NOTE TO USERS

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The Development and Evaluation of a Novel Personal Air Sampling Canister for the Collection of Gases and Vapors

By

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Abstract

A continuing challenge in occupational hygiene is that of estimating exposure to the multitude of airborne chemicals found in the workplace and surrounding community. Occupational exposure limits (OELs) have been established to prescribe the acceptable time weighted average for many different chemicals. Comparing the OELs to the measured workplace concentration allows occupational hygienists to assess the health risks and the need for control measures. Hence, methods to more effectively sample contaminants in the workplace are necessary to ensure that accurate exposure characterizations are completed. Evacuated canisters have been used for many years to collect ambient air samples for gases and vapors. Recently, increased interest has arisen in using evacuated canisters for personal breathing zone sampling as an alternative to sorbent samplers. A capillary flow control device was designed at McGill University mid 1990s. The flow control device was designed to provide a very low flow rate to allow a passive sample to be collected over an extended period of time. This research focused on the development and evaluation of a methodology to use a small canister coupled with the capillary flow controllers to collect long term time weighted air samples for gases and vapors.

A series of flow rate experiments were done to test the capillary flow capabilities with a 300 mL canister for sampling times ranging from a few minutes to over 40 hours. Flow rates ranging from 0.05 to 1.0 mL/min were experimentally tested and empirical formulae were developed to predict flow rates for given capillary geometries. The low flow rates allow for the collection of a long term air sample in a small personal canister.

Studies to examine the collection of air contaminants were conducted in laboratory and in field tests. Air samples for six volatile organic compounds were collected from a small exposure chamber using the

capillary-canisters, charcoal tubes and diffusive badges at varied concentrations. The results from the three sampling devices were compared to each other and to concentration values obtained by an on-line gas chromatography. The results indicate that the capillary-canister compares quite favorably to the sorbent methods and to the on line GC values for the six compounds evaluated.

Personal air monitoring was conducted in a large exposure chamber to assess the effectiveness of the capillary-canister method to evaluate breathing zone samples. In addition, field testing was performed at a manufacturing facility to assess the long term monitoring capabilities of the capillary-canister. Precision and accuracy were found to parallel that of sorbent sampling methods.

The capillary-canister device displayed many positive attributes for occupational and community air sampling. Extended sampling times, greater capabilities to sample a broad range of chemicals simultaneously, ease of use, ease of analysis and the low relative cost of the flow controller should allow for improvements in exposure assessment.

Résumé

Un des défits à relever en hygiène du travail est celui d'estimer l'exposition à une multitude de composés chimiques en milieu de travail et dans la communauté environnante. Des limites d'exposition occupationnelles ont été établies pour une exposition moyenne pondérée pour plusieurs de ces composés chimiques. Une comparaison de ces limites d'exposition avec les mesures de concentrations en milieu de travail, permet aux hygiénistes industriels d'évaluer les risques à la santé et de déterminer le besoin de mesures de contrôle. L'utilisation de méthodes d'échantillonnage éfficaces s'avère donc nécessaire pour assurer la fiabilité des mesures d'exposition obtenues. Une méthode d'échantillonnage basée sur l'utilisation de cannettes évacuées pour le prélèvement de composés organiques volatiles et gaz rencontre ces exigences depuis plusieurs années. Récemment, il y a eu un regain d'intérêt pour l'utilisation de cannettes évacuées pour la collecte d'échantillons personnels dans la zone respiratoire en tant qu'alternative à l'utilisation de tubes de charbon activé. Un instrument basé sur l'utilisation d'un tube capillaire pour le contrôle du débit d'air dans une cannette évacuée a été mise au point à l'université McGill en 1997. Cet instrument a été élaboré pour permettre un échantillonnage passif à un débit relativement bas pour une période prolongée. Dans le cadre des travaux de recherche, une méthodologie unique a été développée et évaluée. Cette nouvelle méthodologie, pour la mesure de vapeurs organiques et gaz , s'appuie sur l'utilisation d'une petite cannette évacuée munie d'un contrôleur de débit capillaire pour la collecte d'échantillons d'air ambiant intégrés pendant une période prolongée.

Une série de déterminations de débits d'air a été menée pour évaluer la capacité du contrôleur capillaire à échantillonner avec une cannette évacuée de 300 ml pour des périodes de temps allant de quelques minutes à 40 heures et plus. Une gamme de débits de 0,05 à 1,0 ml ont été testés et une formule empérique a été obtenue pouvant prédire un débit pour un capillaire d'une

certaine géométrie. Ces débits relativement bas ont permis la collecte d'échantillons personels d'air ambiant dans une petite cannette évacuée pendant une période prolongée.

Des études se penchant sur l'échantillonnage de contaminants de l'air ont été menées dans le laboratoire et sur le terrain. Des échantillons d'air contenant six composés organiques volatils ont été prélevées simultanément dans une chambrette environnementale avec des tubes de charbon activé , des collecteurs passifs à diffusion et des cannettes munies d'un contrôleur capillaire (cannette-capillaire). Les résultats obtenus avec les trois genres d'échantillonneurs ont été comparés l'un à l'autre et à ceux d'un chromatographe à phase gazeuse utilisé pour mesurer la concentration des composés dans la chambre d'essaie en temps réel. Ces tests ont indiqué que les résultats obtenus avec l'échantillonneur cannette-capillaire se comparaient favorablement avec ceux obtenus avec les échantillonneurs à base de charbon activé et aux valeurs du chomatographe à phase gazeuse pour les six composés organiques évalués.

Un échantillonnage personnel a été mené dans une chambre d'exposition pour évaluer l'éfficacité de l'échantillonneur canette-capillaire à prélever des échantillons d'air dans la zone respiratoire. En plus, un échantillonnage sur le terrain a été conduit en milieu de travail pour une semaine complète de travail pour évaluer la capacité de cet échantillonneur pour la collecte d'échantillons pour une période de temps prolongée sur le terrain. L'exactitude et la précision des résultats obtenus rivalisent celles obtenues avec des méthodes basées sur l'utilisation du charbon active

L'échantillonneur cannette-capillaire a démontré des qualités supérieures pour l'échantillonnage d'air en milieu de travail et dans la communauté. Des periodes d'échantillonnage prolongées, une plus grande capacité pour le prélèvement simultané d'une grande gamme de composés organiques volatils, la facilité

d'utilisation, la facilité d'analyse et le coût relativement bas du contrôleur capillaire contribuent tous à une amélioration appréciable de l'évaluation d'expositions aux contaminants volatils et gazeux.

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Contributions of Authors

This thesis is written in the form of four manuscripts, each of which comprises one chapter, an overall introduction and literature review that introduce the topics of study, with overall conclusions that summarize the results. All of the manuscripts were authored by Alan Rossner and co-authored by Jean-Pierre Farant. Alan Rossner carried out all the experimental studies and prepared the manuscripts. Dr. Farant supervised and advised during the development of the manuscripts.

The first manuscript, "Development of a Flow Controller for Long-term Sampling of Gases and Vapors Using Evacuated Canisters" (Chapter 4), was submitted to *Environmental Science and Technology*, in January 2002. Philippe Simon is listed as a co-author because this work is a link to his previous work. David P. Wick is a physicist who reviewed the mathematical model developed by Philippe Simon. The manuscript is accepted and currently in revision. Chapter 5 is entitled, "A Novel Personal Air Sampling Device for Collecting Volatile Organic Compounds: A Comparison to Charcoal Tubes and Diffusive Badges", was submitted to *American Industrial Hygiene Association Journal* in June 2002. Chapter 6 is entitled; "Performance of Small Evacuated Canisters for the Collection of Personal Air Samples" will be submitted to *Applied Occupational and Environmental Hygiene* in July 2002. Dr. Adolf Vyskocyl, University of Montreal, coordinated the exposure scenarios for the test subjects that enable the air sampling to be preformed. Stephanie Warner provided back up support for the air sampling investigation. Both are listed as co- authors.

Chapter 7 is entitled," Field Evaluation of Small Evacuated Canisters for the Collection of Long Term Samples During a Solvent Cleaning Operation", will be submitted to *Applied Occupational and Environmental Hygiene* in September 2002. Jean-Pierre Farant supervised the development.

Please note that bridging text preceding each manuscript is provided to ensure

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CHAPTER 1 INTRODUCTION

Occupational hygienists have historically focused on recognition, evaluation and control of hazards in the occupational environment. The traditional form of evaluation has been air sampling of chemicals in industrial environments to assess exposure. Over the last decade this traditional role has expanded to include more environmental monitoring, microbial monitoring, biological monitoring and air sampling in non-industrial work environments.[1-3] This expanded focus requires that occupational hygienists become familiar with an ever-increasing number of sampling techniques and exposure assessment strategies. The data collected from occupational sampling campaigns are used for many different purposes, ranging from compliance monitoring to epidemiological studies and risk assessments.[4,5] Often the data is used for a very different application than the original reason for collecting the air sample.[6] As an example, from a health effect point of view, work place monitoring is used to estimate dose, while a regulatory view focuses air sampling on compliance. This multiple application of air sampling data suggests that more emphasis be placed on choosing both the correct sampling methodology and exposure assessment strategies. In addition, one must focus on the overall system; exposure monitoring cannot be separated from industrial process, waste or by products. One must take a systematic approach to sampling strategy to ensure an adequate characterization of all exposures is performed.

Prior to the initiation of any sampling campaign one must always answer fundamental questions such as, who, where, when, how and how long should sampling be performed. The "who" and the "how long" concepts are of greatest interest with respect to this research. The ability to conduct personal sampling for long periods of time can provide useful information when performing health hazard assessments. This research project focused on the modification and evaluation of a new instrument to assess exposure to gases and vapors for long periods of time (hours to weeks). The research also developed new exposure

assessment strategies for evaluating the long-term average exposures using this new air sampling method.

Compliance exposure assessments are performed by regulatory inspectors and more frequently performed by employers, required to do so under regulatory requirements such as, Commission de la Santé et de la Sécurité du Travail (CSST), Quebec, Ontario Ministry of Labour, and United States-Occupational Safety and Health Administration (OSHA).[7-9] Historically, occupational hygienists usually measure the exposures by collecting samples on one or more workers in a similarly exposed group (workers with the same job description and location).[10] Based on the results of the collected samples, the employer performs a "practical risk assessment", which is defined as: Risk = (1/exposure limit) * exposure.[11] The employer decides on whether the group of workers is "overexposed" to a defined occupational exposure limit (OEL). If the samples are found to be below the OEL, the company is considered to be in compliance and no additional action is required.[9] However, if any measurement exceeds the OEL, the company is legally and ethically required to reduce the employees' exposure. This type of air monitoring approach is referred to as "Compliance Monitoring" because it focuses on the exceedance of a single point standard as opposed to a long-term average exposure over a series of days or weeks.

A variety of techniques are available to sample gases and vapors in occupational environments.[12-14] These techniques include solid sorbents, chemically treated filters, liquid absorbers, evacuated containers, bags and cold traps.[13] Each method has its own set of limitations that may include efficiency, flexibility, reliability, accuracy, precision, ease of use and cost effectiveness. As time passes, each technique has been continually revised and updated as collection techniques improve and exposure limits were lowered. The National Institute for Occupational Safety and Health (NIOSH) has published methods for approximately 500 airborne contaminants. Each method has an overall uncertainty associated with it. These uncertainties are based on both the air

sampling and analytical components of the method and are often referred to as the standard analytical error.[13] They allow the occupational hygienist some level of confidence that the exposure values are valid. However, to fully consider risk, these sampling and analytical uncertainties must also be considered along with the uncertainties associated with exposure assessment.[11,15,16] Variability in exposure assessment factors such as duration of sample, time of day, number of workers sampled, and worker activities during sampling, may contribute more uncertainty to the final exposure level than all of the sampling and analytical errors combined.

As one approaches an air sampling problem involving gases and vapors, the limitations of the chosen method must always be considered. These limitations often require the occupational hygienist to modify his/her exposure assessment strategies. Often the occupational hygienist cannot collect the number of samples necessary to make appropriate conclusions concerning exposures and control measures. As a result, professional judgment is substituted for data. In addition, Rappaport (1991) and Hewitt (1997) both concluded that measurement error is most frequently a small component of the total variation in exposure monitoring, and that increasing sample size could diminish the importance of sampling and analytical error.[17,18] Hence, devices that allow for increased sample numbers and increased sample duration should be developed and implemented to provide additional and more reliable exposure data.[17,19] Increasing the quantity and quality of data collected for occupational exposures to gases and vapors will benefit both the worker and the occupational health profession.[20]

Simon (1997) developed a flow control-sampling device that allows occupational hygienists to extend the sampling time for gases and vapors.[21] The device consisted of a deactivated capillary column used to control airflow into an evacuated canister. The small diameter of the capillary combined with the length, resulted in a very low airflow rate into the canister. Figure 1.1 displays a

conceptual diagram of Simon's device. The design was awarded a patent for "proof of concept".[22]

This flow control device has many possible applications and may not have the limitations that occur with the current approved means of collecting occupational air samples for gases and vapors.[9,15,23] However, before the flow controller can be used, an effective personal sampler must be developed and a methodology for use of the device must be developed and evaluated.

A review of the history of the implementation of new sampling devices allows one to appreciate the enormous effort it takes to develop a concept into a widely accepted sampling methodology. Palmes first presented the passive diffusive badge in a 1973 paper.[24] It then took 25 years until the regulatory agencies, such as OSHA and standard setting agencies such as ANSI and ISO, developed protocols for use of passive badges.[25] Table 1.1 provides a review of the history of diffusive badge development. From this extended implementation period, it could be concluded that not enough emphasis was placed on the modification, evaluation, and implementation of passive diffusive badges by researchers earlier on in their existence. Extensive testing to explore parameters such as reverse diffusion and variations in uptake rate should have been considered early in the development of the diffusion badges. Therefore, it is important to state that the capillary-canister is not just a device used to collect gases and vapors; it is potentially a completely new sampling methodology that may allow for significant improvement in data collection once boundaries for its use can be established.

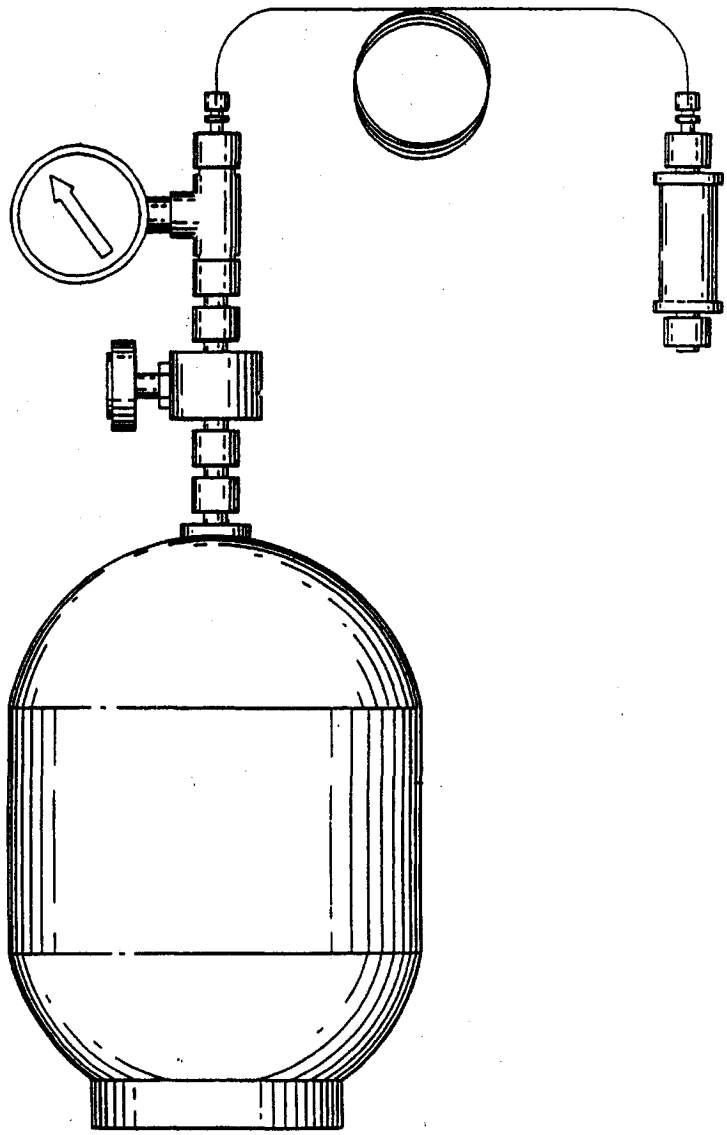

Figure 1.1 Capillary flow controller with a 1 L canister.[21]

Table 1.1 History of diffusion badges

1973	Palmes paper
1977-1980	Development of first commercial diffusive samplers
1980-1983	Characterization of diffusive samplers in the laboratory and field, refinement of theories governing operation
1983-1985	Further development of diffusive samplers; initial development of testing protocols
1986	Luxembourg Conference
1987-1989	Attempts to harmonize protocols fail; no further testing by U.S. Government; SKC begins using NIOSH protocol; beginning of the disappearance of many samplers, including Pro-Tek, Minimonitor, Gasbadge
1990-1994	U.K. Health & Safety Executive publishes methods featuring diffusive samplers; work begins on European standard protocol (EN838)
1994	Beginning of ISEA initiative to develop test protocol; testing begins at OSHA
1995	Publication of EN838 and MDHS 80; testing begins on samplers for the AIHA PAT program
1996	Beginning of ASTM initiative to develop test protocol; Joint Committees technical session at AIHCE
1997	Publication of MDHS 88; first official AIHA Laboratory Accreditation Proficiency Testing round
1998	Publication of first OSHA method; first professional development course on diffusive samplers at the American Industrial Hygiene Conference

(Adopted from Harper, 1998[25])

The research reported herein addresses the investigation of a personal flow control canister-sampling device for use in a variety of occupational exposure assessment strategies. The device consists of a small canister (300 mL) constructed of polished stainless steel, connected to a specially designed capillary to control the airflow into the canister. Figure 1.2 shows a conceptual diagram of the device that was built and tested. The canister is placed under a vacuum prior to sampling, and then air enters the canister because of a pressure differential. As long as the pressure differential between the outside atmosphere and the inside of the canister does not exceed approximately 0.50 atm, the flow rate will remain constant if the device acts similarly to a sharp-edge critical orifice.[26] The system was designed to allow for sampling times ranging from several minutes to several months, depending upon the canister size and capillary geometry. Flow rates ranging from 0.05 mL/min to 1 mL/min were examined. The low sampling flow rate is a unique characteristic of the capillary-canister. At these very low flow rates, samples can be collected for extended periods of time, smaller canisters can be used to collect personal samples and the simplicity of the sampler reduces maintenance issues. Additional details concerning the function of the flow control device will be provided later. The device will be referred to as a capillary-canister device for the remainder of this research.

To test the functionality of the device, it was used in a set of laboratory and field experiments to evaluate its performance with respect to NIOSH criteria and European Community criteria for development of new sampling methods.[27,28] The goal of this research is to establish a framework of sampling conditions that allow the capillary-canister to be used as an effective tool for collecting air sampling data. The research also developed exposure assessment strategies for long-term occupational exposures, where long-term sampling will be defined as greater than 8-hour sampling periods.

The Pressure differential between the ambient atmosphere (P_{atm}) and the inside of the canister (P_{can}) provides the air movement. Canister pressure (P_{can}) is maintained below 0.5 P_{atm}

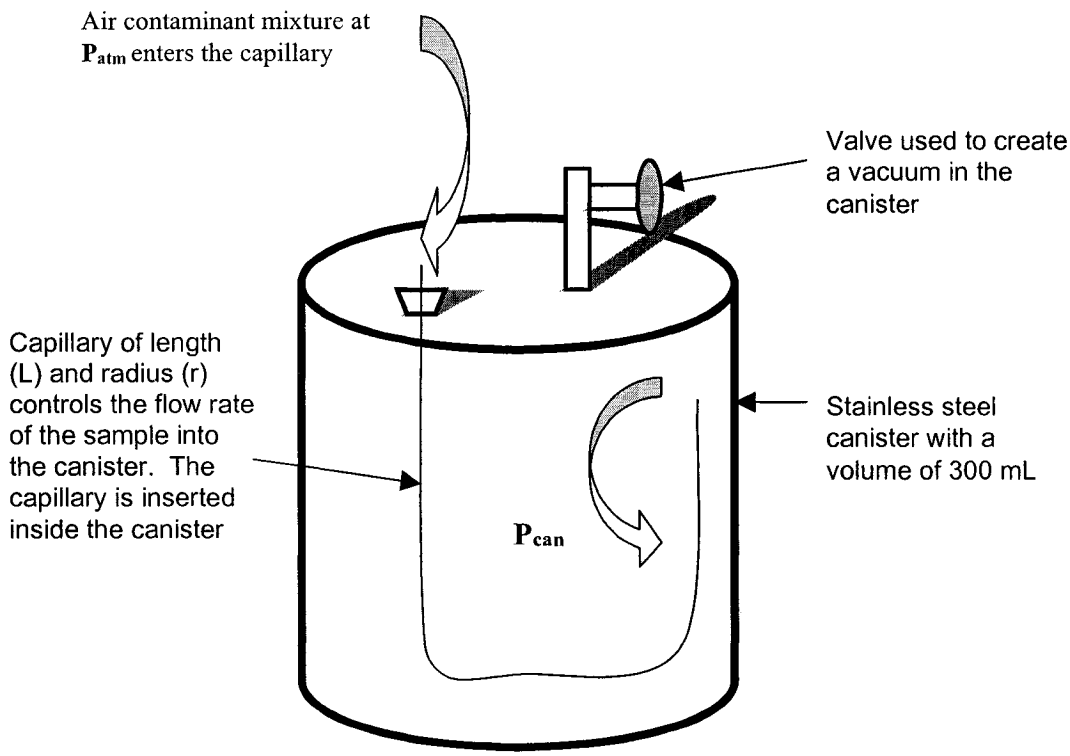

Figure 1.2 Conceptual diagram of the capillary-canister device

1.1 Organization of the Thesis

This research developed and tested a methodology for the use of the capillary flow control device with a modified canister for personal occupational hygiene sampling. This research was separated into four phases. Each phase established the foundation for the next phase. The thesis is comprised of a literature review, four manuscripts linked by a bridging section and an overall conclusion section. In addition, four appendices (A-D) provide supporting information for each phase of the research. A short summary of each phase is provided below.

- Phase one of the research involved designing a functioning sampling device, evaluating the actual air flow rates, evaluating empirical models developed by Simon (1997) and developing additional empirical models to predict airflow rate for specific capillary geometries.

- Phase two evaluated the device's performance with respect to currently approved sampling methods for gases and vapors. This phase assessed the accuracy and precision of the capillary-canister under varying environmental conditions in a small chamber. The canister's performance was compared to an on-line GC, charcoal tubes and charcoal badges.

- Phase three addressed the personal air sampling aspects of the capillary-canister. A group of individuals exposed to styrene in a controlled toxicology experiment were sampled using charcoal tubes, charcoal badges and the capillary-canisters. The styrene concentrations were generated in an 18 m^3 chamber occupied by five subjects for six hours. The measurements were repeated at four concentrations.

- The fourth phase of the research examined the advantages of using the capillary-canister device for field sampling in the aluminum industry. This phase also provided information concerning long-term average monitoring,

40-hours, for Stoddard solvent in an industrial cleaning operation. The long-term average exposures provided an understanding of the capillary-canister performance in an actual industrial environment. The canisters results were compared to charcoal badges.

The following literature review provides insight into the current occupational hygiene methods of air sampling gases and vapors, and their limitations; as well as the proposed use and benefit of capillary-canister device in exposure assessment strategies.

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CHAPTER 2 LITERATURE REVIEW

Occupational hygiene investigations rely to a large extent on integrated personal sampling performed in the breathing zone of workers. Area samples rarely provide the necessary information to determine employee exposure.[1,2] For personal sampling devices to be effective, it must allow for freedom of movement for the worker, worker acceptability, ease of use, durability, sustain corrosive and/or flammable environments, allow for stability of the analyte until it can be transported to the laboratory for analysis and provide accurate time weighted average assessments of exposure.[3] To ensure air sampling is successfully completed, many factors must be considered before equipment is taken into the field. Sampling parameters that need to be considered are: sampling duration, interferences, type of collection devices to be used, personal versus area samples and limitations of the chosen method. The following review provides a brief discussion of important current and proposed methods for integrated monitoring of gases and vapors in occupational hygiene, as well as considering key limitations of each method. Direct reading instruments generally provide instantaneous measurements not integrated averages of air borne concentrations, and therefore will not be evaluated in this review.

2.1 Current Methods of Air Sampling

2.1.1 Sorbent Tubes

Air sampling for gases and vapors has traditionally been performed using charcoal tubes and impingers, and more recently using passive dosimeter badges.[4] Sorbent materials used with air sampling pumps have long been considered the primary standard for collecting organic vapors in occupational hygiene.[5,6] The recommended adsorbent tube for collecting a specific analyte is described by NIOSH in the respective method for that analyte. As an example, NIOSH 1501 prescribes an adsorbent tube containing 150 mg of coconut charcoal divided into 100 mg in the front bed and 50 mg in the back bed for the collection of vapors from aromatic solvents (i.e. toluene, benzene, styrene, etc.).

Air is drawn through the charcoal tube at flow rates ranging from 20 mL to 200 mL per minute, with the flow rate varying for the compound of interest and its respective concentration in the air. The front section of the tube is designed to trap the analyte while the back section is used to ensure that no analyte passes through the tube. Such a breakthrough would indicate sample loss and therefore underestimate the workers' exposure. The two-section tube has become standard for most occupational hygiene sorbent tubes.[8] The concentration of the airborne contaminant is found by using the mass of the analyte divided by the sampling flow rate and the time sampled to obtain the volume of air that passes through the tube. The resulting concentration in milligrams per cubic meter (mg/m^3) is referred to as a time weighted average (TWA) concentration, (eq 2.1) and can be compared to the OEL for the compound of interest.

$$TWA = \frac{\sum_{i=1}^{n} C_i T_i}{T_n} \qquad (2.1)$$

The initial use of sorbent tubes is documented in the literature in the 1960s. Evaluation of the advantages and disadvantages of using sorbent tubes is well documented in the literature for collection of gases and vapors.[5,8-12] While the method does provide accurate reproducible results, the accuracy and precision of charcoal tube sampling are affected by many factors and will be discussed in the limitations section 2.1.4.

2.1.2 Diffusive Badges

The concept of diffusion sampling was introduced in 1973 by Palmes and is still being evaluated today for its effectiveness.[13-20] Diffusive badges are sampling devices that collect gases and vapors by diffusion of the chemical of interest across a membrane, where a concentration gradient exists between the ambient air and the collection sorbent. These badges operate on the principle of Fick's first law of diffusion.[21] Various passive dosimeter badges are commercially available for sampling organic vapors. The samplers are designed in a variety of

shapes and sizes. However, most diffusive badges used to sample volatile organic vapors contain a layer of charcoal to adsorb the organic vapors. The amount and number of layers of charcoal may vary between different manufacturers. Each diffusive sampler operates by collecting a known amount of a chemical from the atmosphere based on some of the physical properties of the chemical being sampled. The theoretical basis for diffusive sampling is now well established.[22] The diffusion process is related to the mass uptake being defined by the concentration gradient, time of exposure, and area of the sampler. The basic expression of Fick's law is as follows:

$$J = \frac{D(C_e - C_o)}{L} \qquad (2.2)$$

$$Q = \frac{(DA)\,t\,(C_e - C_0)}{L} \qquad (2.3)$$

where, J = diffusive flux (g/cm^2-sec)

D = coefficient of diffusion (cm^2/sec)

A = cross sectional area of diffusion path (cm^2)

L = length of diffusion path (cm)

C_e = external concentration (g/cm^3)

C_o = concentration at the interface of the sorbent (g/cm^2), assumed to be zero

Q = mass uptake (g)

t = sampling time (sec)

The method for calculating the atmospheric concentration is essentially the same as is used for the active sampling system. The expression DA/L is defined as the sampling rate and has units of cm^3/sec. The manufacturers of the badges generally certify flow rates for their specific badges for a number of chemicals of interest. The collected sample is analyzed and the total mass of the analyte on

the badge is determined. The concentration is calculated by subtracting the amount of material found in the blank (X_b) from the sample amount (X_1) dividing that value by the sampling rate multiplied by the time (t) sampled (volume of air sampled). The formula used is as follows:

$$C = \frac{(X_1 + X_2) - X_b}{Flow\ Rate\ t} \tag{2.4}$$

X_2 is only used when the badge has a backup section. The above formula only provides an accurate concentration when the appropriate corrections for desorption efficiency, temperature, and pressure have been made.

The diffusive badges were marketed to be inexpensive, lightweight, easy to use, and well accepted by workers as opposed to the active sampling methods. In 1986 an international conference on diffusive sampling was held in Luxembourg.[14] At the symposium, the Commission of the European Communities concluded that: 1) The theoretical basis for diffusive sampling is confirmed by laboratory and field trials. 2) Active and diffusive sampling are complementary approaches, having areas of applicability that may overlap. Each has its role in a strategy of monitoring worker exposures. 3) In general, there seems to be no significant difference between the accuracy and precision of diffusive sampling and those of other monitoring systems such as active pump sampling. 4) Diffusive samplers, like other methods of sampling, are acceptable as long as the limitations are recognized.[23]

While the symposium concluded that diffusive badges were equivalent to that of the charcoal tubes in many ways, both methods have limitations, but not necessarily always the same limitations. The activated charcoal used in both collection devices is susceptible to influence by environmental factors, which may lead to inaccuracies in the sampling results and limitations for use in collecting samples by occupational hygienists. In a later section, a systematic review of the

primary limitations associated with both methods is provided.

2.1.3 Additional Sampling Methods

A number of alternative methods are available to collect gases and vapors for occupational hygiene investigations. These alternative methods can be used to collect grab samples as well as integrated samples. Evacuated flasks and flexible plastic containers (bags) are often used to collect grab samples for analysis of unknowns. The walls of the container can interact with the contaminant of interest resulting in loss of the analyte and underestimating the concentration. The wall loss is related to the properties of the chemicals of interest and the types of material used to construct the container.[24] Liquid sorbers collect contaminants from the air by an absorption process. Sorption of gases and vapors by chemical reaction depends on the size of air bubbles produced in the sampler and capacity of the liquid to react with the analyte of interest.[5] Controlling the flow rate often allows for appropriate residence time of the air in the liquid and, depending upon design, size of the bubbles to collect the contaminants of interest. Liquid sorbers are difficult to use for occupational hygiene application because the sampling system is not very durable. The glass impingers can break, the liquid can spill and the liquid can be drawn into the sampling pump. For these reasons, liquid sorbers are often not the preferred method of sampling if alternatives are available.

Colorimetric tubes, both grab sample type and long term tubes, are simple to use, with accuracy limited to ± 25 to 35 %.[25] In addition, the colorimetric reaction may be affected by a number of interfering compounds resulting in over or under estimation of exposure. Colorimetric badges are another type of dosimeter used to assess the occupational and ambient exposures to gases and vapors. As with the tubes, colorimetric badges are easy to use and results are almost immediate. However, both badges and tubes are susceptible to interferences, fading of the color over time, sensitive to environmental conditions.[26] In general, the colorimetric tubes and badges are sufficient

screening devices regarded as range-finding devices, but rarely do they provide acceptable results for exposure characterization.

2.1.4 Limitations of Current Sampling Methods

Primary parameters that can affect accuracy include: concentration, capacity, sample time, reverse diffusion, air velocity, device orientation, high relative humidity, elevated temperature, flow rate, unique capacity to adsorb each analyte, displacement of the analyte of interest by another analyte more strongly adsorbed by the sorbent, inability of analytes to adsorb onto the sorbent, storage stability, and ability to desorb the analyte from the sorbent and associated analytical problems.[7,27] Both charcoal tubes and diffusive badges have been tested in controlled atmospheres and used extensively under a variety of field conditions, resulting in acceptable airborne contaminant collection.[14,28] However, the limitations must always be considered when using these methods and interpreting the results. In addition, the limitations of the method do restrict the occupational hygienist's options when developing an exposure assessment strategy. A brief discussion of the aforementioned limitations is presented below.

An important consideration as one reviews the limitations, is the interaction of two or more of these limitations. As an example, if a compound has a reduced affinity for the charcoal, then the effects of high relative humidity may reduce the collection efficiency for that chemical more significantly than for a chemical with a strong affinity for charcoal.

Air Concentration is related to the quantity of sorbent available in the sampler to adsorb the chemical of interest. Sample time, flow rate, capacity, storage stability and reverse diffusion are all related to mass uptake and therefore to the concentration being sampled.[5,29-31] Since the concentration of air contaminants in most industrial settings is not known, accurate results depend upon selecting the appropriate sampling time and sampling rate. The capacity of a charcoal tube or badge is related to the chemical's specific affinity for charcoal.[32] These adsorption principles are the factors that result in limitations for air sampling. If

the sampling rate is too high, the chemical of interest does not have a long enough residence time, thus some of the analyte will be lost and measured concentrations will be less than the actual air concentration.[33] If a backup section exists, the analyte that has broken through will be found there. If the analyte concentration in the backup section is greater than 10 % of the total, then the sample is invalid.[27]

Sampler Saturation and room ventilation rates are two factors that generally do not affect the active sampler, yet do create problems when sampling with diffusive samplers. When the diffusive sampler becomes saturated, the C_o is no longer zero and the uptake rate becomes non-linear (i.e. Fick's law is not followed). Hence, it becomes impossible to determine the concentration collected by the diffusive badge. Backup sections in passive badges and active sorbent tubes have been implemented to protect against saturation of the sampling media.[21,34]

Air Velocity. Passive badges require a minimum face velocity to ensure sufficient air movement across the face of the sampler, thus allowing diffusion to occur at a constant rate. In general, the critical velocity is about 0.13 m/s (25 fpm).[21,35,36] If the face velocity falls below the recommended levels, a lack of new molecules to diffuse across the membrane results and the air borne concentration is under estimated by the diffusive sampler. The stagnation of air essentially reduces the amount of contaminant out side the diffusive membrane resulting in a reduced amount of contaminant inside the sampler. The airflow requirement makes passive badges less effective for area sampling or on workers with limited physical movement. When the air velocities are high over estimation of concentration has been reported.[37] In addition to air flow rates, over estimation of concentration has been observed where the airflow across the membrane is contaminated with droplets that may deposited on the diffusion membrane.[38]

Fick's law also assumes a steady concentration of contaminants. If the concentration fluctuates widely, the sampler may not provide a true concentration because some of the contaminant may be missed. Therefore, turbulent air flow may result in under sampling airborne concentrations.[39]

Sorbent Capacity. In practice, the occupational hygienist must change charcoal tubes several times per day, depending upon the concentration in the work environment. Chemical break through can occur even when low flow rates, 20-30 mL/min are used. The breakthrough rate is related to the concentration being sampled.[40] Diffusive badges generally have a larger adsorption capacity for chemicals, yet they often do not have backup sections. Therefore it is not possible to evaluate if the chemical has broken through. Also, the sampling rate for diffusive samplers must be known before the concentration of a vapor can be determined. Most manufacturers determine the sampling rates empirically. For compounds whose sampling rates have not been determined, the company must theoretically estimate the sampling rate. Feigley (1987) found that theoretical flow rates averaged 27 to 61 % higher than the experimental sampling flow rates reported by manufacturers. Clearly, manufacturers are aware that diffusive samplers deviate from theoretical values and have chosen different approaches for determining sampling rates. These different methods may introduce errors associated with using diffusive badges.[41] As mass uptake approaches the capacity of the sampler diffusion factors may be adversely affected.[42]

Reverse Diffusion. The affinity of a compound for charcoal is related to physical properties such as boiling point and molecular weight. Reverse diffusion may be a significant problem for weakly bound chemical species. The following three conditions can result in underestimation of air borne concentrations: 1. one analyte competes for sorbent sites with other chemicals, including water, 2. high peak exposures followed by very low or no analyte exposures, and 3. storage of diffusive badges for long periods (>1 week). These three conditions can cause the chemical of interest to diffuse off the charcoal back into the atmosphere, for

both charcoal tubes and charcoal badges.[37,42-44]

High relative humidity can significantly reduce adsorption of contaminants on charcoal, resulting in break through and underestimating worker's exposure.[45-49] Breakthrough concentration curves developed by Yoon, 1990, show the need to reduce sampling time by 30-40% at higher relative humidity (>80%) to avoid break through. At concentrations surrounding the OEL for many materials, the sorbent tube will often experience breakthrough within 1-2 hours. Therefore, the occupational hygienist may be required to collect 4-6 sorbent tubes over an eight-hour work shift to document the workers' eight-hour exposure. The need to collect multiple tubes in an eight-hour exposure becomes a practical limitation. This limitation results in increased costs to document worker exposures and, in practice, the end result may be a tendency to extrapolate 1-2 hours of sampling into an eight-hour estimate.

Collection and Desorption Efficiency. The typical work environment contains many mixtures of chemicals. As a result, some chemicals compete for sites on the sorbent and different chemicals may require different materials to desorb the chemical of interest from the sorbent. Each chemical has a unique affinity for the sorbent. This requires that collection efficiency and desorption efficiency for each analyte be experimentally determined.[49] Correction factors for each analyte must be applied to accurately determine the airborne concentration of each analyte. Also, multiple analytes may result in several types of sorbent tubes needed to collect the vapors of interest. If polar compounds are present with non-polar materials the adsorption and desorption efficiency may be affected by the polar compounds displacing the non-polar compounds.[50-52] The airborne concentration or mass uptake also affect the adsorption and desorption. In addition to the competition for active sites, compounds may react with each other and the substrate (sorbent), modifying adsorption efficiency.[53] These issues surrounding adsorption and desorption efficiency result in the need to collect more samples to adequately assess employee exposure.

Temperature affects both active and diffusive samplers by impacting both the flow rate and adsorption rate.[44,54] While the ideal gas law can be used to adjust for temperature fluctuations with respect to the volume sampled, it is more involved to determine how the adsorption rate was affected by the change in temperature. Palmes (1976) found that diffusion coefficients of gases and vapors vary with absolute temperature raised to the power of 1.5. In addition, the volume of a gas varies with temperature, so the concentration per unit volume varies inversely with temperature.[55] As a result, $T^{1.5}/T = T^{0.5}$ and the quantity of material sampled varies as a function of absolute temperature to the power of 0.5. In some cases temperature correction factors are provided by manufacturers to compensate for the variability in diffusion at different temperatures.

The above examples summarize the key limitations encountered with sorbent sampling methods. In each case, the solution is often to collect a larger number of samples to ensure the worker's exposure is accurately characterized. These limitations cause the cost of sampling to rise and, in practice, results in fewer workers being sampled and/or fewer chemicals being evaluated. Development of a new sampling method that does not experience as many limitations would provide for improved exposure assessments.

2.2 Exposure Assessment Strategy

An effective exposure assessment strategy can reduce the risk of over or under estimating workers' exposure and reduce regulatory liabilities.[56,57] Occupational exposures to toxic materials can vary considerably from day to day. The chemical generation rate, ventilation rate, worker mobility and variation in tasks, all contribute to the day-to-day exposure variations.[58] A typical sampling campaign for occupational hygiene consists of identifying the worst-case scenario (i.e. maximum risk employees), collecting breathing zone samples on these employees during a specified time period, and extrapolating the data to

other workers who are believed to have similar exposures. Essentially data is collected on a few employees considered to be representative of the entire group (Similar Exposure Group (SEG) .[59]

A key condition for statistical analysis is that samples must be collected randomly to ensure the samples represent independent measurements. However, this is rarely accomplished in occupational hygiene sample collection. In addition, the number of samples collected (n) is usually small, 3-5. These conditions, common in occupational hygiene sampling, can result in biased estimates of exposure variability. The "worst case" sampling strategy simulates drawing samples from the upper tail of a distribution and therefore the potential that underestimation of exposure is significantly reduced if the worst-case individuals were correctly chosen.

The hypothesis that supports the worst-case strategy, is that if the worst-case employees are not over exposed, then other employees in the exposure group are adequately protected. While the aforementioned hypothesis may not always be correct, it is common practice for two reasons. First, many hygienists are not located at the sampling location and therefore must co-ordinate their sampling with workplace visits. Second, while the OELs may or may not be intended to protect employees from long-term health hazards, they are enforced as single day averages.[60,61] Enforcement agencies do not focus on long-term averages, but on single day average.[62-64] Therefore, employers do not have the incentive to develop long-term sampling campaigns to focus on long-term average exposure. Many private companies are expending considerable effort and resources implementing exposure assessment programs that attempt to prioritize needs, optimize resources and accurately assess worker exposure. Yet, decisions are often made based on the results from one day or less of sampling. Adoption of a set of exposure assessment guidelines for use by practicing occupational hygienists may motivate regulatory agencies to change their philosophy.[65]

2.2.1 Long-Term Exposure Strategy

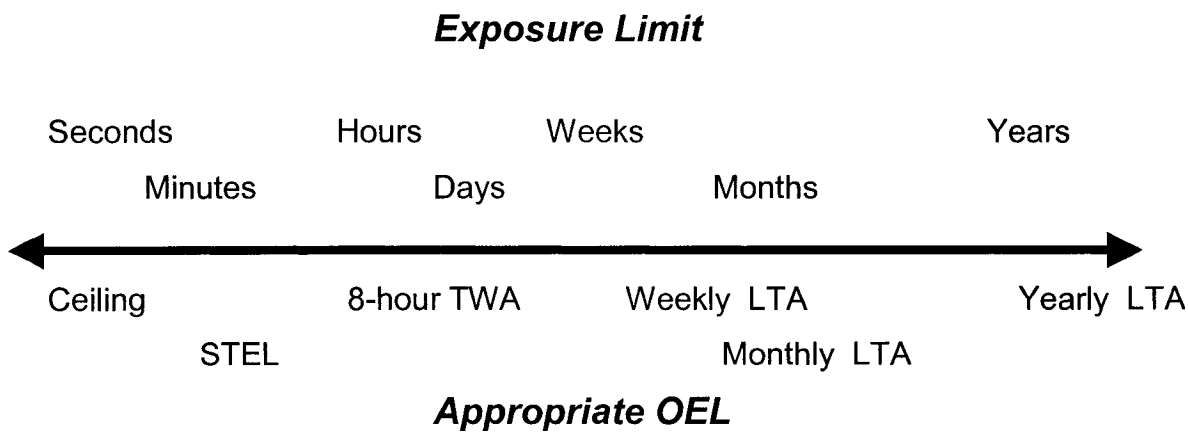
Long-term sampling to assess exposures to chemicals with long-term health effects intuitively seems like a logical approach. However, difficulties can be encountered with long-term sampling. Long-term exposure assessment can be defined as short as an eight-hour day or as long as a working life-time (45 years), depending upon the focus of the individual collecting the sample.[62] The definition is modified to suit the needs of the person performing the exposure assessment. An epidemiologist is usually interested in working life time exposures while the compliance officer's focus is on whether or not the eight-hour exposure exceeds a regulatory limit.[66-68] A component of this review is to consider the meaning of the current definition of the TLVs and OSHA PELs specifically the term "40-hour workweek" in their definitions.[61,69] While the 40-hour workweek concept has been in the literature for decades, few studies have been published that document exposure of workers to hazardous chemicals over a 40-hour period.[69,70] In practice, several eight-hour samples are extrapolated to estimate the workers' long-term average exposure. This is generally done because it is not practical to sample with a charcoal tube and pump or a charcoal badge for five consecutive days. Using the capillary-canister, 40-hour sampling strategy is possible and practical to implement as a field practice.

