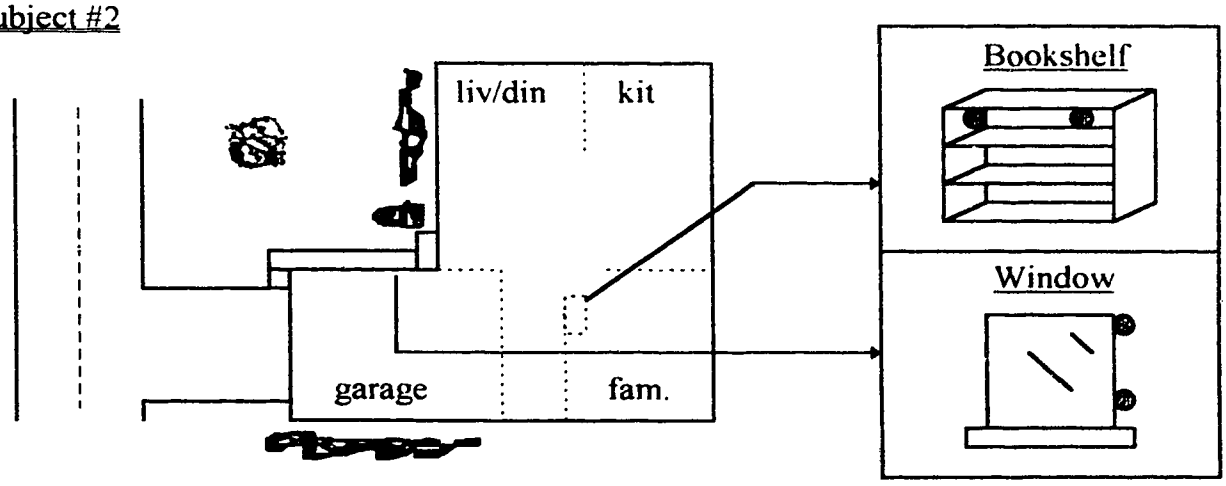
Figure 3.17

Residence Floor Plans

Subject #1



Subject #2



3.5.3 Quality Assurance and Control

The placement of the badges in Figure 3.17 was based on selection criteria designed to maximize the representativeness of the indoor and outdoor air samples. Each of the factors were weighted differently and thus the final decision of badge placement rested primarily on the practical options available for badge placement. The factors considered in the selection of badge locations included:

1. Sufficient ventilation to ensure a constant exchange of air at the face of the sampler.
2. Area where the receptor and other inhabitants occupy most of their time.
3. Indoor samples located at breathing level and away from windows and doors leading to the outside.
4. Outdoor samples at breathing level and facing the major roadway access.
5. Co-located samples located greater than 10cm but less than 2 meters apart.
6. Area where potential interference by the occupants of the home was minimized.

Personal sampling protocol is outlined in Phase II where it is indicated that samplers were to be clipped to the shirt collar in the breathing zone of the host. Both subjects were trained in the simple yet essential procedures for wearing the badge. Volunteers were made aware of the acceptability of removal of the badges when sleeping or bathing, however it was also made clear that sampler time away from the host was to be minimized. Also reinforced was the sensitivity of the Teflon® membrane and the need to only handle the badges by the stainless steel clip.

It is important to note that bias was inherent in the study design as the volunteers were not "blinded" to the sampling. As a result, a Hawthorn effect was created where the volunteers would be expected to act somewhat differently while wearing the badges versus their normal daily activity (Last, 1995). Increasing the probability of this biasing effect was the maintenance of the daily log serving as a constant reminder of how activity affects badge results. Both volunteers were made aware of this and instructed not to second guess their normal actions.

Lastly, field blanks were essential to the quality assurance and control of the pilot study because all samples were transported to a laboratory in Toronto, Ontario for analysis. Field blanks represented any contamination imparted onto the badge both before and after the samples were collected, including during transport. By subtracting field blank values from the results of the exposed samplers, the mass of badge analyte was considered to be reflective of the amount of sample collected over the 24-hour period.

3.5.4 Procedures

1. Upon arrival at the residence, the floor plan and placement of badges was reviewed with the home owner / sample subject.
2. When ready for sampling, all six badges were opened simultaneously with the help of the sample subject.
3. Time and date were recorded on the badges while date, time, and sampler numbers were logged in a field note book.
4. The receptor was then asked to place the badges on each collar; observation of this practice led to constructive comments regarding handling protocol.
5. Indoor and outdoor badges were placed as previously determined.

6. The receptor was reminded of protocol for maintaining daily activity logs. An emergency contact number was given to the host and a time was arranged for sample pick-up.

7. Time was allotted for questions by arriving at the home at least 10 minutes prior to sample pick up. After answering questions, all badges were brought together just prior to the end of the 24 hour sampling period.

8. After the 24 hour exposure, the Teflon® shield was removed, the badges capped, and labeled accordingly. All badges sealed by the volunteer were checked to ensure that the seal was tight.

9. The badges were then packaged in aluminum cans and wrapped with Teflon® tape.

10. To avoid subjecting the badges to a wide range of temperature conditions, the badges were stored at room temperature, packaged in original cardboard boxes and ship by courier to Toronto the following day.

3.5.5 Observations

All samples taken during the pilot study were sent to a Bovar Environmental laboratory in Toronto, Ontario for analysis. Analytical procedures were similar to the Edmonton-base (Enviro•Test) laboratory, with the exception of the method for upgrading the carbon disulfide rinse. Instead of adding an acid to combine with the trace benzene in the CS_2, the contaminant was removed via molecular sieve. Instrumentation used for the analysis included GC-MS(SIM). All results were reported as $\mu g/m^3$ (Appendix 3.13) with corrections for any background contamination in the CS_2. A simple back-calculation using Bovar sampling rates was conducted to translate reported VOC concentration to a badge analyte mass. The desorption efficiency was assumed as 100% and background VOC assumed as non-detectable by

the laboratory in Toronto. Results from two field blanks were taken as the badge background and subtracted from the reported analyte mass.

The objective of the pilot study was to generate badge exposure data for subsequent interpretation based on findings from Phase I through III. Accordingly, all badge masses were adjusted for blanks and desorption efficiency with a description of the environmental parameters of the badge exposure scenario. Appendix 3.14 summarizes the daily activity logs maintained by both subjects over the 24-hour sampling period. Badge results are listed below in Table 3.16.

Table 3.16

Pilot Study Results

Location	Badge	Temp(°C)	Benzene		Toluene	
			ng*	µg/m³**	ng*	µg/m³**
Sub. #1						
Personal	LX04608C	24	550	10.8	1710	37.8
Personal	LX04718C	24	540	10.6	1670	36.9
Indoor	LX04616C	24	320	6.3	800	17.7
Indoor	LX04688C	24	340	6.7	1120	24.8
Outdoor	LX04621C	-11	180	3.5	290	6.41
Outdoor	LX04698C	-11	160	3.1	310	6.86
Blank	LX03742C	24	n/d	-	n/d	-
Sub. #2						
Personal	LX03679C	24	340	6.65	820	18.1
Personal	LX03746C	24	350	6.85	820	18.1
Indoor	LX03804C	24	320	6.26	780	17.3
Indoor	LX03661C	24	310	6.06	760	16.8
Outdoor	LX04751C	-11	130	2.54	140	3.10
Outdoor	LX03671C	-11	100	1.96	80	1.77
Blank	LX03663C	24	n/d	-	n/d	-

* Desorption efficiencies: benzene 103%; toluene 100%

** Concentration calculations were based on 3M sampling rates

Chapter Four: Discussion

4.1 The Experiments

4.1.1 Exposure Chamber

4.1.1.1 Objective One

The first objective of the exposure chamber study was to evaluate the air sampling rate of the OVM-3500 over a range of temperatures and VOC concentrations. In this evaluation, the time-weighted averages of the NIOSH approved charcoal tube reference method were taken as 100% accurate and sampling rates for the badges were back-calculated according to simple diffusion constant equations as previously outlined.

Tables 3.6 and 3.7 provide sampling rate data for benzene and toluene respectively. Over nine trials at three temperatures and concentrations, the mean air sampling rate for benzene was calculated to be 42.7 ± 4.2 L/day with a standard deviation of 10.6L/day. The air sampling rate for toluene was 51.4 ± 8.9L/day with a higher standard deviation of 22.45L/day.

Figure 3.6 clearly shows that the majority of benzene air sampling rates substantially underestimated the "benchmark" rates determined previously by 3M, Bovar, and theoretical calculation. However the sampling rates that were calculated at 5μg/m^3 were generally closer to the benchmark sampling rates than the samples at higher levels. In fact, the mean sampling rate of the three sets of data taken at low level benzene concentrations was 52.5L/day, which was very comparable to the

51.1L/day benzene sampling rate reported by 3M. Sampling rates for toluene are shown in Figure 3.7 as having a much wider but more even distribution around the benchmark rates. The same general trend of increased sampling rate at lower concentrations was also found in the toluene data. Furthermore plottings on both Figures 3.6 and 3.7 indicate that the precision of the samplers decreased with a decrease in VOC concentration. One possible explanation for these trends at lower levels is the variable contribution of background toluene from badge background and background benzene found in the carbon disulfide solvent rinse.

Despite the above deviations from the reference sampling rates, the results showed no trend with temperature, so it was determined that badge sampling rates for both benzene and toluene were not affected by changes in temperature from 24°C, to -5°C, and -15°C.

4.1.1.2 Objective Two

The second objective of the exposure chamber validations was to compare TWAE results generated by the OVM-3500 against measures taken by the SKC charcoal tubes. In this evaluation, 3M sampling rates were used to convert reported badge analyte masses to averaged concentrations in air.

The first evaluation appreciated that both the badge and charcoal tube methods had legitimate sampling inaccuracies of up to ±25%; these ranges were reported and compared in Tables 3.8 and 3.9. There was only one case where the range of benzene measures taken by the badge did not share values with the range of benzene measures

taken by the charcoal tube. This sample was taken at a benzene TWAE of about 5μg/m^3 and under room temperature conditions. The difference between the readings was only slightly outside of the accuracy criteria established in this evaluation and therefore was independently evaluated and deemed to be acceptable. Toluene data was also well correlated with only three data sets having no shared readings at ±25%. Each of the 3 cases were spread evenly over the three temperatures. Again, the differences were small and considered acceptable.

The second evaluation was a simple linear regression analysis of the three data sets for each compound at 24°C, -5°C and -15°C. In all cases, the regressions had a positive y-intercept value and a slope of less than one. Consistent with previous evaluations, there was general underestimation of exposure at high levels and more conformity between badge and charcoal tube results at the lower levels. One finding of this evaluation was that individual regressions for each temperature showed many similarities. In each comparison of benzene readings, the slope of the regression was either 0.65 or 0.64 with y-intercepts ranging between 1.3 and 2.9. Toluene regressions had y-intercepts between 3.4 and 4.2 with slopes of 0.52 at room temperatures, 0.69 at -5°C, and 0.62 at -15°C.

4.1.2 Field Co-location

4.1.2.1 Objective One

The first objective of the field co-location study was to evaluate the air sampling rate of the OVM-3500 in the outdoors at subzero temperatures. In this

evaluation, time-weighted averages from Summa® canisters were considered 100% accurate and sampling rates for the badges were back-calculated according to diffusion constant equations.

Given the results of the exposure chamber study, it was predicted that the low readings expected at the 17th Street Air Monitoring Station would be somewhat overestimated by the badge samples. Table 3.10 lists the data from the station canisters and the mean sampling rates for 9 samples taken over 3 sampling periods at temperatures between -24 to 5°C. The mean air sampling rate for benzene onto the badge was calculated at 60.7 L/day with a standard deviation of 11.6L/day. The air sampling rate for toluene was higher at 68.7 L/day with a standard deviation of 15L/day.

Figure 3.10 clearly shows that the benzene measures correlated well with the benchmark sampling rates with only two of the nine rates not in agreement. Both of these samples were taken during the second scenario that included a period of considerable snowfall and relative humidities over 90%. Relative humidity may have caused the differences between the badge and canister readings, however it was strange that all badges in the set were not affected to the same extent. In fact, one badge was well within the benchmark sampling rate range. Toluene results in Figure 3.11 do not highlight the second sampling day as being different from the other data sets, thus it is assumed that the variable benzene readings were inherent to the badge at these low levels. The toluene readings in the field appear very similar to the

exposure chamber results where both the precision was poor and reference measures somewhat overestimated at low levels.

4.1.2.2 Objective Two

The second objective of the field co-location study was to compare the badge results at 3M rates against the TWAE results reported by the Summa® canisters. The first evaluation under objective two appreciated that both the badge and canister methods had sampling inaccuracies of ±25%. Tables 3.11 and 3.12 report data for benzene and toluene respectively.

Disregarding the data for the first sample set taken on Oct. 24, 1995, the benzene measure comparisons between the badges and canisters were well within the accuracy criterion of this study. Data for toluene was also comparable with seven of nine samples meeting the accuracy criterion. The TWAE values of the two samples were both within a factor of two from the Summa® canister results and this was considered acceptable accuracy given the high imprecision observed for low level toluene measures in the exposure chamber.

The second evaluation was a simple linear regression analysis of the benzene and toluene data. As expected, the reference and test methods were in agreement due to the low concentrations and relatively small range of concentrations being sampled. In all cases the regressions had a positive y-intercept value and a slope of slightly less than one. Construction of a perfect regression at a slope of 1 from the x - y intercept

showed excellent correlation, especially when considering the low level of VOCs being measured.

4.1.3 Personal Sampling

4.1.3.1 Objective One

The first objective of the personal exposure assessment comparison was to evaluate the OVM-3500 sampling rate based on personal pump/charcoal tube TWAE values. In this evaluation, the reference method was again considered 100% accurate and the sampling rates for the badges back-calculated according to diffusion equations.

Table 3.13 summarizes the badge sampling rates for benzene and toluene. Under personal transient exposure scenarios, the overall average air sampling rate for benzene was calculated to be 52.18 L/day with a standard deviation of 17.99L/day. The mean sampling rate for toluene was determined to be 51.98 L/day with a standard deviation of 11.08L/day.

Figures 3.14 and 3.15 show that both benzene and toluene were evenly distributed around the benchmark sampling rates. Interestingly, the first three sample sets, which were taken at lower VOC levels, registered sampling rates at or below the benchmarks rates whereas the final three sets that were taken at higher VOC levels were at or above the benchmarks. This somewhat contradicts both the field and chamber studies where the opposite effect was observed. Notably, the difference

between "high" and "low" in this case was approximately 5 to 10μg/m^3 and any variation could conceivably be caused by inherent imprecision of the badge.