There is no question that interday variability can be extensive, 3-100 fold, in many industrial processes.[69,71,72] To this end, one must conclude that a single day sampling campaign will not be representative of workplace exposures. Roach (1987) suggested that sequential sampling strategies make economical sense. While one can argue that 40 hours is only a fraction of a work year, it is still a significant improvement over the sampling approach of a single eight-hour day sample.[72] **Table 2.1** displays a comparison of exposure times to OEL. The long-term averages (LTA-TWA) have not been established but are recommended by several authors.[62,65,73] These authors suggest LTA-TWA be set at 10% to 25% of the current TLVs for some compounds. In addition, several articles have been published that discuss the smoothing of exposure variability

with respect to long term health effects.[74-78] The use of the long-term monitor will allow for the collection of a 40-hour sample in a variety of different exposure strategies and will allow for comparison to an LTA-TWA. This type of sampling is currently more difficult with charcoal tubes or badges, which would have to rely on multiple tube/badge usage. The recovery of the analyte is impacted with increased storage time as well. In addition, the number of tubes or badges needed would result in unacceptable analytical costs.

Development of an effective exposure assessment requires professional judgment to select the personnel to be sampled, identify the days that should be sampled, and assess the process variability. In an ideal situation, all potentially exposed workers would be sampled and decisions concerning their overexposure would be made for each individual. However, rarely are resources available to sample all workers. Purely random sampling is generally not the desired approach for workplace sampling because of the variability of exposure from worker to worker and the number of workers that would need to be sampled to ensure with some level of certainty that the highest exposed workers were not missed. As an example, if one assumes 20 workers are exposed to similar levels of a chemical in a factory, with 10% of the work group in a highest exposed subgroup, then to be 90% confident that at least one of the subgroup individuals would be sampled, a minimum 13 of the 20 workers must be monitored.[79] This large number of samples is generally not realistic for most occupational hygiene sampling campaigns. It is often the most efficient use of air sampling resources to target the maximum exposed individuals, then collect air sample on them. If sufficient information to identify a maximum exposed group of workers cannot be found then it may be necessary to randomly select employees to sample. However, the random selection results in a large number of samples to ensure statistical confidence that the highest exposed individuals have been identified.

Table 2.1 A Conceptual diagram of the relationship of health effects, averaging time, and occupational exposure limits



Exposure Duration Adverse Effect	Measurement Averaging Time	Occupational Exposure Limit	Example
Seconds/minutes Immediate/acute effects	Instantaneous direct-reading continuous monitoring-- with data logging/alarms	Ceiling STEL[A]	H_2S HCN HCl
Minutes/hours Acute effects	Short - (15-minute) or full-shift TWAs	STEL 8-hour TWA[B]	Solvents
Days/weeks Sub acute/chronic effects	Daily/weekly/monthly TWA	8-hour TWA LTA-OEL[C]	Lead
Years Chronic long-term effects	Annual average exposure	LTA-OEL	Vinyl chloride

[A]STEL = short-term exposure limit

[B]TWA = time-weighted average

[C]LTA-OEL = long-term average-occupational exposure limit

(Tables adopted from Mulhaussen, 1998 [65])

As a result, it often becomes necessary to target the worst-case exposed individuals using a preliminary survey of the physical conditions of the process or operation.

The greater number of samples one can collect for a survey the better the characterization of exposure. If sampling devices become easier to use and more cost effective to employ, even with diminished precision, exposure assessments will improve. The use of the capillary-canister device may provide an efficient method to characterize the mean exposure of workers. Whether this mean should be compared to the current OEL will need to be considered on a chemical-by-chemical basis, the primary consideration being the methods used to develop the occupational health standard.

2.2.2 Exposure Assessment Statistics

Use of a capillary flow control devices with different size canisters may allow for new types of sampling exposure assessment strategies. The improvements to occupational air sampling methods may increase the accuracy and precision of the results. Also, improvement of the "ease of use", innate with this method, will allow for increased data collection resulting in an appropriate number of samples collected to obtain statistically significant results. The atmosphere in a work environment is often determined acceptable when the mean or exceedance fraction is determined to be less than the OEL, where the arithmetic mean is interpreted to be an estimate of long-term (several months to a year) exposure for an employee or group of employees. The exceedance fraction is considered to be the fraction of measurements expected to exceed the OEL. Small numbers of samples(n), often present problems when attempting to decide whether the mean exposure exceeds the OEL. Confidence intervals around a mean allow one to identify the uncertainty in the air sampling data.[68,80,81] Calculation of confidence intervals around a mean can be problematic for small sample sizes and highly varied data (large coefficient of variation). Several authors have suggested methods to accurately calculate the upper and lower confidence limits

around an estimated mean.[64,68,82-86]

The data from occupational hygiene surveys is typically log normally distributed and therefore the confidence intervals are not symmetrical around the mean. It is beyond the scope of this research project to evaluate different methods of calculating confidence limits. However, the issue is raised to emphasize the need to collect sufficient numbers of samples to reduce the risk of arriving at an erroneous conclusion. Therefore, a brief review of the factors surrounding the calculation of confidence intervals is included. Hewett, (1997) evaluated five different methods for mean testing of lognormally distributed data with n values ranging from 5-20.[63] As one would expect, variability between the tests is large for small n values (n=5) and large geometric standard deviations (GSD >2.0) are obtained. An alpha error of 0.05, (the probability of accepting the alternative hypothesis given the null hypothesis is true) and a beta error of 0.01, (the probability of accepting the null hypothesis given the alternative hypothesis is true) are generally considered acceptable. Each test evaluated by Hewett (1997) was designed to allow the occupational hygienist to demonstrate with some level of assurance that the true mean is below or above the OEL. The null hypothesis may take two forms Ho: u $\geq$OEL or Ho: u$\leq$OEL, depending upon the occupational hygienist's view point. Ho: u $\geq$OEL is used when the hygienist is interested in showing that employees are not overexposed. Ho: u$\leq$OEL is appropriate when the hygienist is interested in showing compliance with a legal standard or recommended guidelines. Each hypothesis is based on the arithmetic mean, yet the distribution of the data is assumed to be lognormal as is the case for most occupational hygiene data. Therefore simple upper and lower confidence limit calculations around an arithmetic mean are not appropriate. The various confidence limit methods have been developed to approximate LCL and UCL for small sample sizes using log transformed data. The various tests use different methods of estimating the mean and standard deviation for a data set. The Land Exact test appears to provide the most accurate estimate of confidence intervals.[63] In other words, it provides the confidence limits that are close to the

actual 95% confidence limit. However, the AIHA method and Rappaport & Selvin method show similar confidence limits and are reported to be somewhat easier to calculate. If the upper confidence limit is greater than the LTA-OEL then one can conclude that the true mean may exceed the LTA-OEL and corrective action is necessary to protect the employees.

2.3 Occupational Exposure Limits

The statistical accuracy of the proposed methods for calculating confidence intervals will continue to be debated as will the definition of occupational exposure limits. Many researchers have debated the meaning of OELs and the process by which they are established.[87-95] While this research project focused on the evaluation of a new instrument to assess exposure of gases and vapors, and new exposure assessment strategies, one cannot ignore the relationship of exposure to the exposure limits, and, how exposure limits are applied in practice. A selected review of the literature concerning the concept of occupational exposure limits will be presented here to focus attention on the uncertainties associated with OELs. Several questions that are raised when one reviews definitions of OELs, include: Are they a threshold or are they a long-term average? How did the organizations that developed them intend them to be used? How are they used in practice? While the answers can be debated, a common theme one observes is that a standard is a reference point consisting of a set of guidelines that reflect a society's or an organization's values.

Occupational exposure limits have been used for many years as guidelines to protect workers' health.[96-98] The first set of OELs were established in 1886, published by Karl Bernhard Lehmann.[99] These OELs were quantitative values based on field studies and model exposures based on human and animal exposures. Lehmann introduced dose-response principles which included the theory that exposure to a concentration (C) of identical products for a time (t) will result in identical magnitudes of effect or ($C \times t$ = constant effect). Over the course of several decades, Lehmann and colleagues expanded their list of OELs

to over a hundred compounds. The following is a set of prerequisites they developed for setting OELs in the early 1900's.

1. Complete reversibility of toxic effect at or below the relevant exposure concentrations. This included any accumulation of material over a working lifetime.
2. There should be clear evidence from field experience and/or animal experimentation, of the existence of a threshold of toxic effect.
3. Brief excursions above the OEL (peaks) in the course of a workshift should be regarded as harmless to health, or as tolerable.
4. There should be sufficient knowledge about the mechanism(s) of toxic effect(s) to explain the existence of thresholds.

While these guidelines were developed over a century ago they are still useful in setting OEL's today.[100,101] More recent insight for setting OELs comes from the relationship to exposure, where OELs reflect the maximum level of exposure that is acceptable, however, "acceptable" is defined differently by the standard setting organizations. In addition, the argument has been made that health-based-OELs should be established along with criteria for exposure, monitoring methods, performance guidelines, and exposure assessment strategies that are representative of worker exposure.[102] This inclusion of other factors requires that the established OELs be linked to routes of entry and probability of exposure. The debate becomes further complicated when one considers all the scientific disciplines that are involved in setting OEL standards and the social economic influences. As a result, the standard setting process has considerable uncertainty and the only means to set an OEL is to rely on value judgment. Many different models for establishing OELs exist in the world. Several of the most influential OELs will be reviewed in the following pages.

The American Conference of Governmental Industrial Hygienist (ACGIH), an organization dedicated to the administrative and technical aspects of

occupational and environmental health, publishes occupational exposure limits referred to as Threshold Limit Values (TLV).[69] Some consider TLVs as the most influential OELs in the world.[94] Many countries based their original OELs on the ACGIH TLVs. ACGIH was established in 1938 and still is today a volunteer organization comprised of industrial health professionals from academia, government and industry. It is not a government-funded organization. They began issuing OELs in 1946. TLVs have been established for some 700 compounds and are listed in three categories. Definitions of these categories are as follows:

1. Threshold Limit Value-Time Weighted Average: The time-weighted average concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect.

2. Threshold Limit Value-Short Term Exposure Limit (TLV-STEL): The concentration to which it is believed that workers can be exposed continuously for a short period of time without suffering from irritation, chronic or irreversible tissue damage or narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency, and provided that the daily TLV-TWA is not exceeded. A STEL is defined as a 15-minute TWA exposure, which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA.

3. Threshold Limit Value-Ceiling (TLV-C): The concentration that should not be exceeded during any part of the workday.

Eight-hour time weighted average exposures are generally the most appropriate means of assessing exposure, however, there are certain materials that are acute toxins and STELs or ceiling limits are necessary along with instantaneous

monitoring.[103-106] In the definitions of the TLV-TWA it is stated, "In some instances, it may be permissible to calculate the average concentration for a workweek rather than a workday."[69] However, there are no guidelines explaining which *instances* the 40-hour average would be appropriate to implement. The TLV committee updates the TLVs on an annual basis. Changes are proposed based on current literature reviews and adopted based on committee vote. While these limits are recommended guidelines, they have been cited in legal cases, thus making them more than recommendations in the view of some.[107]

Canada. Each province of Canada has its own process for developing and updating OELs. The specific details for development and the level of enforcement varies from province to province. However, several characteristics are common among the most industrialized provinces. A joint committee of health and safety professionals from labour, management and the ministry is formed to review and update the standards. Public review of proposed standards is required as part of the process. Key criteria include: each OEL has some scientific basis that should be enforceable. Economic factors such as compliance cost, new equipment, costs of operational changes are all factored into setting the OEL. In addition, technical feasibility of compliance with the OEL is considered when setting the standards. Some Canadian OELs are adopted from ACGIH TLVs or other countries such as Germany, Sweden, and the Netherlands.[95] The definitions for the time weighted average and short-term exposure levels are similar to the ACGIH TLVs.

United States. In 1970, the Occupational Safety and Health Administration (OSHA) was formed. It is a regulatory body given the charter to enforce safety and health regulations in the United States. The Permissible Exposure Limits (PELs) are legal airborne limits mandated in US industry. The original PELs were adopted from the 1968 TLVs and have similar definitions for the time weighted average and short-term exposure levels as the ACGIH TLVs.

Economic and technological feasibility are considered when setting new PELs. Labor, management and the public have the opportunity to comment on proposed PELs. However, the process for updating PELs is complicated and political. As a result, less than 30 PELs have been modified since the original PELs were established in 1970. Many PELs are out dated and less than protective.[61]

United Kingdom. In 1989 the Working Group on the Assessment of Toxic Chemicals (Watch Committee) was created. The focus of this committee was to initiate a more in-depth scientific evaluation of OELs in Britain. Individual chemicals are given occupational exposure standards (OES) based on available scientific evidence, that with reasonable certainty, there is no indication that the substance is likely to be injurious to employees if they are exposed by inhalation day after day. The OES is a health-based standard and many originated from the TLVs. If industry cannot reasonably comply with the standard, then WATCH can recommend a maximum exposure limit (MEL). The MEL represents a technological and economically feasible level at which employees are allowed to be exposed. The MEL is not a health-based standard. This duel set of standards allows for flexibility in standard setting procedure, yet it also may introduce more uncertainty in identifying acceptable workplace standards.[102]

European Community. While the TLVs are arguably the most widely used OELs in the world,[95,108] the values have been criticized because the process used to establish them is not based solely on health effects and may be influenced by industry.[109-113] In contrast, the Dutch have used Health Based Recommended (HBR) exposure limits that are generally 4-5 times lower than the TLVs.[114,115] These HBR are established solely on health effect criteria with no social, economic or technical feasibility factors considered. The European community has moved to setting health based OELs using the Commision of European Communities Criteria Documents and Directives.[116-118] These directives embrace the concept of having two types of occupational exposure

levels, each with a different status with respect to compliance and risk reduction. The advantages of a common European approach to the OEL setting process are obvious. German MAKs are based exclusively on scientific information about the health effects, as are the Swedish OELs. When one examines these health-based standards one finds a general downward trend with respect to time. The Swedish standards have dropped on average 3.9 % per year since 1960 and are 70% of their respective TLVs. Both the German MAKs and Swedish OELs are based on comprehensive summaries of toxicological literature and are updated on a routine basis.[94]

China. The Chinese central government began setting OEL standards in the 1950s for chemical and physical agents. The standards are referred to as maximum allowable concentration (MACs). As of 1995, approximately 120 chemical substances are regulated.[119] The standard setting process is similar to the World Health Organization (WHO) two-step process of focusing on setting a health-based exposure limit, then evaluating the social-economic and technical feasibility considerations to define an achievable limit.[120] The Chinese MACs are defined in a similar definition as the ACGIH TLVs. A comparison of 71 Chinese MACs to their corresponding 71 TLVs showed that the TLVs are higher for 72 percent of the chemicals.[119] This comparison as well as the relationship between the Swedish and German OELs seems to support the theory that the process used to set TLVs is influenced by factors other than health.

As one reviews the OELs from different countries, it is found that the process of setting OELs results in different outcomes, even when the standard setting protocols are very similar. This reality has resulted in some groups criticizing the accuracy of OELs and whether they should be used at all. However, regardless of how accurate the OELs, they serve as a guideline in detection of and evaluation of health hazards in the workplace. Regardless of which process is used to set the OELs, there is an initial point at which a quantitative relationship between the dose and effect exists. The long-term value of OELs relies on a

process of continual revision to ensure adequate worker protection.

In practice, OELs are considered "thresholds" by some individuals and "long term average exposure limits" by others.[56,79,113,121] The most widely used interpretation is that the TWA-OEL represents an upper control limit for daily TWA exposure. Based on this interpretation, the long-term average or mean value would be much lower than the daily TWA-OEL because of the distribution of data (i.e., lognormal). The long-term TWA (mean value) would be a central tendency of the distribution and the upper tail would represent the daily threshold limit. An opposing viewpoint is that the risk assessment process used to develop the OELs was based on long-term averaging of the exposure (dose) and therefore OELs are long-term means.[122-124] Several researchers have recommended that the TLVs should be lowered by one third or as much as one-tenth of their current value to be considered as a long term average OELs for chronic disease association.[71,113,121]

Non-Occupational Exposure Limits. In addition to occupational exposure limits promulgated by government regulatory bodies, some agencies have developed guidelines for unique environments. In 1972, the United States National Research Council's Committee on Toxicology (COT) recommended maximum airborne levels for continuous and emergency exposures to spacecraft contaminants. These exposure limits were referred to as Spacecraft Maximum Allowable Concentrations (SMACs).[125] The SMACs were intended to provide guidance for contaminants found in spacecrafts during normal operations and during emergency conditions. Short-term SMACs were developed for emergency conditions ranging from 1-24 hours and were intended to allow occupants to perform necessary task with out causing serious toxic or permanent effects. Long-term SMACs were intended to avoid adverse health effects (either immediate or delayed) and to prevent detrimental change in the crew's performance under continuous exposure to chemicals in an enclosed environment for 180 days. For compounds with carcinogenic effects, the SMACs

were set at levels so that the lifetime risk of cancer is less than 1/10,000. Compounds that affect multiple organ systems were addressed by considering the most sensitive organ system. The relevant information that is considered when establishing a SMAC, includes chemical-physical characteristics, structural activity, in-vitro toxicity test, animal test and human studies. The number of contaminants for which SMACs are developed is continuously expanding with the increased activity on the international space station. As an example, Acetone has SMACs ranging from a 1-hour limit of 500 ppm to a 180 day limit of 22 ppm, and Tricholoroethylene has a 1-hour SMAC of 50 ppm and 180 day SMAC of 2 ppm. These chemicals also have SMACs for 24 hours, 7 days, 30 days that lie somewhere between the 1 hour and 180 day limit.[126,127] The SMACs provide a model for long-term exposure limits that could be used in developing long-term occupational exposure limits.

The National Ambient Air Quality Standards were established in 1970 in the United States and included seven chemicals referred to as priority pollutants.[130] Since the mid 1980s, there has been increasing interest in measuring 600 additional ambient air pollutants from industrial sources to achieve acceptable levels of exposure.[129] These chemicals are present because of combustion processes, point source, mobile sources and fugitive emissions. Ambient air limits (AAL) or acceptable levels are not established at a national level and therefore the individual states and local agencies have turned their attention to establishing AALs. These agencies use a variety of approaches to arrive at an AAL, but given their limited resource, the most common method is to derive an AAL from OEL/TLVs using some safety factor.[130] A common model is shown in equation 2.5.

$$AAL = \frac{OELorTLV}{(4.2)(UF_1)(UF_2)} \qquad (2.5)$$

where:

AAL = ambient air limit (ug/m^3),

OEL = occupational exposure limit (ug/m^3),

4.2 = adjustment for difference in weekly duration of exposure, 168 h/40h

UF1 = uncertainty factor to adjust for possible increased susceptibility of some people in the public versus the work force

UF2 = uncertainty factor to adjust for small margin of safety inherent in the OEL

While this approach may lack scientific rigor it is simple and can readily set AAL for many chemicals. The concept of using occupational levels to set ambient levels that will protect health, clearly introduces uncertainties on top of the already existing uncertainties of the OELs ability to reduce the risk of disease. This example method of deriving AAL is presented to further display the multitude of uncertainty associated with the exposure assessment process.

The future will likely see refined methods of setting exposure limits and uniform application of methods of estimating confidence limits around a mean of exposure data. At present, occupational health standards are enforced by inspectors in North America based on a very small number of samples in an exposure assessment.[95,102] As a result, the uncertainty in the sampled values can lead to variability in how the regulation is applied. If one considers the uncertainty of small sample sizes, the inter-day variability, and then comparing those numbers to the uncertainty associated with setting the OELs, one realizes that interpreting the occupational hygiene data is often about managing uncertainty. Given all these uncertainties, the error associated with taking measurements may be a small fraction of the overall uncertainties. The

fundamental problem of limited resources, resulting in collecting a limited number of samples, extrapolating that data to a large number of workers, to represent extended periods of time, will always result in considerable variability in the exposure assessment process.[61,131] Development of sampling methods that are easier to use, economical, reliable, and more versatile will allow the occupational hygienist to reduce the amount of extrapolation necessary to adequately characterize worker exposures because they should be able to increase the sample size for any given sampling campaign. This research will attempt to address these issues by integrating a capillary-canister device into occupational sampling strategies.

2.4 Capillary-Canister Device

As discussed in Section 1.0, it is important to review the history of the implementation of new sampling devices to understand the challenges of developing and implementing a new device such as the capillary-canister. The fact that it took 25 years from the publishing of the initial paper until the regulatory agencies developed a protocol for use of diffusive badges reflects the difficulty in getting a new device accepted among the occupational hygiene community.[132] It should be realized that many parallels could be drawn between the development of the diffusive badge sampler and the developmental process the capillary-canister must go through. A similar result is expected, the capillary-canister, like other methods of sampling, should be acceptable as long as the limitations are recognized and boundaries are understood. Essentially, the capillary-canister is in the initial prototype phase and the device as well as the methodology will require additional scientific research both in the laboratory and field before the occupational hygiene community accepts it.

The capillary-canister can be used to collect whole air samples of many different gases and vapors. It can be thought of as a passive sampling device because it does not use a sampling pump. The system was designed and modified to allow

for maximum flexibility for sampling duration and for type of contaminant. The flow control device has a demonstrated range of sampling time of several minutes to several months.[133-134] When evaluating the effectiveness of the flow controller combined with evacuated canisters to sample gases and vapors for occupational hygiene investigations, one must understand the advantages and disadvantages of canister sampling. In addition, the parameters that control air flow into the canister must be understood well enough so that flow rates can be predicted. The key design aspects and the advantages and drawbacks to using canisters and the flow controllers to collect whole air samples will be discussed in this section.

Evacuated chambers have been used for years as a means of collecting whole air samples for volatile organic compounds (VOC).[135-137] These evacuated canisters are polished stainless steel canisters, with interiors coated with patented passivate processes. They have been used to collect airborne samples ranging from short-term grab samples to 24-hour integrated samples. The canisters have been evaluated by a number of researchers with respect to stability, storage time, recovery, humidity and other parameters.[136-138] Canisters were also shown to accurately determine trace levels of volatiles in ambient air.[139] However, over and under estimations have been reported by several sources depending upon the chemical being sampled.[137,140-142] United States Environmental Protection Agency (EPA) procedures TO-14 and TO-15 were developed to establish standardized methods to clean, prepare, sample and analyze low concentrations of VOC in ambient air. These methods define the necessary steps to sample VOC by passively collecting a whole air sample in a canister.[143-146] The benefits of canisters is that they can be transported to field sampling locations and used under highly varied field conditions with little effort. However, to date commercially available canisters have been used as area samples and sampling time has been limited to 24 hours for large 6-liter canisters.

Simon (1997) designed a flow control device that allowed for long-term sampling using evacuated 1 and 6-liter canisters. In his research, long-term was defined as weeks or even months of continuous sampling. The flow control device is a passive controller that allows contaminated air to pass into the canister at low flow rates. A fused silica capillary column functions as a restricting orifice to control the flow rate. The columns tested by Simon (1997) were 0.05 mm and 0.1 mm in diameter. The sampling rate was established by using different lengths of capillary column calculated on the basis of experiments derived from the Hagen-Pouiselle fluid flow and the ideal gas law. In Simon's design, the capillary column was housed in a metal or plastic case, approximately 3 cm x 3 cm and was connected to the canister using swagelok fittings. A 0.5 fritted filter was used to prevent particulate from blocking the flow controller.[133,147]

Experimentally, the capillary flow controller allowed for extended sampling periods, ranging from a few hours to a few weeks resulting in flow rates down to 0.05 mL/min.[134] The pressure differential between the ambient atmosphere and the atmosphere inside the canister provides the driving force for the airflow. Flow rate is a function of the capillary length and diameter. The flow controller was designed to allow for broader use of evacuated canisters, where if necessary an integrated sample could be collected for a full month or in small personal canisters. This extended sampling time can improve the exposure assessment strategies used for environmental and occupational air sampling.[61] A detailed analysis of the theory is presented in Simon (1997), as well as a proposed mathematical model.[133] He assumed the flow rate to be relatively constant through the capillary tube for a defined sampling period. Another way of considering this is that the flow rate is constant from initial pressure (P_o) to pressure at some time (t), {P (t)}, where t is the time it takes to fill 50% or less of the canister. However, the assumption of constant flow rate was shown not to be valid in this research. A summary of the theory of air flow through the capillary is presented here to provide the reader with a general understanding of the original design and function of the capillary flow controller.

The principles governing the airflow through the capillary into the canister are represented by two equations, the *Hagen-Poiseuille* and the *Ideal Gas Law*.[148,149] The capillary is a limiting orifice, yet it does not act as a critical orifice in this sampling system. An appropriate equation for steady, incompressible, laminar flow through a straight circular tube of constant cross section is the *Hagen-Poiseuille* (2.6) equation:

$$Q = \frac{\pi(P_o - P_L)r^4}{8\mu L} \qquad (2.6)$$

Where Q is the airflow rate, r is the radius, μ dynamic viscosity of air and L is the length of the pipe (capillary). When a laminar flow of a Newtonian fluid is established, the volumetric flow rates between the inlets of a pipe are related to pressure gradient, viscosity of the fluid and pipe dimensions. Assumptions include: incompressible fluid, laminar flow (Reynolds number (Re) < 2100), the fluid behaves like a continuum and the flow is not valid for tubes where the molecular mean free path can be higher than the tube diameter. The mean free path of air (6.33×10^{-8} m at atmospheric pressure) is considerably smaller than the smallest capillary diameter of 5×10^{-5} m used in the experiments. Finally, if the Hagen-Poiseuille equation is valid under steady state conditions the flow should be time dependent.

A second relationship, the ideal gas law, was used to characterize the relationship between sampling time and the geometry of the system: capillary length, capillary diameter and size of the canister.

$$PV = nRT \qquad (2.7)$$

Many gas mixtures including air behave like an ideal gas under specified conditions. Pressure (P) and the amount of gas in the canister (n) were considered functions of sampling time. As the container fills with gas, the internal

pressure P(t) rises and the number or moles n(t) of an air-contaminant mixture in the canister increases proportionally with sampling time. This new expression is as follows:

$$P(t) = \frac{n(t)RT}{V_s} \tag{2.8}$$

where, V_s is the volume of the canister. The objective at this point was to obtain an expression that shows the relationship between the molar content of the canister {n(t)} and the flow rate delivered by the capillary flow controller {Q(t)}. The relationship between flow rate to sample volume is:

$$V(t) = \int_0^t Q(t)dt \tag{2.9}$$

A key assumption for model development was that the flow rate remains relatively constant, within the operating range of the passive sampler. As observed with a critical orifice, the volumetric flow rate remains reasonably constant during the time it takes to fill half a canister.

Finally, V(t) was defined as the final sampled volume (V_f) which is equal to 0.5 times the sampler's volume (V_s). A capillary of length (L), and radius (R) will restrict the air flow rate (Q) entering the canister during a time period (t). The expression is displayed using the constants K_5 and K_6.

$$L = \frac{k_6 r^4 t}{e^{\frac{V_f}{K_5}} - 1} \tag{2.10}$$

where $$K_5 = \frac{P_{atm} V_s \bar{V}}{RT} P_{atm}, \qquad K_6 = \frac{\pi RT}{8\mu V_s \bar{V}} \tag{2.11, 2.12}$$

Experimental data have shown that the theoretical and experimental results are somewhat in agreement for laminar flow of incompressible fluids in circular tubes or pipes, where laminar flow is defined when the Reynolds number, Re=pV(2R)/ μ, is <2100.[148] Simon's model over estimated flow when compared to experimental data. This resulted in the need to develop empirical equations to allow for accurate prediction of flow rates for different geometries. The empirical equations provided reasonable approximations of actual flow, but still overestimated the actual flow rates.

In the Hagen-Poiseuille equation, length is inversely proportional to the flow rate and directly related to the fourth power of the radius. Therefore, adjusting the length and the radius of a capillary allows one to establish many flow rates. Frictional losses associated with the gas traveling down a length of tubing results in a slower flow rate and ultimately a longer sampling time to collect the same volume of air. This combination of adjustment of length and radius allows for a wide range of flow rates, ranging from 0.05 to 50 mL per minute. While Simon (1997) documented the flow characteristics of the capillary flow controller and compared his mathematical model to his experimental data, additional testing was necessary to fully characterize flow rate. In addition, Simon's research focused on sampling weeks to months while a primary interest of this research is to evaluate the usefulness of using the capillary flow controller as a small personal canister for 8 to 40 hour sampling.

The advances in analytical instrumentation have allowed for increased detection limits with reduced amounts of analyte. This advancement allows for the possibility of using smaller canisters than traditionally used. A 300 mL canister can be used to collect a whole air sample and the material can be directly injected into a GC for analysis of compounds in the ppm range.

2.4.1 Canister Limitations

The personal-canister flow controller provides many advantages over charcoal

sorbent sampling. Because the gases or vapors are being sampled as a "whole air sample" the problems associated with adsorption, desorption efficiency and dilution are not encountered. Also, problems with overloading the sorbent, reverse diffusion, ventilation rate, diffusion constants are not a concern when sampling with the capillary-canister. However, several factors may affect the results when sampling with capillary-canisters. These include relative humidity, temperature, recovery, storage stability and interfering chemicals.

Stability of VOC in canisters has been well documented.[24,142,150-152] While stability of chemicals in the canisters is chemical specific, the majority of the loss is seen with concentrations in the ppb range. Kelly and Holdren, (1995) evaluated the applicability of using canisters to evaluate 52 Hazardous Air Pollutants under the US Clean Air Act of 1990 by summarizing a series of studies that examined stability of VOC and Polar VOC.[150] The compounds evaluated were in the ppb range and were reported in % change/days. As an example, methyl ethyl ketone changed 14% in 21 days, styrene, changed 8% in 32 days and toluene changed 20 % in 21 days. Wai-mei et al. (2001) examined the stability of 143 volatile organic compounds in canisters for up to 4 months.[152] The authors reported average losses of all 143 compound studied, 7.3 % loss in the first week increasing to an average loss of 14.4 % after 4 months. Six percent of the 143 were found to decrease by more than 30 %. All concentrations examined were in the ug/m^3 (ppb) range. Both Kelly et al. and Wai-mei et al. concluded that stability of VOC in canisters were acceptable for most compounds. The stability of chemicals in canisters is a result of the chemicals and physical properties of the chemical in question. Stability is affected by interaction of a number of key factors including: vapor pressure, polarity, water solubility, humidity in the canister, pressure, temperature, characteristics of the canister surface, reactivity of the compounds with other species, and the history of use of the canister. Several of the factors affecting stability will be reviewed here, however, a detailed review can be found in Kelly et al (1995), Wei-mei et al (2001) and Coutant, et al. (1993).[150,152,153]

Relative humidity is closely linked to storage stability. Henry's law partition coefficient (C_{water}/C_{air}) of 2x 10 10^{-2} to 2.5 x 10^{6} for VOC and the reactivity in water, ranging from a few minutes to many months, both have relevance with respect to VOC stability in canisters.[149] VOC that are non-polar such as, aliphatics and aromatics, display little loss during storage times of less than 14 days. The water vapor reduces the ability of the chemical to interact with the walls of the canister. However, chemicals that are considered polar volatile organic compounds (i.e., alcohols and ketones), are more water soluble (greater Henry's constant), more reactive and, thus have demonstrated less stability in the canisters while awaiting analysis.[153] Several researchers found that the stability in humidified canisters was very good and the stability in dry canisters was relatively poor for periods of seven days and longer.[137,139,140] The use of 100% humidified air to pressurize the canisters provides an improved stable environment for most VOC. It should be noted that all studies found in the literature, considered the stability of polar VOC at ambient environmental conditions in the parts per billion range. At the significantly higher concentrations found in the occupational setting, humidity may prove to be less significant.

The stability of a compound in the canister may be affected by interaction of many of the factors previously mentioned. As with the humidity, all these factors are expected to have a reduced affect at the higher concentrations found in the occupational environment because of the mass of contaminant in the sampling canister. The ratio of concentration to water vapor, or active sites on the walls will likely minimize the losses for many of the factors cited above, i.e. the water can reach its saturation level without removing a significant portion of the VOC from the canister air. However, the reactivity with other compounds in the canister air may be increased with increased concentrations; resulting in increased losses at higher concentrations.

Recovery of some compounds from the canisters has been shown to be a problem as well. Reproducing the same concentration inside a canister proved

challenging at low concentrations. In addition, delivering a consistent amount of sample to the gas chromatograph can contribute to the overall loss of sample. While the authors did not quantify this loss, it was discussed briefly in their papers.[150,152] Table 2.2 displays a summary of the advantages and disadvantages of canister sampling and other methods of sampling gases and vapors.

Table 2.2 Comparison of methods for collection of volatile organic compounds

Method of Collection	Major Advantages	Major Disadvantages
Sorbents/impingers	(1) Simple and convenient for sampling, transport, and recovery	(1) Contamination and Interferences
		(2) Competition for adsorption
	(2) Large volumes of air sampled	(3) Sorbents limited by breakthrough volume
	(3) Minimal effects from water vapor	(4) Compound-dependent recovery
Bags (Teflon, Tedlar, Mylar, Etc.)	(1) Allows collection of 10 to 100 *l*	(1) Difficult to clean
		(2) Fragile
		(3) Sample loss and contaminant influx through permeation
		(4) Short self-life
		(5) Wall loss
Glass bulbs	(1) Can be thoroughly cleaned	(1) Limited sample volume
	(2) Good sample recovery	(2) Fragile
Metal canisters	(1) Can be thoroughly cleaned	(1) Limited sample volume
	(2) Good sample recovery	(2) Large and bulky for personal sampling
	(3) Rugged	(3) Evaluation against approved methods.
	(4) Can be pressurized to increase sample volume	(4) Wall Loss
	(5) Long sampling periods	(5) Reactions inside the canisters
	(6) Multiple chemicals	
	(8) No break through	
	(9) Simple to use	

(Adopted from Jayanty, 1989.[24])

2.5 Analysis of Data

One of the objectives of this research is to evaluate the performance of the capillary-canister sampling method using the European community and NIOSH criteria with respect to overall uncertainty. Both methods have protocols for development and evaluation of sampling and analytical methods. These protocols require that the sampling method provide results that are within ±25% of the "true value", 95% of the time.[154-156]

The variability of measurements on replicate samples about the mean of the population of measurements can be found by taking the standard deviation divided by the mean. The value is commonly referred to as the coefficient of variation (CV) or the relative standard deviation (RSD),

$$CV = \frac{Standard \quad Deviation}{Mean} \tag{2.13}$$

Bias (B) is defined as the relative discrepancy between the mean of the distribution of measurements obtained with the method and the true value or reference value. These discrepancies cannot be corrected and therefore are considered in the overall accuracy of the method.

$$Bias = \frac{\mu}{\mathrm{T}} - 1 \tag{2.14}$$

where μ is the mean and T is the true value. Using the precision and the bias one can calculate the overall uncertainty using the following formula:

$$Overall\ Uncertainty = \frac{\left| \bar{x} - x_{ref} \right| + 2s}{x_{ref}} \times 100 \tag{2.15}$$

where: $\bar{x}$ is the mean value of the results of a number of repeated samples, x_{ref} is the accepted reference value, and s is the standard deviation of the measurements.[156]

While the combination of precision (variance) and accuracy (bias) may seem inappropriate from a mathematical point of view, it is a common practice in the area of occupational hygiene and is employed for the development and evaluation of new and modified sampling methods.[154,156] The accuracy and precision of the analytical portion of this research, using GC, is well documented in Environmental Protection Agency (EPA) methods and will not be reviewed here.[145,146]

2.6 Summary

The variability of sampling data, the uncertainties of OELs and variability of the industrial process will always be components in the overall uncertainty of evaluating worker or community risk. However, the ability to collect more samples will allow for better exposure characterization which in turn leads to the development of a better risk assessment. The fundamental problem of limited resources, resulting in a limited number of samples collected, extrapolating that data to a large number of workers, to represent extended periods of time, will always be a challenge faced by occupational hygienist. Development of sampling methods that are easier to use, economical, reliable, and more versatile will allow the occupational hygienist to reduce the amount of extrapolation necessary to adequately characterize exposures. This research will attempt to address some of these issues by modifying and evaluating a capillary-canister device and integrating it into occupational sampling strategies.

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CHAPTER 3 RESEARCH OBJECTIVES

The over all goal of this research is to develop a functioning personal capillary-canister sampling device that could be used to collect gas and vapor samples from industrial and community atmospheres. The device was evaluated in a controlled environment (the laboratory) and field experiments for its performance with respect to established methods for collecting a variety of organic vapors. In addition, flow rates were evaluated under a variety of conditions to examine the variability of the flow rate provided by the capillary flow control device.

The research is supported by the following objectives:

1. Evaluate the current models used to predict airflow rate through the capillary flow controller and develop new empirical models to more accurately predict flow rate.

2. Compare the performance of the capillary-canister sampling device to existing methods for sampling gases and vapors in a controlled laboratory setting.

3. Evaluate the performance of the capillary-canister device as a personal sampling device with respect to existing methods for sampling gases and vapors in a field environment.

4. Evaluate capillary-canister sampling device with respect to the following parameters:

Ease of use	Recovery rate
Precision	Accuracy
Capacity	Multiple chemicals
Humidity	Flexibility of sampling time

5. Estimate the bias, precision and overall uncertainty of the capillary-canister device.

6. Examine long-term air sampling strategies using the capillary-canister device.

CHAPTER 4 Development of a flow controller for long-term sampling of gases and vapors using evacuated canisters

When the work for this thesis started, the capillary flow controller had recently been patented and canisters were primarily being used to collect area samples with mass flow controllers used to control flow rate. The literature contained limited information that investigated the usefulness of canisters as personal samplers. In particular, comparison of canister samples to sorbent samples and the development of a canister small enough to wear as a personal sampler did not exist.

This chapter presents the initial development of a methodology for air sampling with small canisters equipped with capillary flow controllers. The initial step required an evaluation of the fundamental flow characteristics of the capillary flow controller, building upon the work presented by Simon, (1997)[a]. An important issue that is addressed in this chapter is the assumption by Simon (1997) that the flow rate was relatively constant throughout the sampling period. Upon defining the flow characteristics, preliminary air sampling results were examined experimentally to explore the functionality of the capillary-canister as a sampler. Additional information can be found in appendix A for this chapter.

The detailed examination of the flow characteristics was considered imperative before the next phase of the research could be completed. Without a thorough understanding of the flow characteristics, the air monitoring data would be difficult to effectively analyze.

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[a] **Simon P:** Long term integration sampling to characterize airborne volatile organic compounds in indoor and outdoor environments. PhD Thesis, McGill University, Montreal, Canada (1997).

Abstract

Anthropogenic activities contribute to the release of a wide variety of volatile organic compounds (VOC) into microenvironments. Developing and implementing new air sampling technologies that allow for the characterization of exposures to VOC can be useful for evaluating environmental and health concerns arising from such occurrences. A novel air sampler based on the use of a capillary flow controller connected to evacuated canisters, (300 mL, 1 L and 6 L) was designed and tested. The capillary tube, used to control the flow of air, is a variation on a sharp-edge orifice meter. It essentially controls the velocity of the fluid (air) as a function of the properties of the fluid, tube diameter and length. A model to predict flow rate in this dynamic system was developed. The mathematical model presented here was developed using the Hagen-Poiseuille equation and the ideal gas law to predict flow into the canisters used to sample for long periods of time. Hagen-Poiseuille equation shows the relationship between a flow rate, pressure gradient, capillary resistance, fluid viscosity, capillary length and diameter. The flow rates evaluated were extremely low ranging from 0.05 to 1 mL per minute. The model was compared with experimental results and was shown to over estimate the flow rate. Empirical equations were developed to more accurately predict flow for the 300 mL, 1 L and 6 L canisters used for sampling periods ranging from several hours to one month. The theoretical and observed flow rates for different capillary geometries were evaluated. Each capillary flow controller geometry that was tested, was found to generate very reproducible results, RSD < 2%. Also, the empirical formulae developed to predict flow rate given a specified diameter and capillary length, were found to predict flow rate within 6% of the experimental data. Exposing samplers to airborne styrene vapors allowed for comparison of the effectiveness of capillary flow controller to diffusion sampling and to the on-line gas chromatograph. The capillary flow controller was found to exceed the performance of the diffusion samplers in this comparison.

4.1 Introduction

There are a large variety of situations and pollutants in both indoor and outdoor environments that dictate the need for air sampling of gases and vapors. Developing and implementing air sampling technologies that allow for the characterization, and study of the transportation and distribution of VOC in the environment will improve our overall understanding of the effects of VOC on our environment and health. In addition to global concerns, exposure to airborne levels of VOC in the workplace is a concern in many industrial facilities.

Sampling of volatile organic compounds (VOC) using solid sorbent materials and passivated stainless steel canisters has been conducted for many years for environmental and occupational hygiene investigations.[1-5] Sorbent materials, such as activated charcoal and Tenax Æ used with air sampling pumps have long been considered the primary standard for collecting many organic vapors from air in occupational environments.[6-7] Selection of an appropriate sorbent is important because the chemical characteristics of different VOC affect their affinity for the sorbents. Also, sorbents can be affected by environmental conditions such as humidity and temperature, and by factors such as competition for active sites and concentration of the contaminants.[8-10] While sorbent materials have been effective, inherent limitations of the methods may make the evacuated canisters an appropriate alternative when developing a sampling strategy.