Lastly, sampling rate bias caused by the lower temperature conditions was not observed in the personal sampler data set. Considerable time was spent in environments of extreme cold (Appendix 3.11) during the final three sampling scenarios. The calculated sample rates for this time indicated that the colder temperatures may have actually increased the sample rate of the badge, however these differences could have been caused by normal badge variation.

4.1.3.2 Objective Two

The second objective of the personal exposure assessment validation was to compare the charcoal tube TWAE values against the OVM-3500 measures based on 3M sampling rates. The first evaluation under objective two appreciated that both the badge and charcoal tube methods had sampling inaccuracies of ±25%. Tables 3.14 and 3.15 report data for benzene and toluene respectively.

There was only 1 data set of the 24 compared that did not meet the ±25% accuracy criterion set out in this evaluation. The one reading that was slightly outside of the standard limits was a low level benzene measure of 1.3 μg/m^3. This comparison was judged acceptable and the entire data set was considered to be within acceptable limits of accuracy. Once again, review of the data did not suggest any biasing effect caused by changing temperatures and there were no indications that transient exposures affected badge performance.

The second evaluation was a simple linear regression analysis of the twelve data sets for benzene and toluene exposure measures. The correlation of benzene was almost perfect with a y-intercept of 0.68 and a slope of 0.97. Similarly, the toluene regression was excellent with a y-intercept of 0.49 and a slope of 1.13 indicating slight badge overestimation of TWAE. This overestimation of toluene concentrations at low levels was consistent with both the chamber and field sampling validations.

4.2 Sampler Evaluation

4.2.1 Accuracy

As a NIOSH accepted method, the pump/charcoal tube sampler was assumed to have an accuracy range of ±25%. Notably, this accuracy criterion was intended for personal sampling at workplace concentrations over a typical work day. During phases I and III the pumps were used over 4 and 24 hours respectively and at maximum NIOSH flow rates of 200 mL/min. Given that the SKC tube was used in this investigation for purposes other than that intended by NIOSH, it is assumed its ±25% is a somewhat conservative guideline for confidence around "true" measures.

The accuracy of the second reference method, Summa® canisters, was also assumed as ±25%. As stated earlier, direct injection of VOC standards into the canister produced results at ± 5% accuracy. Actual sampling in the field is assumed to

have a higher accuracy tolerance (± 25%) because the mechanism for supplying air from the outside to the Summa® canister could potentially increase sampling bias.

All results that are presented in this report as a TWAE should be taken in context as the median of a range of values. In fact, this entire study was a comparison of ranges, not single values. As such, common statistical analyses such as regression analyses that were used to evaluate agreement between badges and reference methods were only constructed as useful indications of correlation and must be interpreted with recognition of the potential legitimate variation of the exposure data.

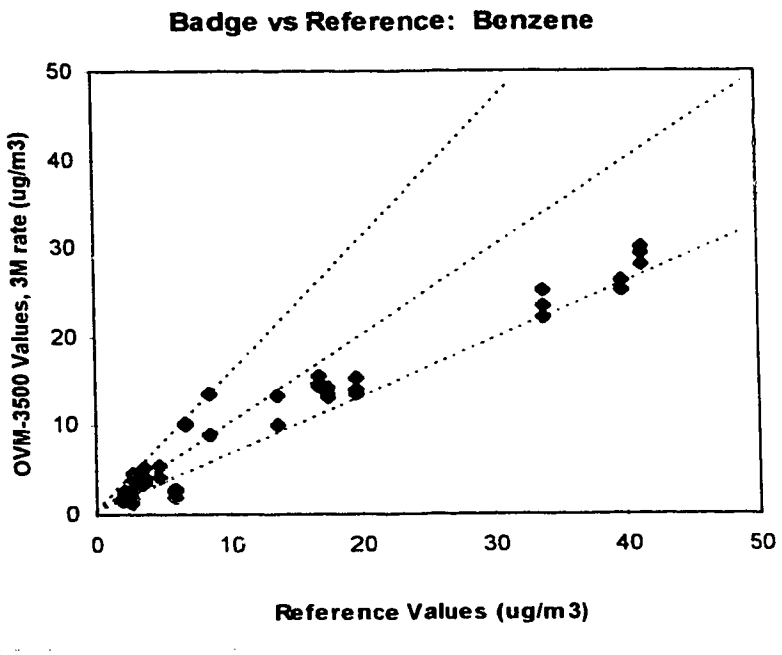
4.2.1.1 Accuracy: Benzene

For all of the 48 benzene samples collected and compared against reference methods, only 4 did not meet the ±25% accuracy criterion. Of the four values that did not meet this standard, most were at low levels and none were more than a factor of 2 from the reference TWAE. When assuming the 3M sampling rate of 51.12 L/day for benzene collection from air, all correlations were positive with agreement being maximized within a concentration range of 5 to 20 $\mu g/m^3$.

Figure 4.1 provides data points for all comparisons of badge measures of benzene at 3M sampling rates against reference sampler TWAEs. Imposed on the graph is a range of values representing perfect correlation at ± 25%. Overall badge accuracy was estimated through consideration of the results of the ± 25% accuracy criterion evaluations and a qualitative interpretation of Figure 4.1. The practical accuracy limits of the OVM-3500, when used for measuring ambient benzene over 24

hours, was determined to be ±25% at TWAEs of 5 to 20μg/m^3, and ±50% for readings outside of this range.

Figure 4.1

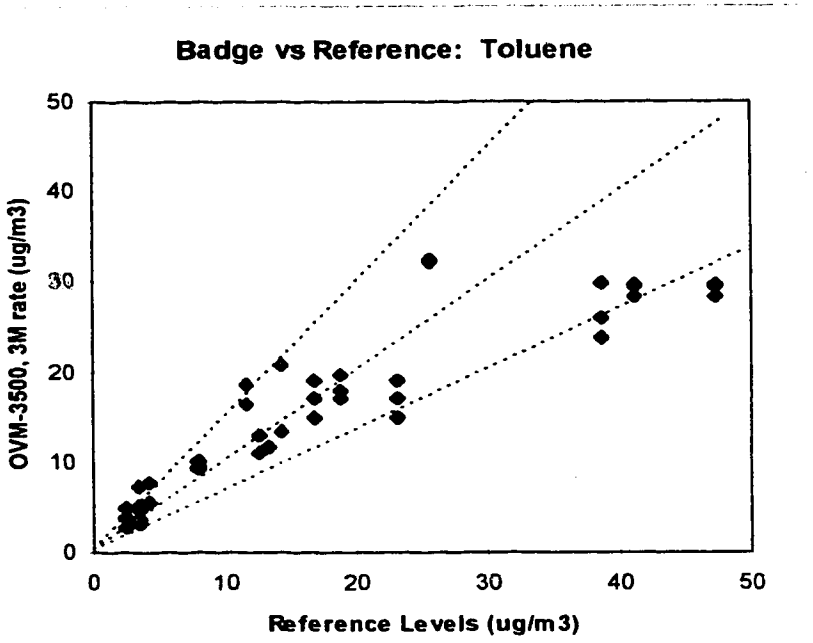


4.2.1.2 Accuracy: Toluene

For all of the 48 toluene badge measures that were compared against reference methods, only 3 did not meet the ± 25% accuracy criterion. Of these three values, most were at low levels and none were more than a factor of 2 from the reference TWAE. When assuming the 3M sampling rate of 45.2 L/day for toluene collection from air, all correlations were positive with agreement between the methods maximized at levels between 5 to 30 μg/m^3.

Figure 4.2 provides data points for all comparisons of badge measures of toluene against reference sampler TWAEs. Imposed on the graph is a range of values representing perfect correlation at ± 25%. Overall badge accuracy was estimated through consideration of the results of the ± 25% accuracy criterion evaluations and a qualitative interpretation of Figure 4.2. The practical accuracy limits of the OVM-3500, when used for measuring ambient toluene over 24 hours, was determined to be ± 25% at 5 to 30μg/m^3 and ± 50% for readings above and below this range.

Figure 4.2



4.2.2 Precision

Quantification of badge precision for measuring ambient VOCs over 24 hours was calculated by assuming a typical exposure value for benzene and toluene and

calculating precision based on the overall standard deviation of the badge sampling rates. 10 $\mu g/m^3$ was assumed as a typical benzene exposure and 20 $\mu g/m^3$ for toluene. The mean plus/minus standard deviation calculations for the sampling rates were:

Benzene: 48.8 ± 14.5L/day

Toluene: 53.8 ± 20.6L/day

Assuming typical exposure levels, calculations of masses of VOC collected on the badge were made according to the average sampling rates (above) and then translated back to TWAE values via 3M sampling rates.

A typical 10 $\mu g/m^3$ TWAE values for benzene was translated to a mean of 9.4$\mu g/m^3$ and a standard deviation of 2.8 $\mu g/m^3$ corresponding to 5.6 $\mu g/m^3$ for 95% confidence bounds, or about 55% of the assumed 10 $\mu g/m^3$ TWAE. A final estimate of badge precision for measuring benzene included a review of the data and consideration that this ± 55% figure included the highly variable low level sampling rates in the study. Accordingly, benzene TWAE readings of 5 $\mu g/m^3$ and above were considered to vary up to ± 25% while measures below 5 $\mu g/m^3$ varied up to ± 50%.

A typical 20 $\mu g/m^3$ TWAE value for toluene was translated to a mean of 23.8 $\mu g/m^3$ and a standard deviation of 9.1 $\mu g/m^3$, corresponding to 18.2 $\mu g/m^3$ for 95% confidence bounds, or about 90% of the assumed 20 $\mu g/m^3$ TWAE. A final estimate of badge precision for measuring toluene included a review of the data and consideration that this ± 90% figure included the extremely variable low level sampling rates in the study. Accordingly, all badge measures of toluene that were

above 10 $\mu g/m^3$ were considered to vary up to ± 25%, while measures of toluene below 10 $\mu g/m^3$ were considered to vary up to ± 90%.

4.2.3 Representativeness

Time-weighted average concentrations were not representative of the variability of VOC exposures during the sampling duration. Furthermore, it must be clear that the above calculations for accuracy and precision do not pertain to any of the variations or spikes averaged out by the TWAE. Rather, these confidence limitations are strictly related to confidence of the reported mean values alone.

In addition, all exposure data generated by the OVM-3500 were only representative of the air that came into contact with the face of the badge. Personal and ambient measures assume that the concentration reaching the badge is equivalent to the concentration of air being breathed or the air within the particular microenvironment of the ambient sample. The main point is that the analytes collected by the badges in this research were NOT necessarily the analytes that were found distributed in the exposure chamber, around the air monitoring station, or in the breathing zone of the receptor - this was an assumption.

The data quality objectives for representation have been met by exposing the badges to scenarios that would be expected to be encountered in a typical community exposure study in Alberta. Both personal and ambient validations were performed at temperatures characteristic of a northern winter climate. In addition, all analytical and

sampling methodologies were selected as tangible protocols for a larger and more general community-based study.

Lastly, sample size selection for each of the three phases was based on both t-statistic confidence and practical research limitations. All data reported in this study includes appropriate statistical descriptions of distribution and explicit expressions of uncertainty.

4.2.4 Completeness

Completeness is a measure of the amount of valid data obtained from the research compared to the amount expected under absolutely correct conditions. The following are short discussions of the potential sources of bias that may have caused research findings to be deviant from absolute accuracy.

4.2.4.1 Temperature

Subzero temperatures were introduced as a potential source of bias due to potential impairment of the sampling rate according to diffusion coefficient calculations and potential enhancement of sample collection caused by increased adsorption efficiency. As stated in the experiment discussions, there was no obvious effect of temperature on the badge sampling rates. It is possible that the two factors canceled each other whereby decreased temperatures did impair VOC diffusivity but increased adsorption efficiency decreased the amount of sorbate lost due to reverse diffusion. In short, the data in this thesis demonstrated that even though theory

warrants a correction factor at temperatures below 24°C, empirical evidence suggests that corrections were not required to subzero temperatures of -15°C.

4.2.4.2 Relative Humidity

Potential bias related to relative humidity was seen once during the study and this occurred during the second field samples taken from the 17th Street Air Monitoring Station. In this case, increased relative humidity appeared to affect sampler precision but accuracy remained consistent with other sampler results. Interpretations of the data suggest that badge performance was somewhat affected by the higher humidity but the extent of the effects were minimal and considered inconclusive.

4.2.4.3 Transient Exposure

The effect of transient exposure was consistent with the Hori study (1993) that demonstrated how the OVM-3500 was responsive to changes in VOC concentrations at the badge interface. Also apparent in this research was the minimal effect of transient temperature exposure scenarios on the badge sampling rate over a 24 hour sampling duration.

4.2.4.4 Sampler Efficiency

Evidence of desorption of badge sorbate (sampler efficiency) was seen in the exposure chamber experiments where sampling rates decreased with increased VOC concentration. It is theorized that the badges lost a given proportion of VOC over the

24 hour samples and that this loss was not as apparent at lower concentrations due to benzene contributions from the CS_2 rinse and toluene backgrounds on the badges.

For example, assume that 10% of the benzene collected by the badge was desorbed to the air over the 24 hour sampling period and that 25 ng of benzene was added to each badge aliquot during analysis. At 50 $\mu g/m^3$ the badge would collect 2556 ng at a 51.12 L/day sampling rate; 10% or 257 ng would be lost during sampling and 25 ng would be gained during analysis, resulting in a net loss of 232 ng. When consider a 5 $\mu g/m^3$ TWAE, the badge would collect 256 ng; with 26 ng lost during sampling and 25 ng gained during analysis, resulting in a much more accurate measure.

Again, this is only a theory and although it may be refuted, the data from the exposure chamber experiments clearly indicated an underestimation of benzene and toluene levels at higher concentrations.

4.2.4.5 Face Velocity

The effect of face velocity has been well documented by both 3M and independent researchers. According to the literature, the badge has a wide range of operable face velocities making it resistant to biasing of results. Deployment of the first sample set of badges at the 17th Street Station required re-sampling due to lack of circulation. This was corrected in the field protocol to make the sample data more complete. Similarly, air circulation rates in the chamber were set to satisfy the needs of the badges; for example, the lowest flow rate used in the experiment was

approximately 500 mL/min (720 L/day) which exceeded the total sampling rate of the badges (153 L/day) by about a factor of 5.

4.2.4.6 Sample Analysis

All analytical work, except for the pilot study, was performed by Envirotest Laboratories in Edmonton. The firm had formal accreditation with 3M and considerable experience working with the OVM-3500. Unfortunately, all of their practice analyzing the 3M badge was for TWAE determination of occupational samples. As such, their well established methods were based on FID and, in some cases, PID/FID detection.

As outlined earlier, the analytical method of choice for analyzing the 24-hour ambient samples is GC-MS(SIM). Envirotest had recently purchased a used unit from another firm and allocated it to this study. Unfortunately, there were several problems with the equipment early in the study and many of the initial samples required reworking. With the equipment overhauled, the sample results implied a considerable background of benzene from the internal standard in the CS_2 rinsing solvent. All results were corrected for this high background and lower levels of deuterated benzene were used in subsequent analyses. This type of learning curve was expected, however the results generated from the first set of samples processed by Envirotest must be viewed with caution.

4.2.5 Comparability

Subzero temperature chamber tests over 24 hours and ambient VOC concentrations were parameters indicative of an experimental design geared to a northern Canadian community. The results of the first deployment of field co-located samplers appeared to underestimate ambient levels of both benzene and toluene by a factor of about five. This did not compare with the results of the chamber studies, in fact if badge values were consistent with the chamber results they should have been slightly higher than the reference method. A decision was made to change the sampling protocol and the first set of samples were eliminated from the experiment interpretations. The revised procedures included putting the badges under the exposure chamber, directly exposed to the outdoor air. Ironically, after deploying samples in the pilot study it was clear that these field validations were very comparable to actual residential samples located in direct contact with ambient air under a protective soffit overhang.

The personal sampling protocol was based on communications with Health Canada (Otson, 1996). Bovar Environmental (Fellin, 1996), and Alberta Health (Kindzierski, 1995). Combining ideas and findings from previous and ongoing sampling programs ensured that the results of this research would be comparable to the sampling protocol used in future Total Human Exposure studies.

4.3 The Pilot Study

4.3.1 Subject #1

On the afternoon of February 4th, 1996, a set of six OVM-3500 samplers were deployed at the home of "Subject #1" located in the south-western region of Edmonton. Subject #1 was a smoker who lived in a relatively new and well insulated home with three other family members. The sample duration was 24 hours and two samples were collected from the receptor, an indoor location, and an outdoor location. Time-weighted average exposure measurements were collected and compared to effectively demonstrate the ability of the OVM-3500 to measure benzene and toluene in a Total Human Exposure study.

Section 2.2.2.5 and 2.2.3.5 provide a discussion of previous studies that included similar measurements of benzene and toluene. Based on these studies, approximate TWAEs were predicted for Subject #1:

Benzene

Outdoor: 2.6 to 3.4μg/m^3 (Cheng, 1996)
Indoor: 3 x outdoor or 7.8 to 10.2μg/m^3 (Wallace, 1989)
Personal: greater than predicted Fort McMurray average of 10μg/m^3 because of smoking status

Toluene

Outdoor: 4.6 to 7.1μg/m^3 (Cheng, 1996)
Indoor: 5 x outdoor or 23 to 35.5μg/m^3 (Montgomery, Kalman, 1989)
Personal: greater than predicted Fort McMurray average of 20μg/m^3 because of smoking status

4.3.1.1 Exposure Assessment

Badge analyte masses determined by Bovar Environmental (Table 3.16) were imported into Table 4.1 for calculation of time-weighted average exposure concentrations using 3M air sampling rates. Appropriate corrections and confidence limits were applied according to the findings of the validation studies.

Table 4.1

Pilot Study TWAE, Subject #1

Placement	Benzene Mass (ng)	Benzene TWAE ($\mu g/m^3$)	Toluene Mass (ng)	Toluene TWAE ($\mu g/m^3$)
Personal	550	10.8 ± 2.7	1710	37.8 ± 18.9
Personal	540	10.6 ± 2.6	1670	36.9 ± 18.5
Indoor	320	6.3 ± 1.6	800	17.7 ± 4.4
Indoor	340	6.7 ± 1.7	1120	24.8 ± 6.2
Outdoor	180	3.5 ± 1.8	290	6.4 ± 1.6
Outdoor	160	3.1 ± 1.6	310	6.9 ± 1.7

4.3.1.2 Interpretation

As expected, the TWAE concentrations of benzene and toluene were higher for samples taken indoors versus outdoors, with even higher levels at the receptor. These results were consistent with the literature and further emphasized the need for personal monitoring for true assessment of exposure. After studying the data more closely, it was thought that the ratio of indoor to outdoor benzene was surprisingly low for a home with a smoker. The information from the personal activity log suggested that the resident smoker did not smoke indoors and went outside whenever a cigarette

was desired. A follow-up phone call to the study volunteer confirmed that this was, and always has been, the case. Indoor toluene measures were substantially higher than outdoor which indicated that the majority of toluene in the receptor environment was originating from indoor sources and not from source emissions in the outdoors.

Further study of the personal daily activity logs indicated that this volunteer spent a relatively large portion of time traveling in his automobile to various inner city destinations. Furthermore, Subject #1 smoked a total of 9 cigarettes and fried bacon on the morning of February 5th. After reviewing the exposure data, it was surprising that personal exposures to benzene were not higher than measured, however toluene exposures corresponded well with the high amount of local city driving.

An estimate of the health risks associated with the personal TWAE data generated from this pilot study was determined by matching exposure results to previously published risk estimates. This exercise was not meant as a full health risk assessment, rather the main objective was to demonstrate the use of the exposure data in assessing health risks according to federal health risk literature.

The average toluene exposure that Subject #1 received over the 24 hour sampling period was found to be two orders of magnitude below the CEPA (1992b) guideline, while TWAE levels for benzene equated to a risk, with reference to Table 2.4, of approximate 1 in 10 000 chance per 70 year lifetime (IRIS, 1995a) of contracting leukemia. This risk estimate is provided as an illustration only and it should be taken literally because of the extremely limited sampling performed.

4.3.2 Subject #2

On the afternoon of February 4th, 1996, a set of six OVM-3500 samplers were deployed at the home of "Subject #2" which was located a short distance east of Edmonton in Sherwood Park. Subject #2 was a non-smoker who lived in a relatively new and well insulated home with three other family members. The sampler duration was 24 hours and two samples were collected from the receptor, an indoor location, and outdoor location. Time-weighted average exposure measurements were collected and compared to demonstrate the ability of the OVM-3500 to measure VOCs in a Total Human Exposure study.

Section 2.2.2.5 and 2.2.3.5 provided a discussion of previous studies that included similar measurements of benzene and toluene. Based on these studies, approximate TWAEs were predicted for Subject #2:

Benzene

Outdoor: 2.6 to 3.4μg/m^3 (Cheng, 1996)
Indoor: 3 x outdoor or 7.8 to 10.2μg/m^3 (Wallace, 1989)
Personal: less than or equal to the predicted Fort McMurray average of 10μg/m^3

Toluene

Outdoor: 4.6 to 7.1μg/m^3 (Cheng, 1996)
Indoor: 5 x outdoor or 23 to 35.5μg/m^3 (Montgomery, Kalman, 1989)
Personal: less than or equal to the predicted Fort McMurray average of 20μg/m^3

4.3.2.1 Exposure Assessment

Badge analyte masses determined by Bovar Environmental (Table 3.16) were imported onto Table 4.2 for calculation of time-weighted average exposure

concentrations using 3M air sampling rates. Appropriate corrections and confidence limits were applied according to the findings of the validation studies.

Table 4.2

Pilot Study TWAE, Subject #2

Placement	Benzene Mass (ng)	Benzene TWAE ($\mu g/m^3$)	Toluene Mass (ng)	Toluene TWAE ($\mu g/m^3$)
Personal	340	6.7 ± 1.7	820	18.1 ± 4.5
Personal	350	6.9 ± 1.7	820	18.1 ± 4.5
Indoor	320	6.3 ± 1.6	780	17.3 ± 4.3
Indoor	310	6.1 ± 1.5	760	16.8 ± 4.2
Outdoor	130	3.5 ± 1.8	140	3.1 ± 2.3
Outdoor	100	3.1 ± 1.6	80	1.8 ± 1.3

4.3.2.2 Interpretation

As expected, the TWAE concentrations of benzene and toluene were higher for samples indoors versus outdoors. Interestingly however, the personal sampler TWAEs were almost identical to the readings for indoor air in the receptor's residence. This ratio of indoor to personal exposure levels was not consistent with the literature but made sense after reading the daily activity log of the volunteer subject. Subject #2 resided in the same residence where the indoor samples were taken for a total of 23 hours and 40 minutes during the 24 hour sample period. Although the sample size is very limited, there is the suggestion that the indoor samples were placed in an area of the home that was very representative of personal exposures throughout.

After studying the data more closely, it was determined that the ratio of indoor to outdoor benzene and toluene measured in the home of Subject #2 was almost identical to that of Subject #1. Subject #2 was possibly atypical with a limited range of personal activities over the 24 hour period. (Appendix 3.14) Toluene levels were lower outside the home of Subject #2 which may be explained by either lower amounts of traffic or, more likely, fugitive emissions from Subject #1 cigarettes increasing the readings on the Subject #1 outdoor badges. Regardless, indoor levels were virtually identical and this is very reflective of the similar construction of the two homes and demographic make-up of the two families.

An estimate of health risks associated with the personal TWAE data generated from the pilot study was determined by matching exposure results to previously published risk estimates. Once again, this exercise was not meant as a full health risk assessment, rather the main objective was to demonstrate the use of the exposure data in assessing health risks according to federal health risk literature.

The average toluene exposure that Subject #2 received over the 24 hour sampling period was found to be two orders of magnitude below CEPA (1992b) guidelines, while TWAE levels for benzene equated to a risk, with reference to Table 2.4, of between 1 in 10 000 and 1 in 100 000 chance per 70 year lifetime (IRIS, 1995a) of contracting leukemia. This risk estimate is provided as an illustration only and it should not be taken literally because of the extremely limited sampling performed.

4.4 Community Exposure Assessment

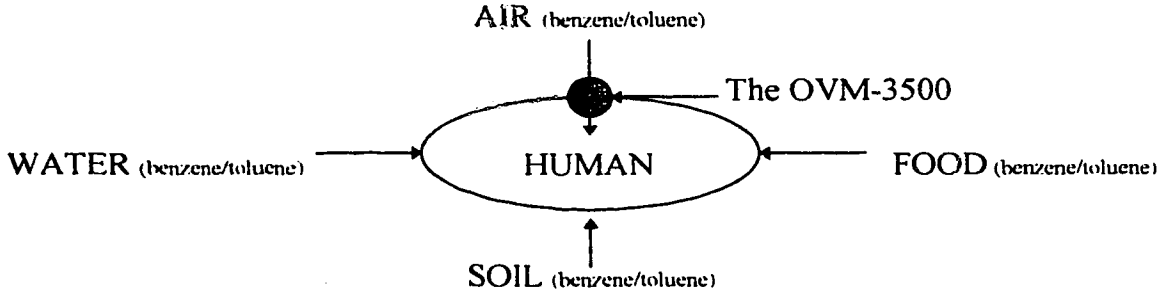
4.4.1 THE and the OVM-3500

As demonstrated in several studies, including the pilot in this research, conventional ambient monitoring does not accurately reflect personal exposure. Stations function to measure seasonal trends or short term variations in air contaminant levels caused by industrial or domestic emissions. At best, a community air monitoring station provides an indication of overall community air but gives no impression of the variable levels of contaminants found in microenvironments both in and outside of local homes.

Figure 4.3 is a rendition of the conceptual model of THE (Total Human Exposure) presented as the first figure in this thesis. In this model, the OVM-3500 badge is placed on the human receptor to achieve a representative measure of actual exposure to airborne benzene and toluene. The exposure equation becomes even more complicated when other pathways are considered in a multimedia perspective of exposure assessment.

Figure 4.3

Total Human Exposure and the OVM-3500



Personal badge samplers are a tool to help researchers gather personal samples in an ergonomically friendly manner. The easy use of the badge promotes voluntary commitment from a community and compliance from those participating in the study. Invaluable experience gained during the pilot study made it clear that members of the sampled household often hold a keen interested in the research. In fact, community sampling programs require a substantial commitment by the investigator to meet the needs of the study population. Investigators must have an ability to communicate and possess sound knowledge of environmental science.

4.4.2 THE and Public Policy

In 1993, CanTox Inc. modeled plume dispersions of 32 chemical emissions leaving the Syncrude Mildred Lake facility en route to Fort McMurray. At the same time, the federal and provincial governments have invested heavily into maintaining ambient air monitoring stations in the community to measure fluctuations of these contaminants in the outdoor air. An underlying purpose for conducting these studies is to protect human health, however based on the research findings ambient monitoring fails to accurately reflect personal exposure. Recognizing this shortcoming, it would be essential to integrate a Total Human Exposure rationale into the process to better understand the need to protect human health.

Chapter Five: Conclusions

There are two conclusions made from the results obtained during the exposure chamber experiments. The first is that the badge underestimated measures of VOCs at high levels and overestimated measures at low concentrations. Fortunately, the range between these extremes included the concentrations that were most likely to be measured during a typical 24 hour community exposure assessment. It is theorized that much of the error at the lower concentrations was due to a decrease in precision of the badge. Compromised precision was thought to be primarily attributed to the inherent variability of background contaminants on either the badge or in the analytical extraction solutions.

The second conclusion, based on the chamber results, refutes the current belief that sampling rates decrease with temperature as there were no indications at either -5 nor -15°C that this was the case. In fact, the sampling rates often increased with decreased temperatures during the chamber tests. Based on exposure chamber results, it is concluded that temperature had no effect on the badge sampling rate with final judgment pending on the results of Phases II and III.

Co-location of the badge at the 17th Street Monitoring station served to test the badge sampling rate under actual outdoor conditions and subzero temperatures. Based on exposure chamber data, it was predicted that the badge would not be affected by temperature but would slightly overestimate the low ambient VOC concentrations. The results of the field trials were consistent with the observations made during the

exposure chamber experiments, with the exception that the correlations against the reference method were stronger in the field.

Conclusions pertaining to the personal sampling validations were based not only on the level of badge conformity with the charcoal tube reference method but also with the consistency of the results in the previous phases. The TWAE levels measured during Phase III were highly correlated with the reference method. This was expected given that the measures were within the range where badge accuracy was highest during the exposure chamber study. Phase III results also showed that the OVM-3500 performed as well during transient exposures as it did under constant exposures in the field and in the lab. Furthermore, the badge sampling rate was NOT adversely affected during exposures of several hours at temperatures well below -30°C.

Taken together, Phases I, II, and III agree with the thesis and combine to support two conclusions:

1. When using the 3M air sampling rates for benzene and toluene, the OVM-3500 can measure time-weighted average exposures within acceptable margins of error at ambient levels over 24 hour sampling durations.
2. Temperatures between 24 and -15°C do not significantly affect the air sampling rate of the OVM-3500 during exposures over 24 hour sampling durations.