Canisters have been used for many years to evaluate the airborne levels of VOC in ambient air. Studies have shown reasonably good stability and recovery of many contaminants.[11-14] However, over and under estimations have been reported by several sources depending upon the chemical being sampled. [15-18] United States Environmental Protection Agency (EPA) procedures TO-14 and TO-15, as well as ASTM D 4844, were developed to establish standardized methods to clean, prepare, sample, and analyze low concentrations of VOC in ambient air using canisters. These methods define the necessary steps to

sample VOC using sub atmospheric pressures to passively collect a whole air sample in a canister.[5,19,20] The airflow into the canister is typically controlled using a mass flow controller. These flow devices generally allow for sampling periods from a few minutes to 24 hours, depending upon the canister size and contaminant of interest (8 hours using 400 milliliter (mL) and up to 24 hours using six liter (L) canisters). A capillary flow controller was developed to control low flow rates of air into a sampling canister. This capillary flow controller was developed at McGill University and allowed for extended sampling periods, ranging from a few hours to a few weeks,[21] resulting in flow rates down to 0.05 mL/min. The pressure differential between the ambient atmosphere and the atmosphere inside the canister provides the driving force for the airflow. The flow rate is a function of the capillary length and diameter. The flow controller was designed to allow for broader use of evacuated canisters, where if necessary an integrated sample could be collected for a full month or in a very small canister. This extended sampling time can improve the exposure assessment strategies used for environmental and occupational investigations.[22] It is important to recognize that the long-term sampling is not appropriate if the capture of the short term fluctuations in concentration are of interest. Measurement of acutely toxic compounds would not be appropriate over a long period of time.

In this paper, we describe the development and testing of a capillary flow controller for use with evacuated canisters for long-term sampling of gases and vapors. Research was initiated to explore the possibility of extending the length of time one can collect a whole air sample in an evacuated canister. To this end, a mathematical model and empirical formulae have been developed to predict the airflow through the flow controller for different sampling periods. The mathematical model was a reasonable approximation of flow rate, but failed to match the experimental data within acceptable tolerances. As a result, empirical formulae were developed using the experimental data to predict flow rate and sampling time. The information provided here is the first phase of a series of experiments that evaluated area and personal exposures to organic vapors using

canisters in chamber and field studies. Once the flow characteristics of the device had been established, the next objective of the study was to assess the capillary flow controller in laboratory and field tests to show the device collects representative air samples. A comparison of the canisters using the novel capillary flow controller to two other air sampling devices was completed in the laboratory and in field test. It is beyond the scope of this article to present the results of a full compliment of air sampling experiments. However, preliminary air-sampling tests will be presented here to show "proof of concept" of the effectiveness of the capillary flow controller in field sampling. A future article will present more detailed results of laboratory and field tests.

4.2 Experimental Method

4.2.1 Capillary Flow Controller

The sampling system consists of a capillary flow controller connected to a canister which may vary in volume from 300 mL to 6 L. Each capillary flow controller is a deactivated fused silica capillary column of a given diameter and length. Figure 4.1 shows a conceptual diagram of the flow controller. Different capillary diameters are commercially available and were cut to specific lengths to control flow rate to a desired level. Capillary columns having internal diameters of 0.05 mm and 0.1 mm with an external diameter of 0.4 mm were used throughout this study. Larger diameters are commercially available, however, they do not provide the restriction necessary to control the flow rates to the very low ranges necessary for long-term sampling. The flow controllers were configured to perform long-term passive sampling to collect gaseous contaminants. Sampler configurations depended upon whether the samplers were going to be used for personal sampling or area (micro environment) sampling.

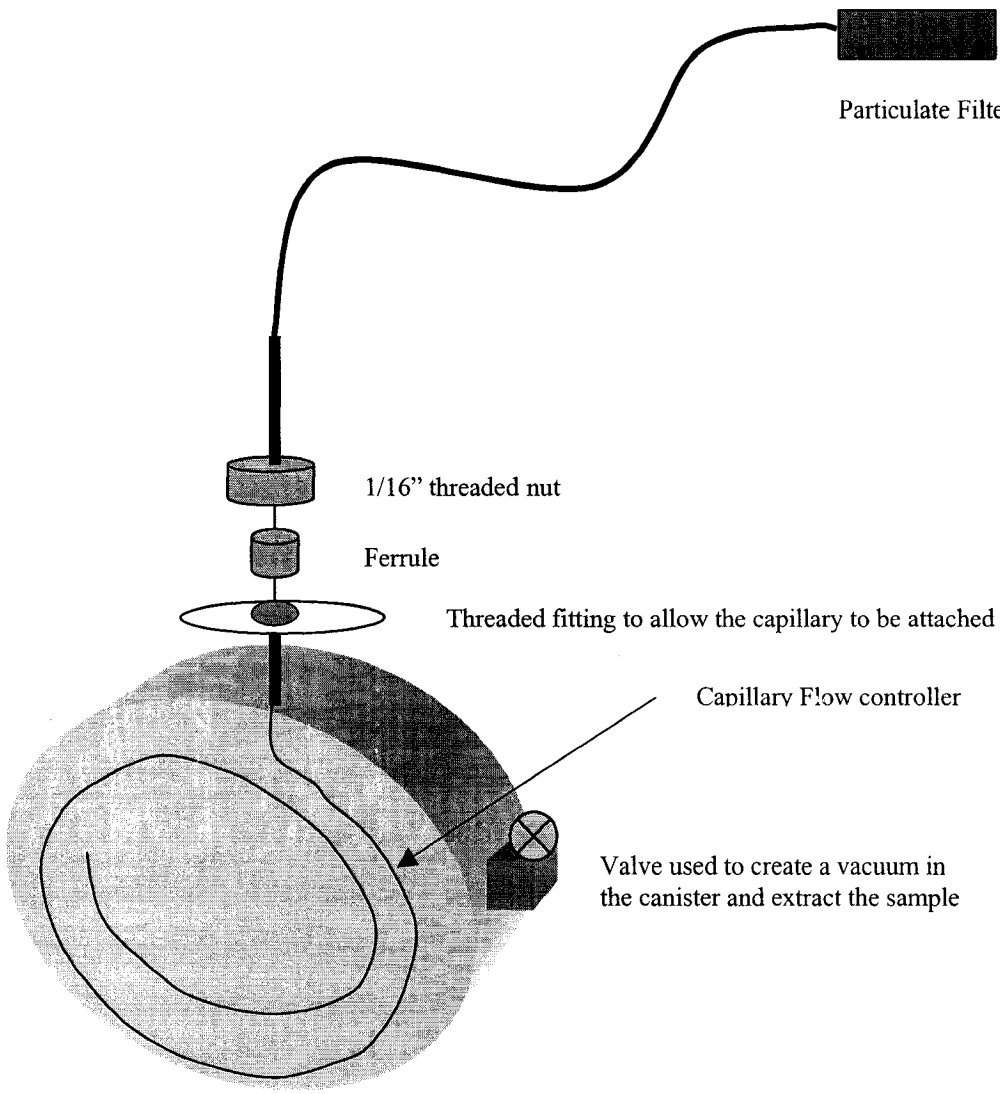

Figure 4.1 Personal whole air sampler with the capillary flow controller mounted inside the 300 mL stainless steel canister.

The canisters used to collect the sample ranged from 300 mL to 6 L. EPA procedure TO-15 presents a detailed description of protocols for sampling with canisters. This research used the sub-atmospheric procedures described in TO-15 and is summarized as follows. A sub-atmospheric canister is prepared by evacuating and filling the canister three times with nitrogen to clean it, and then evacuating it to 0.05 torr. The initial vacuum is then measured, the sampler is placed in the desired sampling location and the valve is opened. After the sample is collected, the valve is closed and the canister is transported to the laboratory where the post sampling pressure is measured and the total volume sampled is recorded. The canister is then pressurized to 1.5 to 2 atmospheres with humidified nitrogen. Analysis using a gas chromatograph equipped with a flame ionization detector (GC-FID) or connected to a mass spectrometer (GC/MS) is performed.

4.2.2 Theory and Model

Model development and validation was performed over several years. The initial research was conducted by Simon (1997),[23] where the flow rate was assumed to be relatively constant through the capillary tube for any sampling period (t) during which the capacity of the canister never exceeds 50%.

The principles governing the airflow through the capillary into the canister are represented by the *Hagen-Poiseuille* equation and the *Ideal Gas Law.*[24,25] The volumetric flow rate for steady, incompressible, laminar flow of a Newtonian fluid through a straight circular tube of constant cross section is described by the *Hagen-Poiseuille* equation:

$$Q = \frac{\pi (P_o - P_L) r^4}{8 \mu L} \qquad (4.1)$$

where Q is the air flow rate, r is the radius, L is the length of the tube (capillary), μ is the dynamic viscosity of air, and P_o and P_L represent the inlet and outlet

pressures respectively. In addition, this relationship is valid for fluids that behave like a continuum where the molecular mean free path is smaller than the tube diameter. The mean free path of air (6.33×10^{-8} m at atmospheric pressure) is considerably smaller than the smallest capillary diameter of 5×10^{-5} m used in these experiments.

Additional assumptions were made to characterize the behavior of this passive ambient air sampler using a capillary flow controller. Although the internal sample container pressure and, hence the volumetric flow rate is a function of time for this device, the rate at which these variables change is very small so that the process can be characterized as being pseudo steady-state. Based on this hypothesis, the Hagen-Poiseuille equation was modified (Eq 4.22).

$$Q(t) = \frac{\pi(P_{atm} - P(t))r^4}{8\mu L} \qquad (4.2)$$

The ideal gas law (Eq 4.3), was used to characterize the relationship between pressure and volume sampled.

$$PV = nRT \qquad (4.3)$$

Many gas mixtures including air, behave like an ideal gas under specified conditions. As the container fills with gas, the internal pressure P(t) rises and the number of moles n(t) of an air-contaminant mixture in the canister increases proportionally with sampling time. Hence, using the same pseudo steady state hypothesis, we represent the ideal gas law as in eq 4.4

$$P(t) = \frac{n(t)RT}{V_s} \qquad (4.4)$$

where V_s is the fixed volume of the canister. The sample volume V(t) is obtained from the flow rate delivered by the capillary flow controller {Q(t)} and sampling time (t). The relationship is defined by eq 4.5.

$$V(t) = \int_0^t Q(t)dt \tag{4.5}$$

A key assumption for model development was that the flow rate remains relatively constant, within the operating range of the passive sampler. As observed with a critical orifice, the volumetric flow rate remains reasonably constant during the time it takes to fill half a canister.[25] Following the pseudo steady state assumption, the sample volume is written as in eq 4.6.

$$V(t) = Q(t)t \tag{4.6}$$

The sampled volume is related to the molar content. Using the molar volume (V') at standard temperature and pressure the following equation is obtained (eq 4.7).

$$n(t) = \frac{V(t)}{V'} = \frac{Q(t)t}{V'} \tag{4.7}$$

Combining equations 4.4 and 4.7, a relationship for the variation of pressure in a sample container as a function of volumetric flow rate controlled by the capillary is obtained, eq 4.8.

$$P(t) = \frac{RTQ(t)t}{V_s V'} \tag{4.8}$$

This relationship can be used to obtain a mathematical model for predicting the geometry of a capillary column for the design of the flow controller. Combining equation 4.2 and 4.8 results in:

$$Q(t) = \frac{K_1}{1 + K_2 t} \tag{4.9}$$

where the constants K_1 (m^3s^{-1}) and K_2 (s^{-1}) are defined as:

$$K_1 = \frac{\pi P_{atm} r^4}{8\mu L} \tag{4.10}$$

$$K_2 = \frac{\pi R T r^4}{8 \mu L V_s V'} \tag{4.11}$$

Again, combining equations (4.2 and 4.8), the pressure variable P(t) was obtained by eliminating the flow rate variable Q(t) resulting in:

$$P(t) = \frac{K_3 P_{atm} t}{K_4 - K_3 t} \tag{4.12}$$

where the constants K_3 (in kg $m^3 s^{-2}$) and K_4 (in kg $m^3 s^{-2}$) are defined as:

$$K_3 = \frac{\pi R T r^4}{V'} \tag{4.13}$$

$$K_4 = 8 \mu V_s L \tag{4.14}$$

As an iterative step, the flow rate expression can be integrated according to equation 4.5 to determine sampled volume as a function of time. Integrating equation 4.9 with respect to time results in:

$$V(t) = K_5 \ln\left(1 + \frac{K_6 r^4}{L} t\right) \tag{4.15}$$

where K_5 (m^3) and K_6 (m^{-3} s^{-1}) are:

$$K_5 = \frac{P_{atm} V_s V'}{RT} \tag{4.16}$$

$$K_6 = \frac{\pi R T}{8 \mu V_s V'} \tag{4.17}$$

The final sampled volume (V_f) is defined as $V_s/2$ where the canister volume is V_s. Equation 4.15 can be rearranged to solve for L, a capillary of given length, with radius (r) that will restrict the air entering the canister during a time period (t)

for a canister size (V_s). The expression is displayed using the constants K_5 and K_6 as defined above.

$$L = \frac{K_6 r^4 t}{e^{\frac{V_f}{K_5}} - 1} \tag{4.18}$$

The above model provides a basis for mathematical simulation used to estimate the capillary geometry and length of sampling time, given a certain size canister. This model was evaluated using experimental data and compared to empirical equations generated to predict airflow rates.

4.2.3 Experimental Techniques

A system was constructed that allowed for continuous measurement of airflow through capillaries of various lengths and diameters. This system was built to evaluate the mathematical model and to test the flow rate through different capillary flow controllers. The system consisted of a pressure transducer (Omega model PX 305 0-15) connected to a 300 mL canister. Data transmission from a meter (Omega model Dpi-C24) connected to the pressure transducer and to a computer was accomplished using a RS-232 standard cable with a 25-pin connector. A data acquisition program in Visual Basic was used to continuously collect the data and an Excel macro was created to transfer the data to a usable format. To eliminate all possible leakage, a canister was designed from welded stainless steel with a flanged vacuum fitting used for connecting the pressure transducer to the welded canister. The valve used to connect the canister to a vacuum pump was fixed to the canister using flanged vacuum fittings and o-rings. This canister used to test the flow rates was specially designed to eliminate leaks and was not used to collect air samples.

A capillary of a desired length and diameter was connected to the canister using a graphite ferrule and a threaded 1/16" nut. The canister was evacuated down to 0.1 torr. The canister was monitored for 30 minutes before the test to ensure the system was not leaking. If the meter had not displayed a leak in 30 minutes,

where a leak was defined as an increase of pressure greater than 0.2 torr, the test was started. Pressure readings were recorded until the internal pressure of the canister reached 450 torr, a pressure that represents a volume of approximately 60% of the canister volume. Upon completion of each test, the data was transferred to a spreadsheet and a macro was run to perform the necessary calculations to convert pressure readings to flow rate values in milliliters per minute (mL/min).

The mean flow rate for each test was calculated between 1 to 380 torr, which is the pressure that corresponds to filling 50% of the canister with air. The mean value was considered to be a good approximation of the average flow rate for the entire sampling time. However, because the flow rate was slowly decreasing over the entire sampling period and the rate at which it changed was not linear, a second method, integration, was used to calculate the average flow rate for each capillary. The data was plotted and the area under the curve was integrated to obtain an average flow rate as the canister filled to approximately 50% (P= 380 torr). The second method will be referred to as the integrated method. Twelve capillary lengths were tested for diameter 0.05 mm and eight capillary lengths were tested for the 0.1 mm diameter capillary. Six replicates were run for each capillary length. A mean flow rate was calculated for all replicates, with the resulting value plotted against the length of the capillary.

Air Sampling Methods. Styrene is a frequently encountered industrial chemical. Traditional methods of air sampling included collection with solid sorbents in both active and passive samplers.[26] During the development of the canister-capillary device, the opportunity arose to evaluate the atmosphere in a large (18.1 m^3) exposure chamber. The chamber was going to be used in a series of tests for a toxicology study. To validate the concentrations inside the chamber, styrene levels were documented using an on-line GC, passive diffusion badges and the capillary-canisters. At a later date during the actual exposure studies, monitoring was performed at the four different exposure concentrations. The data presented here is only from static (area) samples inside the chamber while

a concentration of 5 parts per million was generated for six hours as a background test.

The canisters used to air sample were designed at McGill and built by Meriter, Inc. San Jose, CA. Canisters and valves were made of a high purity polished stainless steel to reduce sample loss. Six 3M-diffusion badges (3M Company, Minneapolis, MN) and six canisters were placed in the chamber for approximately six hours. The chamber (2.45 x 2.2 x 3.35 m) had a series of vents in the ceiling providing down draft air flow throughout the chamber. Air flow into the chamber was held constant with a variable speed motor connected to a fan calibrated to produce 6768 liter per minute. The styrene was introduced into the chamber in the air flow at 0.1 mL/min. An on-line gas chromatograph (Varian CP-3800 with a capillary column - HP-1, 30 m x 0.53 mm x 2.65 um film thickness) was used to monitor the styrene concentrations every few minutes for the entire six hours. The GC sample was drawn from the chamber using a Teflon line and a sampling pump, and then sent through a 10 position valve directly to the injection port. The mean concentration for the six-hour sample period inside the chamber was 21.8 mg/m^3 ± 1.36 with an n of 60. The static samples were arranged inside the chamber at an approximate height of 1.25 meters off the floor and approximately 1 meter distance between each of the samples. The bias associated with each sampling method was calculated by comparing the on-line GC concentrations to the diffusion badges and the canister method.

4.3 Results and Discussion

The experimental data was collected in two phases. First the capillary flow controller was evaluated for long-term sampling, where long-term is defined as a one week to one month period. The second phase of the study included evaluation of capillary flow controllers for shorter sampling periods, 2 to 50 hours. The experimental data was collected and compared to a mathematical model

and several empirical models. The purpose of the mathematical model was to allow for prediction of average flow rates and length of the capillary columns for specified sampling campaigns. The model was not intended to characterize the behavior of airflow in the capillary (i.e. turbulent, or laminar, or transitional).

4.3.1 Mathematical Model

A series of calculations were made to estimate the sampling times and flow rates from different length capillaries using the mathematical model (eq. 18). The results of these calculations are presented in Table 4.1. The total sampling period was estimated in days for four different capillary diameters and nine different capillary lengths.

Table 4.1 Estimation of sampling times (days) based on capillary geometries using the mathematical model and a 500 mL air sample collected with a 1 L sample container using the capillary flow controller of length (M).

Column ID	Capillary Column Length (m)								
(mm)	0.1	0.25	0.5	0.75	1	2	5	10	30
0.05	0.68	1.69	3.38	5.06	6.75	13.5	33.8	67.5	202
0.1	0.04	0.011	0.21	0.32	0.42	0.84	2.11	4.22	12.7
0.18	0.004	0.01	0.02	0.03	0.04	0.08	0.2	0.4	1.21
0.25	0.001	0.03	0.01	0.01	0.01	0.02	0.05	0.11	0.32

Figure 4.2 shows the relationship between flow rate and capillary length from experimental data and predicted numbers using the model. While the model has the same general trend as the experimental data, it clearly overestimates the flow rate. The mathematical model presented here overestimates the actual flow rate of capillary flow controllers with specified geometries. An attempt was made to explain the poor fit of the model early on in the research by examining the actual internal diameter of the capillary. Ten cross sectional areas of a capillary column

were viewed with an electron microscope, identifying a ± 5% variability in diameter. This small amount of variability did not explain the overestimation of the model therefore additional microscopy was not pursued. The errors are likely a result of the assumptions used to develop the model. The assumption that may contribute the most to the error, is the compressibility of the air as it passes through the capillary. As a result, an attempt was made to obtain empirical formulae that better approximate the flow rate.

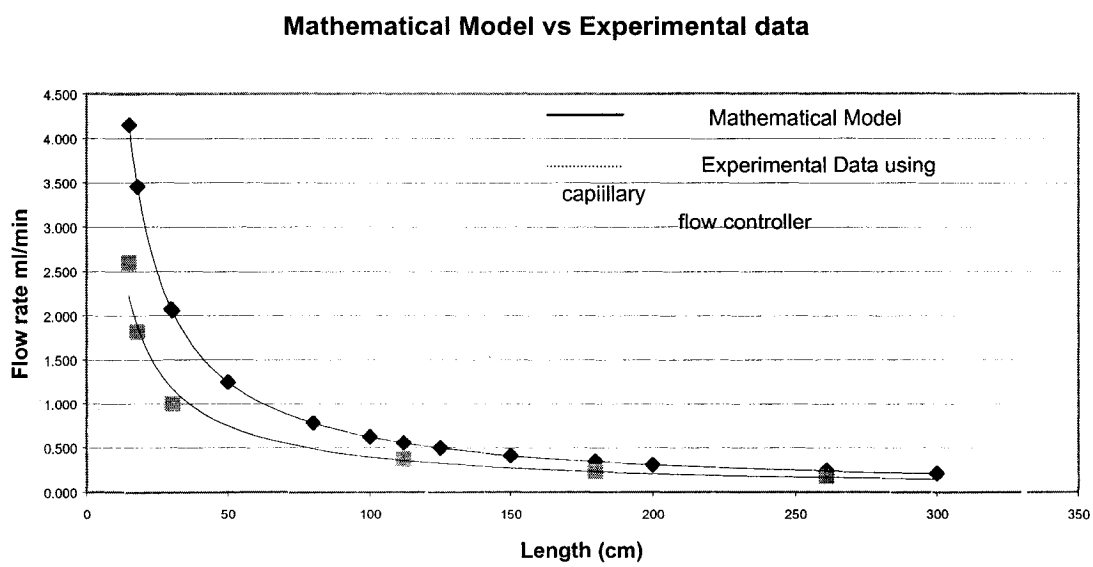

Figure 4.2 Comparison of experimental flow rate data versus flow rates calculated from the mathematical model obtained with various lengths of capillary 0.1 mm in diameter.

4.3.2 Empirical Model

To obtain an empirical model for a specific capillary geometry of the capillary flow controller, an appropriate means of estimating actual flow rates was investigated. The empirical model allowed for prediction of flow rates for given lengths of capillaries. Empirical models were obtained for both capillary diameters for long-term sampling (hours to months). A series of experiments were run using various lengths of capillary to control flow into 300 mL, 1 and 6 liter canisters to

evaluate sampling times. These experiments yielded a relationship that can be used to predict flow rate for a specific capillary length and sample periods for a given canister volume.

Results were very reproducible with relative standard deviations (RSD) for each length ranging from 0.9 % to 1.8 % for the replicated tests. Figure 4.3 is a typical plot of one of the more than 100 individual tests run. Examination of Figure 4.3 shows that a gradual decrease in flow rate occurs as the pressure differential diminishes. The experimental data for all the capillary tests displayed this same relationship. The flow rate decreases very slowly as the canister fills or as the pressure differential diminishes between the outside and the inside of the canister. The frictional losses associated with the geometry of the capillary dictate the flow rate and the rate at which it changes. The experimental data shows that flow rate change for a specific capillary length was not linear, and the data was better fit using a specific quadratic equation for each capillary length. The empirical model was obtained by using the average flow rate for a series of capillary lengths. Because the flow rate is diminishing during a sampling period, it became necessary to identify an appropriate means of selecting an average flow rate for a given sampling period.

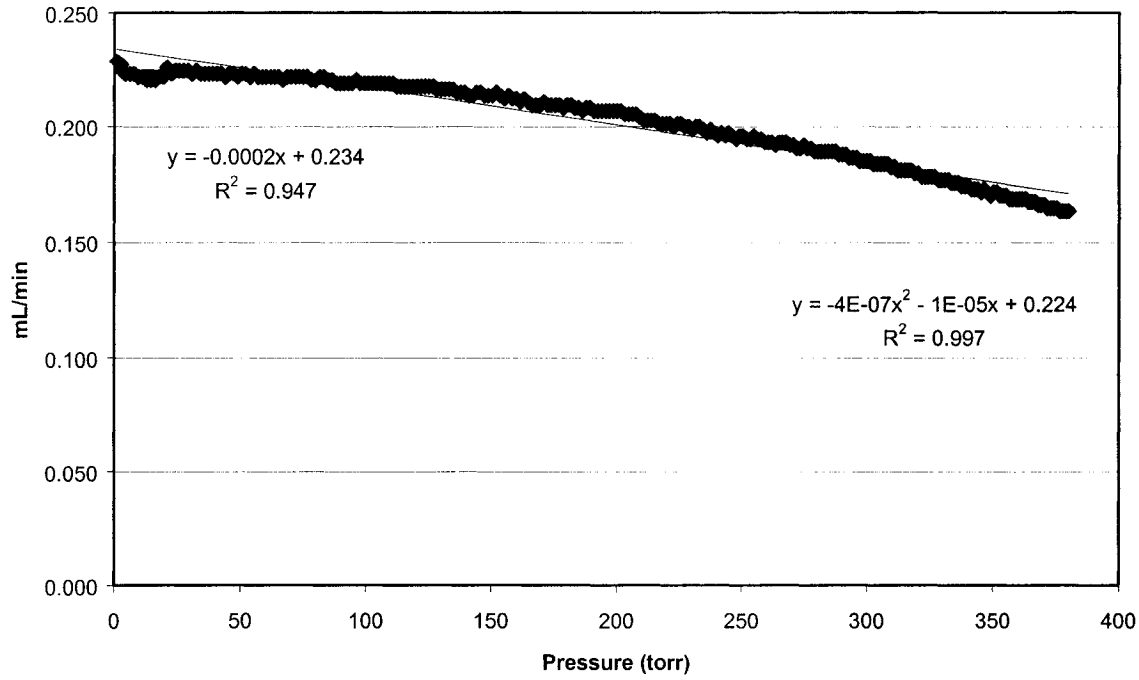

Figure 4.3 Example of a typical experimental flow rate. This data was obtained using a 12 cm capillary flow controller of 0.05 mm diameter. A linear fit (y= -0.0002x + 0.2341, R^2 = 0.9471) and quadratic fit (y= -4E-07x^2 – 1E-05x + 0.2241, R^2=0.9976) of these data points are shown.

Table 4.2 Comparison of the two methods used to estimate flow rate from the experimental data for the entire sampling period of an individual capillary: 1. Mean flow rate, 2. Integrated flow rate. No statistical significant difference between the two methods was observed, $p>0.05$.

(A)

Capillary	**Diameter 0.05 mm**		
Length (cm)	Mean (mL/min)	Integrate (mL/min)	% Difference
5	0.548	0.548	1.21
6	0.389	0.389	0.40
7	0.356	0.356	0.48
7.5	0.325	0.324	0.14
8	0.309	0.308	0.40
9.5	0.253	0.259	2.40
10	0.235	0.244	3.86
12	0.204	0.206	1.72
20	0.121	0.121	0.30
30	0.075	0.076	1.33
40	0.067	0.067	2.11
50	0.053	0.054	2.00
		Mean difference	**1.76**

(B)

Capillary	**Diameter 0.1 mm**		
Length (cm)	Mean (mL/min)	Integrate (mL/min)	% Difference
30	1.191	1.170	1.74
50	0.717	0.715	0.74
80	0.444	0.445	0.45
100	0.372	0.370	0.88
125	0.301	0.302	0.84
150	0.252	0.253	0.86
200	0.211	0.211	1.02
300	0.124	0.124	0.98
		Mean difference	**0.93**

In Table 4.2, a comparison of two methods of estimating flow rate for an entire sampling period, mean flow rate and integrated flow rate, are displayed. The mean flow rate was calculated by summation of flow rate measurements taken every 3 minutes for the entire sampling period, where sampling period was defined as the time it took to fill 50% of the canister. The integrated flow rate was found by integrating the quadratic equation obtained for each experimental test for each capillary length. While it is always most appropriate to integrate to find the area under a curve, a comparison to the mean value was done to examine the difference. Given that the mean flow rates between the two methods was not significant, $p < 0.05$, the simpler method of calculating the mean may be useful. Linear regression was also performed on the two methods resulting in no statistical difference between the two resulting lines. The average flow rate for each specific capillary was then used to establish the empirical model for each diameter capillary. Figure 4.4 is a plot of flow rates versus length of the 0.05 mm and 0.1 mm diameter capillaries. The equations that result from the plot of flow vs. length became the empirical model used to predict flow rates.

As with orifice meters, the empirical relationship between flow and pressure was developed by calibration. These empirical relationships are preferred over the mathematical model because they reflect more accurate flow rates. The model is dependant on understanding the frictional loss factors of the capillary tubes, the relationship between pressure change and fully developed laminar flow, and the compressibility of the air. While the mathematical model is an approximation, the empirical equations can be used to predict flow rate within 6% of the actual flow rate. The 6% error is well within the accuracy provided by air sampling pumps. For field use of the capillary flow controller with a 300 mL canister or with larger canisters, a calibration curve can be developed for a set of capillary lengths to show the expected flow rates. Once the calibration is complete for a capillary length, no additional calibration is necessary. Unlike an air sampling pump, the capillary flow controller would not require field calibration.

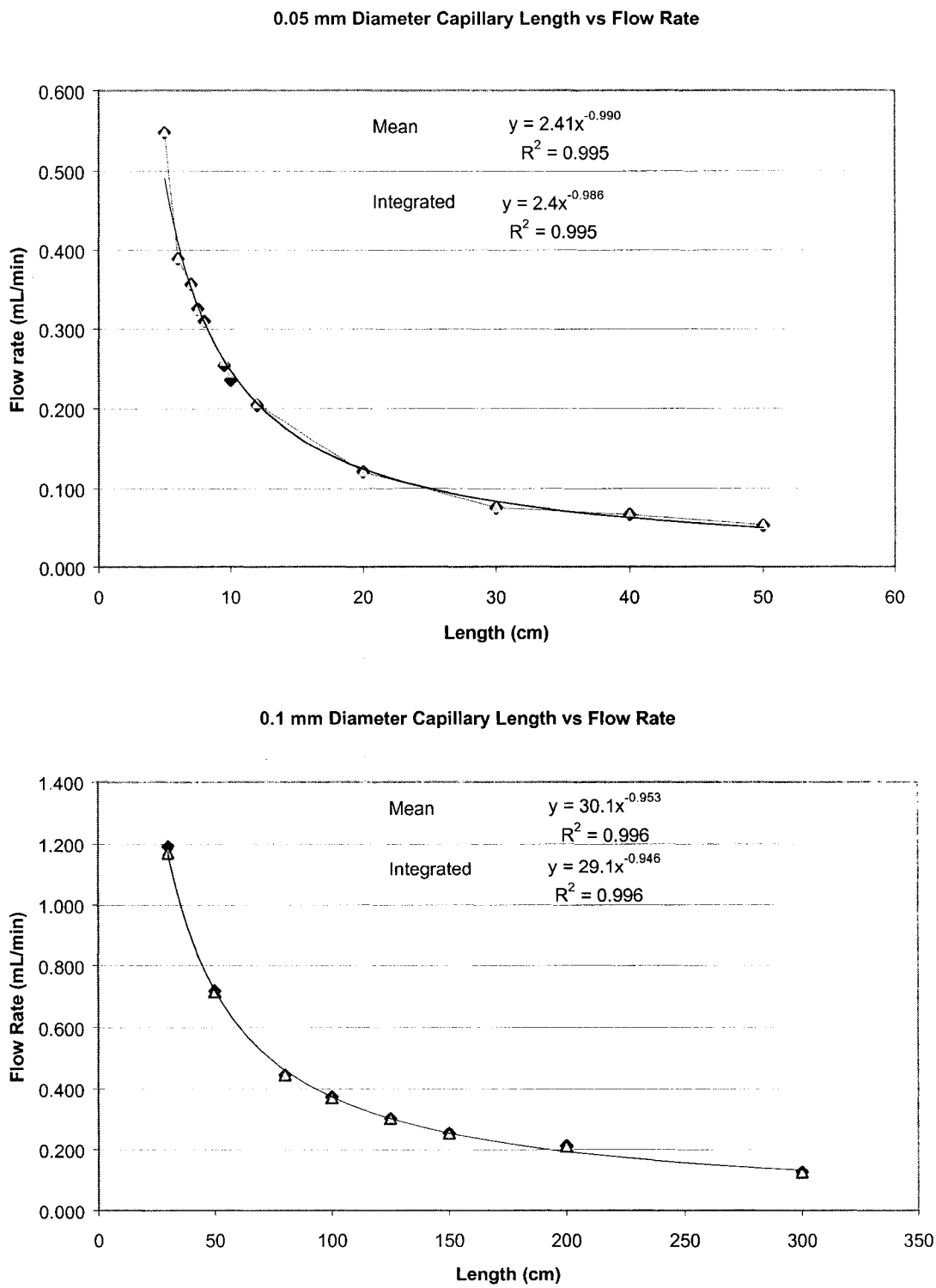

Figure 4.4 Relationship between capillary length and flow rate for capillaries of diameters 0.05 and 0.1 mm. Both mean values and integrated values are represented. The equation represents the empirical model and can be expressed as y (flow rate) = 2.41/x (capillary length).

Table 4.3 displays a comparison of the mathematical, empirical and experimental flow rates through the capillary flow controller. While the data was very consistent, the shorter capillaries, < 6 cm, begin to show deviation from the empirical models. The deviation was thought to be a result of "end effects" associated with the short length tubes.[23] This was not investigated further because the short capillaries resulted in flow rates too great to be useful for this type of air monitoring (hours to days).

Table 4.3. Comparison of two methods for predicting flow rate through a 0.1 mm and 0.05 mm diameter capillary flow controller. The percent difference is calculated by comparing the experimental flow rate to the models.

(A) 0.05 mm Diameter Capillary Flow Controller

Length	Mathematical Model		Empirical Model		Experimental Flow Rate		
cm	mL/min	% Diff	mL/min	% Diff	mL/min	Std Dev	RSD %
5	0.777	41.8	0.492	-10.2	0.548	0.006	1.09
6	0.648	66.5	0.411	5.5	0.389	0.009	2.31
7	0.555	55.9	0.352	-1.0	0.356	0.004	1.12
7.5	0.518	59.9	0.329	1.5	0.324	n/a	
8	0.486	57.7	0.309	0.24	0.308	n/a	
9.5	0.409	57.3	0.260	0.54	0.259	0.006	2.32
10	0.389	56.9	0.248	1.4	0.244	0.006	2.46
12	0.324	56.5	0.207	0.30	0.206	0.005	2.43
20	0.194	55.2	0.125	2.9	0.121	0.002	1.65
30	0.130	56.6	0.083	9.6	0.076	0.004	5.26
40	0.097	54.0	0.063	-6.4	0.067	0.001	1.49
50	0.078	56.0	0.050	-6.9	0.054	0.001	1.85

(B) 0.1 mm Diameter Capillary Flow Controller

Length	Mathematical Model		Empirical Model		Experimental Flow Rate		
cm	mL/min	% Diff	mL/min	% Diff	mL/min	Std Dev	RSD %
30	2.073	77.1	1.173	0.27	1.170	0.0150	1.315
50	1.244	73.9	0.721	0.83	0.715	0.0100	1.329
80	0.777	74.6	0.461	3.52	0.445	0.0050	1.062
100	0.622	68.1	0.372	0.65	0.370	0.010	2.732
125	0.497	64.7	0.301	-0.30	0.302	0.0040	1.451
150	0.415	63.8	0.253	0.02	0.253	0.0040	1.481
200	0.311	47.3	0.192	-8.81	0.211	0.0030	1.593
300	0.207	67.1	0.131	5.42	0.124	0.0020	1.701

The focus of this research was to develop and demonstrate the usefulness of using very low flow rates to sample vapors and gases. The data has shown that the capillary device allows for very repeatable flow rates for collecting whole air samples. The fact that the delivered flow rate of the capillary flow controller slowly decreases over the sampling time could result in a small underestimation of exposure depending upon concentration fluctuations in the sampled atmosphere. However, given that the sampler is designed to be used to characterize the average exposure of a target population over long periods of time, peak values or short fluctuations are generally not a concern with this type of sampling. As a result, the change in flow over time, a 15 -20% drop over a week or longer periods, depending upon the length of capillary, should be acceptable for most sampling campaigns.[27,28] It is important to note that although the flow rate changes, the total amount of air collected is always known for canister samples. It is determined by measuring the pressure differential that resulted during the sampling period. Therefore, the uncertainty in this sampling system does not arise from not knowing the total volume of air collected, as with a sorbent-sampling pump arrangement, but from the timing of the fluctuations in concentration during a given sampling period. As an example, if short fluctuation in peak concentration occurs early in the sampling period, this may result in a small under estimation of exposure when compared to concentration peaks occurring at the end of the sampling period. The benefit of characterizing exposure for longer sampling periods, days to weeks, as opposed to a few hours, makes the fluctuation in flow rate an acceptable bias. In addition, because the change in flow rate can be determined or predicted for any given length of capillary, air sampling campaigns can be modified to meet the needs of the exposure assessment strategy.[29,30]

An assessment of the styrene concentration in an exposure chamber was conducted to evaluate the effectiveness of the capillary-canister sampling system. Sampling results are displayed in Table 4.4. A comparison of the mean concentrations sampled by diffusion badges and canisters to the reference value,

shows a negative bias for the methods, 20% and 9 % respectively. These mean concentration values are the result of six badges and six canisters located in six different positions in the room. Both the diffusion badges and the canisters under sampled chamber concentration with respect to the reference value. However, at GC sample location (location six), the bias drops to 15 % for the badges and 3 % for the canisters. The reduction in bias could suggest that the concentration is not uniform across the chamber, yet this is speculative with this few numbers of samples for this test. The results of this preliminary test were very positive in that they showed the capillary flow controller could indeed measure representative concentrations of contaminant at flow rates below 0.5 mL/min. This preliminary information allowed for further testing at lower flow rates and with a variety of VOC in a small laboratory chamber and in field studies in a manufacturing setting. Similar results were obtained in more extensive testing. These are provided in a subsequent article.

Table 4.4 Comparison of styrene concentrations found in the exposure chamber sampled by diffusion badges and capillary canisters. An on-line GC was used to measure the reference values.

		Badge		Canister	
		mg/m^3	Concentration	mg/m^3	Concentration
Sample Location	Time (hr)		% Bias		% Bias
1	323	18.15	16.75	19.86	8.89
2	323	15.29	29.87	21.48	1.47
3	323	16.54	24.13	18.05	17.19
4	323	18.12	16.89	18.07	17.11
5	323	17.89	17.94	20.05	8.05
*6	323	18.46	15.34	21.19	2.78
Mean		17.41	20.15	19.78	9.25
Standard Deviation		1.24		1.35	
Relative Standard Deviation		7.10		6.80	

Reference Value (n=60) 21.8 mg/m^3 ±1.36 (5.11 ± 0.32 ppm)

*Sample 6, both the badge and canister were located with in 3 cm of the GC sampling location.

Air monitoring in an industrial or community environment for time intervals of days or weeks can be very useful when characterizing the long-term exposure of occupants or areas of interest. The low flow rates provided by the capillary flow system allow for extended air sampling intervals with small volume canisters. The current sorbent air sampling methodologies, tubes with sampling pumps and passive badges, do not provide for extended sampling periods. The option of changing the sorbent tube or badge every few hours becomes difficult if not impossible and costly when attempting to characterize a group of potentially exposed individuals for extended periods. Also, canisters with mass flow controllers do not have the capability to sample at the very low flow rates of the capillary-canister. One system currently available (Entech Instruments, Inc, CA) has the capability to sample 24 hours using a 6 L canister. The capillary-canister technology can extend the sampling time to 30 days. In addition to the longer sampling time, the capillary flow controller is simple and inexpensive when compared to a mass flow controller. These two attributes can be beneficial for field sampling devices.

Experimental testing of the flow controller has shown that the flow rate results are very reproducible and can be predicted using a mathematical equation. While the mathematical model overestimates flow, it is useful to approximate the flow rates for selecting the sampling time or capillary length. The empirical equations obtained from the data presented here can be applied to accurately assess the flow rate and therefore the sampling time.

It is our conclusion, that the capillary flow controller is a beneficial sampling device, because it provides the capability to sample personnel and areas to characterize long-term exposure to airborne concentrations of gases and vapors. This capability is not as readily available with other air sampling techniques.

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CHAPTER 5: A Novel Personal Air Sampling Device for Collecting Volatile Organic Compounds: A Comparison to Charcoal Tubes and Diffusive Badges.

Following the successful development of empirical formulae that predict flow rate in capillaries of varying geometries, as described in the previous chapter, attention was turned to examining the performance of the capillary-canister device as a sampling system. The focus of this chapter was to compare the capillary-canister to sorbent sampling methods in a controlled environment. It was necessary to examine the new sampler in a controlled environment to identify the conditions under which the sampler successfully collected air samples. A key aspect of this phase of the research was to examine the extremely low flow rates provided by the capillary flow controller and whether this low flow rate could result in collecting a representative air borne sample. The flow rates provided by the capillary flow controller are more than two orders of magnitude below the traditional flow rates used to collect personal samples.

This chapter provides experimental data that details the performance of the capillary-canister device with respect to established sampling sorbent methods. Supporting information for this chapter is provided in Appendix B

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Note: The text of this article has been reformatted in accordance with the McGill Thesis Preparation Guidelines.

Abstract

Evacuated canisters have been used for many years to collect ambient air samples for gases and vapors. Recently, significant interest has arisen in using evacuated canisters for personal breathing zone sampling as an alternative to sorbent sampling. A novel flow control device was designed and built at McGill University. The flow control device was designed to provide a very low flow rate, < 0.5 mL/min, to allow a passive sample to be collected over an extended period of time. Previous experiments run at McGill have shown agreement between the mathematical and empirical models to predict flow rate. The flow control device combined with an evacuated canister (capillary-canister device) was used in a series of experiments to evaluate its performance against charcoal tubes and diffusive badges. Air samples of six volatile organic compounds were simultaneously collected in a chamber using the capillary-canister device, charcoal tubes and passive dosimeter badges. Five different concentrations of the six volatile organic compounds were evaluated. The results from the three sampling devices were compared to each other and to concentration values obtained using an on-line gas chromatograph (GC). Eighty-four samples of each method were collected for each of the six chemicals. Results indicate that the capillary-canister compares quite favorably to the on-line GC and to the charcoal tubes, $p>0.05$ for the majority of the tests. The capillary-canister device was found to be more accurate for the compounds evaluated, easier to use, and easier to analyze than charcoal tubes and passive dosimeter badges.

5.1 Introduction

A continuing challenge in occupational environments is that of estimating worker exposure to the multitude of airborne chemicals found in the workplace. Occupational exposure limits (OELs) have been established to prescribe the acceptable time weighted average exposure for many different chemicals. Comparing the OELs to the measured workplace concentrations allows for an assessment of risk and the need for control measures. Hence, methods to more

effectively sample contaminants in the workplace or other microenvironments are necessary to ensure that accurate exposure characterizations are obtained.

A variety of techniques are available to sample gases and vapors in occupational environments and outdoor microenvironments.[1-8] These techniques include solid sorbents, chemically treated filters, liquid absorbers, and evacuated containers. Each method has limitations that may include collection efficiency, flexibility, analyte stability, accuracy, precision, ease of use and cost effectiveness. Collection techniques are continually revised and updated to improve the overall accuracy of the sampling system and to define the limitations of the technique.

Volatile organic compounds have traditionally been collected on both sorbent tubes with calibrated personal air-sampling pumps[9-13] and diffusive badges.[14-17] Three key decisions that need to be made before starting a sampling campaign for volatile organic compounds (VOC) include: the selection of an adsorbent, sampling equipment, and an analytical method. The choice of sorbent is closely linked to the analytical technique and will define the chemicals that can be quantified. Whichever sorbents are chosen, environmental conditions present during sampling can affect the sample collection. High relative humidity, elevated temperatures, airborne concentrations, all may limit the effectiveness of the sampling technique.[18-20] In addition, stability after sampling, adsorption and desorption efficiency, may vary widely between VOC, making it difficult to sample multiple VOC with one sorbent.

As an alternative to sorbents, small canisters have recently become commercially available for use as personal air samplers to collect whole air samples. [8] One and six liter canisters have been used for a number of years for environmental and industrial hygiene area sampling of VOC. Limited data is available in the literature that compares personal sorbent sampling to personal canister samples. Studies have shown reasonably good stability and recovery of many contaminants in canisters.[21-27] However, over and under estimations have

been reported by several sources depending upon the analyte of interest.[28-31] United States Environmental Protection Agency (EPA) procedures TO-14 and TO-15 and ASTM D 5466-93 were developed to establish standardized methods to clean, prepare, sample and analyze low concentrations of VOC in air using canisters.[1,4,32] Whole air sampling is now widely used to collect stationary ambient air samples in indoor and outdoor environments.[33-35]

A critical aspect of sampling with an evacuated canister is the rate of flow of sample into the canister. The airflow into the canister is typically controlled using a mass flow controller. Current devices allow for sampling times up to 24 hours with a 6-liter canister, and approximately 8 hours with the 400 mL canisters.[8] In the interest of extending the sampling period of canisters, a capillary flow controller was developed to allow for low flow rates of air into a canister. This capillary flow controller was developed at McGill University,[36] and allowed for extended sampling periods, ranging from a few hours to a few weeks;[37,38] with flow rates down to 0.05 mL/min. Figure 5.1 displays the basic design of the capillary flow controller-canister. The flow rate of the capillary flow controller is a function of the capillary length and diameter. The pressure differential between the ambient atmosphere and the atmosphere inside the canister provides the driving force for the airflow. This extended sampling capability can improve the exposure assessment strategies used for environmental and occupational investigations.[39] The theory and experimental data describing the details of the capillary flow controller are presented elsewhere.[37,38] A brief review of the airflow concepts of the capillary flow controller will be presented here.

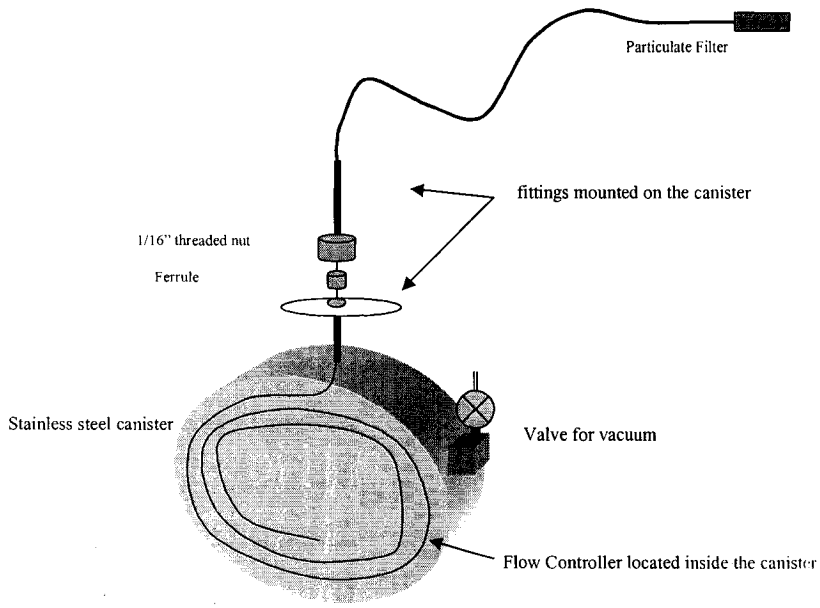


Figure 5.1 Personal whole air sampler: capillary flow controller with 300 mL canister

Simon, 1997 developed a mathematical model and empirical model to predict the airflow rate through the capillary flow controller for different sampling periods.[37] Empirical formulae developed from experimental data were found to be the most accurate means of predicting flow rate and sampling time.[38] In the same manner that a critical orifice is used, once the flow rate was established for a particular capillary length and diameter, it could be connected to an evacuated canister and used repeatedly to sample contaminants of concern without re-calibrating the flow rate. While experimental data showed the flow rate was found to diminish very slowly over the sampling period, it was determined to be

an acceptable bias if the container volume was filled to less than 50% capacity.[37,38] This bias associated with this small reduction in flow rate as the canister fills is more acceptable in canisters than sorbent tubes. The final sampled volume can be determined with canisters, thus, allowing for an accurate determination of concentration.

To allow for an appropriate assessment of personal exposures to chemicals in the work or community environment, it is important to have cost effective, lightweight, easy to use, devices that cause minimal disruption to the wearer. The focus of this paper is to compare the performance of a capillary flow controller-canister system to widely used sampling techniques for VOC: charcoal tubes and diffusive badges.[41,42] The three methods were evaluated in a series of chamber studies. Charcoal tubes are considered to be the standard method for personal monitoring VOC in the workplace,[43,44] diffusive badges have been well established as acceptable measures since the 1980s for personal monitoring of VOC,[17] and canisters have been well established for years as acceptable for collecting indoor and outdoor area samples.[33] The primary parameters affecting accuracy include: concentration, capacity, sample time, reverse diffusion, air velocity, device orientation, high relative humidity, elevated temperature, flow rate, unique capacity to adsorb each analyte, displacement of the analyte of interest by other analytes, inability of analytes to adsorb onto the sorbent, storage stability, and ability to desorb the analyte from the sorbent and associated analytical problems.[45]

Both charcoal tubes and diffusive badges have been tested in controlled atmospheres and used extensively under a variety of field conditions, resulting in acceptable airborne contaminant collection. However, the limitations must always be considered when using these methods and interpreting the results. The limitations are well documented in the literature and will not be further reviewed here.[46-54] The parameters listed above can result in problems with sorbent sampling methods. The solution is often to collect a larger number of

samples to ensure the worker's exposure is accurately characterized. These limitations can cause the cost of sampling to rise and, in practice, results in fewer workers being sampled and/or fewer chemicals being evaluated. Development of a new sampling method that can be used in a broader range of circumstances would provide for improved exposure assessments. Therefore, the primary issue that was addressed in this research was to determine if very low air sampling flow rates allow for the collection of air samples that are representative of atmospheric concentrations. Conditions such as the size of the canister, the recovery of the chemical, and the effect of relative humidity were all considered during this evaluation. While this paper presents laboratory chamber studies, field studies were also conducted to assess the capillary-canister system in the field environment and will be presented in a future article.

The following compounds were collected on the charcoal tubes, badges and in the canisters using the capillary flow controller: isopropyl alcohol, ethyl acetate, methyl ethyl ketone, cyclohexane, toluene, and perchloroethylene. The compounds were selected to represent a spectrum of VOC that may be encountered in occupational or microenvironments and would allow for a broad comparison of the performance of charcoal sorbents and the capillary-canister method. While it is recognized that charcoal is not the recommended sorbent for polar VOC such as isopropyl alcohol and methyl ethyl ketone, the relative correlation between the methods was the primary point of interest. A multiple sorbent could have been chosen for a comparison, however, charcoal is the most common sorbent used in workplace monitoring for VOC, therefore, one sorbent was selected for the collection of all six contaminants.

5.2 Methods and Materials

Five different concentrations of the six VOC were generated in a small chamber to compare collection efficiency of charcoal tubes, badges and the canister system. All chemicals used were reagent grade (Fisher Scientific or Sigma-

Aldrich). The effect of humidity on sample collection was also evaluated at three different humidity levels. The evaluation process involved assessing both the precision and accuracy of each method. European standards, EN 482: *Workplace atmospheres-General requirements for the performance of procedures of the measurement of chemical agents*, and EN 838: *Workplace atmospheres-Diffusive samplers for the determination of gases and vapours-requirements and test methods*, were used as guidelines to establish the protocol for testing the capillary-canister method.[55,56] Precision was evaluated by using replicate samplers, six charcoal tubes (SKC 226-09, Pittsburgh, PA), six charcoal badges (3M 3500 Organic Vapor Badges, Minneapolis, MN) and six canisters (Scientific Instrumentation Specialist, Moscow ID), exposed at each of the five concentrations. An on-line gas chromatograph was used to measure the "reference concentration" in the chamber, allowing for an assessment of the accuracy of the three methods. The overall uncertainty of the method was assessed as follows:

$$\text{Overall Uncertainty (OU)} = \left[\frac{\left| \bar{x} - x_{ref} \right| + 2s_{\bar{x}}}{x_{ref}} \right] \times 100 \quad (5.1)$$

where:

$\bar{x}$ is the mean value of the results of a number (n) of repeated measurements;

x_{ref} is the reference value of the chamber concentration;

$s_{\bar{x}}$ is the standard deviation of the measurements[56]

This equation can be separated into two sections, bias and precision. The bias is the deviation from the reference value and the precision is the deviation among the replicate values of each test. Bias is the first portion of the equation and the precision is the second value. In this research, a test was defined as an eight hour sampling of each of six volatile organic compounds using three different

methods simultaneously: evacuated canisters, charcoal tubes and diffusion badges. To correctly estimate the overall uncertainty for the methods, several factors must be understood and controlled. These factors include: concentration, relative humidity and temperature; all canisters, badges and tubes were exposed to the same levels of each. These parameters were controlled using a dynamic dilution system connected to a small exposure chamber. The system allowed for continual monitoring of the internal concentration, the temperature, and relative humidity in the exposure chamber. In addition, the system provides a uniform airborne concentration for sampling with charcoal tubes, badges and canisters, allowing for inter- and intra- comparison of the results from each test.

The system used to generate vapors in the sample chamber and monitor the concentration, temperature and relative humidity is shown in Figure 5.2. A description of the system is provided below to emphasize several details. Charcoal tubes, badges and canister samples were exposed in the chamber for all experiments in this research. Compressed gas cylinders supplied pure dry air at a constant flow rate to a humidification system. The air then passed by a syringe pump (kd Scientific, Inc., Boston, MA) that injected the mixture of the six VOC into the air stream. The VOC-air mixture flowed into a 1 L mixing chamber located in an oven set at 40° C. The syringe pump was adjusted to different flow rates to establish the concentration of interest for the respective experiments. The airflow rate was held constant for all experiments at 1 liter per minute. The oven was placed in the system to ensure complete and uniform evaporation of the solvent from the syringe pump. A second 1 L chamber was placed downstream from the oven to allow for additional mixing of the solvent vapors with air and measurement of temperature and relative humidity. The mixture of air and solvent vapors was then passed into the 2-liter sample chamber. Six fixed sample locations were established in the chamber. Precaution was taken to ensure that all three sampling methods were clustered within a 2 cm radius of each other for all experiments.

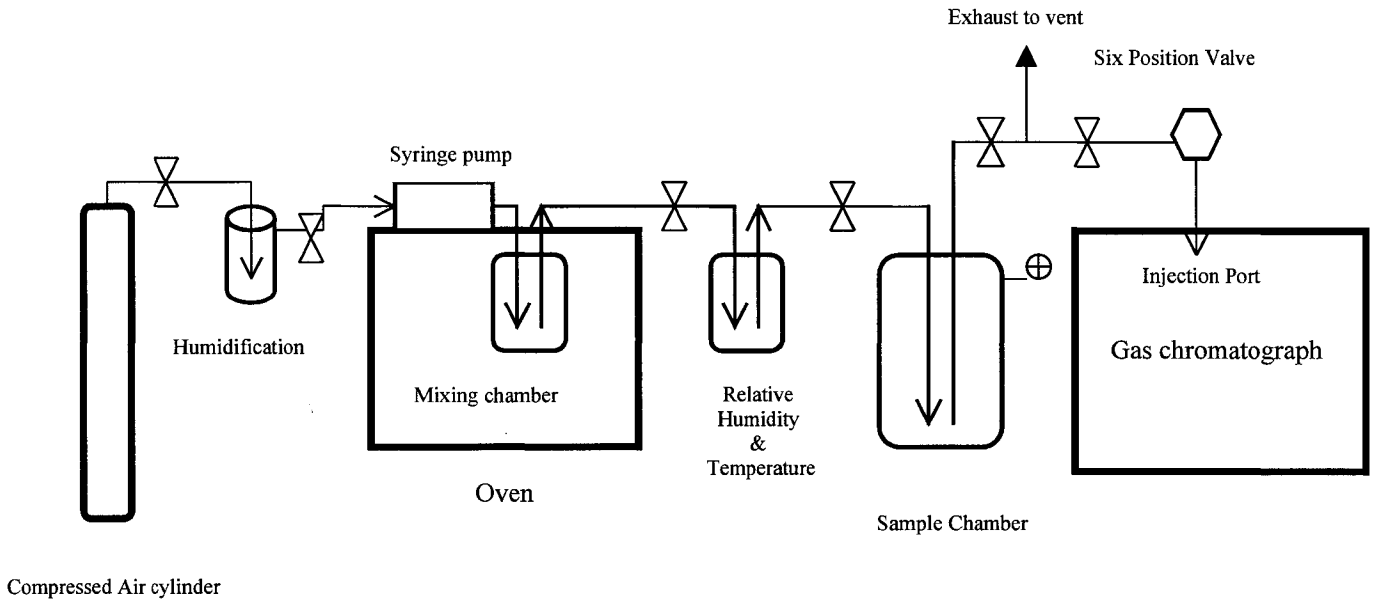


Figure 5.2 Solvent generation system and on-line gas chromatograph

Figure 5.3 shows the configuration of the samplers; only one configuration is shown for clarity. A series of needle valves were used to connect each charcoal tube to the chamber. The flow controllers for each canister were placed into the chamber, allowing the chamber air to be drawn into the canister through the capillary flow controller. The diffusive badges were suspended from the top of the chamber. Airflow rate was monitored throughout the system using eight calibrated rotameters. On-line analysis was performed using a Hewlett Packard gas chromatograph model 5890 series II equipped with a six-position valve and a 1.0 mL sample loop connected to the chamber. The valve allowed for direct injection of the chamber air into the GC. This provided for near-real time monitoring of the chamber concentrations during each test.

5.2.1 Mixture

A mixture of organic solvents was used to generate the airborne concentration inside the chamber. Solvents included: iso-propanol, ethyl acetate, methyl ethyl ketone, cyclohexane, toluene, and perchloroethylene. To eliminate any variability associated with the solvent mixture, a batch of the mixture was made at the beginning of the chamber experiments and used throughout. The six chemicals were mixed in proportions that approximated the ratio of their respective Threshold Limit Values (TLVs).[57] Table 5.1 displays the physical and chemical properties of the VOC and the ratio of the mixture.

5.2.2 Sampling and Analysis: Charcoal Tubes and Badges

Prior to the start of sampling for each test, the chamber was allowed to equilibrate to the target concentration for the respective test. The concentration was considered to be constant when three on-line GC results showed less than 3% change in peak areas over a 30-minute period. Large charcoal tubes, 400 mg/200 mg, (SKC 226-09) were used for all the tests. The large tube allowed for continuous sampling with no breakthrough.

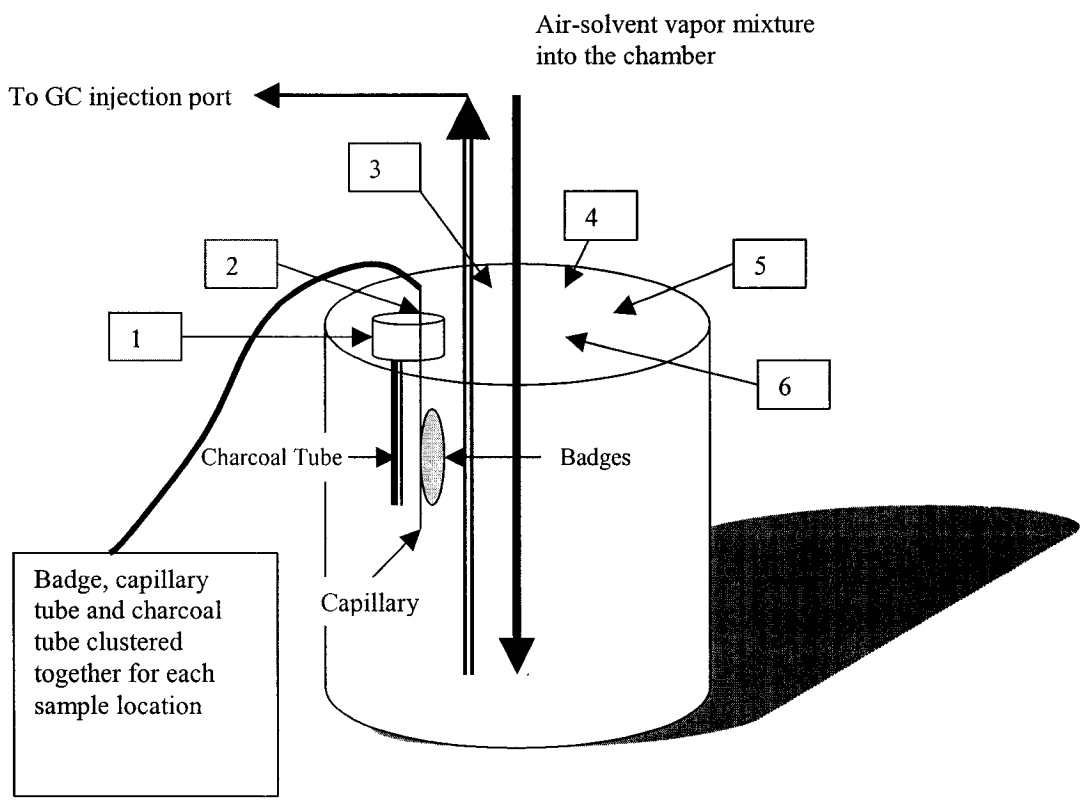


Figure 5.3 Sampling chamber with six sample locations identified; one sampling configuration is shown.

Table 5.1 Chemical and physical properties of solvents and the solvent ratio in the mixture used to generate solvent concentrations

Name (CAS #)	Formula	Mol. W gm/mol	Density gm/ml	TLV mg/m^3	Mixture %	Desorp. Efficiency mean (SD)[1]	Canister Recovery mean (SD)[2]
Cyclohexane (110-82-7)	C_6H_{12}	84.16	0.7781	1030	20	101 (2.1)	97 (2.2)
Ethyl Acetate (141-78-6)	$C_4H_8O_2$	116.16	0.898	1440	32	99.8 (2.8)	1.00 (2.0)
Isopropyl Alcohol (67-63-0)	C_3H_8O	60.1	0.7851	983	20	69.8 (11.6)	95 (5.0)
Methyl Ethyl Ketone (78-93-3)	C_4H_8O	72.11	0.805	590	12	88 (3.5)	1.01 (1.8)
Perchloroethylene (127-18-4)	C_2Cl_4	165.83	1.6311	170	8	97 (1.5)	98 (2.8)
Toluene (108-88-3)	C_7H_8	92.12	0.866	188	8	98 (1.2)	98 (2.4)

[1] **Desorption effeciency for charcoal tubes and badges, n=10**

[2] **Canister recovery was based on n=36 for each compound**

Flow rates were constant at approximately 30 mL/min for each charcoal tube using a calibrated needle valve (SKC Adjustable Low Flow Holders, 224-26-02). The duration of each test was approximately eight hours. Upon completion of air sampling, the charcoal tubes were stored in a freezer for not more than 36 hours before analysis was performed. The front and back section of charcoal was removed from the glass tubes and placed in separate 10 mL glass vials. Two milliliters of carbon disulfide (CS_2) was added to each vial to desorb the collected VOC. The vials were gently agitated for 30 minutes and then an aliquot of the CS_2 solution was transferred into auto sampler vials per NIOSH method 1501.[54] All samples were analyzed using a Hewlett-Packard gas chromatograph (GC) 5890 series 2 equipped with a flame ionization detector and a Hewlett Packard auto sampler model 7673. A Supelco VOCOL capillary column, 0.53 mm diameter, 30 m long and having a film thickness of 3.0 um was used for analysis (Supelco, Inc., Bellefonte, PA). The GC temperature program was the following: initial temperature 80°C, ramp 5 °C to 120 °C and the injector and detector temperatures were held steady at 250 °C and 300 °C, respectively. Sets of calibration standards were prepared for each solvent for each test. The standards were always run at the same time as the charcoal tubes, badge samples and canisters.

The methods for analyzing charcoal tubes and badges for the VOC used in this research have been investigated extensively, therefore, desorption efficiencies are well documented. However, a series of desorption standards were run to ensure desorption efficiencies were similar to the published information.[54] Ten charcoal tubes and 10 badges were injected with known amounts of analyte, allowed to equilibrate for 24 hours, and then desorbed in the same manner as the airborne samples. In addition, blank samples were run with every test to evaluate the integrity of the sampling media.

5.2.3 Analysis of the Capillary-canister sampler

Air sampling with the canisters was done simultaneously with the charcoal tubes and badges. The six capillary flow controllers were extended into the sampling chamber and positioned within 2 centimeters of their respective charcoal tubes and badges. The length of time the canister samples were collected was approximately the same as the sorbent media. Six 1 L stainless steel canisters from Scientific Instrumentation, Moscow, Idaho, were selected for use in this phase of research. The capillary flow controllers (Deactivated fused silica, J&W Scientific, Folsom, CA) installed on each canister were approximately 90 cm long by 0.1 mm inside diameter, providing a flow rate of ~0.4 mL/min. Prior to each test, canisters were filled with humidified zero nitrogen and allowed to stand for at least 24 hours to determine the cleanliness of each canister. The canister was then evacuated and pressurized for a total of three cycles with humidified nitrogen to ensure the canisters were clean. In preparation for the sub-atmospheric sampling, the canister was evacuated to 0.05 mm Hg. When the canister valve is opened, the pressure differential causes the sample to flow into the canister, slowly filling over a period of eight hours. Upon completion of the test, the valves were turned off and the canisters were then pressurized to approximately 1200 mm Hg with humidified pure nitrogen. The pressurized canisters were allowed to stand for 12 hours, and then analyzed with a Hewlett-Packard gas chromatograph (GC) model 5890 series 2 equipped with a flame ionization detector. This GC is the same as the one used to monitor the chamber concentrations during all the tests. A HP-5 capillary column with dimensions of 0.32 mm diameter, 50 m long and a film thickness of 1.05 um was used in this GC. While the column is different than the VOCOL column used to analyze the sorbent samples, it provided adequate separation of all compounds. The concentrations collected in the canisters were within an order of magnitude of TLVs for all six compounds of interest. Therefore, the levels found in the canister were in the ppm range; as a result, the canisters could be analyzed by direct injection of the sample into the GC. A special fitting was designed to allow the canister to be connected directly to the six-position valve that was connected to

the GC injection port. A rotameter was connected to the exit port of the six-position valve to monitor the amount of sample passed through the valve. This ensured that the sample lines were purged of any residual material before the sample was injected.

Gas standards for each VOC were generated at different concentrations to develop a calibration curve for the canister samples. The mass of the analyte from the canister samples was determined by comparing the gas chromatographic area of the analyte to the calibration curve. The concentration collected by the canister from the atmosphere in the chamber was calculated by adjusting for the dilution that occurs when the canister is pressurized.

5.2.4 Experimental Conditions

In the initial series of experiments, the temperature and relative humidity were held constant, at 24°C and ~ 5% RH, while the concentration of the six different VOC were varied. The concentration of four compounds, isopropyl alcohol, ethyl acetate, methyl ethyl ketone and cyclohexane were varied from 10-80% of their respective TLVs. The concentration for the toluene was varied from 25-175% of its TLV and perchloroethylene was varied from 50-350% of its TLV. The second series of experiments examined the effects of humidity. Air borne concentrations were held relatively constant at approximately 30% of the TLV for the four compounds and 50 and 100% for toluene and perchloroethylene respectively, while the relative humidity was varied from <5, 50, 80, to 90%.

5.3 Results & Discussion

A series of experiments were conducted to evaluate the effectiveness of using a novel personal air sampler to collect gases and vapors. The flow rates used to collect the samples were approximately 0.4 mL/min. Charcoal tubes and charcoal diffusion badges simultaneously exposed to the same environmental

conditions as the personal canisters were used to compare the performance of the personal canisters. In addition, a gas chromatograph connected to the sampling chamber was used to determine the reference concentration for each test. The GC values allowed for an assessment of accuracy of the charcoal tubes, badges and canisters. In addition, replicate samplers for each method allowed for estimation of precision.

The reference concentration, as measured by the on-line gas chromatograph (GC), was compared to that obtained with the three field sampling methods. The GC values for each test were collected directly from the exposure chamber throughout the duration of the test. The mean GC values are a result of 25-30 measurements taken during the course of each of the fourteen individual tests. Each test was approximately eight hours long with GC measurements taken approximately every 20 minutes throughout the eight-hour period. The GC values can be considered near-real-time samples and are accepted as an appropriate reference value because of the number of replicate values collected, the variability of the values throughout the sampling period (RSD ~3-4%), frequency of external calibration and the proximity of the GC inlet to the three field sampling methods.

5.3.1 Sampling Accuracy of the Canisters, Charcoal Tubes and Diffusive Badges

Table 5.2 A-F displays the mean GC values for each test and the mean values for the three air sampling methods. The table shows tests run at different concentrations and at different humidity levels (RH). Test one to six were run at <5% RH, test seven to twelve were run at 50% RH and tests 13 and 14 were run at 80 and 90% RH respectively.

Table 5.2 Overall uncertainty of diffusion badges, charcoal tubes and capillary canisters.

A

Isopropyl Alcohol (TLV = 983 mg/m^3)

	[A] On-line GC		Canister			Charcoal Tubes			Badges		
	Reference		mean	RSD	Overall	mean	RSD	Overall	mean	RSD	Overall
Test [B,C]	mg/m^3	RSD%	mg/m^3	%	Uncertainty	mg/m^3	%	Uncertainty	mg/m^3	%	Uncertainty
1	100.6	4.2	99.3	10.8	22.6	135.7	12.4	**68.3**	105.5	2.0	9.0
2	188.9	3.0	170.4	5.8	20.3	143.0	15.9	**48.4**	215.0	12.6	**42.5**
3	186.9	3.3	158.5	6.8	26.6	199.0	28.8	**67.7**	271.6	6.0	**62.8**
4	189.0	4.0	179.4	6.2	16.9	179.9	11.1	26.0	280.0	17.6	**100.4**
5	387.7	3.3	335.9	4.9	21.9	356.0	10.4	27.2	414.5	3.8	**15.1**
6	501.0	14.7	470.2	7.6	20.4	570.0	8.0	**32.0**	458.0	3.0	14.1
7	120.8	5.9	118.6	4.3	10.3	84.6	7.7	**40.7**	88.4	5.7	**35.1**
8	255.5	3.7	214.0	5.4	25.3	162.4	10.2	**49.4**	151.9	5.6	**47.2**
9	261.7	3.1	213.5	8.1	**31.7**	222.5	2.6	19.4	104.4	2.7	**62.3**
10	261.3	6.1	251.2	5.9	15.1	233.4	5.6	20.7	99.4	4.3	**65.2**
11	494.7	4.1	465.9	5.3	15.8	507.5	3.1	9.0	251.0	3.2	**52.5**
12	783.7	5.2	743.4	4.2	13.1	453.2	12.1	**56.2**	229.2	3.3	**72.7**
13	252.2	3.9	239.9	2.5	9.6	150.0	8.6	**50.8**	151.8	2.8	**43.1**
14	258.4	2.0	262.4	5.1	11.9	95.7	5.5	**67.1**	114.5	2.9	**58.3**

B

Methyl Ethyl Ketone (TLV = 590 mg/m^3)

	[A] On-line GC		Canister			Charcoal Tubes			Badges		
	Reference		mean	RSD	Overall	mean	RSD	Overall	mean	RSD	Overall
Test [B,C]	mg/m^3	RSD%	mg/m^3	%	Uncertainty	mg/m^3	%	Uncertainty	mg/m^3	%	Uncertainty
1	61.9	4.7	65.6	7.0	20.8	56.7	12.6	**31.5**	38.3	3.3	**42.2**
2	117.6	2.5	115.9	5.0	11.3	143.0	12.3	**51.6**	99.0	9.0	**31.0**
3	114.7	3.2	108.0	8.5	21.9	N/A			115.0	26.2	**52.9**
4	117.7	2.7	112.0	4.1	12.7	N/A			N/A		
5	227.6	21.0	202.1	5.1	20.3	244.0	6.2	20.6	116.0	23.5	**73.0**
6	311.9	14.0	314.4	8.4	17.8	248.9	1.3	22.2	157.9	2.8	**52.3**
7	72.2	6.0	69.5	8.8	20.6	48.8	5.1	**39.3**	86.6	5.8	**33.8**
8	157.2	3.7	149.6	4.1	12.7	94.9	5.6	**46.4**	94.9	5.6	**46.4**
9	161.0	3.2	153.3	4.7	13.7	107.3	2.8	**37.1**	94.7	1.9	**43.4**
10	162.6	2.3	147.0	7.8	23.6	122.2	5.3	**32.8**	106.6	5.8	**42.1**
11	305.8	4.0	301.6	6.7	14.5	226.5	4.0	**31.9**	218.8	3.1	**32.8**
12	486.9	5.1	456.2	5.0	15.7	407.0	6.2	26.7	198.4	3.3	**61.9**
13	157.3	4.3	149.3	1.8	8.5	26.6	16.5	**88.7**	111.2	2.4	**32.7**
14	162.1	2.2	151.0	3.4	13.1	14.1	15.2	**93.9**	90.8	5.1	**49.7**

C

Ethyl Acetate TLV = 1440 mg/m^3

	[A] On-line GC		Canister			Charcoal Tubes			Badges		
Test [B,C]	Reference mg/m^3	RSD%	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty
1	181.1	4.7	184.9	7.8	18.0	185.8	14.0	**31.2**	205.7	7.9	**31.5**
2	344.8	2.5	355.9	4.8	13.2	355.0	10.8	25.1	421.0	8.0	**41.6**
3*	314.5	3.5	318.4	8.3	18.0	170.6	18.1	**65.4**	202.1	3.6	**40.3**
4*	343.9	2.7	328.0	3.8	12.0	180.0	6.5	**54.5**	285.0	4.0	23.7
5	742.2	3.8	671.8	7.1	22.3	796.0	7.6	23.6	755.0	24.8	**52.2**
6	913.3	13.9	939.0	8.8	20.9	849.0	4.3	15.0	822.0	3.1	15.5
7	217.6	5.9	200.3	8.3	23.3	204.9	6.1	17.3	227.5	6.0	17.1
8	460.1	3.5	433.8	4.9	15.0	392.2	4.0	21.6	255.5	6.0	**51.1**
9	470.7	3.3	446.9	5.3	15.2	463.1	2.3	6.1	244.1	2.7	**51.0**
10	474.8	2.4	430.6	7.8	23.5	449.1	5.3	15.5	277.4	6.7	**49.4**
11	899.0	5.1	894.5	6.7	13.9	898.0	3.0	6.1	570.0	2.9	**40.3**
12	1424.6	5.0	1359.0	5.0	14.2	1414.1	6.9	14.4	518.3	3.0	**65.8**
13	460.1	4.3	434.0	2.0	9.5	452.4	4.4	10.3	294.0	2.5	**39.3**
14	470.2	2.0	391.7	2.8	21.3	454.1	4.8	12.8	348.6	4.1	**32.0**

* Co-elution between MEK and Ethyl acetate resulted in quantification difficulties for the charcoal tubes

D

Cyclohexane TLV = 1030 mg/m^3

	[A] On-line GC		Canister			Charcoal Tubes			Badges		
Test [B,C]	Reference mg/m^3	RSD%	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty
1	99.7	4.9	105.4	8.5	23.8	104.2	14.2	**34.1**	70.8	8.3	**40.8**
2	191.6	2.5	200.1	4.6	14.1	190.0	9.8	20.2	129.0	7.3	**42.4**
3	183.6	3.7	179.9	7.6	16.8	185.5	6.4	13.9	117.2	3.5	**40.7**
4	189.8	4.7	189.8	3.4	6.7	194.0	4.3	11.0	135.0	3.9	**34.4**
5	399.0	5.0	363.0	4.6	17.4	422.3	4.6	15.6	163.9	25.1	**79.5**
6	515.1	12.9	536.3	8.5	21.9	482.0	2.5	11.2	278.0	3.3	**49.6**
7	117.7	5.8	109.1	7.8	21.8	129.7	6.6	24.8	128.8	6.1	22.8
8	254.9	4.4	245.8	4.9	13.1	248.1	5.1	12.6	144.7	6.1	**50.1**
9	259.3	3.5	254.3	4.5	10.7	273.0	2.9	11.3	138.0	2.6	**49.5**
10	259.0	6.1	238.3	9.3	25.1	263.6	5.1	12.2	157.3	6.8	**47.6**
11	497.2	3.6	507.9	7.1	16.8	444.0	2.2	14.7	295.9	2.8	**43.8**
12	792.0	4.7	752.4	11.3	26.5	691.0	6.0	23.2	269.0	2.9	**68.0**
13	249.8	4.4	235.4	2.2	9.8	237.6	3.2	11.0	106.9	2.8	**59.6**
14	254.4	2.1	257.8	3.7	8.9	210.9	3.5	22.9	149.8	4.2	**46.0**

Toluene TLV = 188 mg/m^3

	[A] On-line GC		Canister			Charcoal Tubes			Badges		
Test [B,C]	Reference mg/m^3	RSD%	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty
1	44.4	4.5	47.2	7.4	22.1	40.1	9.6	26.9	30.8	8.3	**42.2**
2	83.8	2.6	84.2	5.8	12.2	73.1	9.7	29.8	54.9	9.3	**46.7**
3	82.3	3.1	78.0	10.4	24.9	78.1	8.1	20.4	52.3	4.1	**41.7**
4	84.2	2.8	83.2	8.3	17.6	84.4	7.6	15.6	60.3	5.4	**36.1**
5	170.6	3.7	148.8	4.7	21.0	166.7	8.5	18.8	77.8	29.4	**81.2**
6	223.8	14.8	219.2	6.8	15.4	234.4	4.7	14.5	146.2	2.8	**38.4**
7	53.5	5.9	46.8	7.1	24.9	54.7	7.6	17.9	62.0	5.4	28.5
8	112.8	3.3	111.4	5.1	11.3	104.7	6.0	18.4	69.9	5.4	**44.7**
9	115.5	4.3	110.0	4.0	12.4	113.5	5.5	12.6	66.8	1.7	**44.1**
10	116.5	2.4	156.8	7.5	**54.7**	111.6	5.3	14.3	75.7	6.6	**43.6**
11	217.9	4.2	266.6	10.1	**47.0**	200.3	2.9	13.4	143.7	3.1	**38.1**
12	347.0	4.9	368.7	11.1	29.8	316.0	2.8	13.9	131.7	3.1	**64.4**
13	113.3	4.2	115.2	5.3	12.4	57.6	7.4	**56.7**	77.2	2.3	**34.9**
14	113.5	2.8	104.1	6.9	21.0	99.4	4.1	19.6	80.0	4.5	**35.8**

F
Perchloroethylene TLV 170 mg/m^3

	[A] On-line GC		Canister			Charcoal Tubes			Badges		
Test [B,C]	Reference mg/m^3	RSD%	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	RSD %	Overall Uncertainty
1	83.7	4.4	76.5	0.0		75.1	11.3	**30.6**	59.2	7.4	**39.8**
2	159.3	2.5	183.0	6.7	**30.2**	159.8	10.1	20.5	117.0	4.7	**33.4**
3	155.2	3.3	145.2	8.2	21.8	155.1	7.3	14.6	107.0	4.1	**36.8**
4	159.3	4.2	143.2	4.3	17.9	164.5	8.4	20.7	122.3	4.2	29.7
5	323.4	3.9	279.3	5.4	23.0	321.1	7.0	14.5	178.6	29.5	**77.4**
6	421.2	15.5	414.4	14.5	**30.1**	403.7	2.4	8.8	268.0	6.6	**44.7**
7	100.7	6.2	96.9	7.6	18.5	106.2	7.0	20.2	120.2	5.2	**31.8**
8	212.6	3.3	202.9	8.6	21.0	203.6	5.6	14.9	135.3	5.1	**42.9**
9	217.7	5.2	216.1	3.1	7.0	225.1	6.0	15.8	132.2	1.2	**40.8**
10	218.8	2.7	216.3	9.0	18.9	220.9	4.9	10.8	135.9	5.1	**44.3**
11	410.6	4.2	408.9	7.2	14.8	380.7	1.1	9.3	252.4	3.0	**42.2**
12	650.7	5.0	607.9	4.2	14.4	613.3	2.7	10.9	316.4	2.9	**54.2**
13	213.6	4.1	201.2	1.9	9.5	232.7	4.8	19.5	118.4	1.9	**46.7**
14	212.6	2.7	213.8	3.6	7.8	200.6	3.9	13.1	160.3	4.4	**31.3**

[A] GC REF. Is the Reference concentration established at the time of sampling using an on-line gas chromatograph, n. (~n=25 to 30)
[B] Relative Humidity Levels: Tests 1 to 6 < 5%, 7 to 12 - 50%, 13 - 80%, 14 - 90% [C] Temperature was held constant for all tests at 24.6 +/- 0.4 °C
[D] Each test has an n of six per sampling method * Statitical difference was observed using a t-test, $p<0.05$

Based on the EN 482 standard, if the overall uncertainty (as defined in the introduction) exceeds 30% for concentrations ranging from 0.5 to 2 times the limit value, the method does not meet the general performance requirements for determining the concentration of air borne chemical agents in the work environment. The EN 482 standard also uses a criterion of <50% for concentrations ranging from 0.1 to 0.5 times the limit value. The challenge concentrations for the compounds used in this research ranged from 0.1 to 3.5 times the chosen limit value, which was the Threshold Limit Value (TLV). The more stringent value of 30% was chosen as an overall uncertainty criterion for acceptable air sampling devices for all tests in this research.

5.3.2 Canisters

No significant difference between the GC values and canister samples for the majority of the 14 tests of each of the 6 compounds, where 67 of 84 t-tests for two sample means showed $p > 0.05$. The tests that showed significant difference were usually a result of the variability (RSD) in the canister method as compared to the on-line GC. This data is displayed in Table 2 A-F, and shows that the canisters collect a representative sample for the six volatile organic chemicals tested. The overall uncertainty values are also shown in this table.

The overall uncertainty (OU) for the individual tests of the canister samples were found to be less than 30% for all fourteen tests for Isopropyl alcohol, methyl ethyl ketone, ethyl acetate, and cyclohexane. Toluene was found to exceed 30% in two (test 10,11) of the fourteen tests. Further examination of the two toluene data sets reveals that the precision is similar to the other chemicals tested, yet the bias was high, overestimating exposure by as much as 35%. The over estimation was determined to be the result of contamination that occurred in the sampling and analysis process during these experiments. It was unclear as to the specific nature of the contamination. However, toluene was used by other researchers in the laboratory for experiments unrelated to this research during

the time frame of tests 10 and 11. A small amount of toluene in the system used to pressurize the canisters appeared to have been the source of contamination. The overall uncertainty of the canister method for perchloroethylene was found to be acceptable for eleven of fourteen tests. Test two and six were found to have OU values just over the 30% at 30.1 and 30.2%. The data from test one for perchloroethylene was lost due to analytical instrumentation failure.

All six chemicals were found to be within the 30% criterion for the high relative humidity tests, 13 and 14. As expected the relative humidity had no noticeable affect on the canister sampling.

Each sampling method was compared to the GC values to assess bias. The overall uncertainty of each method is expressed in Table 2 A-F as a function of bias and precision. The bias values are represented in the overall uncertainty value listed in the table. Bias values for the canister method were relatively constant from chemical to chemical, ranging from 1 to 10% for the fourteen tests for methyl ethyl ketone, ethyl acetate, cyclohexane, toluene, and perchloroethylene. The range of the bias for Isopropyl alcohol was somewhat larger at 1.3 to 18%. The bias was found to be negative for 66 of the 84 canister concentrations, indicating that the canisters under estimated exposure in 75% of the tests. The underestimation was small and consistent with the percent analyte recovery from canister.

Table 5.3 Aggregate uncertainty for each chemical

	Canisters	SD	Char. Tubes	SD	Badges	SD
IsoPropyl Alcohol	18.14	7.36	41.30	19.31	53.55	30.04
Methyl Ethyl Ketone	15.43	5.48	43.33	24.42	45.31	13.21
Ethyl Acetate	16.53	5.53	23.41	17.15	39.25	14.41
Cyclohexane	16.13	6.82	16.46	7.19	48.14	13.93
Toluene	24.36	13.46	20.18	11.38	43.92	43.93
Perchlorothylene	17.12	8.52	16.29	16.29	40.10	15.65

n=14
SD = Standard Deviation

An aggregate overall uncertainty that included all tests for each chemical was calculated to estimate the performance of the canisters for all concentrations and all the different levels of relative humidity tested. The aggregate OU values for the canisters ranged from 15 to 24% for the six compounds evaluated and are displayed in Table 5.3. The individual overall uncertainty values and the aggregate values indicate that the canister method performed within acceptable guidelines for all six compounds tested at the five different concentrations and different relative humidity levels.

5.3.3 Charcoal Tubes and Diffusion Badges

A comparison was made between the canister method and charcoal tubes to evaluate the relationship between the two field methods. In addition, charcoal badges were also evaluated with respect to the canisters. An analysis of variance (ANOVA) was conducted on the data from the charcoal tubes, badges and canisters. The mean values for the badge samples underestimated the concentration by 25-35% for all chemicals tested. As a result, the ANOVA for the mean values of three field samplers were statistically different. However, t-tests between the charcoal tubes and canisters showed no significant difference

between the two methods for most of the 14 tests. Excluding the polar organic compounds, Isopropyl alcohol and methyl ethyl ketone, 80% of the t-tests were found to show no statistically significant difference between the two methods, $p > 0.05$. The tests that showed significant difference were usually a result of the variability (RSD) in the charcoal tube method as compared to the canisters.