The Alberta Oilsands Community Exposure and Health Effects Assessment Program is being developed by Alberta Health and other groups to identify linkages between human exposure to environmental toxicants and the prevalence of disease. The findings of the thesis indicate that the 3M Organic Vapour Monitor #3500 is suitable for use in the assessment of personal exposure to ambient volatile organic compounds both directly at the receptor and within common indoor and outdoor microenvironments. This conclusion is based on the successful validation of this sampling methodology within acceptable margins of error under environmental conditions that would be expected in the community of Fort McMurray.

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Appendices

Appendix 2.1

Calculation of Diffusion Coefficient

The following is an excerpt from 3M (1993). Accurate estimations of diffusion coefficient may be determined through the Wilks and Lee Modification (Ind. Eng. Chem. 47, 1253 [1955]) of the equation by Hirschfelder, Bird, and Spots (Trans. Am. Soc. Mech. Engrs., 71921 [1949[) as outlined in J.H. Perry (Chem. Engrs. Handbook).

Hirschfelder Equation

$$Dg = \frac{BT^{3/2}\sqrt{1/M_1 + 1/M_2}}{P\, r_{12}^{2}\, I_D}$$

Where,

Dg = gas diffusivity (cm^2/sec)

B = $[10.7 - 2.46\sqrt{1/M_1 + M_2}] \times 10^4$

T = absolute temperature (°K)

M_1, M_2 = molecule weight of components 1 and 2

P = absolute pressure (atm)

r_{12} = collision diameter A°

I_d = collision integral for diffusion function of kT/ε_{12}

$\varepsilon 12/k$ = $\sqrt{(\varepsilon_1/k) \bullet (\varepsilon_2/k)}$

k = Boltzmann constant (1.38 x 10-6 erg/°K)

ε = energy of molecule interaction (ergs)

ε/k = 1.15 Tb = 1.92 Tm

T_b = temperature of component boiling point

T_m = temperature of component melting point

Appendix 3.1

Enviro•Test Laboratory Results

Lab Work Order: E510634
Date Received: 10/25/95

- chamber QA/QC
- first field samples

Lab Work Order: E511215
Date Received: 11/09/95

- chamber samples
- field samples

Lab Work Order: E511529
Date Received: 11/27/95

- chamber samples
- field samples

Lab Work Order: E601028
Date Received: 12/19/95

- field samples
- personal samples
- chamber samples

Lab Work Order: E601390
Date Received: 01/31/96

- personal samples

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107 - 111 Research Drive, Saskatoon Saskatchewan S7N 3R2 Telephone (306) 668-8370 Fax (306) 668-8383
Bay 3, 10919 - 96 Avenue, Grande Prairie T8V 3J4 Telephone (403) 539-5196 Fax (403) 539-6295
Unit F - 1420 Clarence Avenue, Winnipeg, Manitoba R3T 1T6 Telephone (204) 452-8104 Fax (204) 477-8719

CHEMICAL ANALYSIS REPORT

UNIVERSITY OF ALBERTA
13-130 CLINICAL SCIENCES BLDG
EDMONTON, ALBERTA
T6G 2G3

DATE: December 22, 1995

ATTN: VINCE GAGNER

Lab Work Order #:	E510634	**Sampled By:**	VINCE GAGNER
Project Reference:	NOT SUBMITTED	**Date Received:**	10/25/95
Project P.O.#:	NOT SUBMITTED		

Comments:

APPROVED BY:

Larry Serbin
Project Manager

ALL SAMPLES WILL BE DISPOSED OF AFTER 30 DAYS FOLLOWING ANALYSIS. PLEASE CONTACT THE LAB IF YOU REQUIRE ADDITIONAL SAMPLE STORAGE TIME.

ACCREDITED BY: (Edmonton)
CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL) - For specific tests registered with the Association
STANDARDS COUNCIL OF CANADA - Organic & Industrial Hygiene analysis as registered with the Council
AMERICAN INDUSTRIAL HYGIENE ASSOCIATION (AIHA) - Industrial Hygiene analysis registered by AIHA
AGRICULTURE CANADA - Pesticide in Fruits and Vegetables, pesticides and PCP in meat

CERTIFIED BY: (Calgary)
CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL) - For specific tests registered with the Association

BENZENE AND TOLUENE ANALYSIS ON CHARCOAL TUBES:

LAB SAMPLE #:	SAMPLE ID	RESULTS (µg/Front/Back) Benzene	Toluene
E5-10-634-01A	10-18-A-1-F	ND/ND	0.10/ND
E5-10-634-02A	10-18-A-2-F	ND/ND	0.10/ND
E5-10-634-03A	10-19-A-1-B	ND/ND	ND/ND
E5-10-634-04A	10-19-A-2-B	ND/ND	ND/ND
E5-10-634-05A	10-23-A-1-F	0.47/ND	0.55/ND
E5-10-634-06A	10-23-A-2-F	0.40/ND	0.52/ND
E5-10-634-07A	10-23-A-1-B	0.31/ND	0.52/ND
E5-10-634-08A	10-23-A-2-B	0.35/ND	0.54/ND
E5-10-634-09A	10-24-A-1-F	1.74/ND	2.06/ND
E5-10-634-10A	10-24-A-2-F	1.89/ND	2.07/ND
E5-10-634-11A	10-24-A-1-B	1.81/ND	2.08/ND
E5-10-634-12A	10-24-A-2-B	1.72/ND	2.07/ND

Results not corrected for desorption efficiency.

BENZENE AND TOLUENE ANALYSIS ON 3M ORGANIC VAPOUR MONITORS:

LAB SAMPLE #:	SAMPLE ID	RESULTS (µg/badge) Benzene	Toluene
E5-10-634-13A	10-24-P-05346C	0.14/ND	0.14/ND
E5-10-634-14A	10-24-P-05330C	ND/ND	0.25/ND
E5-10-634-15A	10-24-P-05402C	ND/ND	ND/ND
E5-10-634-16A	10-24-P-05221C	ND/ND	0.95/ND

Results not corrected for desorption efficiency

NOTE#1: Blank 3M Badges showed toluene background in the range of 0.1 to 0.5 µg. Results were corrected by removing this average of the blank results (see quality control data below).

NOTE#2: Detection limits are reported based on calculations discussed below. Values are reported to 0.10µg and two decimal places for each analyte for client information only. Note comments below for true detection limits.

METHODOLOGY:

SAMPLE ANALYSIS: Front and back charcoal tube sections, and 3M absorbent pads were placed in 4mL glass vials and 2.0mL desorbing solution was added. The vials were then shaken for a minimum thirty minutes to desorb the samples. The desorbing solution was prepared by acid washing (nitric/sulfuric acid) analytical grade carbon disulfide to remove residual benzene. Deuterated benzene and toluene (benzene d6, toluene d8) were added to give concentrations of $\simeq 3\mu g/mL$ respectively. The resulting solution was used for desorption of all samples, spikes, desorption efficiency tests and calibration solutions.

Analysis was performed by gas chromatography with mass spectrometric detection operating in selected ion mode monitoring ions specific for deuterated and undeuterated benzene and toluene. The deuterated compounds act as sample specific and analyte specific internal standards but do not interfere in the analytical when analyzed by GC/MSD.

Calibration solutions were prepared at levels of approximately 0.1, 1.0 and 10μg/mL each analyte in desorbing solution. Each set of calibration solutions was analyzed before and after each set of samples and at a frequency of at least every fifteen analyses.

DESORPTION EFFICIENCY: Desorption efficiencies were tested at the three calibration levels in duplicate for 3M badges by adding 2.0mL of each calibration standard solution to blank absorption pads in 4mL glass vials. The vials were shaken for thirty minutes and the resulting solutions analyzed as described above. Charcoal tubes desorption efficiency was also tested at the three levels in duplicate by adding blank front sections of charcoal tubes to vials and treating in the same manner as 3M charcoal pads.

BLANK ANALYSES: Blank desorbing solution was analyzed in triplicate to determine benzene and toluene background levels. Although the acid washed CS_2 did not show detectable amounts of benzene or toluene, the desorbing solution did show levels of approximately 0.05μg/mL benzene from contribution of small amounts of undeuterated benzene in the deuterated benzene d_6. Toluene was not detected in the desorbing solution to a level of 0.01μg/mL. All resulting analyses areas were corrected for this background before proceeding with any calculations.

Blank charcoal tubes were analyzed in duplicate. Six blank 3M badges (two as field blanks and two as sampling media blanks as supplied by client) were analyzed to determine badge background of the analytes. All results were corrected for average solvent background contributions prior to determining sampler backgrounds.

SPIKES: Ten charcoal tubes front sections were spiked by adding 10μL of spiking solution to front charcoal sections in desorption vials. Four blank 3M charcoal pads were spiked at two levels in duplicate by adding 10μL of spiking solution at two concentration levels. The samples were desorbed and analyzed in the same manner as the samples. All results were corrected for solvent background and media background before determining percent recoveries.

QUALITY CONTROL - RESULTS SUMMARY:

Blanks	µg benzene	µg toluene
Blank solution (average)	0.27	ND
Blank charcoal tubes (solvent corrected)	0.04	0.02
	0.11	0.04
Charcoal tube average	0.07	0.03
Blank 3M badges (solvent corrected)	ND	0.29
	0.08	0.49
	ND	0.17
	0.13	0.33
	ND	0.45
	0.13	0.28
3M badge average	0.06	0.34

Desorption Efficiencies	(µg)	Benzene (%)	Toluene (%)
Charcoal tubes			
	17.6	102.1	98.5
	17.6	98.8	100.0
	average	100.4	99.3
	2.54	98.0	87.9
	2.54	94.5	94.3
	average	96.3	91.1
	0.25	147.0	94.1
	0.25	97.3	94.4
	average	122.2	94.3
3M badges			
	17.6	105.8	100.0
	17.6	101.6	98.1
	average	103.7	99.1
	2.54	105.8	101.6
	2.54	101.7	92.1
	average	99.9	96.9
	0.25	92.2	91.8
	0.25	97.5	77.3
	average	94.8	84.6

SPIKE RESULTS:

		µg Benzene	µg Toluene
Charcoal Tubes			
	Spike Level	0.725	4.52
	µg obtained	0.82	4.59
		0.77	4.33
		0.79	4.40
		0.57	4.46
		0.77	4.42
		0.79	4.39
		0.75	4.54
		0.73	4.53
		0.75	4.46
	average (µg)	0.753	4.45
	percent recovery	103.9	98.5
	coefficient of variation	0.095	0.018
3M Badges			
	Spike level	0.725	4.52
	µg obtained	0.81	3.79
		0.64	4.54
	average (µg)	0.725	4.17
	percent recovery	100.0	91.9
	range (µg)	0.17	0.75
	Spike level	0.290	1.81
	µg obtained	0.22	1.22
		0.18	1.15
	average (µg)	0.200	1.18
	percent recovery	69.0	65.2
	range (µg)	0.04	0.07

Detection Limit Calculation:

The desorbing solution benzene background (estimated at representing approximately 0.3 μg per badge) was used to calculate benzene detection limit. The raw benzene areas were standardized to the internal standard variation, multiplied by response factor to obtain μg benzene and then mean and standard deviation were calculated. The 99% confidence range was calculated using the formula:

$$\bar{X} \pm t \frac{s}{\sqrt{(n)}}$$

$\bar{x}$ = sample mean (0.316)
t = t-statistic for 99% confidence (4.032) For n degrees of freedom
s = standard deviation (0.082)
n = degrees of freedom (6)

$$0.316 \pm 4.032 \frac{0.082}{\sqrt{(n)}}$$

0.316 ± 0.135 μg benzene

The range reported above represents 99% two sided confidence range based on the standard deviation adjusted by the t-statistic for six degrees of freedom. This is equivalent to three standard deviations for large degrees of freedom. Based on this information the following information was calculated.

Benzene:

MDL - Minimum detection limit (assumed at 3 S.D.) - 0.14μg (rounded to 0.2 μg)
RDL - Reliable detection limit (liberal)(4.66 S.D.) - 0.21μg (rounded to 0.2μg)
LOQ - Limit of quantitation (conservative) (10 S.D.) - 0.45μg (rounded to 0.5μg)

Similar background levels for toluene were not available to perform the same calculation to determine toluene limits of detection and quantitation. However, certain assumptions can be made from the chromatographic data obtained. First is that the analysis is linear down to instrument noise levels. Based on peak heights of samples E5-10-634-01A and 02A which are reported at 0.10μg, a detection limit estimated at three times instrument noise can be estimated at 0.02μg. From this number the following data can then be extrapolated.

Toluene:

MDL - Minimum detection limit (estimated at 3 S.D.) - 0.02μg
RDL - Reliable detection limit (liberal) (4.66 S.D.) - 0.03μg
LOQ - Limit of quantitation (conservative 10 S.D) - 0.07μg

For toluene, however, the 3M background observed in the blank badges analyses can be used to calculate toluene detection limit based on the whole sampling and analytical process. Since toluene was detected in the desorbing solvent. correction for solvent background was not necessary. The toluene detection limit was for the whole sampling and analytical process can be calculated in the same manner as benzene where X represents average toluene badge background.

where $\overline{X}$ represents average toluene badge background,

$\overline{X} = 0.335$ $0.335 \pm 0.213\mu g$ toluene (99% confidence based on $\pm$ 3 S.D.)
$t = 4.032$
$s = 0.118$
$n = 6$

Toluene quantitation limit is therefore $0.71\mu g$ (ten standard deviations) for total sampling and analytical process. This toluene detection limit used data which included variations in background levels of toluene on the 3M badges. Therefore the toluene detection limit represents measurable detection limit for the whole sample measurement including variation in badge background.