An important consideration when sampling with sorbent materials is the affinity of the chemical compound of concern for the sorbent. Polar organic compounds have a relatively low affinity for charcoal; as a result, a different sorbent such as silica gel is often preferred as a collection media.[19,46] The overall uncertainty associated with these tests for the charcoal tubes is consistent with the polarity of the compounds used in the tests. Isopropyl alcohol and methyl ethyl ketone, the two most polar compounds tested, were found to have an aggregate OU exceeding 40%. The charcoal tubes effectively collected the ethyl acetate, cyclohexane, toluene and perchloroethylene; aggregate OU were less than 25%.

Diffusion badges displayed similar precision as the charcoal tubes, but underestimated the concentration. The aggregate OU for all chemicals for the badges ranged from 39 to 53%. Desorption and analysis of the badges was performed in the same manner as the charcoal tubes and recovery of the analyte did not deviate from the published data. Therefore, the collection of the sample was considered the primary source of error. Diffusion badge sampling is sensitive to velocity of airflow across the sampler.[58] The system was designed to produce airflow in the chamber similar to the air flow patterns a worker moving about a factory may encounter. While the minimum flow of 0.2 m/s (25 ft/min) was initially designed into the chamber at the sample locations, airflow patterns during the actual tests likely fell below the 0.1 m/s across the badge. This low airflow resulted in a reduced amount of analyte available to diffuse across the badge membrane. As a result, the badge data was found to underestimate the contaminant concentration in the atmosphere of the chamber, (i.e. poor accuracy). The relative standard deviations (RSD) for the badge data show

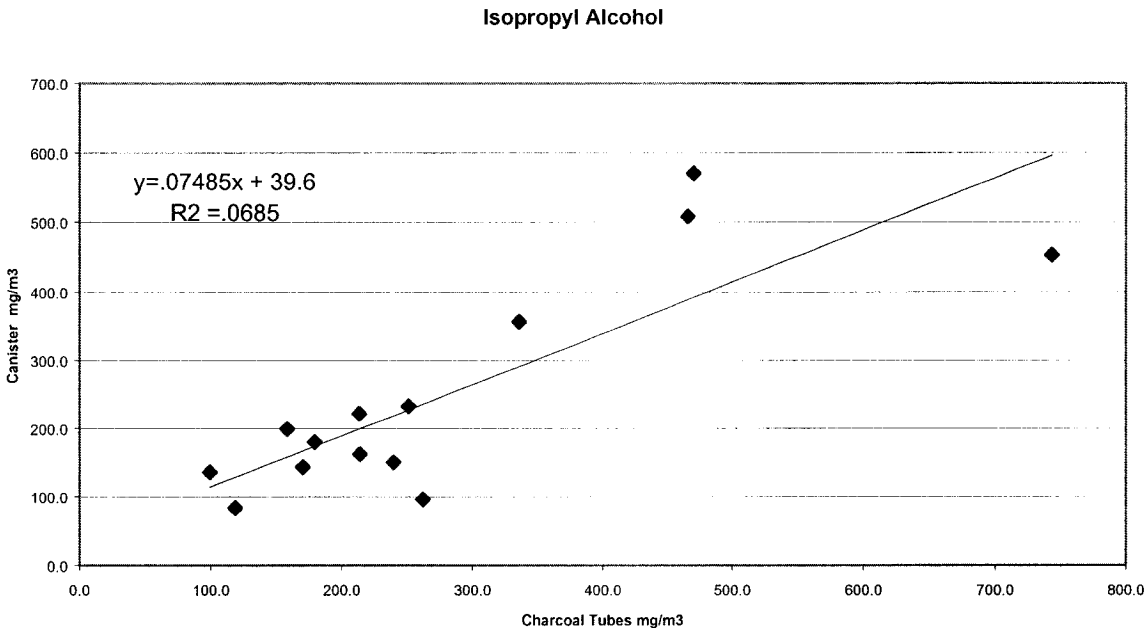
similar precision to that of the other two methods. Combined accuracy and precision of the badges are demonstrated in the elevated overall uncertainty.

5.3.4 Correlation of Canister and Charcoal Samplers

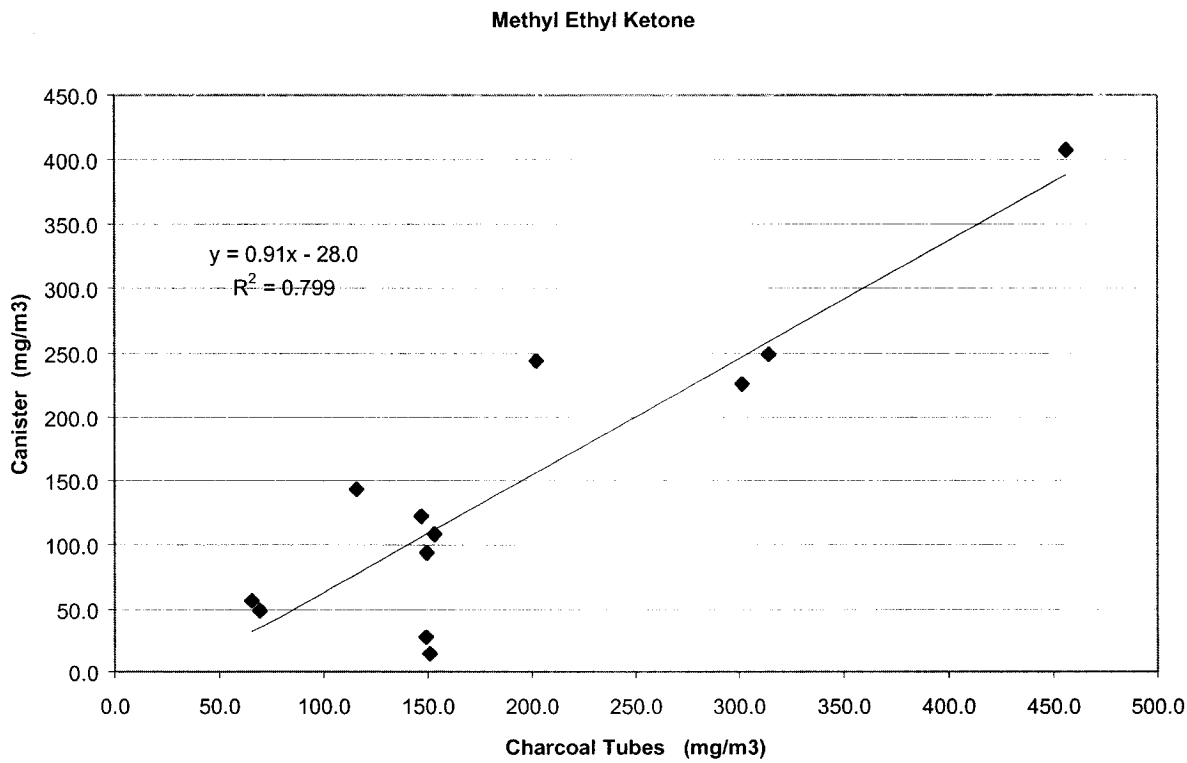
The overall uncertainty of the three methods provides a comparison to the true concentration based on the gas chromatograph values. By plotting the canister results against the charcoal tube results, one can assess the performance of the two methods with respect to each other. Figure 4 A-F shows the relationship of the two sampling methods for the six different compounds.

Each data point represents six replicate measurements. Four compounds, ethyl acetate, cyclohexane, toluene and perchloroethylene show an R^2 value greater than 0.90. The two more polar compounds, isopropyl alcohol and methyl ethyl ketone, display relatively poor correlations (< 0.8). Slope values of the regression line for all compounds, except isopropyl alcohol, ranged from 0.86 to 1.05, indicating a relationship of approximately 1:1. One would expect the poor correlation for the polar organic materials because of the reduced affinity for charcoal.[19,46]

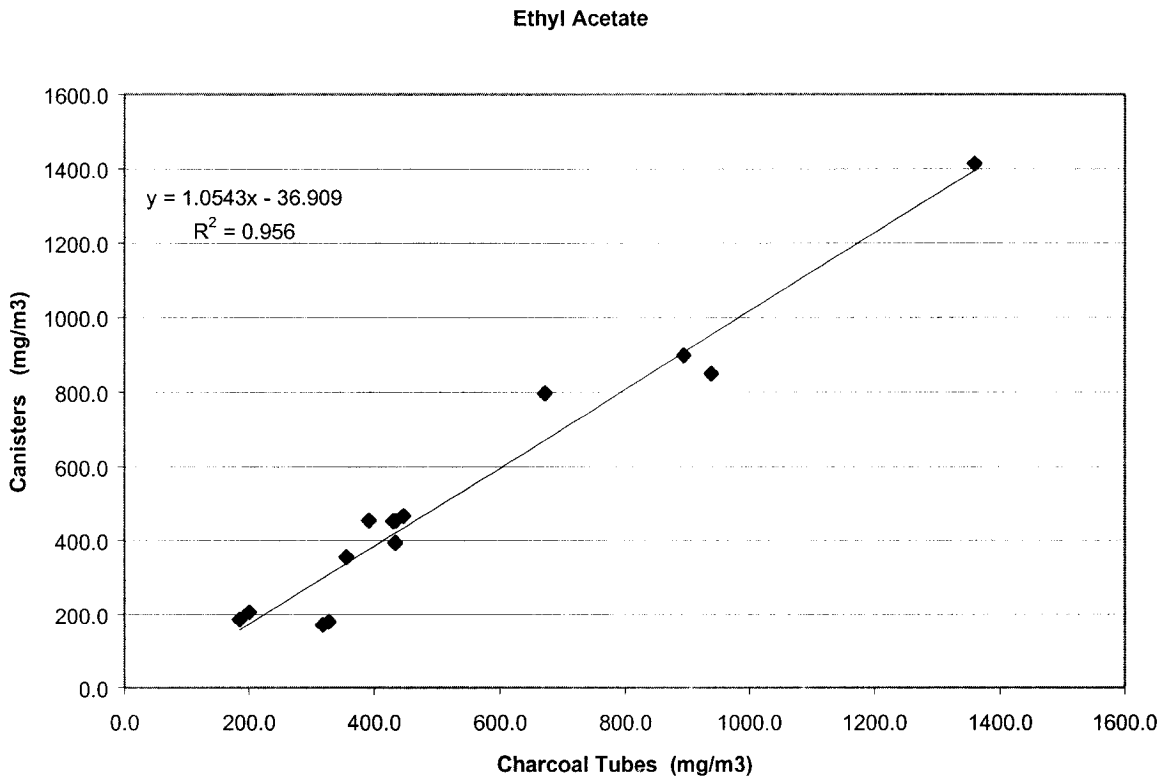
(A)


Isopropyl Alcohol
y=.07485x + 39.6
R2 =.0685
Canister mg/m3
Charcoal Tubes mg/m3
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
0.0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0

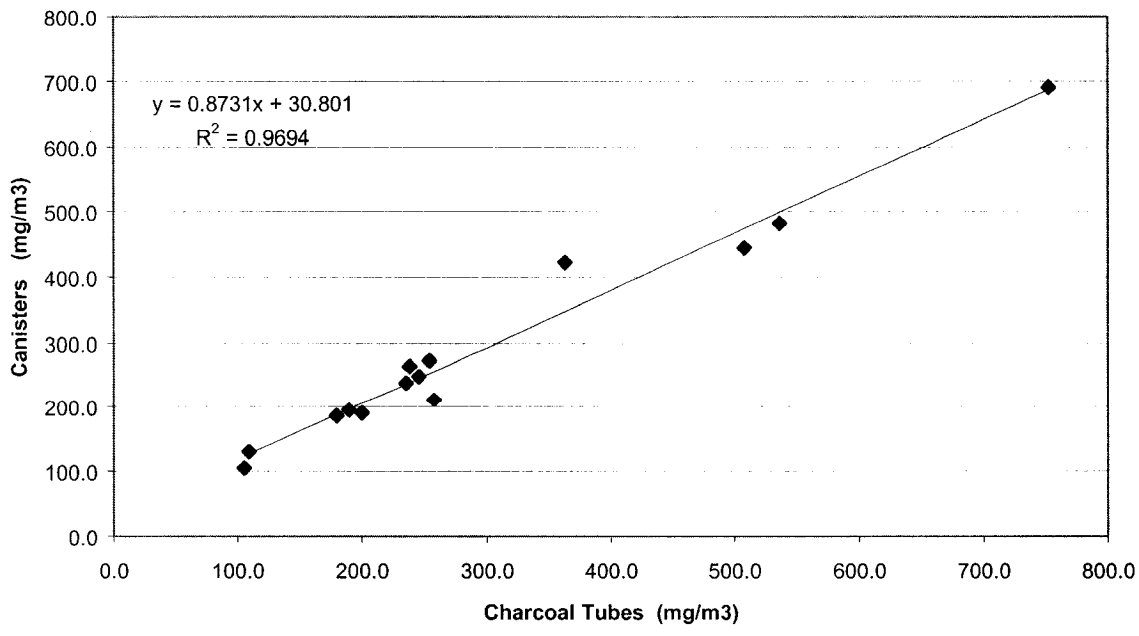
(B)


Methyl Ethyl Ketone
y = 0.91x - 28.0
R2 = 0.799
Canister (mg/m3)
Charcoal Tubes (mg/m3)
450.0
400.0
350.0
300.0
250.0
200.0
150.0
100.0
50.0
0.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
450.0
500.0

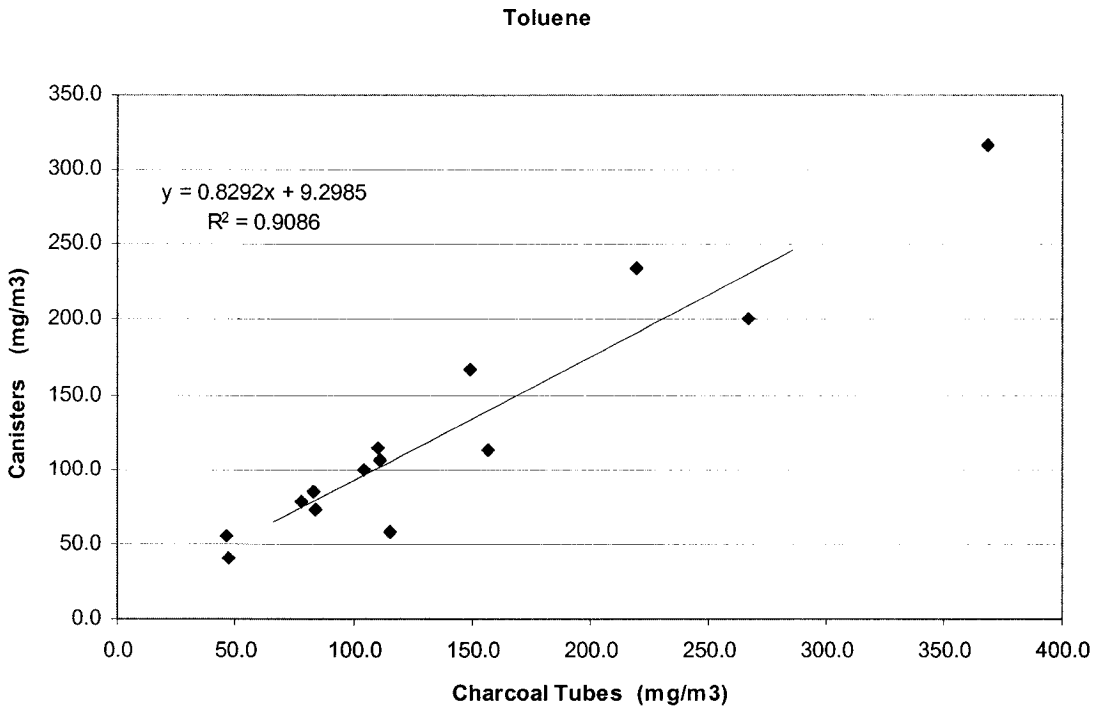
(C)


Ethyl Acetate
y = 1.0543x - 36.909
R2 = 0.956
Canisters (mg/m3)
Charcoal Tubes (mg/m3)
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
1400.0
1600.0

(D)


Cyclohexane
y = 0.8731x + 30.801
R2 = 0.9694
Canisters (mg/m3)
Charcoal Tubes (mg/m3)
0.0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0

(E)



(F)

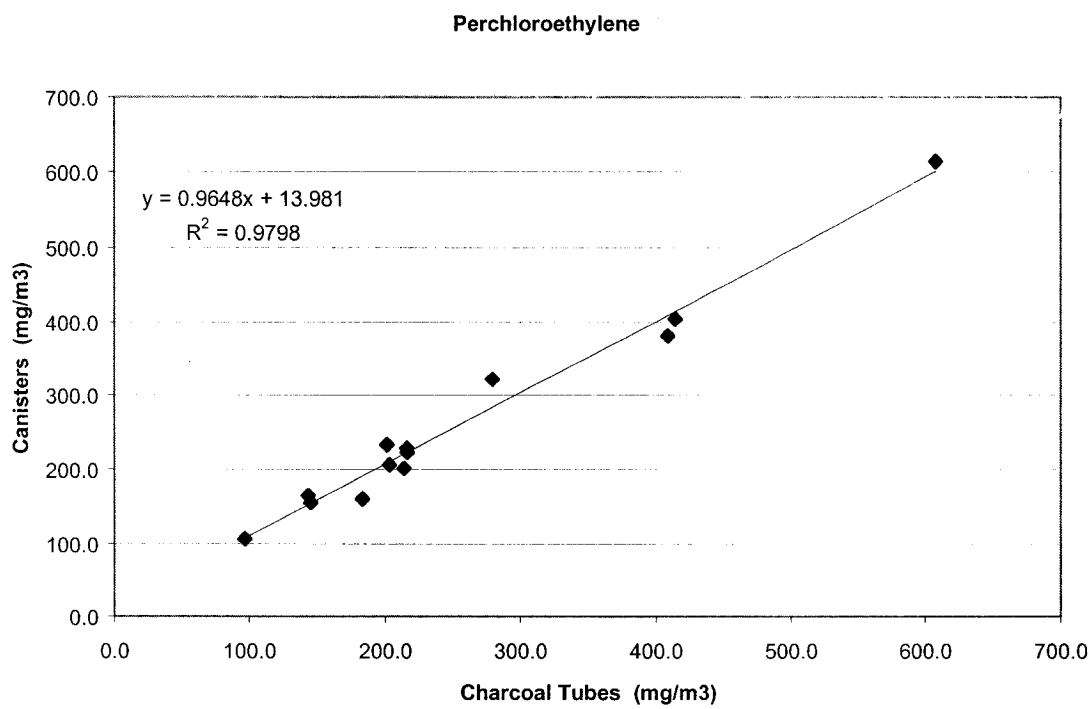


Figure 5.4 Comparison of charcoal tubes and capillary-canister samples for the collection of six organic solvents.

5.4 Conclusions

The capillary-canister system performed within the acceptable guidelines when compared to an on-line GC and to field sorbent sampling methods. While statistically significant differences may be observed in some tests between the results from canister and near-real-time samples (GC results), the differences were generally small and there were very good correlations between the canister results, the near-real-time results and the charcoal tubes. When compared to sorbent methods, canisters provide the ability to sample a wider range of compounds, a wider range of concentration (ppb to ppm), and for longer periods of time. The canister sampling system was found to perform adequately for all six compounds tested using guidelines put forth by European Committee for Standardization, CEN 482.

The low flow rate of 0.4 mL/min allowed for representative sample collection. These low flow rates, below 1 mL/min, are of value because they allow the use of canisters for long-term air sampling. Also, these low flows allow for the use of smaller canisters adapted as personal samplers and used to assess exposures in industry or microenvironments. Validation of canisters as personal samplers will provide the hygienist with an additional tool when developing strategies for exposure assessment. Finally, a qualitative benefit observed by the authors during the course of this research, was the ease of analysis for the canisters when compared to the sorbent methods. The limited sample preparation time for the canisters and the ability to perform replicate analysis on each whole air sample was a noticeable benefit.

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Chapter 6 Performance of Small Evacuated Canisters for the Collection of Personal Air Samples

A traditional industrial hygiene function is measuring air borne exposures, with the preferred method being personal breathing zone samples. Breathing zone samples, samples collected from the collar or lapel area[a], provide the most accurate assessment of an individual's exposure, because they capture the contaminant in the immediate environment surrounding the individual's breathing zone. Variables such as the interaction of the individual with the source(s) of contamination, the proximity of the individual to an industrial process, the mobility of the individual, and the environmental changes that may occur during the air monitoring can all be better assessed if samples can be collected in the breathing zone. As discussed in Chapter 5, the capillary-canister device can effectively collect a larger number of compounds and at a wider range of concentrations as compared to the sorbent samplers. The ability to use a capillary-canister device for breathing zone samples would provide industrial hygienists with a valuable tool to access worker exposures to multiple chemical compounds.

In this chapter, a series of experiments are discussed that compared the use of the capillary-canister device to sorbent tubes and badges in the breathing zone of individuals in a large exposure chamber. The individuals wore all three sampling devices throughout a series of six-hour exposure scenarios. These experiments provide an assessment of how well the capillary-canisters perform as personal breathing zone sampling devices. Additional information is provided in Appendix C.

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Note: The text of this article has been reformatted in accordance with the McGill Thesis Preparation Guidelines.

[a]**Guffey SE, Flanagan M E, van Belle G:** Air Sampling at the Chest and Ear as Representative of The Breathing Zone, Amer. Ind. Hyg. Assoc. J., 62:416-427 (2001).

Abstract

Evaluation of small-evacuated canisters compared to sorbent sampling methods is essential to ensure the devices accurately monitor airborne contamination. This data, in a controlled environment, will provide practitioners with valuable reference information when considering air-sampling campaigns. Six 300 mL stainless steel canisters were used to collect six-hour breathing zone samples on volunteers exposed to styrene in a large exposure chamber. The canisters are specially designed and equipped with a capillary flow controller. Based on the geometry of the capillary, the airflow into the canisters is controlled to a low flow rate, ~0.3 mL/min. The low sampling flow rate allows for the use of small volume canisters as personal samplers to collect gases and vapors. Charcoal tubes and diffusion badges were simultaneously used to collect side-by-side samples for comparison. In addition, an on-line gas chromatograph (GC) documented the concentration of styrene in the exposure chamber throughout the duration of the exposure. The three methods were found to have no statistical difference when compared to the on-line GC values and to each other. In addition, linear regression analysis between the charcoal tubes and the canisters resulted in very good correlation ($R^2 > 0.95$). An evaluation of the bias and precisions (overall uncertainty) of the capillary-canister method, charcoal tubes and diffusion badges were found to be very comparable and within criteria established by European Committee for Standardization in CEN 482. The results indicate that the capillary-canister sampling device can be used as a personal sampler to provide reliable results that are representative of worker exposure.

6.1 Introduction

Exposure assessment of gases and vapors in the field of occupational hygiene requires representative air samples. The personal breathing zone sample is often the best representation of worker exposure.[1,2] In recent years evacuated canisters have become more common in sampling work place exposures to volatile compounds.[3] The canisters are being used to compliment the traditional sorbent sampling techniques. A 300 mL canister with a novel flow control device was developed at McGill University for use as a personal sampler. The focus of the design was to develop a versatile sampler that is simple to use and could effectively collect multiple compounds in a broad range of concentrations for sampling periods of a few minutes up to a 40 hour work week.[4,5]

Personal canisters with the capillary flow controller are placed under a vacuum, < 1 mm Hg, then a specially designed capillary flow controller connected to the canister is used to passively draw an air sample into the canister over an interval of time, such as an entire day, week or possibly longer. The capillary acts in a similar manner as a critical orifice with the geometry of the capillary controlling the flow. As long as the pressure in the canister does not exceed 380 mm Hg (0.5 atm) during the sampling period, the flow rate remains within acceptable ranges (i.e. relatively constant) and the sample collected in the canister is representative of the concentration in the person's breathing zone.[4-6] The capillary flow controller-canister device will be referred to as a capillary-canister device for the remainder of this article and is displayed in Figure 6.1. The canister provides an integrated sample for the period of time sampled. Analysis in the laboratory can be performed without solvent extraction and for many compounds of interest. The elimination of the solvent extraction reduces the use of hazardous solvents, allows for analysis of the whole sample and provides for multiple analysis of the same canister. Analysis can be performed with GC or a GC/MS can be used to identify unknowns. [7-9]

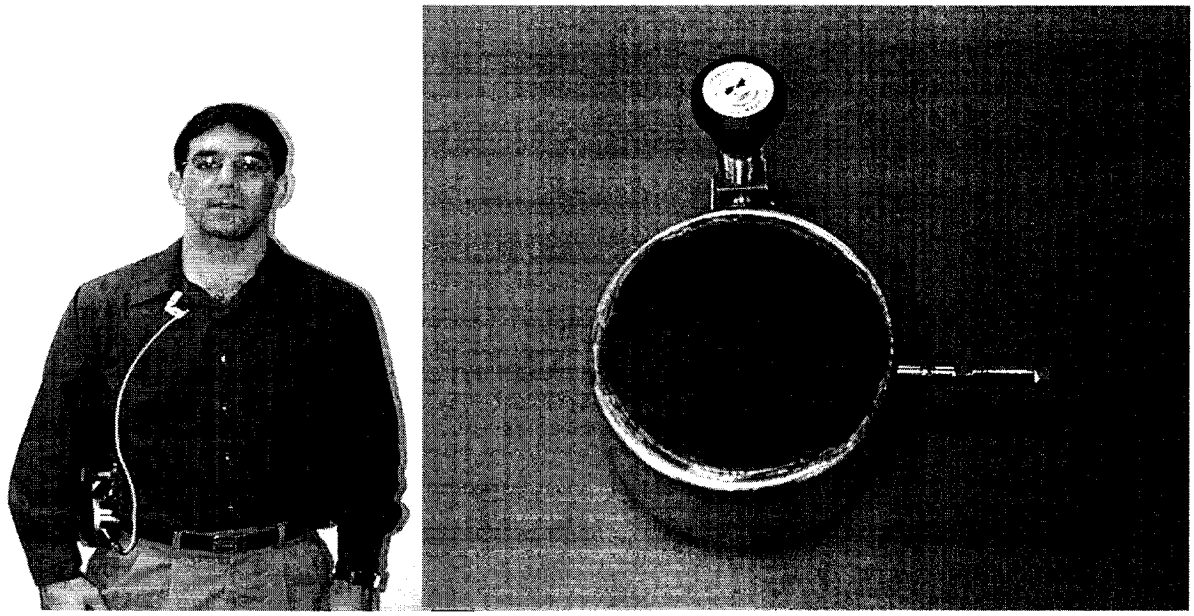

Figure 6.1 Capillary-canister personal air sampler

The capillary-canister sampling system was designed and repeatedly tested over several years in four phases of research at McGill University. The capillary flow control device was initially tested for accuracy of flow rates ranging from 0.05 to 1 mL/min.[5] Simon et al.[10] and Rossner et al.[11] demonstrated the conceptual aspects of the design of the capillary canister system. The capillary-canister system was then tested in a laboratory setting by comparing it to charcoal tubes and diffusive badges in a small exposure chamber.[11] Performance of the capillary-canister system as a personal air sampler on individuals exposed to styrene in a large (18.1 m^3) exposure chamber was the third component of the research and is the focus of this paper. Finally, a field investigation of solvent exposures during a cleaning operation was conducted in a factory environment and will be reported elsewhere.

Previous studies have not addressed the use of evacuated canisters as personal samplers. The purpose of this research was to evaluate the capillary-canister's ability to collect a representative personal sample at a very low flow rate, ~0.3 mL/min. The low flow rate is necessary to collect an eight-hour sample in a small personal canister. Sampling flow rates below 1 mL have not traditionally been used for the collection of occupational hygiene samples. As a result, how

representative are these samples collected at low flow rates is a question that must be evaluated. The replicate samples will allow for an assessment of precision, and the on-line GC will provide an assessment of the accuracy of the capillary-canister system. In addition, two exposure scenarios will include peak concentrations, 2.5 times higher than the constant concentration for the respective scenario. These peak concentrations will allow for an assessment of how well the capillary-canister functions in environments with fluctuating air borne contaminant concentrations.

6.1.1 Styrene Exposure Assessment

Styrene is a volatile liquid used mainly in the manufacture of polymers, copolymers and reinforced plastics, particularly polystyrene and the production of styrene butadiene rubbers. Studies suggest that liver, kidney and neurotoxicity can result from repeated exposure.[12,13] In excess of 90,000 individuals may be exposed to styrene in the workplace in the United States.[14] Exposure levels in the manufacturing processes of reinforced plastics can vary widely, ranging from 20 to 650 mg/m^3.[15-18] Occupational exposure limits include a Threshold Limit Value (TLV) of 85 mg/m^3 [19], a Quebec provincial occupational exposure limit of 213 mg/m^3 [20] and a U S Occupational Safety and Health Administration Permissible Exposure Limit of 426 mg/m^3.[21]

The Department of Environmental and Occupational Health at the University of Montreal, was investigating neurological effects of styrene in the reinforced plastic industry in Quebec, Canada.[22] A component of their research was to expose a group of volunteers to series of different concentrations of styrene for six-hour periods. The justification and details of the toxicology research are beyond the scope of this paper, and will not be reviewed here with the exception of the aspects relating to exposure assessment. The University of Montreal research group was interested in secondary confirmation of the concentrations in their 18.1 m^3 chamber. The primary device was an on-line GC used to monitor

the concentrations for the duration of each exposure scenario. Personal air sampling devices, the focus of this paper, were used to compliment the on-line GC to ensure the chamber concentrations were adequately characterized.

6.2 Methods

6.2.1 Sample Collection

Three personal air-sampling methods were employed to evaluate the concentration of styrene in the large chamber. These three methods, charcoal tubes, diffusive badges and capillary-canisters, were compared to each other and to an on-line GC. Known concentrations of styrene were generated in the chamber while five individuals occupied it for six hours. Two of the methods are traditional methods of air sampling styrene and included collection with solid sorbents for both active and passive samplers.[23-25] The third method, capillary-canister system, was compared to the sorbent methods and to the on-line GC. The multiple methods were used to assess the personal exposures of the individuals in the chamber and to compare styrene levels documented by the on-line GC. [26-28] The GC sample was collected at one location in the chamber while the three field sampling methods were placed at six locations in the chamber. Five samplers were worn by the individuals in the chamber and one was placed adjacent to the location of the GC intake.

All samples were collected in an 18.1 m^3 (2.45 x 2.2 x 3.35 m) chamber located in the Department of Environmental and Occupational Health, University of Montreal. The chamber was rigidly constructed and contained plastic panels on the interior walls and ceiling with a portion of two walls having glass windows for observation of individuals during the tests. The chamber contained a table with five chairs for the participants. Figure 6.2 shows the chamber and the air sample configurations.

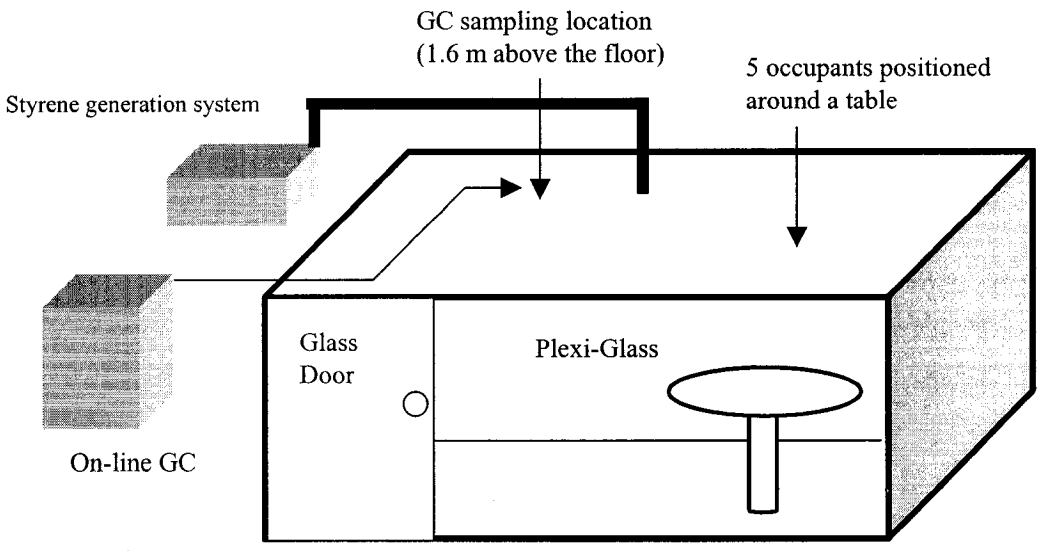

Figure 6.2 Schematic of the 18.1 m^3 exposure chamber

A down draft ventilation system provided a constant flow of air into the room. Airflow was controlled using a calibrated variable speed motor that was set to provide 6768 liters per minute of air into the room. The air was distributed into the room through a series of 16 jets located in the ceiling of the chamber; air exited the room through a series of 6 mm holes perforating the floor. Styrene liquid was introduced into airflow using a small solvent pump and a heated flask. The flow rates of the styrene were adjusted to provide the desired concentration in the chamber, ranging from 0.1 to 1.3 mL/min.

6.2.2 Styrene Exposure Scenarios

The toxicology protocol established six exposure scenarios, where five different individuals were exposed each day and the scenario was run for four days, Friday to Monday.[22] The air monitoring preformed for this research was conducted 1-3 days for five of the six scenarios, 2-6. The exposure scenarios are shown in Table 6.1.

The first scenario was not monitored with the personal samplers because the concentration was repeated in scenario 4. Scenario 2 was monitored but all data for the capillary-canisters was lost due to gas chromatograph failure during scenario 2. Scenario 4 and 5 were designed to be constant concentration throughout the sample period, 21.3 and 213 mg/m^3 respectively. While scenario 3 and 6 were held at 85 and 170 mg/m^3 respectively, with four 15-minute peak concentrations at 213 and 426 mg/m^3 respectively, generated one hour apart. The tests were run from 9:00 am to 3:00 pm with peak concentrations being generated at 11:00 am, 12:15 pm, 1:30 and 2:45 pm. The three field sampling methods were employed in a side-by-side comparison for all scenarios. Charcoal tubes with low flow sampling pumps, passive badges and 300 mL capillary-canisters were placed on subjects just prior to entering the exposure chamber. Each sampler was placed on the subject to collect breathing zone samples with the samplers located on the lapel area of the clothing. The results

of the personal sampling methods were then compared to each other as well as to the on-line gas chromatograph (static sample) that was sampling every few minutes for the entire time the subjects were in the exposure chamber.

Table 6.1 Summary of styrene exposure scenarios

Exposure Scenario For Styrene	Target Concentration mg/m^3	Peaks (4) Conc. mg/m^3	Air (L/min)	Styrene (mL/min)
1	21.3	0	6768	0.1
2	107	0	6768	0.67
3*	85	213	6768	0.53 & 1.3
4	21.3	0	6768	0.1
5	213	0	6768	1.35
6*	170	426	6768	1.06 & 2.7

Note: 1. Tests were run from 9:00 am to 3:00 pm with the start time shifting a few minutes.
2. Test 1 and 2 were not monitored with the personal capillary canisters, but were part of the Toxicology research.
3. Each scenario was repeated four consecutive days, Friday to Monday with personal air sampling occurring 1-3 days each scenario.
* Peak concentrations were generated at 11:00 am, 12:15, 1:30 and 2:45 pm.

6.2.3 Sampling and Analysis

6.2.3.1 On-line GC Methodology

An on-line gas chromatograph model Varian CP-3800 with a flame ionization detector (FID) was used for analysis and was equipped with a fused silica capillary column (J&W Scientific, Folsom, CA) HP-1, 30 m x 0.53 mm x 2.65 um film thickness. Samples were analyzed using a split less injection mode. For all samples the column temperature was maintained at 130°C, while the injector was kept at 160°C and the FID was maintained at 250°C. The GC allowed for the monitoring of the styrene concentrations every few minutes for the entire six hours. The GC sample was drawn from the chamber using a Teflon line and a sampling pump, and then sent through a 10-position valve directly to the injection port. The concentration for the six-hour sample period inside the chamber was an average of 60 analyses done over the six-hour period, providing near-real time monitoring.

6.2.3.2 Charcoal Tubes, Diffusive Badges and Capillary-Canisters

The charcoal tubes and passive badges are established methods that have been used for a number of years, while the 300 mL canister is a method under development. A summary of each method is described. The National Institute of Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM) standard 1501 was used as a guide for sampling and analysis with sorbents. Standard size charcoal tubes (100/50 mg, SKC 226-01, SKC, Eight Four, PA) were used in conjunction with a low flow personal air-sampling pump (SKC 224 series and Gilan113, Sensidyne, Inc. Clearwater, FL).[29] Pumps were calibrated at flow rates between 35 to 75 mL/min. Calibration was performed before and after each day of sampling. The charcoal tubes were placed on tube holders and attached to the lapel of the subject. Each subject was asked to wear the pump for the entire six hours of the test. Upon completion of the test, the sampling train was removed from the subject, and the tubes were capped and placed in a freezer for storage. The tubes were not stored more than five days in the freezer before being analyzed. Sample preparation involved desorbing the charcoal in 2

mL of carbon disulfide for 60 min then 1.0 uL injection into a gas chromatograph. Analysis was performed using a Hewlett Packard 5890 Series II gas chromatograph equipped with a FID. A Supelco – VOCOL capillary column 30 meters x 0.53 mm ID and a 3.0 um film thickness was used to analyze the sorbent samples. Column temperature program for all analyses was maintained at 138°C , with Helium as the carrier gas. [29]

3M Organic Vapor Monitors (OVM) were used in the same manner as the charcoal tubes. A badge was placed on each subject during each scenario. The manufacturer has identified the sampling flow rate of 28.9 ±1.4 mL/min.[30] The badges were transported and stored in the same manner as the charcoal tubes. Desorbing the badge in 2.0 mL of carbon disulfide for sixty minutes was done in preparation for analysis. Badge samples were run using the same GC under the same conditions as the charcoal tubes. Calibration standards were always run along with the samples for both charcoal tubes and diffusive badges.

6.2.3.3 Capillary-Canister

The canisters used in this study were designed at McGill University and built by Meriter, Inc. San Jose, CA. USA. The canisters and valves were made of a high purity stainless steel to reduce the possibility of contamination or sample loss. All canister samples were collected in a 300 mL canister. A deactivated capillary of 0.05 mm in diameter and 10 cm long (J.&W Scientific, Folsom, CA) was connected to each canister. The procedure used to prepare the canisters and sample, was a modified version of the US-Environmental Protection Agency (EPA) TO-15.[8,31,32] The modification was necessary because of the small canister size. Prior to collection, canisters were cleaned by evacuating to a vacuum of 0.05 mm Hg and alternatively flushed with high purity humidified nitrogen three times. Canisters were then evacuated to 0.05 mm Hg and leak tested for at least 24 hours prior to sampling. A Teflon tube (1/8" diameter and 3 feet long) was connected to each canister to allow for sample collection in the

individuals breathing zone.

When the canister is opened, the pressure differential causes the sample to flow into the canister, slowly filling over a period of six hours. Upon completion of the tests, the capillary opening was closed with the use of a fitting. The canisters were then pressurized to approximately 1200 mm Hg with humidified pure nitrogen. The pressurized canisters were allowed to stand for 12 hours and then analyzed with a Hewlett-Packard gas chromatograph (GC) model 5890 series 2 equipped with a FID.[32] A HP-5 capillary column (0.32 mm diameter, 50 m long and a film thickness of 1.05 um) was used for this analysis. The concentrations of styrene collected in the canisters were in the ppm ranges for all scenarios. As a result, the samples did not need to be concentrated using a purge and trap system and could be analyzed by direct injection of the sample into the GC. One mL injections were used for all analysis. A special fitting was designed to allow the canister to be connected directly to the six-position valve that was connected to the GC injection port. Figure 6.3 displays the configuration of the canister analysis system. A rotameter was connected to the exit port of the six-position valve to monitor the amount of sample passed through the valve. This ensured that the sample lines were purged of any residual styrene before the sample was injected.

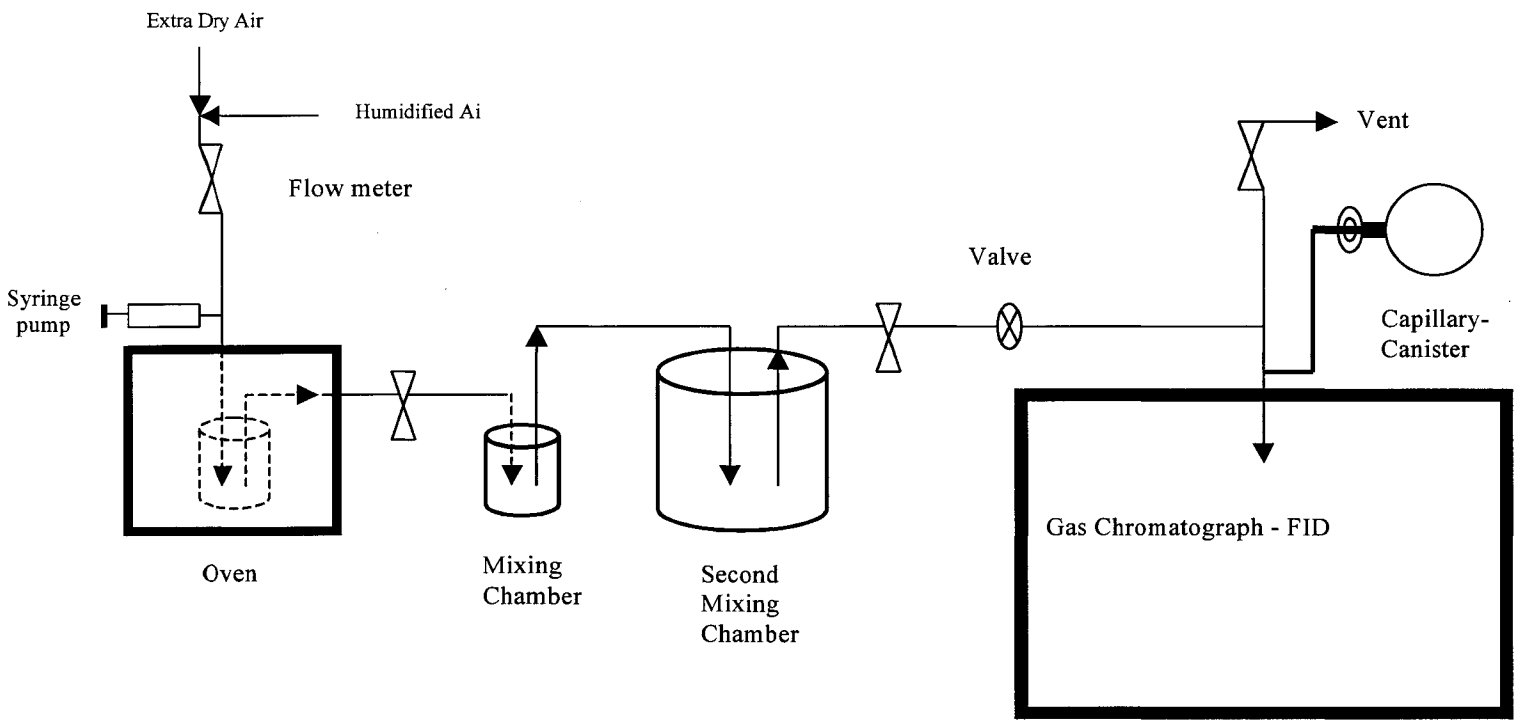

Figure 6.3 Capillary-canister analysis system

6.2.3.4 Data Analysis

The overall uncertainty of the canister, charcoal tube and badge methods were evaluated by examining the bias (accuracy) and precision using the following formula:

$$Overall\ Uncertainty\ (\mathrm{OU}) = \frac{\left|\bar{x} - x_{ref}\right| + 2s_{\bar{x}}}{x_{ref}} * 100 \qquad (6.1)$$

where:

$\bar{x}$ is the mean value of the results of a number n of repeated measurements;

x_{ref} is the reference value of the chamber concentration from the GC;

$s_{\bar{x}}$ is the standard deviation of the mean values ($\bar{x}$).[33,34]

The bias is deviation of the results of a measurement technique from the "true value" of the concentration. Precision is the closeness of the data obtained from repeat measurements. The overall uncertainty was determined by repeated measurements under defined conditions, where the defined conditions were exposure concentration of styrene in the chamber, constant temperature and constant relative humidity on a specific day. In addition, regression analysis between the three air sampling methods and the online GC was performed and expressed as the least squared (R^2) value and the equation of the respective line for each method. The difference between the air sampling methods was evaluated using a student t-test, where $p<0.05$ was considered significant.

6.3 Results & Discussion

The canister performed quite well as a personal sampler when compared to the reference concentration in the chamber. The correlation (R^2) between the online gas chromatograph and the canister sampling system was greater than 0.95 and

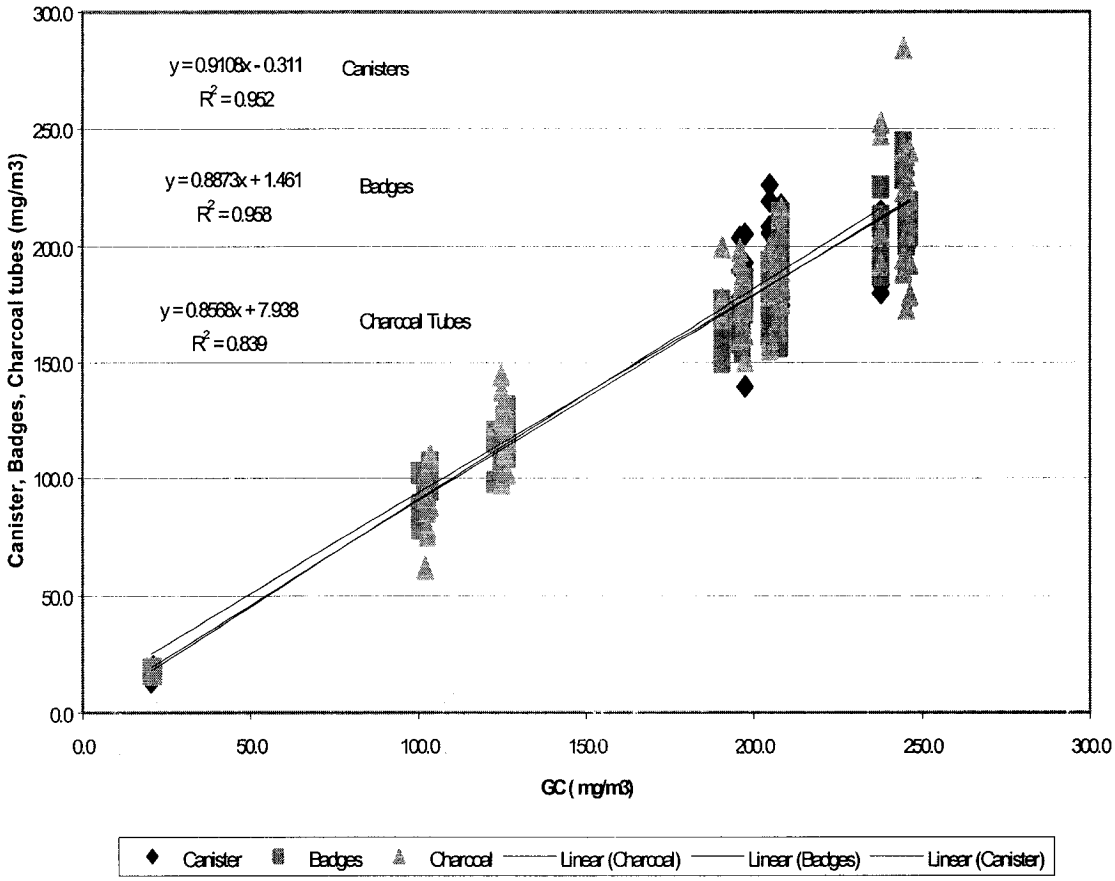

Figure 6.4 Correlation between the styrene concentration measured by gas chromatograph and the concentration measured by capillary-canisters, charcoal tubes and diffusion badges.

displayed a slope approaching 1.0, (y=0.911x –0.311). The diffusion badges displayed a similar correlation to the reference concentration (R^2 = 0.958) and the charcoal tubes were found to have a somewhat lower correlation of R^2 = 0.839. This indicated that all three methods provided representative concentrations of styrene in the chamber. Figure 6.4 displays the relationship of the three personal air sampling methods compared to the on-line GC. No statistical difference was observed between the canister method and the two sorbent sampling methods for all but one test ($p > 0.05$). The one test performed on Nov. 12 did show a significant difference between mean value of the capillary-canisters and diffusive badges ($p=0.044$).

To further evaluate the capillary-canister sampling system the overall uncertainty of the method was calculated to assess the accuracy and precision of the sampler. The sampler was found to meet or exceed the requirements established by European Standard EN 482, *Workplace atmosphere- General requirements for the performance of procedures of the measurement of chemical agents.* The specification of performance required by EN 482 is an overall uncertainty of $\leq$ 50% for concentrations ranging from 0.1 to 0.5 of the chosen occupational exposure limit, in this case the TLV, and $\leq$ 30% for concentrations ranging from 0.5 to 2 TLVs. Table 6.2 displays the mean concentrations for each test and overall uncertainty data for each set of exposures evaluated by all three methods. One canister test was found to exceed the EN 482 criteria, and two charcoal tube tests were found to exceed the 30 % overall uncertainty criteria. The badge data produced the best precision of the three methods and therefore display the lowest overall uncertainty values. This is a result of the relative standard deviation for the badges being approximately 50 % of the other two personal sampling methods. Figure 6.5 shows a bar graph summarizing all three methods for each test.

Table 6.2 Overall uncertainty of diffusion badges, charcoal tubes and capillary-canister associated with styrene collection

	Gas Chromatograph		Canister				Charcoal Tubes				Badges			
Exposure [1]	Reference mg/m^3	Fraction TLV[2]	mean mg/m^3	SD mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	SD mg/m^3	RSD %	Overall Uncertainty	mean mg/m^3	SD mg/m^3	RSD %	Overall Uncertainty
Oct. 27	21.00	0.25	18.50	1.53	8.270	26.48					17.5	0.83	4.743	24.57
Oct. 28	20.45	0.24	15.80	1.71	10.823	**39.46**					17.4	0.83	4.770	23.03
Oct. 15	113.30	1.33	113.00	7.85	6.947	14.12	115.9	7.5	6.5	15.59	99.8	2.50	2.506	16.37
Nov. 10	208.15	2.44	194.70	17.62	9.050	23.39	189.7	17.1	9.0	25.26	203.1	6.09	3.000	8.28
Nov. 12	204.91	2.41	201.90	21.31	10.555	22.27	181.1	5.8	3.2	17.34	179.3	8.96	4.999	21.27
Nov. 24	213.85	2.51	196.40	15.81	8.050	22.95	200.2	26.0	13.0	**30.74**	182.3	10.94	6.001	24.98
Nov. 25	219.82	2.58	182.60	14.42	7.897	**30.05**	199.9	22.0	11.0	29.06	201.1	6.03	3.000	14.01
Nov. 26	221.53	2.60	188.50	12.23	6.488	25.95	190.3	19.5	10.2	**31.69**	195.8	5.87	2.998	16.91
	Aggragate Overall Uncertainly					**25.58**				**24.95**				**18.68**

[1] **n= 5 for each test**

[2] **TLV = 85.2 mg/m^3 (20 ppm)**

[3] **GC Reference is the average concentration measured during the six hour sampling period from n=60 measurements.**

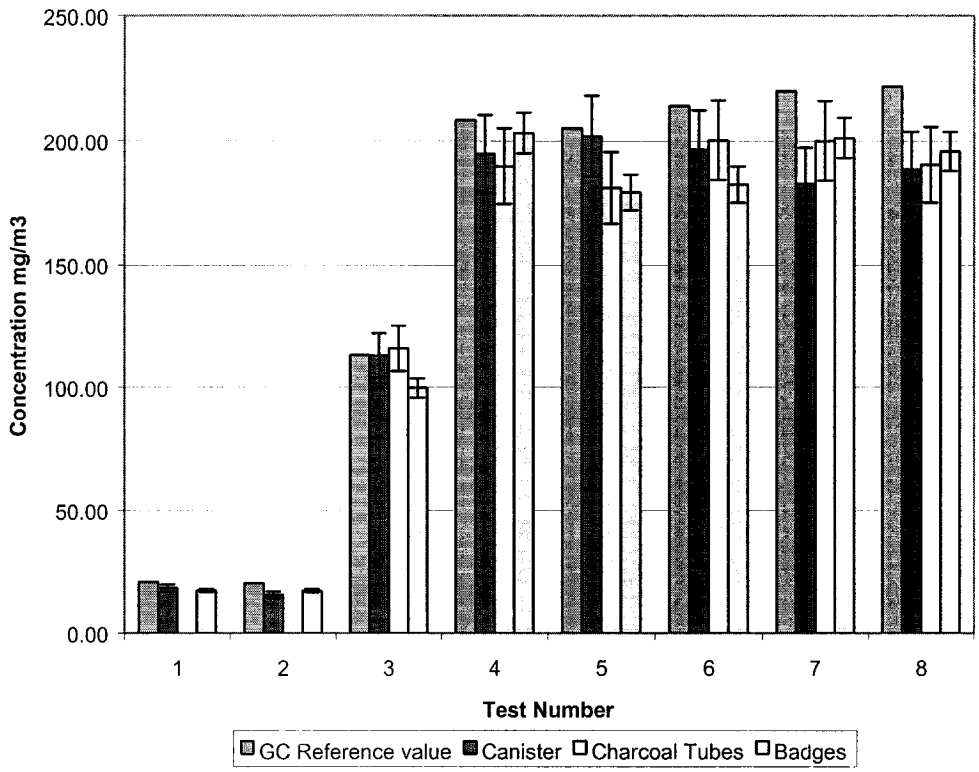

Figure 6.5 Comparison of air sampling methods used to evaluate styrene levels in the 18.1 m^3 exposure chamber (n=6 for each method).

All three methods were found to provide values slightly lower than the GC reference. The ratio of the mean value for the respective sampling method and the GC value were: canisters 0.9, charcoal tubes 0.92, and badges 0.88, and the RSD for the samplers were 8.6, 6.1 and 5%, respectively. One would expect a distribution of data above and below the reference value for the personal air sampling methods, if the GC was the "true concentration" in the breathing zone and there was no systematic errors associated with the experimental setup. However, the GC sample was a static sample and was always drawn from the same location in the chamber. The ~10% underestimation of concentrations measured by the personal samplers may be explained by two conditions: the different orientation of the subjects in the chamber and the steady state concentration in the chamber. The different positions of the individuals in the chamber may account for some deviation from the GC reference values because of somewhat different concentrations in areas of the chamber. Also, the door of the chamber was opened for each test when moving 5 subjects into the chamber at the beginning, allowing for a 5 minute break mid way through, and when the toxicologist enters the chamber twice during the six hour exposure. These activities could effect the steady state concentration in the chamber and may account for some of the variation between the GC values and the personal sampling methods. A series of calculations were done in an attempt to examine if the disturbances that occurred in each test would cause a 5-10 percent reduction in concentration. The static GC sample was located the furthest from the door and would be effected the least by the in-flux of uncontaminated (no styrene) air. The calculations were a simplified form of the well-mixed box mass balance equations, (eq. 6.2 & 6.3) which provide a reasonable estimate of average concentration change with respect to time.[35] The estimates were done to show that this was a plausible explanation and not to construct a model of the styrene concentrations in the room. The results from the calculations support the 5-10% approximate reduction in average room concentration of styrene. Essentially, the steady-state condition did not reflect the actual condition in the chamber for the entire six hours. A reduction in concentration would have

occurred each time the door was opened, resulting in a time weighted average somewhat lower than the concentration predicted by the on-line GC values.

$$C_{Aroom} = \left(C_{Aroom0} - \frac{G_A}{Q} \right) * e^{-\frac{Q(\Delta t)}{V}} + \frac{G_A}{Q} \qquad (6.2)$$

$$C_{Aroom} = \frac{G_A}{Q} * \left(1 - e^{-\frac{Q(\Delta t)}{V}} \right) \qquad (6.3)$$

where, C_A is a concentration of contaminant (mg/m^3), G_A is the generation rate of mg/min of contaminant A, Q is the ventilation rate, (m^3/min), V represents room volume (m^3), t is the time (min).

6.3.1 Peak Exposures

Two exposure scenarios, 3 and 6, included four peak concentrations during the six-hour tests. The scenarios with the peak concentrations provided an opportunity to evaluate the performance of the canister in a controlled environment with fluctuating concentrations. Theoretically, the capillary-controller sampling flow rate should not effect the concentration found in the canister. However, given that the flow rates are below 1 mL/min and diminish slowly over the sampling period, the ability to accurately capture peak concentrations over the course of a sampling period were in question. To evaluate this, the overall uncertainties for the tests with peak concentrations were compared to the tests with constant concentrations using a t-test. No statistically different results were found for the canister method for the scenarios with the peak concentrations compared to the scenarios with the constant styrene concentrations ($p<0.05$). This indicated that in these peak concentrations were adequately captured by the low flow rates of the capillary flow controller.

6.4 Conclusions

The capillary-canister personal sampler was shown to collect representative personal samples for styrene concentrations in a controlled environment for challenge concentrations ranged from 0.25 to 2.5 times the TLV. The capillary canisters showed no statistical difference between sorbent sampling methods. The data obtained did show that the canister sampler under sampled the reference concentration (GC) by ~10%, however, the under sampling was similar to that of charcoal tubes and diffusion badges and was attributed to the manner in which the GC samples were collected. No negative influence occurred due to the peak concentrations generated in the chamber. This is an important factor when considering the performance of a field instrument, because the concentrations frequently fluctuate in the work environment. The overall uncertainty of all canister samples was 25%, this being within the guidelines established by EN 482. The performance in this study suggests that the canisters are well suited for field sampling in occupational hygiene and could effectively complement or replace the more common sorbent-based methods for field sampling. In addition, another benefit when evaluating the usefulness of a field sampling method is the ease of use in sampling and analysis. The canister was simpler to use than the charcoal tubes because no pumps were needed and no calibration was necessary. The analysis of the chemicals in the canisters does not require the use of hazardous chemicals for a desorption step, is less time consuming than the sorbent methods and provides for a wider variety of chemicals to be analyzed from a single sample. While the specific chemical used in this study, styrene, can be adequately collected on charcoal media, the capillary-canister sampler can be used in a much broader application. Multiple chemicals can be collected and widely varied concentrations can be analyzed from a single sample, making the capillary-canister a versatile sampler that may provide advantages for occupational hygiene and community monitoring.

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Chapter 7 Field Evaluation of Small Evacuated Canisters for the Collection of Long Term Samples During a Solvent Cleaning Operation.

A significant effort was made to determine the effects of environmental conditions on the capillary-canister device ability to collect representative samples in the two laboratory chamber studies (Chap 5 & 6). However, there may be some factors that exist under field conditions (work place) that may influence the performance of the capillary-canister device. An example of such factors include, rapidly changing contaminant concentrations, the presence of interfering compounds and changing environmental conditions. A series of experiments were conducted under actual field conditions in a manner consistent with how the capillary-canister is anticipated to be used. In this chapter we examine the final phase of this method development, field testing. We also explore the usefulness of the capillary-canister to sample for extended periods of time, 40 hours.

From the inception of this research, a primary objective was to develop a sampler capable of collecting a long-term sample. The ability to accurately collect an air sample over an extended sampling period could be beneficial for industrial and non-industrial exposure assessments. Whether the sampling environment is a traditional production factory, an office environment, the perimeter of a hazardous waste site, or the community down wind of industrial emissions, the need to assess the airborne contamination over periods greater than 8 hours may be a prudent sampling strategy in some instances. The forty-hour sampling (five consecutive work shifts) is compared to traditional eight hour sampling in a factory environment. A model is also proposed to estimate bias.

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Note: The text of this article has been reformatted in accordance with the McGill Thesis Preparation Guidelines.

Abstract

Small evacuated canisters (300 mL) equipped with a unique capillary flow controller were used to evaluate air borne concentrations of Stoddard solvent. The characteristics of the flow controller allowed for the collection of an air sample for 40 hours (five consecutive work days). Long-term sampling (> 8 hours) is rarely performed in industrial hygiene; however, it may provide valuable information to characterize worker cumulative exposures for some processes. The definition associated with American Conference of Governmental Industrial Hygienist's Threshold Limit Values suggests that the TLVs may be applicable to workweek exposures in addition to 8-hour exposures. A field study was performed to evaluate the feasibility of collecting a 40-hour sample using small canisters. Six canister samplers were used to monitor a cleaning operation for an entire workweek, while 30 diffusive badges, six each day, were simultaneously used to monitor the same process. No statistical difference was found between the time weighted average for the two sampling methods, $p>0.05$. The canister samples integrate the air borne concentrations for an entire workweek and therefore peak concentrations are not explicitly observed. An examination of peak exposures using simulated concentrations was modeled to assess if a bias was associated with the long-term sampling when peak concentrations are present. The bias was determined to be less than 10% for the conditions evaluated. In conclusion, long-term sampling with the small evacuated canisters was found to provide comparable results and was more efficient than sampling with the passive sorbent method.

7.1 Introduction

In order to effectively develop and design control strategies for exposures to air borne contaminants, field measurements are necessary to characterize worker or community exposures. Air sampling methodologies that allow for the efficient collection of field samples can increase the number of samples collected on a potentially exposed group, resulting in a more complete characterization of exposure. Such air sampling methods also provide dependable exposure assessment data necessary to assess occupational and community health risks.[1,2] New air sampling techniques that are cost effective, easy to use and provide accurate results provide another tool to refine the exposure assessment process.

A novel air-sampling device used to collect gases and vapors for extended periods was designed and tested at McGill University in 1997. [3,4,5] The device, an evacuated canister equipped with a special capillary flow controller, was designed to collect a whole air sample from the breathing zone of an exposed individual for time periods ranging from a few minutes to a week. This sampler will be referred to as a capillary-canister device throughout this article. The device was previously compared to charcoal tubes and diffusive badges in both a small chamber (2.0 L) and in a large exposure chamber (18.3m^3), where test subjects wore the capillary-canisters as personal samplers.[6,7] Results of the chamber studies showed a good correlation with the sorbent based sampling methods for multiple chemicals collected over six to eight hour periods. As a follow-up of the chamber evaluation process of the capillary-canister device, and the focus of this article, field testing of the device at an aluminum extruding factory was performed. Capillary-canisters were compared to diffusive badges during a solvent cleaning operation. The test was designed to assess the long-term sampling capabilities, 40 hours, of the canister as compared to a series of diffusive badges used to sample each day for the entire week. The long-term sampling capability of the canister is unique and may be useful for some sampling campaigns.

Occupational hygienists frequently use multiple exposure limits, such as action limits, short-term exposure limits and 8-hour time weighted averages. [8] A long-term exposure limit may be a useful extension of the existing exposure limits. Several authors in the literature have explored the concept of Long Term Average-Occupational Exposure Limits (LTA-OEL), where long-term may apply to 40 hours, weeks, months or years.[9-12] Hewitt (1997) and Rappaport et al. (1991) focused on the statistical aspects and consider the possibility of using a fraction of the 8-hour time weighted average as a LTA-OEL, 10% to 25% of the current TLVs is suggested. Confidence intervals associated with multiple eight-hour air sampling measurements collected over weeks to months could be used to establish the LTA-OEL.[10,11] Mulhausen (1998) et al. suggests an overall strategy of weekly, monthly or yearly LTA-OELs, depending upon the agent, to control the cumulative dose acquired by the employee.[9] Each of the above authors identifies the precautionary note that LTA-OELs must always be used with shorter term OELs to ensure that workers are protected from acute exposures as well. Also, it is recognized that for some chemicals dose rate is important, because multiple short-term high doses can increase the risk of disease even if the long-term cumulative dose is low.

Specific examples of LTA-OELs have been issued by Britain and NIOSH. A British directive was issued in 1978 for vinyl chloride of 3 ppm for a one year standard and 7 ppm for an 8-hour time weighted average.[13,14] The NIOSH 8-hour recommended exposure limit (REL) for coal mine dust was reduced to 1 mg/m^3 in 1995. A long term average exposure to coal mine dust of 0.5 mg/m^3 was used by NIOSH to establish the 1 mg/m^3 eight hour time weighted average. [15] The rational used by NIOSH was based on the 8-hour REL value of 1 mg/m^3 being the 95^{th} percentile of the mean single daily exposures of 0.5 mg/m^3.

In addition to these specific examples, the American Conference of Governmental Industrial Hygienist (ACGIH) Threshold Limit Values-Time Weighted Average (TLV-TWA) definition states, "In some instances, it may be

permissible to calculate the average concentration for a *workweek* rather than a *workday*".[16] This statement clearly implies a LTA-TLV of 40 hours, for some chemicals under some circumstances. However, ACGIH does not provide examples or criteria that would define the "instances" in which the TLV should be considered a work week average. The justifications for these LTA-OEL are made by the respective organizations and will not be further discussed here. The examples are provided to show that occupational hygiene organizations and practitioners have considered LTA-OELs for some agents for a number of years. A sampling device that allows for air sampling longer than eight hours, such as 40 hour sampling, may be useful to examine chronic exposures and how the results compared to existing or future LTA-OELs. Currently, equipment to collect long-term personal samples is not readily available to occupational hygienists.

Interday variability among exposures in the workplace can be extensive, 3-100 fold, in many industrial processes.[11,12,16] If one can effectively capture a 40-hour sample to characterize an exposure for a working week, it could be a significant improvement over the sampling approach of a single eight-hour sample for compounds with chronic toxicity. Intuitively, the 40-hour sample will not characterize the peak exposures one encounters, however it will better estimate the long-term average that reflects the cumulative exposure of the individual. Several articles in the literature conclude that in general, the risk of chronic disease depends upon the mean exposures received over time and that short-term exposures are less likely to influence the long-term disease.[17-20] Also, if the data is assumed to be log-normally distributed, controlling the mean exposure will also likely control the right tail of the log-normal distribution.[21] Rappaport (1991) performed an analysis of the relationship of mean, variance and length of monitoring, concluding that the estimated variance around a mean based upon a weeklong measurement (five shifts) would be less than that of the variance based on measurements of a single shift, assuming sampling is random and for a specific process.[11] Further, he concludes that to obtain the most precise information about the long-term exposures, multi shift sampling should be

considered and any compromise between sample size and precision should always lean toward increasing sample size.

The implementation of the monitoring technique that will allow for the collection of a 40-hour sample could lead to several different exposure strategies and improved characterization of exposure. Examples of extended exposure strategies could include: monitoring five consecutive 8-hour workdays to examine the workweek exposure, selecting five random days to sample over a one-month period or examining a series of tasks that occur over several weeks. These types of sampling strategies are very difficult to perform using sorbent methods. In addition, the sampling and analysis would likely be cost and time prohibitive for most organizations. The use of the capillary-canister device that samples for 40 hours would likely result in greatly reduced labor and analysis costs.[22]

To explore the feasibility of long-term sampling an industrial process that generates gases or vapors throughout the workweek was identified. The long-term sampling is most useful for chemicals with long term health hazards, however, the process chosen for this study was deliberately a chemical of relatively low toxicity to ensure no workers were exposed to elevated levels of chemicals with long term health hazards. In addition, small concentrations of compounds are more difficult to sample and analyze, thus low concentrations provide for a more rigorous test of the sampling system.

7.1.1 Aluminum Fabrication

Access to a solvent cleaning operation in a large aluminum fabrication facility (ALCOA Massena Operations) provided an opportunity to evaluate the performance of the capillary-canister device over 40-hour workweek in an actual industrial environment. A location that had a relatively uniform use of solvents with low concentrations of airborne vapors was of interest to evaluate the performance of the capillary-canister. At the facility, aluminum wire and bar are

cold extruded through dies of various shapes and sizes. The dies are coated with a heavy oil to aid the extrusion process. After a series of extrusions the dies must be removed from the extrusion machine and cleaned. Workers remove the heavy oil from the dies with Stoddard solvent. Using charcoal diffusive badges as a comparison method to measure the concentration of the vapors in the air, the field sampling capabilities of the capillary-canister were assessed. The objectives of this research are to evaluate the capillary-canisters in a field environment and to compare the long-term exposure measurements (40 hours) to sequential eight-hour measurements.

7.2 Methods

The cleaning operation at the aluminum fabrication facility is performed five days a week throughout the year. One worker cleans approximately 40 dies per day. The die is washed with the Stoddard solvent using a hose in the wash basin. The worker then removes the small amounts of aluminum with abrasive paper and small hand tools. Each die requires about 8-10 minutes to clean. Table 7.1 displays the number and types of dies cleaned during the monitoring. The dies range in size from 10 cm in diameter and weighing 10 kg to 40 cm in diameter weighing 50 kg. The actual number and type of dies that are cleaned is dependant upon the production cycles and the types of product being extruded. Six capillary-canisters were used, each canister sampled for the entire 40 hours of the workweek. Simultaneously, 30 diffusive badges were used, 6 each day, to sample for the entire workweek. The two methods were clustered on a ring stand adjacent to a Safety Kleen® wash basin. All samplers were located within 10 cm of each other and within 20 cm of the lip of the wash basin. Figure 7.1 displays a diagram of the sampling configuration. Area sampling was chosen over personal sampling to ensure that replicates could be obtained for each sampling method. It was determined to be impractical to fix 12 samplers to a worker. The area sampling was considered to be somewhat representative of the worker exposure because of the location of the solvent wash basin with respect to the worker's breathing zone. However, the primary focus of the

sampling was not to characterize worker exposures, but to evaluate how the capillary canister performed with respect to the diffusive badges over the entire workweek. Based on information from the company, the concentration of the airborne Stoddard solvent was expected to be low, 5% of the TLV (TLV-TWA = 572.6 mg/m^3).[16]

Table 7.1 Die cleaning process

	Number dies cleaned by size (cm)							
	10 (cm)	15	18	23	30	35	40	**Total**
Week - 1								
Monday	12	10	1	1	0	4	2	30
Tuesday	7	14	3	4	0	6	6	40
Wednesday	16	7	9	6	1	1	1	41
Thursday	9	6	5	6	1	1	0	28
Friday	24	13	9	4	0	2	0	52
Week - 2								
Monday	17	15	0	3	0	0	0	35
Tuesday	12	10	2	2	3	7	2	38
Wednesday	12	13	1	1	1	5	0	33
Thursday	26	11	2	1	0	0	0	40
Friday	20	14	0	0	1	7	0	42

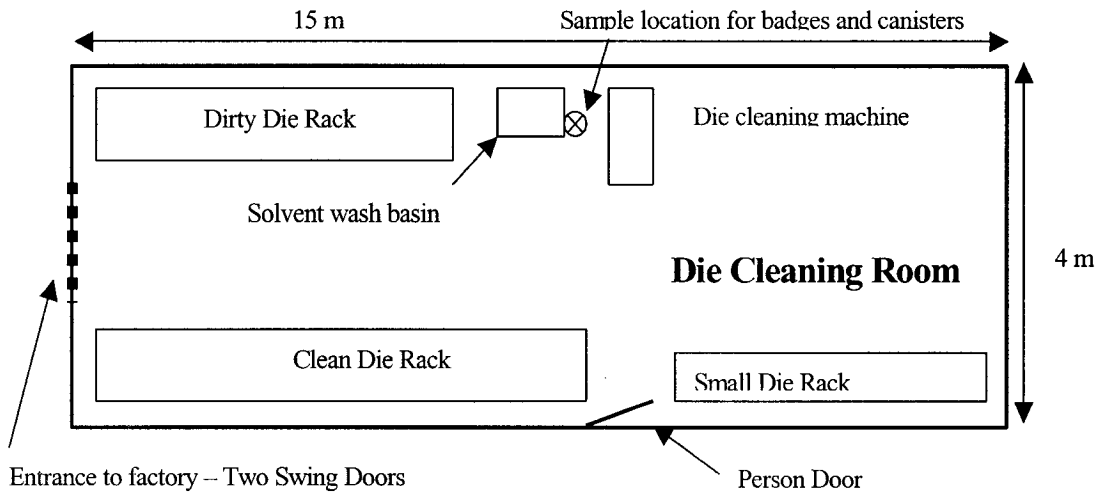

Figure 7.1 Sketch of the die cleaning room. The worker washed the dies in the solvent wash basin and then removed the deposits of aluminum on the table of the die cleaning/honing machine. Factory workers brought in used dies and took out clean dies through the swing doors at the end of the room.

7.2.1 Sampling and Analysis

The material used to clean the dies was Safety-Kleen Premium Solvent® (Safety-Kleen Corp. Columbia SC). It is a light petroleum distillate consisting of a mixture of C_9 to C_{11} compounds, (CAS # 84742-47-8). Common synonyms are Stoddard solvent and petroleum naphtha. The molecular weight and density of decane (C_{10}) are suggested by the manufacturer for use as an approximation for calculating concentrations. Analytical standards were made using the bulk Stoddard and as a cross reference neat decane (J.T. Baker, Phillipsburg, NJ) was used to develop analytical standards.

7.2.2 Capillary Canister

The canisters used in this study were designed at McGill University and built by Meriter, Inc. San Jose, CA. USA. The canisters and valves were made of a high purity stainless steel to reduce the possibility of contamination or sample loss. All canister samples were collected in a 300 mL canister. A deactivated capillary 0.05 mm in diameter and 40 cm long (J.&W Scientific, Folsom, CA) was connected to each canister, providing a flow rate of 0.035 mL/min. The procedure used to prepare the canisters and sample, was a modified version of the US-Environmental Protection Agency (EPA) TO-15.[23,24] Prior to collection, canisters were cleaned by evacuating to a vacuum of 0.05 mm Hg and alternatively flushed with high purity humidified nitrogen three times. Canisters were then evacuated to 0.05 mm Hg and leak tested for at least 24 hours prior to sampling. A Teflon tube (1/8" diameter and 3 feet long) was connected to each canister to allow for sample collection at the solvent wash basin.

The sampling was initiated at approximately 7:00 am each morning and terminated at 3:00 pm each afternoon, Monday through Friday. Each day the canisters were turned off at the end of the shift until the beginning of the next shift. The canisters were then pressurized to approximately 1000 mm Hg with humidified pure nitrogen. The pressurized canisters were allowed to stand for 12 hours, and then analyzed with a Hewlett-Packard gas chromatograph (GC)

model 5890 series 2 equipped with a FID.[24] A HP-5 capillary column (0.32 mm diameter, 50 m long and a film thickness of 1.05 um) was used in this analysis. The concentrations of Stoddard collected in the canisters were in the ppm ranges. As a result, the samples did not need to be concentrated using a purge and trap system and could be analyzed by direct injection of the sample into the GC. One mL injections were used for all analysis. A special fitting was designed to allow the canister to be connected directly to the six-position valve that was connected to the GC injection port. A rotameter was connected to the exit port of the six-position valve to monitor the amount of sample that passed through the valve. This ensured that the sample lines were purged of any residual Stoddard solvent before the sample was injected.

7.2.3 Badges

Six 3M Organic Vapor Monitors (OVM) were placed in close proximity to the six capillary canisters, within 2 cm (3M Company, Minneapolis, Minnesota). At the end of the shift the badges were removed from the ring stand, capped and stored in a freezer until the end of the week when all sets of badges were analyzed. The National Institute of Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM) standard 1550 and a 3M sampling and analysis guide for OVM 3500 were used as guides to sample and analyze the 3M badges for Stoddard solvent. The manufacturer has identified a sampling flow rate of 24.3 mL/min.[25, 26]

Using diffusive badges as area samplers can result in an under estimation of exposure if the airflow across the badge is too low, < 0.2 m/s.[26] The air flow in the shop was measured prior to selecting the area for sampling and several times during the two weeks of sampling. In each case, the airflow was greater than 0.13 m/s (25 fpm) in the sampling area, averaging 0.18 to 0.25 (35 to 50 fpm). The air currents in the room were a result of the air exchange between the die cleaning room and the factory where the extrusion process was performed.

Sample preparation involved desorbing the charcoal in 2 mL of carbon disulfide for 60 min then a 1.0 uL injection into a gas chromatograph was made. Analysis was performed using a Hewlett Packard 5890 Series II gas chromatograph equipped with a FID. A Supelco–VOCOL capillary column 30 meters x 0.53 mm ID and a 3.0 um film thickness was used to analyze the sorbent samples. Column temperature program for all analyses was an initial temperature of 138°C increased to 153°C at 1.5°C per min. Helium was used as a carrier gas.[26] Five calibration standards were prepared and run with each set of samples for the diffusive badges. Standards were prepared by diluting an appropriate amount (1 to 100 uL) of Stoddard solvent in 10 mL CS_2, more dilute standards were prepared by diluting these stock solutions by 1:10 or 1:100.

7.2.4 Data Analysis

The mean and coefficient of variation of the sets of six replicate samples were calculated. An F-test was used to assess whether there are differences in the variance between the two monitors. A $p<0.01$ was considered significant for the F-test. A determination of any systematic difference between the capillary canister method and the diffusive badges were tested using a t-test, where $p<0.05$ was considered significant.[27] Environmental or industrial hygiene field data can be normal or log normal distributed, therefore, the Shapiro-Wilk W-test for normality was completed on both the badge and capillary-canister sampling data. In addition, a non-parametric statistics, the Mann Whitney, test was performed to further evaluate the statistical difference between the mean values of the two sampling methods.[28]

Table 7.2 Example of one day of diffusive badge data

Sample Number	GC Area	Mass ug	Flow Rate mL/min	Time min	Concentration (mg/m3)
29-1	75179	205.8	24.3	450	19.23
29-2	71196	194.9	24.3	450	18.21
29-3	75791	207.5	24.3	450	19.39
29-4	91176	249.6	24.3	450	23.32
29-5	103059	282.2	24.3	450	26.36
29-6	82675	226.4	24.3	450	21.15
Mean	**83179**				**21.3**
STD	**12013**				**3.07**
RSD	**14.40**				**14.40**

7.3 Results & Discussion

Comparison of diffusive badges and capillary canisters were made to evaluate the effectiveness of the capillary-canisters in real world conditions. Table 7.2 displays an example set (one day) of airborne concentrations collected by the diffusive badge. Ten data sets similar to the set presented in Table 2 were collected. The sampling was performed for five consecutive days for two consecutive weeks. The coefficient of variation for the badge data sets ranged from 4 to 16%, with a mean value of 11.5 ± 3.8%. The badge method was used as a benchmark to compare the capillary-canister samplers. Six capillary-canisters were used to collect samples simultaneously with the diffusive badges. However, each capillary-canister collected a one-week sample as opposed to the 8-hour sample collected by the diffusive badges. The mean value of all 30 badges was compared to the average concentration collected by the six capillary-canisters. Table 7.3 displays the airborne concentrations collected by the badges and capillary canisters. The mean and standard deviation values for each day, as measured by the badges, show the variability of the day-to-day airborne concentrations. The Shapiro-Wilk W-test failed to reject a normal distribution and therefore normal statistics were used to evaluate the data sets. No statistically significant difference was observed between the two methods for the mean concentrations for each week sampled using a t-test ($p>0.05$). In addition, an F-test was used to examine if a statistical difference between the variances was observed for the two methods. The test was performed because the first week of data displayed a seemly high variance for the canisters as compared to the badges, while the second week of data showed the opposite relationship. A statistical difference was found for the first week of data ($p=0.09$) yet, the second week did not show a statistically significant difference ($p=0.22$).

Table 7.3 Summary of diffusive badges and capillary-canister data

	N	Mean Week - 1	STD	N	Mean Week - 2	STD
Badges		mg/m^3			mg/m^3	
Monday	6	16.4	1.87	6	30.2	2.13
Tuesday	6	29.1	3.32	6	42.7	1.82
Wednesday	6	15.2	2.22	6	38.0	5.77
Thursday	6	21.6	3.53	6	31.1	3.60
Friday	6	21.3	3.07	6	35.7	3.72
Week long Mean	30	*20.7	5.49	30	*35.5	5.14
Canisters						
Week long Mean	6	*18.7	8.21	6	*33.1	4.07

*No statistically significant difference between the two sampling methods for week long means ($p > 0.05$), where t-statistic for week 1 = 0.73 and week 2 = 0.95 compared to a t critical value of 2.03

The capillary-canisters were found to measure a slightly lower concentration than the badges, 9.6 and 6.6 % respectively for the two weeklong averages. This could indicate that the capillary-canisters were under sampling airborne concentrations to some extent. However, since the coefficient of variations were greater than 11% for both methods for the weeklong mean values, one cannot conclude that the canisters were under sampling.

A series of t-tests were done to evaluate if a significant difference between the 40-hour canister values and daily time weighted average values sampled by the badges. No significant difference was observed between the daily averages and the 40-hour mean value collected by the canister for eight of the 10 days sampled. The second day (Tuesday) of sampling for both weeks were found to have statistically different mean values, $p= 0.023$ and $p= 0.001$. Airborne levels were 30 and 55% higher respectively, on those two days. The number of dies cleaned on either Tuesday was not different than the other days, however, the number of large diameter dies (30, 35, 40 cm) cleaned was 2-3 times the number cleaned on the other days. Therefore, it was concluded that the size of the dies is a determinant factor for exposure because of the amount of solvent used and the manner in which the larger dies are cleaned.

The fluctuations in airborne concentrations observed during a sampling period, as seen on two days of the 10 days sampling, is inevitable and will always be present in workplace and community measurements. The comparison of the eight hour time weighted average samples to the forty hour time weighted average samples was done in this study to examine if there was a difference between the mean values and variances of the two methods. This study only examined two weeks of sampling with the capillary-canisters. To further assess how peak values during the sampling period may affect the final sampled concentration, a series of hypothetical exposure scenarios were simulated. The simulation is designed to examine how the final concentration collected by the

capillary-canisters is affected by peak concentrations occurring at different times during a weeklong sampling campaign. Figure 7.2 displays an example of the hypothetical exposure scenarios and the corresponding estimated exposure concentrations.

7.3.1 Simulation Model for Peak Concentrations

A number of important characteristics of the capillary-canister sampler need to be emphasized here to explain how the simulation model was used. First, the delivered flow rate of the capillary flow controller slowly decreases over the sampling time and this could result in inaccurate estimation of exposure depending upon concentration fluctuations in the sampled atmosphere. Also, the long-term sampling smoothes peak concentrations because the entire weeks sample is collected in the one canister. Given that the sampler is used to characterize the average exposure of a target population over long periods of time, peak values or short fluctuations should generally not be a concern. As a result, the change in flow over time, 15 -20% reduction in flow over a week long sampling period, should be acceptable for most sampling campaigns. To evaluate the amount of sampling bias related to the flow rate slowly decreasing and the occurrence of peak concentrations in sampling environments, several hypothetical scenarios were created to evaluate the error one would encounter if peak values resulted at different times during the sampling period.

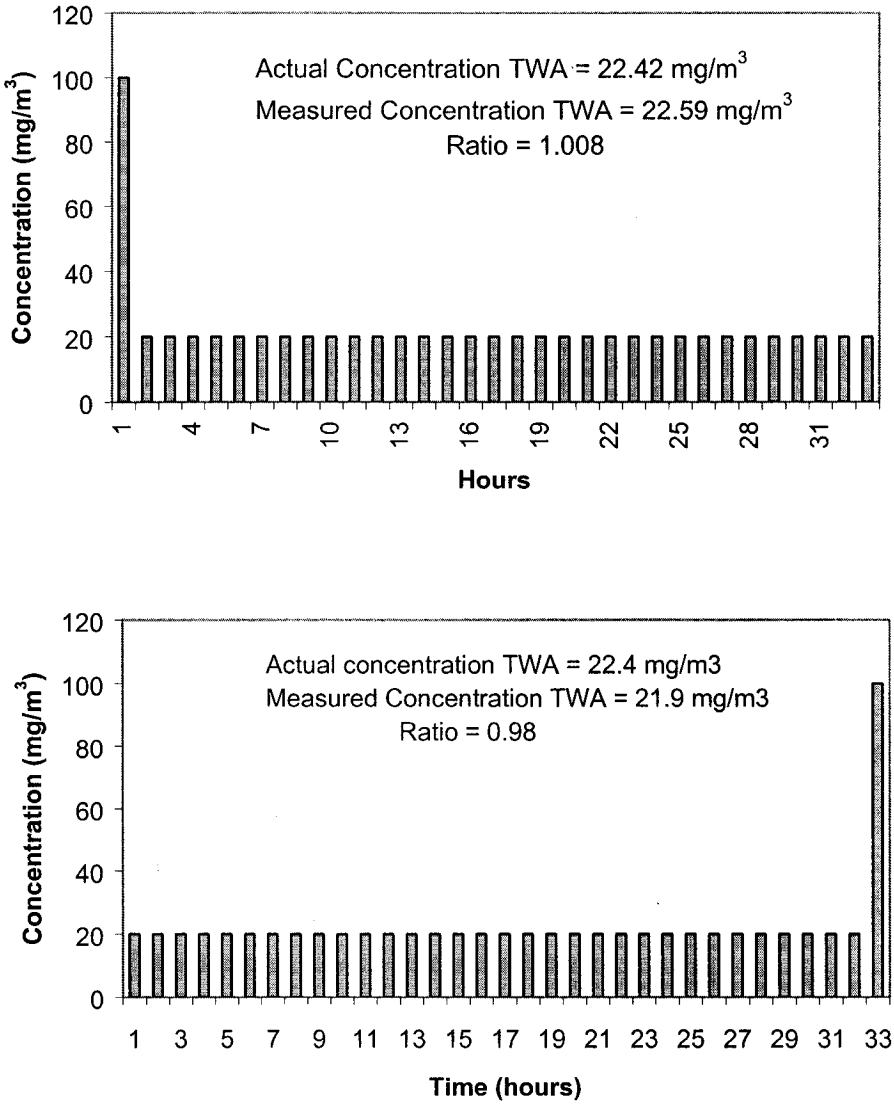

Figure 7.2 Comparison of predicted capillary-canister results for a hypothetical scenario of a process that has an airborne concentration of 20 mg/m^3 with one peak concentration of 100 mg/m^3. The peak concentration is moved from the beginning of the sampling period to the end to show the change in measured concentration.