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Unit F - 1420 Clarence Avenue, Winnipeg, Manitoba R3T 1T6 Telephone (204) 452-8104 Fax (204) 477-8719

CHEMICAL ANALYSIS REPORT

UNIVERSITY OF ALBERTA
13-130 CLINICAL SCIENCES BLDG
EDMONTON, ALBERTA
T6G 2G3

DATE: December 19, 1995

ATTN: VINCE GAGNE

Lab Work Order #: E511215

Sampled By: CLIENT

Project Reference: QUOTE #H2515

Date Received: 11/09/95

Project P.O.#: NOT SUBMITTED

Comments:

APPROVED BY:

Larry Sefbin
Project Manager

ACCREDITED BY: (Edmonton)
CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL) - For specific tests registered with the Association
STANDARDS COUNCIL OF CANADA - Organic & Industrial Hygiene analysis as registered with the Council
AMERICAN INDUSTRIAL HYGIENE ASSOCIATION (AIHA) - Industrial Hygiene analysis registered by AIHA
AGRICULTURE CANADA - Pesticide in Fruits and Vegetables, pesticides and PCP in meat

CERTIFIED BY: (Calgary)
CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL) - For specific tests registered with the Association

E5-11-215 cont'd

BENZENE AND TOLUENE ANALYSIS ON 3M 3500 ORGANIC VAPOR MONITORS:

LAB I.D.	CLIENT I.D.	RESULTS (µg/badge) BENZENE	TOLUENE
E5-11-215-1A	LG06459C	0.22	0.32
E5-11-215-2A	LG06461C	0.21	0.37
E5-11-215-3A	LG06458C	0.21	0.42
E5-11-215-4A	LG05264C	0.77	1.16
E5-11-215-5A	LG05347C	0.71	1.03
E5-11-215-6A	LG06432C	0.73	1.07
E5-11-215-7A	LG05229C	1.26	1.53
E5-11-215-8A	LG05266C	1.36	1.73
E5-11-215-9A	LG05386C	1.19	1.42
E5-11-215-10A	LG08530C	0.28	0.36
E5-11-215-11A	LG06964C	0.23	0.26
E5-11-215-12A	LG06957C	0.23	0.30
E5-11-215-13A	LG08739C	0.79	1.19
E5-11-215-14A	LG08571C	0.84	1.34
E5-11-215-15A	LG06891C	0.78	1.06
E5-11-215-16A	LI3392C	0.22	0.50
E5-11-215-17A	7604C	0.17	0.42
E5-11-215-18A	7803C	0.25	0.50
E5-11-215-19A	7601C	0.27	0.44
E5-11-215-20A	LG05233C	0.15	0.81

Results not corrected for desorption efficiency

BENZENE AND TOLUENE ANALYSIS ON CHARCOAL TUBES:

LAB I.D.	CLIENT I.D.	RESULTS (µg/tube) BENZENE	TOLUENE
E5-11-215-21A	10-31-A-1	0.20/0.08	0.15/N.D.
E5-11-215-22A	10-31-A-2	0.19/0.08	0.14/N.D.
E5-11-215-23A	11-1-A-1	0.90/0.08	1.01/N.D.
E5-11-215-24A	11-1-A-2	0.87/0.08	1.01/N.D.
E5-11-215-25A	11-3-A-1	1.66/0.08	2.01/N.D.
E5-11-215-26A	11-3-A-2	1.66/0.08	2.06/N.D.
E5-11-215-27A	11-7-A-1	0.20/0.07	0.14/N.D.
E5-11-215-28A	11-7-A-2	0.21/0.08	0.15/N.D.
E5-11-215-29A	11-8-A-1	0.86/0.07	1.01/N.D.
E5-11-215-30A	11-8-A-2	0.83/0.07	0.96/N.D.

Results not corrected for desorption efficiency

E5-11-215 cont'd

Spike Recovery

Benzene (%)	Toluene (%)
104.8	104.2
101.6	111.4

Charcoal tubes were spiked with Benzene and Toluene in the amounts of 0.44 µg and 0.42 µg respectively.

Detection limits for the analytes were determined in the next batch of samples submitted (ETL project No. E5-11-529). Based on that information a limit of quantitation has been set at 0.1 µg per analyte per sample. Results are reported to two decimal places and to below the LOQ for client information only. The reliability of this low level data is unknown.

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Unit F - 1420 Clarence Avenue Winnipeg, Manitoba R3T 1T6 Telephone (204) 452-8104 Fax: (204) 477-8713

CHEMICAL ANALYSIS REPORT

UNIVERSITY OF ALBERTA
13-130 CLINICAL SCIENCES BLDG
EDMONTON, ALBERTA
T6G 2G3

DATE: December 27, 1995

ATTN: VINCE GAGNE

Lab Work Order #:	E511529	**Sampled By:**	CLIENT
Project Reference:	H2515	**Date Received:**	11/27/95
Project P.O.#:	NOT SUBMITTED		

Comments:

APPROVED BY:

Larry Serbin
Project Manager

ACCREDITED BY: (Edmonton)	**CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)** - For specific tests registered with the Association **STANDARDS COUNCIL OF CANADA** - Organic & Industrial Hygiene analysis as registered with the Council **AMERICAN INDUSTRIAL HYGIENE ASSOCIATION (AIHA)** - Industrial Hygiene analysis registered by AIHA **AGRICULTURE CANADA** - Pesticide in Fruits and Vegetables, pesticides and PCP in meat
CERTIFIED BY: (Calgary)	**CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)** - For specific tests registered with the Association

BENZENE AND TOLUENE ANALYSIS ON 3M 3500 ORGANIC VAPOR MONITORS:

LAB SAMPLE #:	SAMPLE#:	RESULTS (µg/badge) BENZENE	TOLUENE
E5-11-529-1A	LO02329C	0.05	0.27
E5-11-529-2A	LO02528C	0.03	0.21
E5-11-529-3A	LO02328C	0.06	0.18
E5-11-529-4A	LG08397C	1.57	2.52
E5-11-529-5A	LG06975C	1.50	1.67
E5-11-529-6A	LG06946C	1.61	1.75
E5-11-529-7A	LG08653C	0.15	3.76
E5-11-529-8A	LO02515C	0.14	0.40
E5-11-529-9A	LO02419C	0.16	0.39
E5-11-529-10A	LO01449C	0.16	0.48
E5-11-529-11A	LO02324C	0.02	0.19
E5-11-529-12A	LO01493C	0.17	0.41
E5-11-529-13A	LO01489C	0.13	0.36
E5-11-529-14A	LO01384C	0.16	0.34
E5-11-529-15A	LO01338C	0.74	0.93
E5-11-529-16A	LO01511C	0.76	1.03
E5-11-529-17A	LO01094C	0.82	1.12
E5-11-529-18A	LO02406C	1.36	1.65
E5-11-529-19A	LO02315C	1.35	1.70
E5-11-529-20A	LO02362C	1.41	1.72
E5-11-529-21A	LO02338C	0.05	0.22
E5-11-529-22A	LO02525C	0.03	0.19
E5-11-529-23A	LO02347C	0.04	0.16
E5-11-529-36A	LO01829C	0.20	0.59
E5-11-529-37A	LO01807C	0.23	0.57
E5-11-529-38A	LO01799C	0.21	0.56
E5-11-529-39A	LO02420C	0.11	0.76
E5-11-529-40A	LO02504C	0.12	0.67

Results not corrected for desorption efficiency.

BENZENE AND TOLUENE ANALYSIS ON CHARCOAL TUBES:

LAB SAMPLE #:	SAMPLE#:	RESULTS (µg/badge)	
		BENZENE	TOLUENE
E5-11-529-24A	11-10-A-1	2.04/N.D.	2.48/N.D.
E5-11-529-25A	11-10-A-2	2.14/0.02	2.49/0.01
E5-11-529-26A	11-15-A-1	0.14/0.02	0.15/N.D.
E5-11-529-27A	11-15-A-2	0.49/N.D.	0.22/N.D.
E5-11-529-28A	11-16-A-1	1.06/0.10	1.22/0.01
E5-11-529-29A	11-16-A-2	0.96/N.D.	1.22/N.D.
E5-11-529-30A	11-18-A-1	1.95/N.D.	2.47/0.01
E5-11-529-31A	11-18-A-2	1.98/0.02	2.42/N.D.
E5-11-529-32A	11-22-A-1	0.02/0.01	0.02/N.D.
E5-11-529-33A	11-22-A-2	0.02/0.01	0.03/N.D.
E5-11-529-34A	11-24-A-1	0.02/0.01	0.02/0.01
E5-11-529-35A	11-24-A-2	0.04/0.01	0.02/N.D.
E5-11-529-41A	12-7-A-P	0.59/0.09	4.06/0.01

Results not corrected for desorption efficiency.

The detection limit has been determined as described below.
Results are reported to two decimal places and to below the calculated detection limit for client information only. The reliability of the data reported below the calculated limit of quantitation is unknown.

Detection Limit Determination:

Detection limits for benzene and toluene were determined by analyzing low level solutions of the analytes in carbon disulfide containing deuterated benzene d_6 and toluene d_8 as internal standard. The deuterated species were at a low concentration so as to not contribute non-deuterated analytes to the solutions above a level that is consistent with instrument noise (this is because the neat deuterated compounds may contain small amounts of non-deuterated species). Sixteen analyses were performed to obtain data for the benzene detection determination and nine analysis were performed for toluene. The levels of benzene and toluene analyzed represented 0.088 μg/sample and 0.070 μg/sample of benzene and toluene respectively. These levels represented approximately 3-5 times instrument noise for benzene and approximately 10 times noise for toluene.

The data obtained was calculated as total μg each analyte as would be represented per sample. The mean and standard deviations were calculated. The 99% confidence range was calculated with the t-statistic for each set of data using the formula:

$$\bar{X} \quad \pm t \frac{s}{\sqrt{n}}$$

$\bar{X}$ = sample mean
t = t-statistic for two-sided 99% confidence
(2.947 for 15 degrees of freedom, 3.355 for 8 degrees of freedom)
s = standard deviation
n= no. of samples

On a normal distribution, the 99% two-sided confidence is equivalent to ± 3 standard deviations (corrected for low sample degrees of freedom using the t-statistic correction).

The summarized raw data is presented below as total μg per sample.

Benzene		Toluene	
0.086	0.080	0.045	
0.090	0.080	0.059	
0.113	0.075	0.062	
0.106	0.090	0.042	
0.076	0.056	0.073	
0.097	0.087	0.086	
0.115	0.073	0.088	
0.107	0.076	0.086	
		0.091	
No. of samples	16	No. of samples	9
Std. deviation	0.016	Std. deviation	0.019
t-statistic	2.947	t-statistic	3.355
degrees of freedom (n-1)	15	degrees of freedom (n-1)	8
Minimum detection limit	3 S.D. 0.012	Minimum detection limit	3 S.D. 0.021
Reliable detection limit (liberal)	4.66 S.D. 0.019	Reliable detection limit (liberal)	4.66 S.D. 0.033
Limit of Quantitation (conservative)	10 S.D. 0.041	Limit of Quantitation (conservative)	10 S.D. 0.109

5

Based on the data presented, results will be reported to a limit of quantitation (LOQ) of 0.1 μg each analyte. This is to provide results with a coefficient of variation of 0.1 ($\pm$ 10%) and to take into consideration variations in instrument sensitivities that commonly occur with GC/MS analyses.

ETL Enviro-Test

A DIVISION OF ETL CHEMSPEC ANALYTICAL LIMITED

9936 - 67 Avenue, Edmonton, Alberta T6E 0P5 Telephone (403) 434-9509 Fax (403) 437-2311
Bay 2, 1313 - 44 Avenue N.E., Calgary, Alberta T2E 6L5 Telephone (403) 291-9897 Fax (403) 291-0298
107 - 111 Research Drive, Saskatoon, Saskatchewan S7N 3R2 Telephone (306) 668-8370 Fax (306) 668-8383
Bay 3, 10919 - 96 Avenue, Grande Prairie T8V 3J4 Telephone (403) 539-5196 Fax (403) 539-6295
Unit F - 1420 Clarence Avenue, Winnipeg, Manitoba R3T 1T6 Telephone (204) 452-8104 Fax (204) 477-8719

CHEMICAL ANALYSIS REPORT

UNIVERSITY OF ALBERTA
13-130 CLINICAL SCIENCES
EDMONTON, ALBERTA T6G-2G3

DATE: January 8, 1996

ATTN: VINCE GAGNER

Lab Work Order #: E601028

Sampled By: VINCE GAGNER

Project Reference: NOT SUBMITTED

Date Received: 12/19/95

Project P.O.#: NOT SUBMITTED

Comments:

APPROVED BY:

Larry Sebbin
Project Manager

ACCREDITED BY: (Edmonton)	**CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)** - For specific tests registered with the Association
	STANDARDS COUNCIL OF CANADA - Organic & Industrial Hygiene analyses as registered with the Council
	AMERICAN INDUSTRIAL HYGIENE ASSOCIATION (AIHA) - Industrial Hygiene analyses as registered by AIHA
	AGRICULTURE CANADA - Pesticide in Fruits and Vegetables, pesticides and PCP in meat
CERTIFIED BY: (Calgary)	**CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)** - For specific tests registered with the Association

BENZENE AND TOLUENE ANALYSIS ON 3M 3500 ORGANIC VAPOR MONITORS:

LAB I.D.	CLIENT I.D.	RESULTS (µg/badge) BENZENE	TOLUENE
E6-01-028-1A	LO02477C	0.13	0.70
E6-01-028-2A	LO01777C	0.10	0.70
E6-01-028-3A	LO01793C	0.23	0.78
E6-01-028-4A	LI3397C	0.29	1.09
E6-01-028-5A	LO01832C	0.20	0.40
E6-01-028-6A	LO01906C	0.26	0.53
E6-01-028-7A	LO01808C	0.27	0.41
E6-01-028-8A	LI9837C	1.84	2.55
E6-01-028-9A	LO01735C	1.73	2.32
E6-01-028-10A	LO01720C	1.75	2.21
E6-01-028-17A	LI9746C	0.61	1.56
E6-01-028-18A	LI9764C	0.52	1.61
E6-01-028-19A	LI9868C	0.49	1.04
E6-01-028-20A	LI9817C	0.48	1.00

Results not corrected for desorption efficiency

BENZENE AND TOLUENE ANALYSIS ON CHARCOAL TUBES:

LAB I.D.	CLIENT I.D.	RESULTS (µg,front/back) BENZENE	TOLUENE
E6-01-028-11A	12-11-A-P	0.72/0.16	4.23/N.D.
E6-01-028-12A	12-11-A-P	1.32/0.16	4.46/N.D.
E6-01-028-13A	12-[illegible]	0.29/0.14	0.18/N.D.
E6-01-028-14A	12-[illegible]-2	0.27/0.12	0.19/N.D.
E6-01-028-15A	12-16-A-1	2.26/0.11	3.03/N.D.
E6-01-028-16A	12-16-A-2	2.24/0.11	2.97/N.D.
E6-01-028-21A	12-18-A-H	1.22/0.10	8.17/N.D.
E6-01-028-22A	12-18-A-O	1.59/0.10	3.92/N.D.

Results not corrected for desorption efficiency

	BENZENE	TOLUENE
Mean Spike Recoveries- (%)	106	115
	110	117
	108	117
Limit of quantitation(conservative)-µg:	0.1	0.1

ETL Enviro-Test

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Bay 2, 1313 - 44 Avenue N.E. Calgary, Alberta T2E 6L5 Telephone (403) 291-9897 Fax (403) 291-0298
107 - 111 Research Drive, Saskatoon, Saskatchewan S7N 3R2 Telephone (306) 668-8370 Fax (306) 668-8383
Bay 3, 10919 - 96 Avenue, Grande Prairie T8V 3J4 Telephone (403) 539-5196 Fax (403) 539-6295
Unit F - 1420 Clarence Avenue, Winnipeg, Manitoba R3T 1T6 Telephone (204) 452-8104 Fax (204) 477-8719

CHEMICAL ANALYSIS REPORT

UNIVERSITY OF ALBERTA
13-130 CLINICAL SCIENCES
EDMONTON, ALBERTA T6G-2G3

DATE: February 12, 1996

ATTN: VINCE GAGNER

Lab Work Order #: E601390 **Sampled By:** VINCE GAGNER

Project Reference: NOT SUBMITTED **Date Received:** 01/31/96

Project P.O.#: NOT SUBMITTED

Comments:

APPROVED BY:
Larry Serbin
Project Manager

ACCREDITED BY: (Edmonton)	**CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)** - For specific tests registered with the Association **STANDARDS COUNCIL OF CANADA** - Organic & Industrial Hygene analyses as registered with the Council **AMERICAN INDUSTRIAL HYGIENE ASSOCIATION (AIHA)** - Industrial Hygene analyses as registered by AIHA **AGRICULTURE CANADA** - Pesticide in Fruits and Vegetables, pesticides and PCP in meat
CERTIFIED BY: (Calgary)	**CANADIAN ASSOCIATION OF ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)** - For specific tests registered with the Association

BENZENE AND TOLUENE ANALYSIS ON 3M 3500 ORGANIC VAPOR MONITORS:

LAB I.D.	CLIENT I.D.	RESULTS (μg/badge) BENZENE	TOLUENE
E6-01-028-1A	L19838	0.50	5.36
E6-01-028-2A	L19842	0.73	5.38
E6-01-028-3A	L191719C	0.57	1.04
E6-01-028-4A	L19871C	0.56	0.94
E6-01-390-5A	L19845C	0.72	1.67
E6-01-390-6A	L04717C	0.56	1.66

Results not corrected for desorption efficiency

BENZENE AND TOLUENE ANALYSIS ON CHARCOAL TUBES:

LAB I.D.	CLIENT I.D.	RESULTS (μg,front/back) BENZENE	TOLUENE
E6-01-390-7A	01-24-A-P	2.63/N.D.	32/N.D.
E6-01-390-8A	01-26-A-P	1.68/0.50	3.9/N.D.
E6-01-390-9A	01-30-A-P	4.49/N.D.	8.7/N.D.

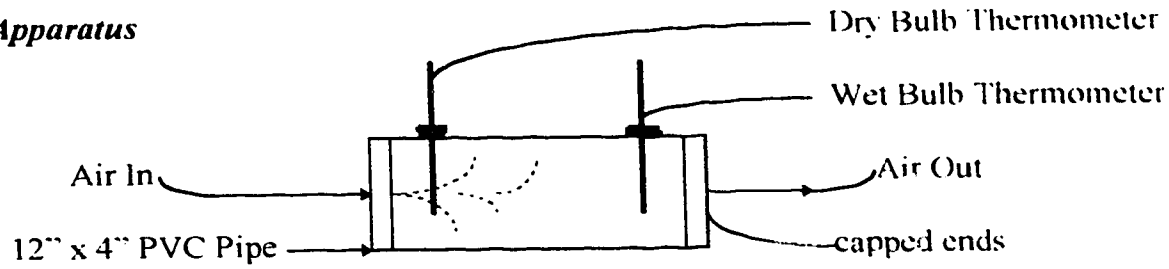
Results not corrected for desorption efficiency

Limit of quantitation(conservative)-μg:	0.1	0.1

Appendix 3.2

Measurement and Calculation of Relative Humidity

Apparatus



Procedures

1. Divert air flows from exposure chamber to the above relative humidity measurement station.

2. Insert dry bulb thermometer at the front of the air flow.

3. Place wet cotton sleeve on wet bulb thermometer (freeze for runs at -15 and -15°C) and insert at the back end of the air flow.

4. Allow 3 minutes for thermometers to adjust and record temperatures.

Observations

Dry Bulb	Wet Bulb	Difference	Dew Point[1]	Relative Humidity[1]
-13.5	-14.5	1	-20.3	57%
-13.5	-14.5	1	-20.3	57%
-13.5	-14	1.5	-23.9	41%
-5	-8.5	3.5	-20.3	28%
-5	-8.5	3.5	-20.3	28%
-5	-8.25	3.25	-18.5	34%
24	10.5	13.5	-2.4	17%
24	11	13	-1.0	19%
24	11.5	12.5	+1.0	22%

[1] R.H. Tables. Atmospheric Environment, (1976) "Psychrometric Tables for a Ventilated Sample at Station Elevations Above 760m", Environment Canada. 00-0063-2203 (4/76)

Appendix 3.3

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Chemical Fill	:	Toluene
Device Type	:	Standard Emission Tube
Length/Geometry	:	2.0 cm.
Part Number	:	117-020-1401
Method of Certification	:	Gravimetric
Certification Number	:	30-56791

Rate: 23.7 ng/min +/- 2 ng/min at 50 deg C
Note:
Date: 14 September 1995 by: J. Ann Banks

VICI

VICI Metronics, Inc.
2991 Corvin Drive
Santa Clara, California 95051 U.S.A.
(408) 737-0550 Telefax: 408-737-0346

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Chemical Fill	:	Benzene
Device Type	:	Standard Emission Tube
Length/Geometry	:	4.0 cm.
Part Number	:	116-040-1400
Method of Certification	:	Gravimetric
Certification Number	:	22-65431

Rate: 17.6 ng/min +/- 10% at 30 deg C
Note:
Date: 14 September 1995 by: J. Ann Banks

VICI

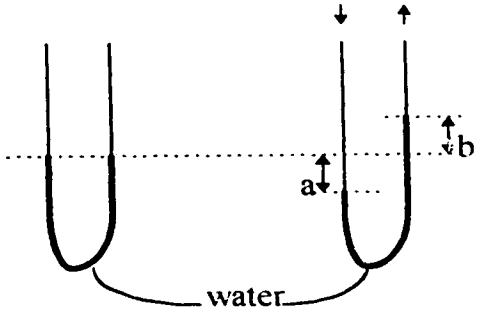
VICI Metronics, Inc.
2991 Corvin Drive
Santa Clara, California 95051 U.S.A.
(408) 737-0550 Telefax: 408-737-0346

Appendix 3.4

Measurement and Calculation of Chamber Pressure

Apparatus

A U-tube manometer is partially filled with water with one open end exposed to the atmosphere and the other end to the pressure of the chamber. The pressure is calculated by measuring the difference in level of the water in the two tube branches.



Calculation at 3L/min
a + b = 0.35 inches of water
= 0.654 mmHg

Calculation at 7L/min
a + b = 1.2 inches of water
= 2.24 mmHg

Calculation at 10L/min
a + b = 2 inches of water
= 3.74 mmHg

Conversions

1 inch of water = 7.355 x 10-2 inches of mercury
1 inch = 25.4 millimeters

Notes

1. Measures were taken at 24°C and 704mmHg.

2. Maximum flow rates used in the experiment are 7000cc/min; assuming that this will create the highest pressure, the contribution of chamber pressure to the sampling mechanism of the badges is < 1%.

Appendix 3.5

Chamber QA/QC Tube Measures: Front vs Back

Date	oct.18-blk,front		oct.19-blk,back		oct.23-1000,front		oct.23-1000, back		oct.24-500,front		oct.24-500,back	
Pump Number	1	2	1	2	1	2	1	2	1	2	1	2
Freezer Temp. (C)	room	room	room	room	room	room	room	room	room	room	room	room
Room Temp. (C)	23	23	23	23	24	24	24	24	24	24	24	24
Atm Press (mmHg)	695.0	695.0	694.0	694.0	696.0	696.0	696.0	696.0	697.0	697.0	697.0	697.0
Vap Press (mmHg)	21.08	21.08	21.08	21.08	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35
Corr. Factor	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89
Bub. Flow Vol. (cc)	100	100	100	100	100	100	100	100	50	50	50	50
Initial Time #1	27.70	26.69	26.86	26.48	26.69	26.59	26.16	26.16	13.41	13.42	13.25	13.10
Initial Time #2	27.58	26.59	26.63	26.42	26.77	26.42	26.35	26.16	13.45	13.42	13.18	13.18
Initial Time #3	27.29	26.80	26.68	26.40	26.65	26.55	26.39	26.20	13.40	13.42	13.19	13.15
Initial Time #4	27.06	26.68	26.72	26.44	26.70	26.57	26.35	26.16	13.47	13.48	13.20	13.13
Initial Time #5	27.18	26.60	26.65	26.47	26.69	26.49	26.33	26.13	13.45	13.39	13.15	13.15
Final Time #1	26.67	26.71	26.30	26.10	26.16	26.16	25.97	25.23	13.25	13.10	13.41	13.37
Final Time #2	26.71	26.71	26.38	26.11	26.35	26.16	25.95	25.31	13.18	13.18	13.44	13.30
Final Time #3	26.75	26.65	26.34	26.20	26.39	26.20	25.95	25.32	13.19	13.15	13.42	13.34
Final Time #4	26.85	26.67	26.40	26.15	26.35	26.16	25.89	25.32	13.20	13.13	13.50	13.30
Final Time #5	26.76	26.65	26.35	26.14	26.33	26.13	26.03	25.30	13.15	13.15	13.49	13.39
Average Time (sec)	27.06	26.68	26.53	26.29	26.51	26.34	26.14	25.73	13.32	13.28	13.32	13.24
Ave Mass Cor (cc/min)	197.31	200.13	200.91	202.75	201.31	202.57	204.16	207.40	200.68	201.15	200.56	201.80
Sample Duration (min)	240	240	240	240	240	240	240	240	240	240	240	240
SKC Tube No.	1018a1f	1018a2f	1019a1b	1019a2b	1023a1f	1023a2f	1023a1b	1023a2b	1024a1f	1024a2f	1024a1b	1024a2b
Benzene Reported (ng)	nd	nd	nd	nd	470	400	310	350	1740	1890	1810	1720
Blank Adjusted (ng)	-	-	-	-	400	330	240	280	1670	1820	1740	1650
Des.Eff.Adjusted (ng)	-	-	-	-	333	275	200	233	1637	1784	1706	1618
Benzene TWAE (ug/m3)	nd	nd	nd	nd	6.9	5.7	4.1	4.7	34.0	37.0	35.4	33.4
Toluene Collected (ng)	100	100	nd	nd	550	520	520	540	2060	2070	2080	2070
Blank Adjusted (ng)	70	70	-	-	520	490	490	510	2030	2040	2050	2040
Des.Eff.Adjusted (ng)	74	74	-	-	486	458	458	477	1897	1907	1916	1907
Toluene TWAE (ug/m3)	1.6	1.5	nd	nd	10.1	9.4	9.3	9.6	39.4	39.5	39.8	39.4

Appendix 3.6

Phase I: SKC Tube Readings

Run# & Date	Blk 1, Nov. 22		Blk 2, Nov. 24		Run 7b, Nov. 15		Run 8, Nov. 16		Run 9a, Nov. 18	
Pump Number	1	2	1	2	1	2	1	2	1	2
Freezer Temp. (C)	(+) 24	(+) 24	(+) 24	(+) 24	(+) 24	(+) 24	(+) 25	(+) 25	(+) 24	(+) 24
Room Temp. (C)	24	24	24	24	24	24	25	25	24	24
Atm Press (mmHg)	705.4	705.4	701.8	705.4	702.0	702.0	701.0	701.0	684.0	684.0
Vap Press (mmHg)	22.35	22.35	22.35	22.35	22.35	22.35	23.88	23.88	22.35	22.35
Corr. Factor	0.90	0.90	0.90	0.90	0.90	0.90	0.89	0.89	0.87	0.87
Bub. Flow Vol. (cc)	100	100	100	100	100	100	100	100	100	100
Initial Time #1	27.10	27.04	26.83	26.87	26.81	27.30	27.00	26.84	26.91	26.75
Initial Time #2	27.20	27.13	26.80	26.90	26.91	27.23	26.98	26.80	26.96	26.68
Initial Time #3	27.16	27.12	26.76	26.88	26.88	27.27	27.07	26.87	26.89	26.65
Initial Time #4	27.16	27.14	26.78	27.05	26.89	27.21	26.95	26.79	26.91	26.71
Initial Time #5	27.13	27.22	26.82	26.98	26.95	27.35	27.01	26.79	26.89	26.67
Final Time #1	26.69	26.61	26.71	26.10	26.52	27.04	26.93	26.71	26.79	26.65
Final Time #2	26.73	26.60	26.75	26.17	26.55	27.03	27.01	26.73	26.72	26.79
Final Time #3	26.65	26.65	26.75	26.21	26.56	26.99	26.95	26.69	26.89	26.70
Final Time #4	26.68	26.60	26.78	26.09	26.58	27.06	26.97	26.77	26.89	26.66
Final Time #5	26.70	26.61	26.77	26.25	26.60	27.05	27.01	26.79	26.81	26.58
Average Time (sec)	26.92	26.87	26.78	26.55	26.73	27.15	26.99	26.78	26.87	26.68
Ave Mass Cor (cc/min)	200.99	201.35	201.01	203.79	201.45	198.27	198.74	200.30	195.08	196.42
Sample Duration (min)	240	240	240	240	240	240	240	240	240	240
SKC Tube No.	1122A1	1122A2	1124A1	1124A2	1214A1	1214A2	1116A1	1116A2	1118A1	1118A2
Benzene Reported (ng)	30	30	30	50	430	390	1160	960	1950	2000
Blank Adjusted (ng)	n/d	n/d	n/d	n/d	360	320	1090	890	1880	1930
Des.Eff.Adjusted (ng)	n/d	n/d	n/d	n/d	300	267	1038	848	1843	1892
Benzene Conc. (ug/m3)	n/d	n/d	n/d	n/d	6.2	5.6	21.8	17.6	39.4	40.1
Toluene Reported (ng)	20	30	30	20	180	190	1230	1220	2480	2420
Blank Adjusted (ng)	n/d	n/d	n/d	n/d	150	160	1200	1190	2450	2390
Des.Eff.Adjusted (ng)	n/d	n/d	n/d	n/d	158	168	1121	1112	2290	2234
Toluene Conc.(ug/m3)	n/d	n/d	n/d	n/d	3.3	3.5	23.5	23.1	48.9	47.4