It is important to remember that although the flow rate changes, the total amount

of air collected is always known for canister samples. Total volume can be determined by measuring the pressure differential that resulted during the sampling period. Therefore, the primary concern is not the total volume of air collected, but the timing of the fluctuations in concentration during a given sampling period. If large peaks occur early in the sampling period, then this may result in under estimating exposure when compared to peaks in concentration occurring at the end of the sampling period. As an example, if a peak exposure occurs for 1 hour early Monday morning as opposed to the late Friday afternoon, the final concentration collected by the capillary-canister for the two different conditions will vary, but the cumulative exposure of the occupants in that environment will be the same.

The simulation model was used to predict the concentration sampled by the capillary canister for a series of hypothetical scenarios with peak concentrations ranging from 30 minutes to 8 hours during a weeklong sample. The simulated conditions evaluated were a constant atmospheric concentration of 20 mg/m^3 with peak values of 100 and 200 mg/m^3 occurring during 30, 60, and 240 minute periods. The entire sampling time was 33 hours, representing an approximate workweek. The times at which the peaks occurred were changed from scenario to scenario to observe how the sampled concentration was affected. If the flow rate of the capillary-canister was constant during the sampling period, the resulting concentration would be equal to the actual concentration in the atmosphere sampled. The sampled time weighted average is calculated using equation 7.1. The flow rate through a specific capillary flow controller can be defined by a quadratic equation. The equation for the capillary used to sample for 33 hours in this simulation was determined experimentally and is shown in equation 7.2. The sampled concentration was compared to the "true time weighted average concentration" or the concentration that would result if the flow rate had not diminished over time. The data for simulation is presented in Figure 7.3.

$$TWA = \frac{\sum_i^n T_i C_i}{T_n} \qquad (7.1)$$

$$Q(t) = \frac{1}{379} \int_1^{380} -3E-07x^2 + 5E-5x + 0.0843 \qquad (7.2)$$

The amount of bias ranged from 0 to 12.2% for the conditions simulated. The worst case scenario was the largest peak (200 mg/m^3) occurring for four hours very early or very late in the sampling period (i.e. A peak in the first hours of a week long sample as compared to a peak during the last hours of the week). The changes in concentration due to the timing of the peak, does effect the estimated exposure of the capillary canister, yet the variability only exceeds 12% when a peak of 10 times the TWA concentration occurs in the first four hours of sampling of the week long sample. Shorter peaks of 0.5 hours and 1 hour were found to produce a bias of less than 5% of the TWA concentrations. As the peak concentrations occur more toward the middle of the sampling period, the bias becomes progressively smaller. The shorter the time period of the peak concentration the less affect it will have on the final concentration and the observed bias. While fluctuating concentrations or excursion values are common in industrial processes, their duration is often short, minutes as opposed to hours. As a result, the bias for capillary-canister sampling device should be in the lower estimations, less than 5%, for most industrial environments for week long sampling.

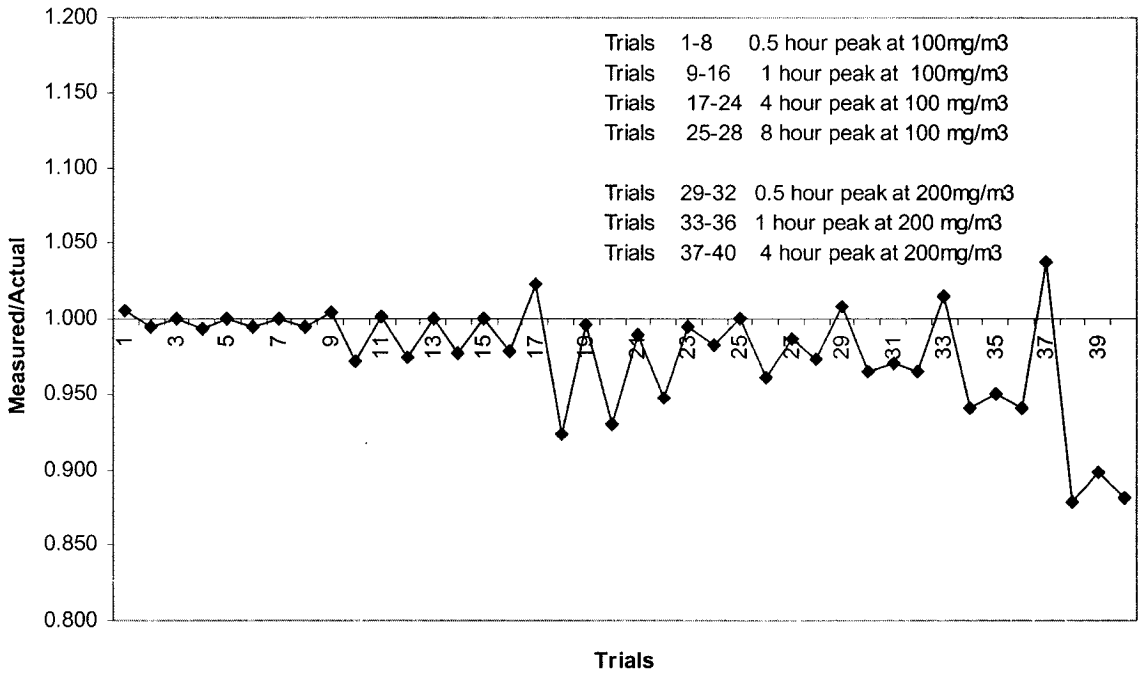

Figure 7.3 Estimated bias associated with the capillary-canister sampler when peak concentrations are present. Data was generated using a simulation model. Each data point represents the TWA for one peak occurring during a 33-hour sampling period. The length and magnitude of the peak concentration was varied as noted on the graph. The difference between the replicate trials is the timing of the peak, such as, trial one has the peak occurring during the first hour of sampling while in trial two the peak occurs in the last hour of sampling. The actual concentration is represented by the TWA for the scenario.

7.4 Conclusions

This study showed no statistical difference observed between the two types of samplers, therefore, the capillary-canister device could effectively collect field samples for extended sampling periods. The capillary-canister integrates the peak concentrations into the weeklong concentration, resulting in a long-term average. The existence and validity of a long term average OELs may be in question, but the data can be used to compare to current OELs or fractions of current OELs. In addition, the long-term sampling data will provide a better estimate of a cumulative exposure to assess long term health effects. It must be emphasized here that all field data were collected at one location involving one process. The ability to extrapolate this data to many types of air sampling conditions, such as highly fluctuating air borne concentrations, is limited. However, the modeling of the estimated bias established guidelines around which the capillary-canister could be used to evaluate a broader range of sampling environments. Since environmental variability is almost always much greater than the error of the measurements, lower levels of sampling and analytical precision can be acceptable to increase the sample size. The field data coupled with the modeled scenarios further supports the capillary-canisters effectiveness in collecting long-term air samples.

In addition, the advantages of reduced sampling and analytical costs are an important factor for the usefulness of the capillary-canister device. The two weeks of sampling resulted in 60 charcoal badges and 12 canister samples; a five-fold reduction in samplers and a five-fold reduction in sample analysis. The cost savings associated with collection and analysis of capillary-canister samples is appreciable.

This work represents the first step in an attempt to understand the realm of possibilities that exist when characterizing long-term exposures in occupational hygiene sampling. Appendix D provides supporting information for this chapter.

The continued modeling of different fluctuating concentrations and additional validation of actual sampling in a wider variety of processes and chemicals will be necessary to examine the performance of the sampler and to consider the value of long term average exposures.

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Chapter 8.0 General Conclusions

This research was concerned with the development and evaluation of the capillary-canister device as a personal air sampler for long-term air sampling of gases and vapors. In Chapter 4, the flow rate characteristics were examined and shown to be very reproducible for capillaries of different geometries. The empirical formulae developed for the predication of the flow rate were found to match the experimental flow rates within a few percent. An assessment of how constant the flow rate is over the sampling period was done to examine the usefulness of the capillary-canister as a long-term sampling device. While it was found that the flow rate slowly diminishes as the canister fills during sampling, understanding how the flow rate changes allowed for the quantification of the potential bias one would encounter during a sampling period. Given the overall uncertainties associated with current air sampling methodologies, the potential bias of the capillary-canister device was found to be well within acceptable guidelines. In addition, the error associated with measurements is small compared to the variability associated with exposures.

In Chapter 5 and 6, the functionality of the capillary-canister was examined in a series of laboratory experiments. When compared to the gold standard, an on-line gas chromatograph, no statistical difference was observed for the chemicals tested. In addition, no statistically significant difference was observed between the capillary-canister results and the sorbent sampling methods used for most compounds tested. For certain chemicals tested, the more polar organic compounds, the sorbent methods did not return an acceptable result while the capillary-canisters performed with acceptable accuracy and precision. The second finding was of particular importance because it showed that the capillary-canister device could be used to effectively sample a wide range of compounds. Also, the range of concentrations of air borne contaminants that the capillary canister can sample is much broader. The sorbent methods experience break through at higher concentrations and during longer sampling periods. These

laboratory tests showed that the capillary-canister device could accurately collect a variety of compounds exceeding the capabilities of the currently used sorbent methods.

An additional benefit of the capillary-canister, while not quantified herein, was the ease and time required for analysis. Once the initial set up of the analytical equipment was complete, the time and effort to analyze the capillary-canister was ~30% that of the time necessary to prepare and analyze the sorbent samples. This observation may lead to more cost-effective strategies in the future.

In Chapter 7, the field evaluation of the capillary-canister was studied to assess its performance in the dynamic conditions of a factory. The long-term, 40-hour, capabilities of the sampling device were also investigated. The variability of the air borne exposures from day to day were statistically different, but no statistically significant difference was observed between the mean values of sorbent method and the capillary-canister method. This finding allowed for the conclusion that the capillary-canister system collected representative samples that reflected the worker's cumulative exposure for a workweek. Long-term sampling can lead to a more complete exposure assessment of worker or community exposures to contaminants that may have long-term health effects.

Given that the airborne concentrations fluctuated during this field sampling, as in most industrial processes, an analysis of the effects of peak concentrations with respect to the diminishing flow rate, as discussed in Chapter 4, was preformed. The simulation model showed that the changing flow rate could create a bias when large peak concentrations are present. The bias is less than 5% for most conditions evaluated, yet can rise to 12 percent for large lengthy peaks occurring on the ends of the sampling period.

The peak analysis links the last phase of the research back to the first

component of the research, the characterization of flow rate. This systems approach for evaluating the capillary-canister device allowed for both the analysis of specific details that could affect the results and the overall functionality of the sampler; resulting in a personal/area sampling device that can be used for a wide variety of industrial and community air sampling campaigns. Since the error associated with sample collection and analysis is usually a small segment of the overall variability of exposure, greater tolerance for error is acceptable for devices that are more effective, allowing for a greater sample size given the same input of resources. The capillary-canister could be a more effective tool for use by occupational hygienists for the assessment of exposures to gases and vapors.

Key advantages of the capillary-canister device as compared to sorbent sampling methods include:

- Low flow rates allow for long term sampling and enable the use of small canisters for personal sampling
- Length of sampling from seconds to weeks
- No field calibration of the device is necessary
- A durable and simple design reduced the possibility of damage and device failure
- No power is required for field air sampling
- Multiple chemicals can be simultaneously sampled from diverse chemical groups: CO_2, CO, CH_4, polar organic compounds, and non-polar organics
- Limited effects by environmental conditions
- Stability of the sample in the canister
- No knowledge of contaminant concentration is necessary
- Whole air sample is collected and the dilution of sample is greatly reduced 1:3 versus 1:1000 for liquid desorption
- Multiple analysis of the same sample is possible
- Ease of analysis

8.1 Contributions to Knowledge

1. Characterization and validation of the flow rates for multiple geometries of the capillary flow controller.

2. Development of new empirical models to more accurately predict flow rate through the capillary flow controllers.

3. Modification of the design of the personal capillary-canister by using a smaller 300 mL canister and inserting the capillary inside the canister.

4. Comparison of the capillary-canister method to online gas chromatograph demonstrating accuracy and precision of the method.

5. Comparison of capillary-canister device to established sorbent-based sampling methods under a variety of concentrations for multiple hydrocarbon vapors. This comparison demonstrated that the capillary-canister performed better overall than sorbent-based methods.

6. Demonstrated that humidity and air velocity did not significantly affect the collection of contaminants.

7. Demonstrated that the capillary-canister can be used as a personal sampling device.

8. Developed and evaluated a long-term sampling methodology for workplace exposure.

8.2 Suggestions for Future Research

Whether one is interested in improvements in current methodologies or development of new sampling technologies, there is a need to focus on reducing the cost and time it takes to collect a sample to increase the number of samples that can be collected per unit investment. In addition, effective air sampling methodologies will always be of value to assess exposure in industry and community environments. Several future research projects are proposed that examine uses of the capillary-canister device. Some of these were briefly tested during the course of this research.

1. Develop a more accurate theoretical model to predict air flow through the capillary flow controller. By eliminating the assumption that air is incompressible, a new mathematical model could be developed. This is a formidable undertaking because it includes advanced fluid mechanics problems and at this point it is unclear if all the equations can be solved.

2. Evaluate the effectiveness of the sampler for a wider range of chemical compounds including sulfur containing hydrocarbons, aldehydes and inorganic priority air pollutants.

3. Develop an analytical methodology to analyze the canisters using solid phase micro extraction (SPME). This could reduce the cost of analysis and could allow for field analysis with portable gas chromatographs. The field analysis would be beneficial at sites where sampling results are quickly needed. Several sets of canisters were analyzed using SPME during the course of this research with very promising results. §

4. Develop and test a more comprehensive model to predict bias associated with peak or fluctuating airborne concentrations.

5. Conduct a detailed cost analysis of using the capillary-canister as compared to other canister and sorbent-based sampling methods.

6. Conduct further field evaluations to examine the performance of the device under a broader range of conditions.

7. A pilot study using the capillary-canister was done to examine the air borne concentration of styrene in the reinforced plastics industry. Capillary-canister samples were collected for 20 consecutive working days in 10 different facilities. Workers were asked to turn the canister on and off each day and record the times. This test showed that the canister could sample for the month long period. The concentrations recorded were questionable because limited information about the work day activities were provided and no secondary device was used to confirm the air borne levels. However, the test did show that the samples were stable for 30 days, the majority of the canisters did not leak and the airborne concentrations were similar to data collected with a direct reading field instrument. A more elaborate study design could show the reliability of the capillary-canister for 30-day periods.

8. Develop and test a long term sampling methodology for using the capillary-canisters in residential environments.

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Appendices A – D

Supporting information is provided in four Appendices, A through D, to give the reader additional information on how the data was collected and analyzed.

Appendix A **Example Flow rate measurement data**

Appendix B **Calculation methods, calibration curves and chromatographs for small chamber laboratory experiments**

Appendix C **Calculation methods and calibration curves for Styrene experiments**

Appendix D **Simulation model and Summary of statistical methods for all experiments.**

Appendix A – Example of Flow rate measurement data

Approximately one hundred replications of flow rate experiments were completed to examine the flow rate through various lengths of capillary tubing. An example of the experimental apparatus used to measure the flow rate and an example of a typical data set are shown.

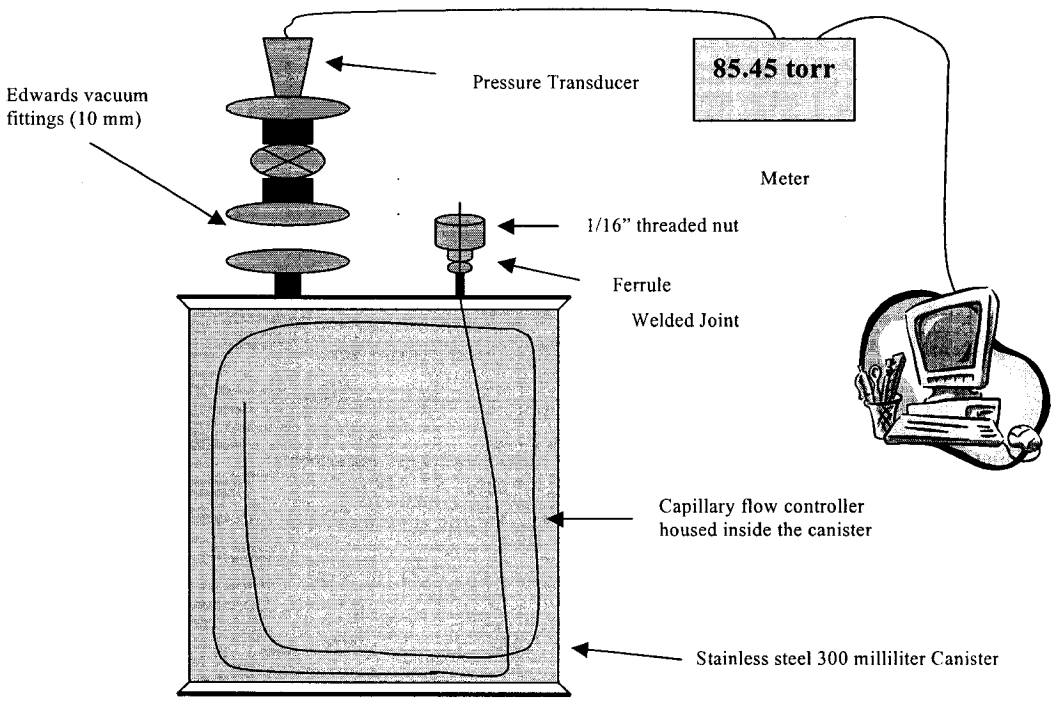


Figure A-1 Flow Rate Testing System for the Capillary Flow Controller

Table A-1 An example of capillary flow test data

Capillary Size: **Diameter 0.05 mm** ml/torr = 0.407895
Length 0.4 m

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
8:34:18	0	0.2	3	0.7	0.095	30	6.2	0.084
8:31:18	3	0.9	3	0.7	0.095	30	6.1	0.083
8:28:17	6	1.6	3	0.6	0.082	30	5.9	0.080
8:25:17	9	2.2	3	0.6	0.082	30	6	0.082
8:22:17	12	2.8	3	0.6	0.082	30	6	0.082
8:19:17	15	3.4	3	0.6	0.082	30	6	0.082
8:16:17	18	4	3	0.5	0.068	30	6	0.082
8:13:17	21	4.5	3	0.7	0.095	30	6.1	0.083
8:10:17	24	5.2	3	0.6	0.082	30	6	0.082
8:07:17	27	5.8	3	0.6	0.082	30	6	0.082
8:04:17	30	6.4	3	0.6	0.082	30	5.9	0.080
8:01:17	33	7	3	0.5	0.068	30	5.9	0.080
7:58:17	36	7.5	3	0.7	0.095	30	6	0.082
7:55:17	39	8.2	3	0.6	0.082	30	5.9	0.080
7:52:17	42	8.8	3	0.6	0.082	30	5.9	0.080
7:49:17	45	9.4	3	0.6	0.082	30	5.9	0.080
7:46:17	48	10	3	0.6	0.082	30	6	0.082
7:43:17	51	10.6	3	0.6	0.082	30	6.2	0.084
7:40:17	54	11.2	3	0.6	0.082	30	6.3	0.086
7:37:17	57	11.8	3	0.5	0.068	30	6.3	0.086
7:34:17	60	12.3	3	0.6	0.082	30	6.4	0.087
7:31:17	63	12.9	3	0.6	0.082	30	6.3	0.086
7:28:17	66	13.5	3	0.6	0.082	30	6.3	0.086
7:25:17	69	14.1	3	0.6	0.082	30	6.3	0.086
7:22:17	72	14.7	3	0.6	0.082	30	6.3	0.086
7:19:17	75	15.3	3	0.7	0.095	30	6.2	0.084
7:16:16	78	16	3	0.8		30	6.1	0.083
7:13:17	81	16.8	3	0.7		30	5.8	0.079
7:10:17	84	17.5	3	0.6	0.082	30	5.7	0.078
7:07:16	87	18.1	3	0.6	0.082	30	5.6	0.076
7:04:16	90	18.7	3	0.5	0.068	30	5.6	0.076
7:01:16	93	19.2	3	0.6	0.082	30	5.6	0.076
6:58:16	96	19.8	3	0.6	0.082	30	5.6	0.076
6:55:16	99	20.4	3	0.6	0.082	30	5.6	0.076
6:52:16	102	21	3	0.5	0.068	30	5.5	0.075
6:49:16	105	21.5	3	0.6	0.082	30	5.5	0.075
6:46:16	108	22.1	3	0.5	0.068	30	5.5	0.075
6:43:16	111	22.6	3	0.6	0.082	30	5.5	0.075
6:40:16	114	23.2	3	0.5	0.068	30	5.4	0.073
6:37:16	117	23.7	3	0.6	0.082	30	5.5	0.075
6:34:16	120	24.3	3	0.5	0.068	30	5.5	0.075
6:31:16	123	24.8	3	0.6	0.082	30	5.5	0.075
6:28:16	126	25.4	3	0.6	0.082	30	5.5	0.075

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
6:25:16	129	26	3	0.5	0.068	30	5.4	0.073
6:22:16	132	26.5	3	0.5	0.068	30	5.5	0.075
6:19:16	135	27	3	0.6	0.082	30	5.6	0.076
6:16:16	138	27.6	3	0.5	0.068	30	5.4	0.073
6:13:15	141	28.1	3	0.5	0.068	30	5.5	0.075
6:10:15	144	28.6	3	0.6	0.082	30	5.6	0.076
6:07:15	147	29.2	3	0.6	0.082	30	5.5	0.075
6:04:16	150	29.8	3	0.5	0.068	30	5.4	0.073
6:01:16	153	30.3	3	0.6	0.082	30	5.5	0.075
5:58:15	156	30.9	3	0.5	0.068	30	5.5	0.075
5:55:15	159	31.4	3	0.6	0.082	30	5.5	0.075
5:52:15	162	32	3	0.6	0.082	30	5.5	0.075
5:49:15	165	32.6	3	0.4	0.054	30	5.4	0.073
5:46:15	168	33	3	0.6	0.082	30	5.6	0.076
5:43:15	171	33.6	3	0.6	0.082	30	5.5	0.075
5:40:15	174	34.2	3	0.5	0.068	30	5.5	0.075
5:37:15	177	34.7	3	0.5	0.068	30	5.6	0.076
5:34:15	180	35.2	3	0.6	0.082	30	5.7	0.078
5:31:15	183	35.8	3	0.6	0.082	30	5.6	0.076
5:28:15	186	36.4	3	0.5	0.068	30	5.6	0.076
5:25:15	189	36.9	3	0.6	0.082	30	5.6	0.076
5:22:15	192	37.5	3	0.5	0.068	30	5.6	0.076
5:19:15	195	38	3	0.6	0.082	30	5.7	0.078
5:16:15	198	38.6	3	0.5	0.068	30	5.6	0.076
5:13:15	201	39.1	3	0.6	0.082	30	5.7	0.078
5:10:15	204	39.7	3	0.6	0.082	30	5.7	0.078
5:07:15	207	40.3	3	0.6	0.082	30	5.7	0.078
5:04:15	210	40.9	3	0.5	0.068	30	5.7	0.078
5:01:15	213	41.4	3	0.6	0.082	30	5.8	0.079
4:58:15	216	42	3	0.5	0.068	30	5.8	0.079
4:55:14	219	42.5	3	0.6	0.082	30	5.9	0.080
4:52:14	222	43.1	3	0.6	0.082	30	5.9	0.080
4:49:14	225	43.7	3	0.5	0.068	30	5.9	0.080
4:46:14	228	44.2	3	0.6	0.082	30	5.9	0.080
4:43:14	231	44.8	3	0.6	0.082	30	5.8	0.079
4:40:14	234	45.4	3	0.6	0.082	30	5.8	0.079
4:37:14	237	46	3	0.6	0.082	30	5.7	0.078
4:34:14	240	46.6	3	0.6	0.082	30	5.6	0.076
4:31:14	243	47.2	3	0.6	0.082	30	5.6	0.076
4:28:14	246	47.8	3	0.6	0.082	30	5.5	0.075
4:25:14	249	48.4	3	0.6	0.082	30	5.4	0.073
4:22:14	252	49	3	0.6	0.082	30	5.3	0.072
4:19:14	255	49.6	3	0.5	0.068	30	5.3	0.072

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
4:16:14	258	50.1	3	0.5	0.068	30	5.3	0.072
4:13:14	261	50.6	3	0.6	0.082	30	5.3	0.072
4:10:14	264	51.2	3	0.5	0.068	30	5.3	0.072
4:07:14	267	51.7	3	0.5	0.068	30	5.3	0.072
4:04:14	270	52.2	3	0.6	0.082	30	5.4	0.073
4:01:14	273	52.8	3	0.5	0.068	30	5.3	0.072
3:58:14	276	53.3	3	0.5	0.068	30	5.3	0.072
3:55:13	279	53.8	3	0.5	0.068	30	5.5	0.075
3:52:13	282	54.3	3	0.6	0.082	30	5.5	0.075
3:49:13	285	54.9	3	0.5	0.068	30	5.5	0.075
3:46:13	288	55.4	3	0.5	0.068	30	5.5	0.075
3:43:13	291	55.9	3	0.6	0.082	30	5.5	0.075
3:40:13	294	56.5	3	0.5	0.068	30	5.5	0.075
3:37:13	297	57	3	0.6	0.082	30	5.5	0.075
3:34:13	300	57.6	3	0.5	0.068	30	5.5	0.075
3:31:13	303	58.1	3	0.5	0.068	30	5.6	0.076
3:28:13	306	58.6	3	0.7	0.095	30	5.6	0.076
3:25:13	309	59.3	3	0.5	0.068	30	5.5	0.075
3:22:13	312	59.8	3	0.6	0.082	30	5.5	0.075
3:19:13	315	60.4	3	0.5	0.068	30	5.5	0.075
3:16:13	318	60.9	3	0.5	0.068	30	5.5	0.075
3:13:13	321	61.4	3	0.6	0.082	30	5.6	0.076
3:10:13	324	62	3	0.5	0.068	30	5.5	0.075
3:07:13	327	62.5	3	0.6	0.082	30	5.5	0.075
3:04:13	330	63.1	3	0.6	0.082	30	5.5	0.075
3:01:13	333	63.7	3	0.5	0.068	30	5.5	0.075
2:58:13	336	64.2	3	0.6	0.082	30	5.5	0.075
2:55:13	339	64.8	3	0.5	0.068	30	5.4	0.073
2:52:13	342	65.3	3	0.6	0.082	30	5.5	0.075
2:49:13	345	65.9	3	0.5	0.068	30	5.4	0.073
2:46:13	348	66.4	3	0.6	0.082	30	5.4	0.073
2:43:12	351	67	3	0.5	0.068	30	5.4	0.073
2:40:13	354	67.5	3	0.5	0.068	30	5.4	0.073
2:37:12	357	68	3	0.6	0.082	30	5.4	0.073
2:34:12	360	68.6	3	0.6	0.082	30	5.4	0.073
2:31:12	363	69.2	3	0.5	0.068	30	5.3	0.072
2:28:12	366	69.7	3	0.5	0.068	30	5.3	0.072
2:25:12	369	70.2	3	0.6	0.082	30	5.4	0.073
2:22:12	372	70.8	3	0.5	0.068	30	5.3	0.072
2:19:12	375	71.3	3	0.5	0.068	30	5.3	0.072
2:16:12	378	71.8	3	0.6	0.082	30	5.4	0.073

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
2:13:12	381	72.4	3	0.5	0.068	30	5.3	0.072
2:10:12	384	72.9	3	0.5	0.068	30	5.4	0.073
2:07:12	387	73.4	3	0.6	0.082	30	5.4	0.073
2:04:12	390	74	3	0.5	0.068	30	5.3	0.072
2:01:12	393	74.5	3	0.5	0.068	30	5.3	0.072
1:58:12	396	75	3	0.6	0.082	30	5.3	0.072
1:55:12	399	75.6	3	0.5	0.068	30	5.3	0.072
1:52:12	402	76.1	3	0.5	0.068	30	5.3	0.072
1:49:12	405	76.6	3	0.6	0.082	30	5.3	0.072
1:46:12	408	77.2	3	0.5	0.068	30	5.2	0.071
1:43:12	411	77.7	3	0.6	0.082	30	5.2	0.071
1:40:12	414	78.3	3	0.5	0.068	30	5.2	0.071
1:37:12	417	78.8	3	0.5	0.068	30	5.1	0.069
1:34:12	420	79.3	3	0.5	0.068	30	5.2	0.071
1:31:11	423	79.8	3	0.5	0.068	30	5.2	0.071
1:28:11	426	80.3	3	0.6	0.082	30	5.2	0.071
1:25:11	429	80.9	3	0.5	0.068	30	5.1	0.069
1:22:11	432	81.4	3	0.5	0.068	30	5.1	0.069
1:19:11	435	81.9	3	0.5	0.068	30	5.1	0.069
1:16:11	438	82.4	3	0.5	0.068	30	5.1	0.069
1:13:11	441	82.9	3	0.6	0.082	30	5.1	0.069
1:10:11	444	83.5	3	0.4	0.054	30	5	0.068
1:07:11	447	83.9	3	0.6	0.082	30	5.1	0.069
1:04:11	450	84.5	3	0.5	0.068	30	5	0.068
1:01:11	453	85	3	0.5	0.068	30	5	0.068
12:58:11	456	85.5	3	0.5	0.068	30	5	0.068
12:55:11	459	86	3	0.5	0.068	30	5	0.068
12:52:11	462	86.5	3	0.5	0.068	30	5	0.068
12:49:11	465	87	3	0.5	0.068	30	5	0.068
12:46:11	468	87.5	3	0.5	0.068	30	5	0.068
12:43:11	471	88	3	0.5	0.068	30	5	0.068
12:40:11	474	88.5	3	0.5	0.068	30	5.1	0.069
12:37:11	477	89	3	0.5	0.068	30	5.1	0.069
12:34:11	480	89.5	3	0.5	0.068	30	5.1	0.069
12:31:11	483	90	3	0.5	0.068	30	5.1	0.069
12:28:10	486	90.5	3	0.5	0.068	30	5.1	0.069
12:25:11	489	91	3	0.5	0.068	30	5.2	0.071
12:22:10	492	91.5	3	0.5	0.068	30	5.2	0.071
12:19:10	495	92	3	0.5	0.068	30	5.2	0.071
12:16:10	498	92.5	3	0.5	0.068	30	5.2	0.071
12:13:10	501	93	3	0.6	0.082	30	5.2	0.071

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
12:10:10	504	93.6	3	0.5	0.068	30	5.1	0.069
12:07:10	507	94.1	3	0.5	0.068	30	5.1	0.069
12:04:10	510	94.6	3	0.5	0.068	30	5.1	0.069
12:01:10	513	95.1	3	0.5	0.068	30	5.1	0.069
11:58:10	516	95.6	3	0.6	0.082	30	5.2	0.071
11:55:10	519	96.2	3	0.5	0.068	30	5.1	0.069
11:52:10	522	96.7	3	0.5	0.068	30	5.1	0.069
11:49:10	525	97.2	3	0.5	0.068	30	5.1	0.069
11:46:10	528	97.7	3	0.5	0.068	30	5.1	0.069
11:43:10	531	98.2	3	0.5	0.068	30	5.2	0.071
11:40:10	534	98.7	3	0.5	0.068	30	5.2	0.071
11:37:10	537	99.2	3	0.5	0.068	30	5.2	0.071
11:34:10	540	99.7	3	0.5	0.068	30	5.2	0.071
11:31:10	543	100.2	3	0.6	0.082	30	5.2	0.071
11:28:10	546	100.8	3	0.5	0.068	30	5.1	0.069
11:25:10	549	101.3	3	0.5	0.068	30	5.2	0.071
11:22:09	552	101.8	3	0.5	0.068	30	5.2	0.071
11:19:10	555	102.3	3	0.5	0.068	30	5.2	0.071
11:16:10	558	102.8	3	0.6	0.082	30	5.2	0.071
11:13:09	561	103.4	3	0.5	0.068	30	5.2	0.071
11:10:09	564	103.9	3	0.5	0.068	30	5.2	0.071
11:07:09	567	104.4	3	0.5	0.068	30	5.2	0.071
11:04:09	570	104.9	3	0.5	0.068	30	5.2	0.071
11:01:09	573	105.4	3	0.5	0.068	30	5.2	0.071
10:58:09	576	105.9	3	0.6	0.082	30	5.2	0.071
10:55:09	579	106.5	3	0.5	0.068	30	5.2	0.071
10:52:09	582	107	3	0.5	0.068	30	5.2	0.071
10:49:09	585	107.5	3	0.5	0.068	30	5.2	0.071
10:46:09	588	108	3	0.6	0.082	30	5.2	0.071
10:43:09	591	108.6	3	0.5	0.068	30	5.1	0.069
10:40:09	594	109.1	3	0.5	0.068	30	5.2	0.071
10:37:09	597	109.6	3	0.5	0.068	30	5.1	0.069
10:34:09	600	110.1	3	0.5	0.068	30	5.2	0.071
10:31:09	603	110.6	3	0.5	0.068	30	5.2	0.071
10:28:09	606	111.1	3	0.6	0.082	30	5.2	0.071
10:25:09	609	111.7	3	0.5	0.068	30	5.2	0.071
10:22:09	612	112.2	3	0.5	0.068	30	5.2	0.071
10:19:09	615	112.7	3	0.5	0.068	30	5.2	0.071
10:16:09	618	113.2	3	0.5	0.068	30	5.2	0.071
10:13:09	621	113.7	3	0.6	0.082	30	5.3	0.072
10:10:08	624	114.3	3	0.4	0.054	30	5.1	0.069

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
10:07:09	627	114.7	3	0.6	0.082	30	5.3	0.072
10:04:08	630	115.3	3	0.5	0.068	30	5.2	0.071
10:01:09	633	115.8	3	0.5	0.068	30	5.2	0.071
9:58:08	636	116.3	3	0.6	0.082	30	5.2	0.071
9:55:08	639	116.9	3	0.5	0.068	30	5.2	0.071
9:52:08	642	117.4	3	0.5	0.068	30	5.2	0.071
9:49:08	645	117.9	3	0.5	0.068	30	5.2	0.071
9:46:08	648	118.4	3	0.6	0.082	30	5.2	0.071
9:43:08	651	119	3	0.4	0.054	30	5.1	0.069
9:40:08	654	119.4	3	0.6	0.082	30	5.3	0.072
9:37:08	657	120	3	0.5	0.068	30	5.1	0.069
9:34:08	660	120.5	3	0.5	0.068	30	5.2	0.071
9:31:08	663	121	3	0.5	0.068	30	5.2	0.071
9:28:08	666	121.5	3	0.6	0.082	30	5.2	0.071
9:25:08	669	122.1	3	0.5	0.068	30	5.2	0.071
9:22:08	672	122.6	3	0.5	0.068	30	5.2	0.071
9:19:08	675	123.1	3	0.5	0.068	30	5.2	0.071
9:16:08	678	123.6	3	0.5	0.068	30	5.2	0.071
9:13:08	681	124.1	3	0.6	0.082	30	5.2	0.071
9:10:08	684	124.7	3	0.4	0.054	30	5.2	0.071
9:07:08	687	125.1	3	0.6	0.082	30	5.3	0.072
9:04:08	690	125.7	3	0.5	0.068	30	5.2	0.071
9:01:07	693	126.2	3	0.5	0.068	30	5.2	0.071
8:58:07	696	126.7	3	0.6	0.082	30	5.2	0.071
8:55:07	699	127.3	3	0.5	0.068	30	5.2	0.071
8:52:07	702	127.8	3	0.5	0.068	30	5.2	0.071
8:49:07	705	128.3	3	0.5	0.068	30	5.2	0.071
8:46:07	708	128.8	3	0.5	0.068	30	5.3	0.072
8:43:07	711	129.3	3	0.6	0.082	30	5.2	0.071
8:40:07	714	129.9	3	0.5	0.068	30	5.2	0.071
8:37:07	717	130.4	3	0.5	0.068	30	5.2	0.071
8:34:07	720	130.9	3	0.5	0.068	30	5.2	0.071
8:31:07	723	131.4	3	0.5	0.068	30	5.2	0.071
8:28:07	726	131.9	3	0.6	0.082	30	5.3	0.072
8:25:07	729	132.5	3	0.5	0.068	30	5.2	0.071
8:22:07	732	133	3	0.5	0.068	30	5.2	0.071
8:19:07	735	133.5	3	0.6	0.082	30	5.2	0.071
8:16:07	738	134.1	3	0.4	0.054	30	5.1	0.069
8:13:07	741	134.5	3	0.6	0.082	30	5.3	0.072
8:10:07	744	135.1	3	0.5	0.068	30	5.2	0.071
8:07:07	747	135.6	3	0.5	0.068	30	5.2	0.071

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
8:04:07	750	136.1	3	0.5	0.068	30	5.2	0.071
8:01:07	753	136.6	3	0.6	0.082	30	5.2	0.071
7:58:06	756	137.2	3	0.5	0.068	30	5.1	0.069
7:55:06	759	137.7	3	0.5	0.068	30	5.2	0.071
7:52:06	762	138.2	3	0.5	0.068	30	5.2	0.071
7:49:06	765	138.7	3	0.5	0.068	30	5.2	0.071
7:46:06	768	139.2	3	0.6	0.082	30	5.2	0.071
7:43:06	771	139.8	3	0.5	0.068	30	5.2	0.071
7:40:06	774	140.3	3	0.5	0.068	30	5.2	0.071
7:37:06	777	140.8	3	0.5	0.068	30	5.2	0.071
7:34:06	780	141.3	3	0.5	0.068	30	5.2	0.071
7:31:06	783	141.8	3	0.5	0.068	30	5.2	0.071
7:28:06	786	142.3	3	0.6	0.082	30	5.2	0.071
7:25:06	789	142.9	3	0.5	0.068	30	5.1	0.069
7:22:06	792	143.4	3	0.5	0.068	30	5.2	0.071
7:19:06	795	143.9	3	0.5	0.068	30	5.2	0.071
7:16:06	798	144.4	3	0.6	0.082	30	5.2	0.071
7:13:06	801	145	3	0.5	0.068	30	5.1	0.069
7:10:06	804	145.5	3	0.5	0.068	30	5.1	0.069
7:07:06	807	146	3	0.5	0.068	30	5.1	0.069
7:04:06	810	146.5	3	0.5	0.068	30	5.2	0.071
7:01:06	813	147	3	0.5	0.068	30	5.2	0.071
6:58:06	816	147.5	3	0.5	0.068	30	5.2	0.071
6:55:06	819	148	3	0.6	0.082	30	5.2	0.071
6:52:05	822	148.6	3	0.5	0.068	30	5.1	0.069
6:49:05	825	149.1	3	0.5	0.068	30	5.2	0.071
6:46:06	828	149.6	3	0.5	0.068	30	5.2	0.071
6:43:05	831	150.1	3	0.5	0.068	30	5.2	0.071
6:40:05	834	150.6	3	0.5	0.068	30	5.2	0.071
6:37:06	837	151.1	3	0.6	0.082	30	5.2	0.071
6:34:05	840	151.7	3	0.5	0.068	30	5.1	0.069
6:31:05	843	152.2	3	0.5	0.068	30	5.1	0.069
6:28:05	846	152.7	3	0.5	0.068	30	5.2	0.071
6:25:05	849	153.2	3	0.5	0.068	30	5.2	0.071
6:22:05	852	153.7	3	0.6	0.082	30	5.2	0.071
6:19:05	855	154.3	3	0.5	0.068	30	5.1	0.069
6:16:05	858	154.8	3	0.5	0.068	30	5.1	0.069
6:13:05	861	155.3	3	0.5	0.068	30	5.1	0.069
6:10:05	864	155.8	3	0.5	0.068	30	5.1	0.069
6:07:05	867	156.3	3	0.5	0.068	30	5.2	0.071
6:04:05	870	156.8	3	0.5	0.068	30	5.2	0.071

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
6:01:05	873	157.3	3	0.6	0.082	30	5.2	0.071
5:58:05	876	157.9	3	0.5	0.068	30	5.1	0.069
5:55:05	879	158.4	3	0.5	0.068	30	5.1	0.069
5:52:05	882	158.9	3	0.5	0.068	30	5.1	0.069
5:49:05	885	159.4	3	0.5	0.068	30	5.1	0.069
5:46:04	888	159.9	3	0.5	0.068	30	5.1	0.069
5:43:05	891	160.4	3	0.5	0.068	30	5.2	0.071
5:40:04	894	160.9	3	0.6	0.082	30	5.2	0.071
5:37:05	897	161.5	3	0.5	0.068	30	5.1	0.069
5:34:05	900	162	3	0.5	0.068	30	5.1	0.069
5:31:04	903	162.5	3	0.5	0.068	30	5.1	0.069
5:28:04	906	163	3	0.5	0.068	30	5.1	0.069
5:25:04	909	163.5	3	0.5	0.068	30	5.2	0.071
5:22:04	912	164	3	0.5	0.068	30	5.2	0.071
5:19:04	915	164.5	3	0.5	0.068	30	5.2	0.071
5:16:04	918	165	3	0.6	0.082	30	5.2	0.071
5:13:04	921	165.6	3	0.5	0.068	30	5.1	0.069
5:10:04	924	166.1	3	0.5	0.068	30	5.1	0.069
5:07:04	927	166.6	3	0.5	0.068	30	5.1	0.069
5:04:04	930	167.1	3	0.5	0.068	30	5.1	0.069
5:01:04	933	167.6	3	0.5	0.068	30	5.1	0.069
4:58:04	936	168.1	3	0.6	0.082	30	5.1	0.069
4:55:04	939	168.7	3	0.5	0.068	30	5	0.068
4:52:04	942	169.2	3	0.5	0.068	30	5	0.068
4:49:04	945	169.7	3	0.5	0.068	30	5.1	0.069
4:46:04	948	170.2	3	0.5	0.068	30	5.1	0.069
4:43:04	951	170.7	3	0.5	0.068	30	5.1	0.069
4:40:04	954	171.2	3	0.5	0.068	30	5.1	0.069
4:37:04	957	171.7	3	0.5	0.068	30	5.1	0.069
4:34:04	960	172.2	3	0.5	0.068	30	5.1	0.069
4:31:04	963	172.7	3	0.5	0.068	30	5.1	0.069
4:28:03	966	173.2	3	0.5	0.068	30	5.1	0.069
4:25:03	969	173.7	3	0.5	0.068	30	5.1	0.069
4:22:04	972	174.2	3	0.6	0.082	30	5.1	0.069
4:19:03	975	174.8	3	0.5	0.068	30	5	0.068
4:16:03	978	175.3	3	0.5	0.068	30	5	0.068
4:13:03	981	175.8	3	0.5	0.068	30	5	0.068
4:10:03	984	176.3	3	0.5	0.068	30	5	0.068
4:07:03	987	176.8	3	0.5	0.068	30	5.1	0.069
4:04:03	990	177.3	3	0.5	0.068	30	5.1	0.069
4:01:03	993	177.8	3	0.5	0.068	30	5.1	0.069