Appendix 3.6

Phase I: SKC Tube Readings (continued)

Run# & Date	Run 4, Nov. 7		Run 5, Nov. 8		Run 6, Nov. 10		Run 1, Oct. 31		Run 2, Nov. 1		Run 3, Nov. 3	
Pump Number	1	2	1	2	1	2	1	2	1	2	1	2
Freezer Temp. (C)	(-) 5	(-) 5	(-) 5	(-) 5	(-) 5	(-) 5	(-) 15	(-) 15	(-) 15	(-) 15	(-) 15	(-) 15
Room Temp. (C)	24	24	24	24	24	24	24	24	24	24	24	24
Atm Press (mmHg)	708.7	708.7	693.7	693.7	704.6	704.6	706.0	706.0	708.5	708.5	705.0	705.0
Vap Press (mmHg)	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35
Corr. Factor	0.91	0.91	0.89	0.89	0.90	0.90	0.90	0.90	0.91	0.91	0.90	0.90
Bub. Flow Vol. (cc)	100	100	100	100	100	100	100	100	100	100	100	100
Initial Time #1	26.90	26.51	26.87	26.61	26.94	26.64	26.64	26.62	26.99	26.45	26.86	26.84
Initial Time #2	26.99	26.54	26.79	26.62	26.94	26.62	26.67	26.85	26.99	26.42	26.89	26.75
Initial Time #3	27.10	26.65	26.81	26.66	26.97	26.65	26.68	26.60	27.04	26.48	26.81	26.83
Initial Time #4	27.05	26.45	26.85	26.63	27.08	26.60	26.58	26.80	27.01	26.48	26.84	26.78
Initial Time #5	27.11	26.51	26.88	26.67	27.00	26.69	26.61	26.65	26.95	26.48	26.86	26.79
Final Time #1	26.80	26.41	26.76	26.45	26.97	26.64	26.81	26.20	26.71	26.69	26.80	26.61
Final Time #2	26.82	26.45	26.76	26.41	26.99	26.63	26.85	26.15	26.73	26.69	26.72	26.65
Final Time #3	26.82	26.48	26.73	26.46	26.96	26.52	26.83	26.27	26.79	26.68	26.80	26.60
Final Time #4	26.80	26.52	26.74	26.50	26.90	26.61	26.79	26.15	26.80	26.67	26.76	26.63
Final Time #5	26.82	26.58	26.82	26.46	26.95	26.64	26.86	26.25	26.79	26.66	26.75	26.61
Average Time (sec)	26.92	26.51	26.80	26.55	26.97	26.62	26.73	26.45	26.88	26.57	26.81	26.71
Ave Mass Cor (cc/min)	201.95	205.08	198.42	200.32	200.38	202.99	202.58	204.71	202.20	204.56	201.70	202.46
Sample Duration (min)	240	240	240	240	240	240	240	240	240	240	240	240
SKC Tube No.	117A1	117A2	118A1	118A2	1110A1	1110A2	1031A1	1031A2	111A1	111A2	113A1	113A2
Benzene Reported (ng)	270	290	930	900	2040	2160	280	270	980	950	1740	1740
Blank Adjusted (ng)	200	220	860	830	1970	2090	210	200	910	880	1670	1670
Des.Eff.Adjusted (ng)	167	183	819	790	1931	2049	175	167	867	838	1637	1637
Benzene Conc. (ug/m3)	3.4	3.7	17.2	16.4	40.2	42.1	3.6	3.4	17.9	17.1	33.8	33.7
Toluene Reported (ng)	140	150	1010	960	2480	2500	150	140	1010	1010	2010	2060
Blank Adjusted (ng)	110	120	980	930	2450	2470	120	110	980	980	1980	2030
Des.Eff.Adjusted (ng)	116	126	916	869	2290	2308	126	116	916	916	1850	1897
Toluene Conc.(ug/m3)	2.4	2.6	19.2	18.1	47.6	47.4	2.6	2.4	18.9	18.7	38.2	39.0

Appendix 3.6

Phase I: SKC Tube Readings (excluded duplicates)

Run# and Date	Run 7a, Nov.15		Run 9b, Dec.16	
Pump Number	1	2	1	2
Freezer Temp. (C)	(+) 24	(+) 24	(+) 24	(+) 24
Room Temp. (C)	24	24	24	24
Atm Press (mmHg)	697.8	697.8	703.0	703.0
Vap Press (mmHg)	22.35	22.35	22.35	22.35
Corr. Factor	0.89	0.89	0.90	0.90
Bub. Flow Vol. (cc)	100	100	100	100
Initial Time #1	26.60	26.56	26.91	26.62
Initial Time #2	26.56	26.47	26.87	26.65
Initial Time #3	26.70	26.56	26.86	26.54
Initial Time #4	26.59	26.53	26.99	26.55
Initial Time #5	26.64	26.51	27.00	26.59
Final Time #1	26.67	26.50	26.50	27.05
Final Time #2	26.75	26.63	26.49	26.99
Final Time #3	26.73	26.63	26.45	26.99
Final Time #4	26.77	26.56	26.51	27.03
Final Time #5	26.76	26.65	26.44	27.00
Average Time (sec)	26.68	26.56	26.70	26.80
Ave Mass Cor (cc/min)	200.56	201.45	201.92	201.17
Sample Duration (min)	240	240	240	240
SKC Tube No.	1115A1	1115A2	1216A1	1216A2
Benzene Reported (ng)	160	490	2300	2280
Blank Adjusted (ng)	90	420	2230	2210
Des.Eff.Adjusted (ng)	75	350	2186	2167
Benzene Conc. (ug/m3)	1.6	7.2	45.1	44.9
Toluene Reported (ng)	150	220	3010	2950
Blank Adjusted (ng)	120	190	2980	2920
Des.Eff.Adjusted (ng)	126	200	2785	2729
Toluene Conc.(ug/m3)	2.6	4.1	57.5	56.5

Appendix 3.7

Phase I: OVM-3500 Results

(Corrected for blank and desorption efficiency)

Chamber Sampling

Date	Run #	Temp	Badge #	Benz. (ng)	Blk Adj.	DE Adj.	Conc. ug/m3	Tol. (ng)	Blk Adj.	DE Adj.	Conc. ug/m3
17-Nov	9a	(+) 25	LOO2406C	1360	1320	1294	25.3	1650	1450	1450	32.1
17-Nov	9a	(+) 25	LO02315C	1350	1310	1284	25.1	1700	1500	1500	33.2
17-Nov	9a	(+) 25	LO02362C	1410	1370	1343	26.3	1720	1520	1520	33.6
15-Nov	8a	(+) 24	LO01338C	740	700	700	13.7	930	730	768	17.0
15-Nov	8a	(+) 24	LO01511C	760	720	720	14.1	1030	830	874	19.3
15-Nov	8a	(+) 24	LO01094C	820	780	780	15.3	1120	920	968	21.4
13-Dec	7b	(+) 24	LO01906C	260	220	244	4.8	530	330	388	8.6
13-Dec	7b	(+) 24	LO01832C	200	160	178	3.5	400	200	235	5.2
13-Dec	7b	(+) 24	LO01808C	270	230	256	5.0	410	210	247	5.5
09-Nov	6a	(-) 5	LG08397C	1570	1530	1500	29.3	2520	2320	2320	51.3
09-Nov	6a	(-) 5	LG06975C	1500	1460	1431	28.0	1670	1470	1470	32.5
09-Nov	6a	(-) 5	LG06946C	1610	1570	1539	30.1	1750	1550	1550	34.3
07-Nov	5a	(-) 5	LG08739C	790	750	750	14.7	1190	990	1042	23.0
07-Nov	5a	(-) 5	LG08571C	840	800	800	15.6	1340	1140	1200	26.5
07-Nov	5a	(-) 5	LG06891C	780	740	740	14.5	1060	860	905	20.0
06-Nov	4a	(-) 5	LG08530C	280	240	267	5.2	360	160	188	4.2
06-Nov	4a	(-) 5	LG06964C	230	190	211	4.1	260	60	71	1.6
06-Nov	4a	(-) 5	LG06957C	230	190	211	4.1	300	100	118	2.6
02-Nov	3a	(-) 15	LG05229C	1260	1220	1196	23.4	1530	1330	1330	29.4
02-Nov	3a	(-) 15	LG05266C	1360	1320	1294	25.3	1730	1530	1530	33.8
02-Nov	3a	(-) 15	LG05386C	1190	1150	1127	22.1	1420	1220	1220	27.0
31-Oct	2a	(-) 15	LG05264C	770	730	730	14.3	1160	960	1011	22.3
31-Oct	2a	(-) 15	LG05347C	710	670	670	13.1	1030	830	874	19.3
31-Oct	2a	(-) 15	LG06432C	730	690	690	13.5	1070	870	916	20.3
30-Oct	1a	(-) 15	LG06459C	220	180	200	3.9	320	120	141	3.1
30-Oct	1a	(-) 15	LG06461C	210	170	189	3.7	370	170	200	4.4
30-Oct	1a	(-) 15	LG06458C	210	170	189	3.7	420	220	259	5.7

Eliminated Duplicate Runs

Date	Run #	Temp	Badge #	Benz (ng)	Blk Adj.	DE Adj.	Conc. ug/m3	Tol. (ng)	Blk Adj.	DE Adj.	Conc. ug/m3
14-Nov	7a	(+) 24	LO01493C	170	130	144	2.8	410	210	247	5.5
14-Nov	7a	(+) 24	LO01489C	130	90	100	2.0	360	160	188	4.2
14-Nov	7a	(+) 24	LO01384C	160	120	133	2.6	340	140	165	3.6
15-Dec	9b	(+) 24	LO01735C	1730	1690	1657	32.4	2320	2120	2120	46.9
15-Dec	9b	(+) 24	LO01720C	1750	1710	1676	32.8	2210	2010	2010	44.5
15-Dec	9b	(+) 24	LI9837C	1840	1800	1765	34.5	2550	2350	2350	52.0

Appendix 3.8

Phase II: OVM-3500 Results

(Corrected for blank and desorption efficiency)

Date	Badge #	Benz.(ng)	Blk Adj	DE Adj.	Tol.(ng)	Blk Adj	DE Adj.
24-Oct	O5346C	140	100	111	140	-	-
24-Oct	O5330C	n/d	-	-	250	50	59
24-Oct	O5402C	n/d	-	-	n/d	-	-
Blank	*O5221C*	*n/d*	-	-	*950*	*750*	882
Temperature Range: 0.7 to 10C, Ave. 5.35C							
Relative Humidity Range: 40 to 76%, Ave. 58%							
Prevailing Wind Velocity and Direction: WNW, 16kph							
05-Nov	L13392	220	180	200	500	300	353
05-Nov	7604C	170	130	144	420	220	259
05-Nov	7803C	250	210	233	500	300	353
Blank	*7601C*	*270*	*230*	256	*440*	*240*	282
Temperature Range: -2.9 to -0.4C, Ave. -1.65C							
Relative Humidity Range: 44 to 96%, Ave. 70%							
Prevailing Wind Velocity and Direction: ENE, 9.2kph							
17-Nov	LO02515C	140	100	111	400	200	235
17-Nov	LO02419C	160	120	133	390	190	224
17-Nov	LO01449C	160	120	133	480	280	329
Blank	*LO02324C*	*20*	-	-	*19*	-	-
Temperature Range: -1.5 to 6.7C, Ave. 2.6C							
Relative Humidity Range: 64 to 92%, Ave. 78%							
Prevailing Wind Velocity and Direction: SSW, 9.7kph							
05-Dec	LO01829C	200	160	178	590	390	459
05-Dec	LO01807C	230	190	211	570	370	435
05-Dec	LO01799C	210	170	189	560	360	424
Temperature Range: -30.6 to -17C, Ave. -24.1C							
Relative Humidity Range: 55 to 70%, Ave. 62.5%							
Prevailing Wind Velocity and Direction: S, 7.3kph							

Meteorological Info.: Environment Canada, (1995). Edmonton International Airport Monthly Meteorological Summary, Atmospheric Environmental Service.

Appendix 3.9

Phase III: SKC Tube Readings

Date	06-Dec		11-Dec		13-Dec		24-Jan		26-Jan		30-Jan	
Pump Number	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
Outside Temp. (C)	(-) 20	(-) 20	(-) 22	(-) 22	(-) 20	(-) 20	(-) 28	(-) 28	(-) 25	(-) 25	(-) 22	(-) 22
Atm Press (mmHg)	704.6	704.6	703.8	703.8	693.0	693.0	704.0	704.0	703.0	703.0	704.5	704.5
Vap Press (mmHg)	22.35	22.35	23.88	23.88	22.35	22.35	22.35	22.35	22.35	22.35	22.35	22.35
Corr. Factor	0.90	0.90	0.90	0.90	0.89	0.89	0.90	0.90	0.90	0.90	0.90	0.90
Bub. Flow Vol. (cc)	100	100	100	100	100	100	100	100	100	100	100	100
Initial Time #1	26.13	25.51	26.83	25.99	26.66	26.67	24.90	25.14	25.23	25.27	24.70	25.03
Initial Time #2	26.14	25.76	26.91	26.05	26.74	26.60	24.92	25.20	25.29	25.28	24.65	25.03
Initial Time #3	26.12	25.70	26.86	26.15	26.91	26.67	25.01	25.10	25.25	25.33	24.59	25.13
Initial Time #4	26.15	25.66	26.90	26.13	26.9[illegible]	26.67	25.13	25.19	25.29	25.35	24.65	25.10
Initial Time #5	26.10	25.69	26.87	26.13	27.00	26.65	25.04	25.21	25.33	25.30	24.67	25.20
Final Time #1	26.35	25.68	27.20	26.25	26.90	26.70	25.23	25.27	24.70	25.03	23.68	24.73
Final Time #2	26.40	25.71	27.09	26.21	26.19	26.68	25.29	25.28	24.65	25.03	23.87	24.59
Final Time #3	26.31	25.67	27.13	26.30	26.23	26.80	25.25	25.33	24.59	25.13	23.80	24.85
Final Time #4	26.45	25.73	27.14	26.31	26.30	26.70	25.29	25.35	24.65	25.10	23.90	24.87
Final Time #5	26.48	25.71	27.20	26.27	26.30	26.71	25.33	25.30	24.67	25.20	23.91	24.83
Average Time (sec)	26.26	25.68	27.01	26.18	26.61	26.69	25.14	25.24	24.97	25.20	24.24	24.94
Ave Mass Cor (cc/min)	205.78	210.43	199.38	205.73	199.61	199.08	214.79	213.95	215.97	213.94	222.90	216.70
Sample Duration (min)	720	720	685	755	680	760	395	985	815	625	738	702
SKC Tube No.	127ap		1211ap		1213ap		0124ap		0126ap		0130ap	
Benzene Reported (ng)	680		880		1480		2630		2180		4490	
Blank Adjusted (ng)	610		810		1410		2560		2110		4420	
Des.Eff.Adjusted (ng)	580.95		771.43		1382.4		2509.8		2068.6		4333.3	
Benzene Conc. (ug/m3)	1.9		2.6		4.8		8.5		6.7		13.7	
Toluene Reported (ng)	4070		4230		4460		32000		3900		8700	
Blank Adjusted (ng)	4040		4200		4430		31970		3870		8670	
Des.Eff.Adjusted (ng)	3776		3925		4140		29879		3617		8103	
Toluene Conc.(ug/m3)	12.6		13.4		14.4		101.1		11.7		25.6	

Appendix 3.10

Phase III: OVM-3500 Results

(Corrected for blank and desorption efficiency)

Personal Sampling

Date	Indoor	Outdoor	Badge #	Benz.(ng)	Blk Adj	DE Adj.	Tol.(ng)	Blk Adj	DE Adj.
	(24C)	(Sub-0)							
06-Dec	93%	7%	LO02420C	110	70	78	760	560	589
06-Dec	93%	7%	LO02504C	120	80	89	670	470	495
11-Dec	92%	8%	LO01777C	100	60	67	700	500	526
11-Dec	92%	8%	LO02477C	130	90	100	700	500	526
13-Dec	92%	8%	LI3397C	290	250	278	1090	890	937
13-Dec	92%	8%	LO01793C	230	190	211	780	580	611
24-Jan	84%	16%	LI9838C	500	460	460	5360	5160	5160
24-Jan	84%	16%	LI9842C	730	690	690	5380	5180	5180
26-Jan	75%	25%	LI9871C	560	520	520	940	740	740
26-Jan	75%	25%	LI9719C	570	530	530	1040	840	840
30-Jan	68%	32%	LI9845C	720	680	680	1670	1470	1470
30-Jan	68%	32%	LX04717C	560	520	520	1660	1460	1460

Appendix 3.11

Phase III: Personal Sampling, Daily Logs

Start Date: December 6th, 1995

Time	Activity
1400	initiate sampling at residence
1430	automobile
1440	Tory Building at UofA
1510	automobile
1530	Revy Hardware
1620	automobile
1630	IKEA
1640	automobile
1650	Safeway
1750	automobile
1800	residence
1830	dinner (ham+bun, salsa+nacho)
1900	dishes
1930	work on computer
2100	brush teeth etc...
2130	go to bed
0200	change to Alpha-1 pump #2
0800	coffee and newspaper
0900	brush teeth, shower, dress
0940	work on computer
1140	lunch (Mr.Noodles/toast)
1200	main living area
1400	terminate samples

Average Temp: -20.4°C
Average RH: 67%
Average wind: 14.5 kph, NNW

Start Date: December 11, 1995

Time	Activity
1000	initiate sampling, Alb.Env.Lab
1105	automobile
1135	Clinical Sci. Blg. UofA
1200	automobile
1210	Albert's Restaurant
1300	McBain Photo
1345	Safeway
1400	automobile
1430	residence
1440	automobile
1500	Concordia College (main campus)
1520	automobile
1530	Concordia College (Braemar)
1540	automobile
1550	Environment Canada
1610	automobile
1620	Alberta Environment
1650	automobile
1700	residence
1730	dinner: noodles, toast cauliflower
1830	main living area
1900	laundry - watch Oilers game
2125	change Alpha-1 pump #2
2130	mark Concordia papers
0045	brush teeth and go to bed
1000	terminate samples

Average Temp: -22.3°C
Average RH: 66%
Average wind: 30 kph, ESE

Start Date: December 13th, 1995

Time	Activity
1605	initiate sampling at Alb.Env.Lab
1630	handling benzene perm. tube
1845	automobile
1900	residence
1915	dinner, spaghetti, salad
2000	main living area
2200	work on computer
0405	change to Alpha-1 Pump #2
0430	brush teeth, go to bed
0820	automobile
0900	Clinical Sci.Blg. UofA
1115	automobile
1140	Mr Sub
1220	automobile
1230	residence (main living area)
1330	automobile
1350	Clinical Sci.Blg. UofA
1530	automobile
1545	Alberta Environment Lab
1605	terminate samples

Average Temp: -19.5°C
Average RH: 65%
Average Wind: 13kph, NW

Start Date: January 24th, 1996

Time	Activity
0600	initiate sampling at residence
0615	automobile
0745	arrive at Novacor (Jeoffrey)
0800	safety orientation
0900	respirator fitting/orientation
1000	Eth.Plant 2, control room
1120	tour of yard
1150	control room
	note: maintenance painting.
1200	breakroom
1300	contractor room
1320	garage: solvent clean gear box
1400	smoking area
1410	tour of compressor units
1440	breakroom
1510	garage
1540	change clothes
1600	automobile
1800	residence, dinner, soup/sandwich
1815	automobile
1830	Clinical Sci. Blg. UofA
2140	automobile
2200	residence
2410	change to Alpha-1 Pump #2
2415	brush teeth, go to bed
0600	terminate samples

Average Temp: -27.6°C
Average RH: 67%
Average Wind: 5.1 kph, S

Start Date: January 26th, 1996

Time	Activity
0535	initiate sampling at residence
0600	automobile
0730	arrive at Ethylene #2
0800	tour of Operator area
0935	breakroom
0950	control room
1100	walk the yard
1115	watched a technician drain oily water lines (blowdowns)
1200	lunch
1230	control room
1250	garage
1330	control room
1345	walk the yard / compressors
1500	breakroom
1515	change clothes
1600	automobile
1750	residence
1800	dinner, spaghetti
1910	change Alpha-1 pump #2
1930	brush teeth, go to bed
0535	terminate sampling

Average Temp: -25°C
Average RH: 66%
Average Wind: 4.8 WNW

Start Date: January 30th, 1996

Time	Activity
0535	initiate sampling at residence
0555	automobile
0730	arrive at Ethylene #2
0745	with Operator, C4 / C5 holding tanks; loading rack (RR cars) ....wore respirator.
0945	control room
1100	meeting with Occ'l Hygiene
1200	lunchroom
1230	walk the yard
1315	garage: valve maintenance
1420	change clothes
1445	drop off safety gear
1500	sign off with security
1520	automobile
1655	car dealership
1730	residence: indoor BBQ burgers
1755	change Alpha-1 pump #2
1930	watch Oilers game
2200	work on computer
2430	brush teeth, go to bed
0535	terminate sampling

Average Temp: -21.7°C
Average RH: 64%
Average Wind: 15.8 kph, W

Appendix 3.12

Volunteer Exposure Subject Information Sheet and Consensus Form

University of Alberta
Edmonton

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492-64[illegible]

Validation of the OVM-3500 Passive Sampling Device
24 Hour Exposure to Environmental Levels of Benzene and Toluene

Principal Investigator

Dr. S. Hrudey

Co-Investigators

Vince Gagner (graduate student)
Dr. W. Kindzierski
Dr. X. Le

Background

You are asked to participate in a voluntary 24 hour validation study of the OVM-3500 sampling device. You have been chosen because you appear trustworthy, reliable, and cognizant of the importance of the proposed research. You are asked to reside in Edmonton over the selected sampling date, and would be expected to continue with normal lifestyle activities during the 24 hour sampling period.

Purpose:

Your participation in this research is expected to help demonstrate the usefulness of the OVM-3500 personal sampler for domestic applications. The information generated from your personal 24 hour sample will enable researchers to evaluate the measurement capability of the badge. Your involvement in the project follows extensive exposure chamber simulation testing, comparative studies at a local field monitoring station, and preliminary 24 hour personal sampling trials performed on an investigator.

Procedures

Participating in this study will involve:

a) Completion of a preliminary questionnaire in late January or early February (at your convenience)
b) 30 minute training and question period for daily activity log and badge handling protocol
c) Concurrent 24 hour placement of 2 badges on yourself (one on each collar); 6 badges in your primary living space; and, 6 badges on the outside of the main entrance to your residence.
d) Maintenance of an activity sheet log over the 24 hour sampling period

Possible Benefits

The possible benefits to you for participating in this study are that you may find that logging your daily activity will give you an appreciation for the many microenvironments you encounter over a typical 24 hour period. You may also feel a sense of satisfaction since your participation could potentially help residents throughout the Province of Alberta.

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Phone: (403) 492-6409
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- Occupational Health 492-6291
- Health Services Administration
- Epidemiology 492-6402
- Environmental Health 492-6452
492-6407

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Possible Risks

There are no risks to you as a participant in this study because you are not asked to expose yourself in any way outside of your normal routine. Results of the exposure assessment will be communicated to you if requested, or if exposure levels exceed the estimated intake of toluene and benzene outlined in the Canadian Environmental Protection Act Priority Substances List, published by Health and Welfare Canada.

Confidentiality

Personal records relating to this study will be kept confidential. However, in addition to the investigators, Alberta Health and Health Canada will have access to your records. Any report published as a result of this study will not identify you by name.

You are free to withdraw from the research study at any time. You will be promptly informed if the study is not undertaken, if it is discontinued, or if any knowledge gained from this study becomes available which could influence your decision to continue in the study.

Please contact any of the individuals identified below if you have any questions or concerns:

Primary Contact

Vince Gagner, Graduate Student, Environmental Health, University of Alberta
(403) 434-6118

Advisory Committee

Principal Investigator
Dr. S. Hrudey, Professor and Director, Environmental Health, University of Alberta
(403) 492-6807

Committee Advisor
Dr. X. Le, Assistant Professor, Environmental Health, University of Alberta
(403) 492-6416

Committee Advisor
Dr. W. Kindzierski, Risk Manager, Alberta Health
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Title of Project: Validation of the OVM-3500 Passive Sampling Device, 24 Hour Exposure to Environmental Levels of Benzene and Toluene

Principal Investigator: Dr. S. Hrudey Phone Number: (403) 492-6807

Co-Investigators: V. Gagner (403) 434-6118
Dr. W. Kindzierski (403) 427-2643
Dr. X. Le (403) 492-6416

	Yes	No
Do you understand that you have been asked to be in a research study?		
Have you read and received a copy of the attached Information Sheet?		
Do you understand the benefits and risks involved in taking part in this research study?		
Have you had an opportunity to ask questions and discuss this study?		
Do you understand that you are free to withdraw from the study at any time, without having to give a reason?		
Has the issue of confidentiality been explained to you, and do you understand who will have access to your records?		

Who explained this study to you? _____

I agree to take part in this study: YES ( ) NO ( )

Signature of Research Subject _____

(Printed Name) _____

Date: _____

Signature of Witness _____

Signature of Investigator or Designee _____

THE INFORMATION SHEET MUST BE ATTACHED TO THIS CONSENT FORM AND A COPY GIVEN TO THE RESEARCH SUBJECT

Appendix 3.13

Bovar Environmental Results

Applications: Community Exposure Assessment

BOVAR Environmental

2 Lappert Ave
Toronto Ontario
Canada M3H 2V2
Phone: 416 630 6333
Fax: 416 630 0439

Vince Gagner
Dept. of Public Health Sciences
Faculty of Medicine
13-103 Clincal Sciences Building
University of Alberta
Edmonton, Alberta, T6G 2G3

March 1, 1996

File: 5416769

TeL: (403)492-8446
Via Fax: (403)492-0364

Dear Mr. Gagner:

Please find attached preliminary Sample Analysis Report for the 14 samples that you submitted for analysis.

Should you have any questions regarding the analysis results or require our other services, please do not hesitate to contact me or Mr. Phil Fellin.

Sincerely,

BOVAR Environmental

Y.Z. TANG, PH.D.
SUPERVISOR
Air Monitoring and Laboratory Services

Encl.

BOVAR Environmental

2 Tippett Road
Toronto Ontario
Canada M3H 2V2
Phone 416-630-6331
Fax 416-630-0506

Sample Analysis Report

Project Number:	5416769
Report Date:	Mar. 01, 1996
Analysis Date:	Feb. 28, 1996
Analytical Method:	GC/MSD
Sample Type:	3M Samplers
Results	Unit: µg/m3
	Blank Corrected: no

Sample	Benzene	Toluene
1-LX04698C	2.82	6.34
2-LX04718C	9.74	34.66
3-LX04616C	5.75	16.55
4-LX04621C	3.28	6.11
5-LX04608C	9.86	35.40
6-LX04688C	6.20	23.15
7-LX03663C	N	N
8-LX03746C	6.21	16.96
9-LX03671C	1.83	1.73
10-LX03742C	N	N
11-LX03661C	5.57	15.66
12-LX03679C	6.05	17.07
13-LX03804C	5.68	16.23
14-LX04751C	2.40	2.95
Detection Limits	0.54	0.62

Comments	N = Below Detection Limit
Analyst	Quang Tran, M.Sc.
Lab Manager	Philip Fellin, M.Sc.

Appendix 3.14

Pilot Study: Personal Sampling, Daily Logs

Subject #1

Start Date: February 4th, 1996

Time	Activity
1225	initiate sampling at residence
1240	wash dishes
1245	outside for a smoke
1300	automobile
1320	arrive at coffee shop, smoke a cigarette outside
1330	enter coffee shop
1400	automobile
1410	arrive home, smoke cigarette outside
1420	main indoor living area
1500	bedroom for a nap
1615	main living space
1700	outside for a smoke
1730	automobile
1800	hockey arena
1915	outside arena for a smoke
1930	automobile
2000	main indoor living area
2200	outside for a smoke
2210	main living area
2400	to bed
0900	main living area - coffee
0915	outside for a smoke
0930	shower, change
1000	outside for a smoke
1015	automobile
1030	church
1145	automobile
1200	arrive home - outside for a smoke
1205	kitchen, fry bacon and eggs
1225	terminate sample

Subject #2

Start Date: February 4th, 1996

Time	Activity
1445	initiate sampling at residence
1540	work on computer (bedroom)
1725	load recyclables to truck
1730	automobile
1735	unload recyclables from truck
1740	automobile
1745	main living area
1800	work on computer
1835	main living area
1850	work on computer
1930	main living area - dinner
2055	work on computer
2220	main living area
2245	bedroom
2320	to bed
1100	get up and shower
1115	main living space - breakfast
1230	work on computer
1425	main living space
1445	terminate sample

Ave. Temp: -11.4°C
Ave. RH: 84%
Ave. Wind: 16.5 NNE

Note: Subject #1 smoked on the **back** step of the house