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
3:58:03	996	178.3	3	0.5	0.068	30	5.1	0.069
3:55:03	999	178.8	3	0.5	0.068	30	5.1	0.069
3:52:03	1002	179.3	3	0.5	0.068	30	5.1	0.069
3:49:03	1005	179.8	3	0.5	0.068	30	5.1	0.069
3:46:03	1008	180.3	3	0.5	0.068	30	5.1	0.069
3:43:03	1011	180.8	3	0.5	0.068	30	5.1	0.069
3:40:03	1014	181.3	3	0.6	0.082	30	5.1	0.069
3:37:03	1017	181.9	3	0.5	0.068	30	5	0.068
3:34:03	1020	182.4	3	0.5	0.068	30	5	0.068
3:31:03	1023	182.9	3	0.5	0.068	30	5	0.068
3:28:03	1026	183.4	3	0.5	0.068	30	5	0.068
3:25:02	1029	183.9	3	0.5	0.068	30	5	0.068
3:22:03	1032	184.4	3	0.5	0.068	30	5	0.068
3:19:03	1035	184.9	3	0.5	0.068	30	5	0.068
3:16:02	1038	185.4	3	0.5	0.068	30	5	0.068
3:13:02	1041	185.9	3	0.5	0.068	30	5	0.068
3:10:02	1044	186.4	3	0.5	0.068	30	5	0.068
3:07:03	1047	186.9	3	0.5	0.068	30	5	0.068
3:04:02	1050	187.4	3	0.5	0.068	30	5	0.068
3:01:02	1053	187.9	3	0.5	0.068	30	5	0.068
2:58:02	1056	188.4	3	0.5	0.068	30	5.1	0.069
2:55:02	1059	188.9	3	0.5	0.068	30	5.1	0.069
2:52:02	1062	189.4	3	0.5	0.068	30	5.1	0.069
2:49:02	1065	189.9	3	0.5	0.068	30	5.1	0.069
2:46:02	1068	190.4	3	0.5	0.068	30	5.1	0.069
2:43:02	1071	190.9	3	0.5	0.068	30	5.1	0.069
2:40:02	1074	191.4	3	0.5	0.068	30	5.1	0.069
2:37:02	1077	191.9	3	0.5	0.068	30	5.1	0.069
2:34:02	1080	192.4	3	0.5	0.068	30	5.1	0.069
2:31:02	1083	192.9	3	0.6	0.082	30	5.1	0.069
2:28:02	1086	193.5	3	0.5	0.068	30	5	0.068
2:25:02	1089	194	3	0.5	0.068	30	5	0.068
2:22:02	1092	194.5	3	0.5	0.068	30	5	0.068
2:19:02	1095	195	3	0.5	0.068	30	5	0.068
2:16:02	1098	195.5	3	0.5	0.068	30	5	0.068
2:13:02	1101	196	3	0.5	0.068	30	5	0.068
2:10:02	1104	196.5	3	0.5	0.068	30	5	0.068
2:07:02	1107	197	3	0.5	0.068	30	5	0.068
2:04:02	1110	197.5	3	0.5	0.068	30	5	0.068
2:01:02	1113	198	3	0.5	0.068	30	5	0.068
1:58:02	1116	198.5	3	0.5	0.068	30	5	0.068

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
1:55:01	1119	199	3	0.5	0.068	30	5	0.068
1:52:01	1122	199.5	3	0.5	0.068	30	5	0.068
1:49:01	1125	200	3	0.5	0.068	30	5	0.068
1:46:01	1128	200.5	3	0.5	0.068	30	5	0.068
1:43:01	1131	201	3	0.5	0.068	30	5	0.068
1:40:01	1134	201.5	3	0.5	0.068	30	5	0.068
1:37:01	1137	202	3	0.5	0.068	30	5.1	0.069
1:34:01	1140	202.5	3	0.5	0.068	30	5	0.068
1:31:01	1143	203	3	0.5	0.068	30	5	0.068
1:28:01	1146	203.5	3	0.5	0.068	30	5.1	0.069
1:25:01	1149	204	3	0.5	0.068	30	5.1	0.069
1:22:01	1152	204.5	3	0.5	0.068	30	5.1	0.069
1:19:01	1155	205	3	0.5	0.068	30	5.1	0.069
1:16:01	1158	205.5	3	0.5	0.068	30	5.1	0.069
1:13:01	1161	206	3	0.5	0.068	30	5.1	0.069
1:10:01	1164	206.5	3	0.6	0.082	30	5.1	0.069
1:07:01	1167	207.1	3	0.4	0.054	30	5.1	0.069
1:04:01	1170	207.5	3	0.5	0.068	30	5.1	0.069
1:01:01	1173	208	3	0.6	0.082	30	5.2	0.071
12:58:01	1176	208.6	3	0.5	0.068	30	5.1	0.069
12:55:00	1179	209.1	3	0.5	0.068	30	5.1	0.069
12:52:01	1182	209.6	3	0.5	0.068	30	5.1	0.069
12:49:00	1185	210.1	3	0.5	0.068	30	5.1	0.069
12:46:00	1188	210.6	3	0.5	0.068	30	5.1	0.069
12:43:00	1191	211.1	3	0.5	0.068	30	5.1	0.069
12:40:00	1194	211.6	3	0.6	0.082	30	5.1	0.069
12:37:00	1197	212.2	3	0.4	0.054	30	5	0.068
12:34:00	1200	212.6	3	0.6	0.082	30	5.1	0.069
12:31:00	1203	213.2	3	0.5	0.068	30	5	0.068
12:28:00	1206	213.7	3	0.5	0.068	30	5	0.068
12:25:00	1209	214.2	3	0.5	0.068	30	5	0.068
12:22:00	1212	214.7	3	0.5	0.068	30	5	0.068
12:19:00	1215	215.2	3	0.5	0.068	30	5	0.068
12:16:00	1218	215.7	3	0.5	0.068	30	5	0.068
12:13:00	1221	216.2	3	0.5	0.068	30	5	0.068
12:10:00	1224	216.7	3	0.5	0.068	30	5	0.068
12:07:00	1227	217.2	3	0.5	0.068	30	5	0.068
12:04:00	1230	217.7	3	0.5	0.068	30	5	0.068
12:01:00	1233	218.2	3	0.5	0.068	30	5	0.068
11:58:09	1236	218.7	3	0.5	0.068	30	5	0.068
11:55:09	1239	219.2	3	0.5	0.068	30	5	0.068
11:52:09	1242	219.7	3	0.5	0.068	30	5	0.068

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
1:55:01	1119	199	3	0.5	0.068	30	5	0.068
1:52:01	1122	199.5	3	0.5	0.068	30	5	0.068
1:49:01	1125	200	3	0.5	0.068	30	5	0.068
1:46:01	1128	200.5	3	0.5	0.068	30	5	0.068
1:43:01	1131	201	3	0.5	0.068	30	5	0.068
1:40:01	1134	201.5	3	0.5	0.068	30	5	0.068
1:37:01	1137	202	3	0.5	0.068	30	5.1	0.069
1:34:01	1140	202.5	3	0.5	0.068	30	5	0.068
1:31:01	1143	203	3	0.5	0.068	30	5	0.068
1:28:01	1146	203.5	3	0.5	0.068	30	5.1	0.069
1:25:01	1149	204	3	0.5	0.068	30	5.1	0.069
1:22:01	1152	204.5	3	0.5	0.068	30	5.1	0.069
1:19:01	1155	205	3	0.5	0.068	30	5.1	0.069
1:16:01	1158	205.5	3	0.5	0.068	30	5.1	0.069
1:13:01	1161	206	3	0.5	0.068	30	5.1	0.069
1:10:01	1164	206.5	3	0.6	0.082	30	5.1	0.069
1:07:01	1167	207.1	3	0.4	0.054	30	5.1	0.069
1:04:01	1170	207.5	3	0.5	0.068	30	5.1	0.069
1:01:01	1173	208	3	0.6	0.082	30	5.2	0.071
12:58:01	1176	208.6	3	0.5	0.068	30	5.1	0.069
12:55:00	1179	209.1	3	0.5	0.068	30	5.1	0.069
12:52:01	1182	209.6	3	0.5	0.068	30	5.1	0.069
12:49:00	1185	210.1	3	0.5	0.068	30	5.1	0.069
12:46:00	1188	210.6	3	0.5	0.068	30	5.1	0.069
12:43:00	1191	211.1	3	0.5	0.068	30	5.1	0.069
12:40:00	1194	211.6	3	0.6	0.082	30	5.1	0.069
12:37:00	1197	212.2	3	0.4	0.054	30	5	0.068
12:34:00	1200	212.6	3	0.6	0.082	30	5.1	0.069
12:31:00	1203	213.2	3	0.5	0.068	30	5	0.068
12:28:00	1206	213.7	3	0.5	0.068	30	5	0.068
12:25:00	1209	214.2	3	0.5	0.068	30	5	0.068
12:22:00	1212	214.7	3	0.5	0.068	30	5	0.068
12:19:00	1215	215.2	3	0.5	0.068	30	5	0.068
12:16:00	1218	215.7	3	0.5	0.068	30	5	0.068
12:13:00	1221	216.2	3	0.5	0.068	30	5	0.068
12:10:00	1224	216.7	3	0.5	0.068	30	5	0.068
12:07:00	1227	217.2	3	0.5	0.068	30	5	0.068
12:04:00	1230	217.7	3	0.5	0.068	30	5	0.068
12:01:00	1233	218.2	3	0.5	0.068	30	5	0.068
11:58:09	1236	218.7	3	0.5	0.068	30	5	0.068
11:55:09	1239	219.2	3	0.5	0.068	30	5	0.068
11:52:09	1242	219.7	3	0.5	0.068	30	5	0.068

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
11:49:09	1245	220.2	3	0.5	0.068	30	5	0.068
11:46:09	1248	220.7	3	0.5	0.068	30	5	0.068
11:43:09	1251	221.2	3	0.5	0.068	30	5	0.068
11:40:09	1254	221.7	3	0.5	0.068	30	5	0.068
11:37:09	1257	222.2	3	0.5	0.068	30	5	0.068
11:34:09	1260	222.7	3	0.5	0.068	30	5	0.068
11:31:09	1263	223.2	3	0.5	0.068	30	5	0.068
11:28:09	1266	223.7	3	0.5	0.068	30	5	0.068
11:25:09	1269	224.2	3	0.5	0.068	30	5	0.068
11:22:08	1272	224.7	3	0.5	0.068	30	5	0.068
11:19:09	1275	225.2	3	0.5	0.068	30	5	0.068
11:16:09	1278	225.7	3	0.5	0.068	30	5	0.068
11:13:09	1281	226.2	3	0.5	0.068	30	5	0.068
11:10:08	1284	226.7	3	0.5	0.068	30	5	0.068
11:07:08	1287	227.2	3	0.5	0.068	30	5	0.068
11:04:08	1290	227.7	3	0.5	0.068	30	5	0.068
11:01:08	1293	228.2	3	0.5	0.068	30	5	0.068
10:58:08	1296	228.7	3	0.5	0.068	30	5	0.068
10:55:08	1299	229.2	3	0.5	0.068	30	5	0.068
10:52:08	1302	229.7	3	0.5	0.068	30	5	0.068
10:49:08	1305	230.2	3	0.5	0.068	30	5	0.068
10:46:08	1308	230.7	3	0.5	0.068	30	4.9	0.067
10:43:08	1311	231.2	3	0.5	0.068	30	4.9	0.067
10:40:08	1314	231.7	3	0.5	0.068	30	4.9	0.067
10:37:08	1317	232.2	3	0.5	0.068	30	4.9	0.067
10:34:08	1320	232.7	3	0.5	0.068	30	4.9	0.067
10:31:08	1323	233.2	3	0.5	0.068	30	4.9	0.067
10:28:08	1326	233.7	3	0.5	0.068	30	5	0.068
10:25:08	1329	234.2	3	0.5	0.068	30	4.9	0.067
10:22:08	1332	234.7	3	0.5	0.068	30	4.9	0.067
10:19:08	1335	235.2	3	0.4	0.054	30	5	0.068
10:16:08	1338	235.6	3	0.5	0.068	30	5	0.068
10:13:08	1341	236.1	3	0.5	0.068	30	5	0.068
10:10:07	1344	236.6	3	0.5	0.068	30	5	0.068
10:07:07	1347	237.1	3	0.5	0.068	30	5.1	0.069
10:04:07	1350	237.6	3	0.5	0.068	30	5.1	0.069
10:01:07	1353	238.1	3	0.6	0.082	30	5	0.068
9:58:07	1356	238.7	3	0.4	0.054	30	5	0.068
9:55:07	1359	239.1	3	0.5	0.068	30	5	0.068
9:52:07	1362	239.6	3	0.6	0.082	30	5.1	0.069

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
9:49:07	1365	240.2	3	0.4	0.054	30	4.9	0.067
9:46:07	1368	240.6	3	0.5	0.068	30	5	0.068
9:43:07	1371	241.1	3	0.5	0.068	30	5	0.068
9:40:07	1374	241.6	3	0.6	0.082	30	5	0.068
9:37:07	1377	242.2	3	0.5	0.068	30	4.9	0.067
9:34:07	1380	242.7	3	0.4	0.054	30	4.9	0.067
9:31:07	1383	243.1	3	0.6	0.082	30	5	0.068
9:28:07	1386	243.7	3	0.4	0.054	30	4.9	0.067
9:25:07	1389	244.1	3	0.6	0.082	30	5	0.068
9:22:07	1392	244.7	3	0.4	0.054	30	4.9	0.067
9:19:07	1395	245.1	3	0.5	0.068	30	4.9	0.067
9:16:07	1398	245.6	3	0.5	0.068	30	5	0.068
9:13:07	1401	246.1	3	0.5	0.068	30	4.9	0.067
9:10:07	1404	246.6	3	0.5	0.068	30	4.9	0.067
9:07:07	1407	247.1	3	0.5	0.068	30	4.9	0.067
9:04:07	1410	247.6	3	0.5	0.068	30	4.9	0.067
9:01:06	1413	248.1	3	0.5	0.068	30	4.9	0.067
8:58:07	1416	248.6	3	0.5	0.068	30	4.8	0.065
8:55:07	1419	249.1	3	0.5	0.068	30	4.9	0.067
8:52:07	1422	249.6	3	0.4	0.054	30	4.8	0.065
8:49:06	1425	250	3	0.6	0.082	30	4.9	0.067
8:46:06	1428	250.6	3	0.4	0.054	30	4.8	0.065
8:43:06	1431	251	3	0.5	0.068	30	4.9	0.067
8:40:06	1434	251.5	3	0.5	0.068	30	4.9	0.067
8:37:06	1437	252	3	0.5	0.068	30	4.9	0.067
8:34:06	1440	252.5	3	0.5	0.068	30	4.8	0.065
8:31:06	1443	253	3	0.4	0.054	30	4.8	0.065
8:28:06	1446	253.4	3	0.6	0.082	30	4.9	0.067
8:25:06	1449	254	3	0.4	0.054	30	4.8	0.065
8:22:06	1452	254.4	3	0.5	0.068	30	4.9	0.067
8:19:06	1455	254.9	3	0.5	0.068	30	4.8	0.065
8:16:06	1458	255.4	3	0.5	0.068	30	4.8	0.065
8:13:06	1461	255.9	3	0.5	0.068	30	4.8	0.065
8:10:06	1464	256.4	3	0.5	0.068	30	4.8	0.065
8:07:06	1467	256.9	3	0.4	0.054	30	4.8	0.065
8:04:06	1470	257.3	3	0.5	0.068	30	4.8	0.065
8:01:05	1473	257.8	3	0.5	0.068	30	4.8	0.065
7:58:06	1476	258.3	3	0.5	0.068	30	4.8	0.065
7:55:06	1479	258.8	3	0.5	0.068	30	4.8	0.065
7:52:05	1482	259.3	3	0.4	0.054	30	4.8	0.065
7:49:05	1485	259.7	3	0.5	0.068	30	4.9	0.067

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
7:46:05	1488	260.2	3	0.5	0.068	30	4.9	0.067
7:43:05	1491	260.7	3	0.5	0.068	30	4.9	0.067
7:40:05	1494	261.2	3	0.5	0.068	30	4.9	0.067
7:37:05	1497	261.7	3	0.4	0.054	30	4.9	0.067
7:34:05	1500	262.1	3	0.5	0.068	30	5	0.068
7:31:05	1503	262.6	3	0.5	0.068	30	4.9	0.067
7:28:05	1506	263.1	3	0.5	0.068	30	4.9	0.067
7:25:05	1509	263.6	3	0.5	0.068	30	4.9	0.067
7:22:05	1512	264.1	3	0.5	0.068	30	4.8	0.065
7:19:05	1515	264.6	3	0.5	0.068	30	4.8	0.065
7:16:05	1518	265.1	3	0.5	0.068	30	4.8	0.065
7:13:05	1521	265.6	3	0.5	0.068	30	4.7	0.064
7:10:05	1524	266.1	3	0.5	0.068	30	4.7	0.064
7:07:05	1527	266.6	3	0.5	0.068	30	4.7	0.064
7:04:05	1530	267.1	3	0.4	0.054	30	4.7	0.064
7:01:05	1533	267.5	3	0.5	0.068	30	4.7	0.064
6:58:04	1536	268	3	0.5	0.068	30	4.7	0.064
6:55:04	1539	268.5	3	0.4	0.054	30	4.6	0.063
6:52:05	1542	268.9	3	0.5	0.068	30	4.7	0.064
6:49:04	1545	269.4	3	0.5	0.068	30	4.6	0.063
6:46:04	1548	269.9	3	0.4	0.054	30	4.6	0.063
6:43:04	1551	270.3	3	0.5	0.068	30	4.7	0.064
6:40:04	1554	270.8	3	0.5	0.068	30	4.6	0.063
6:37:04	1557	271.3	3	0.5	0.068	30	4.6	0.063
6:34:04	1560	271.8	3	0.4	0.054	30	4.6	0.063
6:31:04	1563	272.2	3	0.5	0.068	30	4.6	0.063
6:28:04	1566	272.7	3	0.4	0.054	30	4.6	0.063
6:25:04	1569	273.1	3	0.5	0.068	30	4.7	0.064
6:22:04	1572	273.6	3	0.4	0.054	30	4.6	0.063
6:19:04	1575	274	3	0.5	0.068	30	4.7	0.064
6:16:04	1578	274.5	3	0.5	0.068	30	4.6	0.063
6:13:04	1581	275	3	0.4	0.054	30	4.6	0.063
6:10:04	1584	275.4	3	0.5	0.068	30	4.6	0.063
6:07:04	1587	275.9	3	0.5	0.068	30	4.6	0.063
6:04:04	1590	276.4	3	0.4	0.054	30	4.6	0.063
6:01:03	1593	276.8	3	0.5	0.068	30	4.6	0.063
5:58:04	1596	277.3	3	0.5	0.068	30	4.6	0.063
5:55:04	1599	277.8	3	0.4	0.054	30	4.6	0.063
5:52:03	1602	278.2	3	0.5	0.068	30	4.6	0.063
5:49:04	1605	278.7	3	0.4	0.054	30	4.6	0.063
5:46:03	1608	279.1	3	0.5	0.068	30	4.7	0.064

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
5:43:03	1611	279.6	3	0.4	0.054	30	4.6	0.063
5:40:03	1614	280	3	0.5	0.068	30	4.7	0.064
5:37:03	1617	280.5	3	0.5	0.068	30	4.6	0.063
5:34:03	1620	281	3	0.4	0.054	30	4.6	0.063
5:31:03	1623	281.4	3	0.5	0.068	30	4.7	0.064
5:28:03	1626	281.9	3	0.5	0.068	30	4.7	0.064
5:25:03	1629	282.4	3	0.4	0.054	30	4.6	0.063
5:22:03	1632	282.8	3	0.5	0.068	30	4.7	0.064
5:19:03	1635	283.3	3	0.5	0.068	30	4.6	0.063
5:16:03	1638	283.8	3	0.4	0.054	30	4.6	0.063
5:13:03	1641	284.2	3	0.5	0.068	30	4.7	0.064
5:10:03	1644	284.7	3	0.4	0.054	30	4.7	0.064
5:07:03	1647	285.1	3	0.5	0.068	30	4.8	0.065
5:04:03	1650	285.6	3	0.5	0.068	30	4.8	0.065
5:01:03	1653	286.1	3	0.5	0.068	30	4.8	0.065
4:58:03	1656	286.6	3	0.4	0.054	30	4.8	0.065
4:55:03	1659	287	3	0.5	0.068	30	4.8	0.065
4:52:03	1662	287.5	3	0.4	0.054	30	4.8	0.065
4:49:02	1665	287.9	3	0.5	0.068	30	4.9	0.067
4:46:02	1668	288.4	3	0.5	0.068	30	4.9	0.067
4:43:03	1671	288.9	3	0.5	0.068	30	4.9	0.067
4:40:02	1674	289.4	3	0.5	0.068	30	4.9	0.067
4:37:02	1677	289.9	3	0.5	0.068	30	4.9	0.067
4:34:02	1680	290.4	3	0.5	0.068	30	4.8	0.065
4:31:02	1683	290.9	3	0.5	0.068	30	4.9	0.067
4:28:02	1686	291.4	3	0.4	0.054	30	4.9	0.067
4:25:02	1689	291.8	3	0.5	0.068	30	4.9	0.067
4:22:02	1692	292.3	3	0.5	0.068	30	4.9	0.067
4:19:02	1695	292.8	3	0.5	0.068	30	4.9	0.067
4:16:02	1698	293.3	3	0.5	0.068	30	4.8	0.065
4:13:02	1701	293.8	3	0.5	0.068	30	4.8	0.065
4:10:02	1704	294.3	3	0.5	0.068	30	4.7	0.064
4:07:02	1707	294.8	3	0.4	0.054	30	4.7	0.064
4:04:02	1710	295.2	3	0.6	0.082	30	4.7	0.064
4:01:02	1713	295.8	3	0.5	0.068	30	4.6	0.063
3:58:02	1716	296.3	3	0.4	0.054	30	4.5	0.061
3:55:02	1719	296.7	3	0.5	0.068	30	4.5	0.061
3:52:02	1722	297.2	3	0.5	0.068	30	4.5	0.061
3:49:02	1725	297.7	3	0.4	0.054	30	4.4	0.060
3:46:02	1728	298.1	3	0.5	0.068	30	4.4	0.060
3:43:01	1731	298.6	3	0.4	0.054	30	4.4	0.060

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
3:40:02	1734	299	3	0.5	0.068	30	4.4	0.060
3:37:01	1737	299.5	3	0.4	0.054	30	4.4	0.060
3:34:01	1740	299.9	3	0.5	0.068	30	4.4	0.060
3:31:01	1743	300.4	3	0.4	0.054	30	4.3	0.058
3:28:01	1746	300.8	3	0.4	0.054	30	4.4	0.060
3:25:01	1749	301.2	3	0.5	0.068	30	4.4	0.060
3:22:01	1752	301.7	3	0.4	0.054	30	4.4	0.060
3:19:01	1755	302.1	3	0.4	0.054	30	4.4	0.060
3:16:01	1758	302.5	3	0.5	0.068	30	4.4	0.060
3:13:01	1761	303	3	0.4	0.054	30	4.3	0.058
3:10:01	1764	303.4	3	0.5	0.068	30	4.3	0.058
3:07:01	1767	303.9	3	0.4	0.054	30	4.3	0.058
3:04:01	1770	304.3	3	0.4	0.054	30	4.3	0.058
3:01:01	1773	304.7	3	0.5	0.068	30	4.4	0.060
2:58:01	1776	305.2	3	0.4	0.054	30	4.3	0.058
2:55:01	1779	305.6	3	0.5	0.068	30	4.3	0.058
2:52:01	1782	306.1	3	0.4	0.054	30	4.2	0.057
2:49:01	1785	306.5	3	0.4	0.054	30	4.3	0.058
2:46:01	1788	306.9	3	0.4	0.054	30	4.3	0.058
2:43:01	1791	307.3	3	0.4	0.054	30	4.3	0.058
2:40:01	1794	307.7	3	0.5	0.068	30	4.4	0.060
2:37:01	1797	308.2	3	0.4	0.054	30	4.3	0.058
2:34:00	1800	308.6	3	0.5	0.068	30	4.3	0.058
2:31:00	1803	309.1	3	0.4	0.054	30	4.3	0.058
2:28:00	1806	309.5	3	0.4	0.054	30	4.3	0.058
2:25:00	1809	309.9	3	0.4	0.054	30	4.3	0.058
2:22:00	1812	310.3	3	0.5	0.068	30	4.3	0.058
2:19:00	1815	310.8	3	0.4	0.054	30	4.3	0.058
2:16:00	1818	311.2	3	0.4	0.054	30	4.3	0.058
2:13:00	1821	311.6	3	0.5	0.068	30	4.3	0.058
2:10:00	1824	312.1	3	0.4	0.054	30	4.3	0.058
2:07:00	1827	312.5	3	0.4	0.054	30	4.3	0.058
2:04:00	1830	312.9	3	0.5	0.068	30	4.3	0.058
2:01:00	1833	313.4	3	0.4	0.054	30	4.3	0.058
1:58:00	1836	313.8	3	0.4	0.054	30	4.3	0.058
1:55:00	1839	314.2	3	0.4	0.054	30	4.3	0.058
1:52:00	1842	314.6	3	0.5	0.068	30	4.4	0.060
1:49:00	1845	315.1	3	0.4	0.054	30	4.3	0.058
1:46:00	1848	315.5	3	0.4	0.054	30	4.3	0.058
1:43:00	1851	315.9	3	0.5	0.068	30	4.3	0.058
1:40:00	1854	316.4	3	0.4	0.054	30	4.3	0.058

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
1:37:00	1857	316.8	3	0.4	0.054	30	4.3	0.058
1:34:00	1860	317.2	3	0.5	0.068	30	4.4	0.060
1:31:00	1863	317.7	3	0.4	0.054	30	4.3	0.058
1:27:59	1866	318.1	3	0.4	0.054	30	4.3	0.058
1:25:00	1869	318.5	3	0.5	0.068	30	4.4	0.060
1:21:59	1872	319	3	0.4	0.054	30	4.3	0.058
1:19:00	1875	319.4	3	0.4	0.054	30	4.3	0.058
1:16:00	1878	319.8	3	0.4	0.054	30	4.4	0.060
1:12:59	1881	320.2	3	0.5	0.068	30	4.4	0.060
1:09:59	1884	320.7	3	0.4	0.054	30	4.3	0.058
1:06:59	1887	321.1	3	0.5	0.068	30	4.4	0.060
1:03:59	1890	321.6	3	0.4	0.054	30	4.3	0.058
1:00:59	1893	322	3	0.4	0.054	30	4.3	0.058
12:57:59	1896	322.4	3	0.5	0.068	30	4.4	0.060
12:54:59	1899	322.9	3	0.4	0.054	30	4.3	0.058
12:51:59	1902	323.3	3	0.4	0.054	30	4.3	0.058
12:48:59	1905	323.7	3	0.5	0.068	30	4.4	0.060
12:45:59	1908	324.2	3	0.4	0.054	30	4.3	0.058
12:42:59	1911	324.6	3	0.4	0.054	30	4.3	0.058
12:39:59	1914	325	3	0.5	0.068	30	4.4	0.060
12:36:59	1917	325.5	3	0.4	0.054	30	4.3	0.058
12:33:59	1920	325.9	3	0.4	0.054	30	4.3	0.058
12:30:59	1923	326.3	3	0.5	0.068	30	4.4	0.060
12:27:59	1926	326.8	3	0.4	0.054	30	4.3	0.058
12:24:59	1929	327.2	3	0.4	0.054	30	4.3	0.058
12:21:59	1932	327.6	3	0.5	0.068	30	4.3	0.058
12:18:59	1935	328.1	3	0.4	0.054	30	4.3	0.058
12:15:58	1938	328.5	3	0.4	0.054	30	4.3	0.058
12:12:59	1941	328.9	3	0.5	0.068	30	4.3	0.058
12:09:59	1944	329.4	3	0.4	0.054	30	4.3	0.058
12:06:58	1947	329.8	3	0.4	0.054	30	4.3	0.058
12:03:58	1950	330.2	3	0.5	0.068	30	4.3	0.058
12:00:58	1953	330.7	3	0.4	0.054	30	4.3	0.058
11:57:58	1956	331.1	3	0.4	0.054	30	4.3	0.058
11:54:58	1959	331.5	3	0.4	0.054	30	4.4	0.060
11:51:58	1962	331.9	3	0.5	0.068	30	4.4	0.060
11:48:58	1965	332.4	3	0.4	0.054	30	4.3	0.058
11:45:58	1968	332.8	3	0.4	0.054	30	4.3	0.058
11:42:58	1971	333.2	3	0.5	0.068	30	4.4	0.060
11:39:58	1974	333.7	3	0.4	0.054	30	4.3	0.058
11:36:58	1977	334.1	3	0.4	0.054	30	4.3	0.058

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
11:33:58	1980	334.5	3	0.5	0.068	30	4.3	0.058
11:30:58	1983	335	3	0.4	0.054	30	4.3	0.058
11:27:58	1986	335.4	3	0.5	0.068	30	4.3	0.058
11:24:58	1989	335.9	3	0.4	0.054	30	4.2	0.057
11:21:58	1992	336.3	3	0.4	0.054	30	4.3	0.058
11:18:58	1995	336.7	3	0.4	0.054	30	4.3	0.058
11:15:58	1998	337.1	3	0.5	0.068	30	4.4	0.060
11:12:58	2001	337.6	3	0.4	0.054	30	4.3	0.058
11:09:57	2004	338	3	0.4	0.054	30	4.3	0.058
11:06:58	2007	338.4	3	0.4	0.054	30	4.3	0.058
11:03:58	2010	338.8	3	0.5	0.068	30	4.3	0.058
11:00:57	2013	339.3	3	0.4	0.054	30	4.3	0.058
10:57:57	2016	339.7	3	0.4	0.054	30	4.3	0.058
10:54:57	2019	340.1	3	0.5	0.068	30	4.3	0.058
10:51:57	2022	340.6	3	0.4	0.054	30	4.2	0.057
10:48:57	2025	341	3	0.5	0.068	30	4.2	0.057
10:45:57	2028	341.5	3	0.4	0.054	30	4.1	0.056
10:42:57	2031	341.9	3	0.4	0.054	30	4.1	0.056
10:39:57	2034	342.3	3	0.4	0.054	30	4.2	0.057
10:36:57	2037	342.7	3	0.4	0.054	30	4.2	0.057
10:33:57	2040	343.1	3	0.5	0.068	30	4.2	0.057
10:30:57	2043	343.6	3	0.4	0.054	30	4.1	0.056
10:27:57	2046	344	3	0.4	0.054	30	4.1	0.056
10:24:57	2049	344.4	3	0.4	0.054	30	4.2	0.057
10:21:57	2052	344.8	3	0.4	0.054	30	4.2	0.057
10:18:57	2055	345.2	3	0.4	0.054	30	4.2	0.057
10:15:57	2058	345.6	3	0.4	0.054	30	4.2	0.057
10:12:57	2061	346	3	0.5	0.068	30	4.2	0.057
10:09:57	2064	346.5	3	0.4	0.054	30	4.2	0.057
10:06:57	2067	346.9	3	0.4	0.054	30	4.2	0.057
10:03:56	2070	347.3	3	0.4	0.054	30	4.2	0.057
10:00:57	2073	347.7	3	0.4	0.054	30	4.2	0.057
9:57:56	2076	348.1	3	0.5	0.068	30	4.2	0.057
9:54:56	2079	348.6	3	0.4	0.054	30	4.1	0.056
9:51:57	2082	349	3	0.4	0.054	30	4.2	0.057
9:48:57	2085	349.4	3	0.4	0.054	30	4.2	0.057
9:45:56	2088	349.8	3	0.4	0.054	30	4.2	0.057
9:42:56	2091	350.2	3	0.5	0.068	30	4.2	0.057
9:39:56	2094	350.7	3	0.4	0.054	30	4.1	0.056
9:36:56	2097	351.1	3	0.4	0.054	30	4.1	0.056
9:33:56	2100	351.5	3	0.4	0.054	30	4.1	0.056

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
9:30:56	2103	351.9	3	0.4	0.054	30	4.1	0.056
9:27:56	2106	352.3	3	0.4	0.054	30	4.1	0.056
9:24:56	2109	352.7	3	0.5	0.068	30	4.1	0.056
9:21:56	2112	353.2	3	0.4	0.054	30	3.9	0.053
9:18:56	2115	353.6	3	0.4	0.054	30	3.9	0.053
9:15:56	2118	354	3	0.4	0.054	30	3.9	0.053
9:12:56	2121	354.4	3	0.4	0.054	30	3.9	0.053
9:09:56	2124	354.8	3	0.4	0.054	30	3.8	0.052
9:06:56	2127	355.2	3	0.4	0.054	30	3.8	0.052
9:03:56	2130	355.6	3	0.4	0.054	30	3.8	0.052
9:00:56	2133	356	3	0.4	0.054	30	3.8	0.052
8:57:56	2136	356.4	3	0.4	0.054	30	3.8	0.052
8:54:55	2139	356.8	3	0.3	0.041	30	3.8	0.052
8:51:55	2142	357.1	3	0.4	0.054	30	3.8	0.052
8:48:55	2145	357.5	3	0.4	0.054	30	3.8	0.052
8:45:55	2148	357.9	3	0.4	0.054	30	3.8	0.052
8:42:55	2151	358.3	3	0.3	0.041	30	3.8	0.052
8:39:55	2154	358.6	3	0.4	0.054	30	3.8	0.052
8:36:55	2157	359	3	0.4	0.054	30	3.8	0.052
8:33:55	2160	359.4	3	0.4	0.054	30	3.8	0.052
8:30:55	2163	359.8	3	0.4	0.054	30	3.8	0.052
8:27:55	2166	360.2	3	0.4	0.054	30	3.8	0.052
8:24:55	2169	360.6	3	0.3	0.041	30	3.7	0.050
8:21:55	2172	360.9	3	0.4	0.054	30	3.8	0.052
8:18:55	2175	361.3	3	0.4	0.054	30	3.8	0.052
8:15:55	2178	361.7	3	0.4	0.054	30	3.8	0.052
8:12:55	2181	362.1	3	0.3	0.041	30	3.8	0.052
8:09:55	2184	362.4	3	0.4	0.054	30	3.8	0.052
8:06:55	2187	362.8	3	0.4	0.054	30	3.8	0.052
8:03:55	2190	363.2	3	0.4	0.054	30	3.8	0.052
8:00:55	2193	363.6	3	0.4	0.054	30	3.8	0.052
7:57:55	2196	364	3	0.3	0.041	30	3.8	0.052
7:54:55	2199	364.3	3	0.4	0.054	30	3.9	0.053
7:51:55	2202	364.7	3	0.4	0.054	30	3.9	0.053
7:48:55	2205	365.1	3	0.4	0.054	30	3.9	0.053
7:45:55	2208	365.5	3	0.4	0.054	30	3.9	0.053
7:42:54	2211	365.9	3	0.3	0.041	30	3.9	0.053
7:39:54	2214	366.2	3	0.4	0.054	30	4	0.054
7:36:54	2217	366.6	3	0.4	0.054	30	3.9	0.053
7:33:55	2220	367	3	0.4	0.054	30	3.9	0.053
7:30:54	2223	367.4	3	0.4	0.054	30	3.9	0.053

Time (s)	Time (min)	Pressure	dt min	dP torr	ml/min	dt min	dP torr	ml/min
7:27:54	2226	367.8	3	0.4	0.054	30	3.9	0.053
7:24:54	2229	368.2	3	0.4	0.054	30	3.8	0.052
7:21:54	2232	368.6	3	0.4	0.054	30	3.8	0.052
7:18:54	2235	369	3	0.4	0.054	30	3.8	0.052
7:15:54	2238	369.4	3	0.4	0.054	30	3.8	0.052
7:12:54	2241	369.8	3	0.4	0.054	30	3.8	0.052
7:09:54	2244	370.2	3	0.3	0.041	30	3.8	0.052
7:06:54	2247	370.5	3	0.4	0.054	30	3.9	0.053
7:03:54	2250	370.9	3	0.4	0.054	30	3.9	0.053
7:00:54	2253	371.3	3	0.4	0.054	30	3.9	0.053
6:57:54	2256	371.7	3	0.3	0.041	30	3.8	0.052
6:54:54	2259	372	3	0.4	0.054	30	3.9	0.053
6:51:54	2262	372.4	3	0.4	0.054	30	3.9	0.053
6:48:54	2265	372.8	3	0.4	0.054	30	3.9	0.053
6:45:54	2268	373.2	3	0.4	0.054	30	3.9	0.053
6:42:54	2271	373.6	3	0.4	0.054	30	3.9	0.053
6:39:54	2274	374	3	0.4	0.054	30	3.8	0.052
6:36:53	2277	374.4	3	0.4	0.054	30	3.8	0.052
6:33:54	2280	374.8	3	0.4	0.054	30	3.8	0.052
6:30:54	2283	375.2	3	0.3	0.041	30	3.7	0.050
6:27:53	2286	375.5	3	0.4	0.054	30	3.8	0.052
6:24:53	2289	375.9	3	0.4	0.054	30	3.8	0.052
6:21:53	2292	376.3	3	0.4	0.054	30	3.8	0.052
6:18:53	2295	376.7	3	0.4	0.054	30	3.8	0.052
6:15:53	2298	377.1	3	0.4	0.054	30	3.8	0.052
6:12:53	2301	377.5	3	0.3	0.041	30	3.8	0.052
6:09:53	2304	377.8	3	0.4	0.054	30	3.9	0.053
6:06:53	2307	378.2	3	0.4	0.054	30	3.9	0.053
6:03:53	2310	378.6	3	0.3	0.041	30	3.9	0.053
6:00:53	2313	378.9	3	0.4	0.054	30	4	0.054
5:57:53	2316	379.3	3	0.4	0.054	30	4	0.054
5:54:53	2319	379.7	3	0.4	0.054	30	4	0.054
5:51:53	2322	380.1	3	0.4	0.054	30	4	0.054

Empirical Models for Predicting Flow Rate for Capillary Length (L)

Capillary Diameter 0.05 mm:

$$Flow\ \text{rate(y)} = 2.4\text{L}^{-0.986}$$

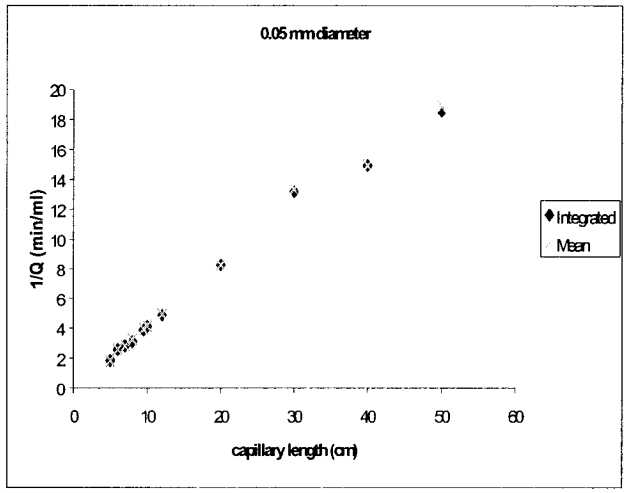
Capillary Diameter 0.10 mm:

$$Flow\ \text{rate(y)} = 29.12\text{L}^{-0.947}$$

Table A-2 Regression Data comparing the integrated flow rate method to the mean flow rate method. Both lines fall within the confidence intervals of each other.

0.05 mm Diameter Capillary

Length	Integrated		Mean	
cm	ml/min	min/ml	ml/min	min/ml
5	0.548	1.8248175	0.548	1.824818
6	0.389	2.5706941	0.389	2.570694
7	0.356	2.8089888	0.356	2.808989
8	0.324	3.0864198	0.309	3.236246
9.5	0.259	3.8610039	0.253	3.952569
10	0.244	4.0983607	0.242	4.132231
12	0.206	4.8543689	0.204	4.901961
20	0.121	8.2644628	0.121	8.264463
30	0.076	13.157895	0.075	13.33333
40	0.067	14.925373	0.067	14.92537
50	0.054	18.518519	0.053	18.86792



INTEGRATED DATA REGRESSION
SUMMARY OUTPUT for all points

Regression Statistics	
Multiple R	0.99498
R Square	0.989985
Adjusted R	0.988872
Standard E	0.612456
Observatio	11

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	333.70321	333.7032	889.6318	2.62E-10
Residual	9	3.3759234	0.375103		
Total	10	337.07914			

	Coefficients	*Standard Err*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	**0.339973**	0.2920433	1.16412	0.274306	-0.320675	1.000622
X Variable	**0.375854**	0.0126013	29.8267	2.62E-10	0.347348	0.40436

MEAN DATA REGRESSION
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.994951
R Square	0.989927
Adjusted F	0.988808
Standard E	0.6215
Observatic	11

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regressior	1	341.6365	341.6365	884.4687	2.68E-10
Residual	9	3.476357	0.386262		
Total	10	345.1129			

	Coefficients	*Standard Err*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	**0.337293**	0.296356	1.138135	0.284454	-0.333111	1.007696
X Variable	**0.380296**	0.012787	29.74002	2.68E-10	0.351369	0.409223

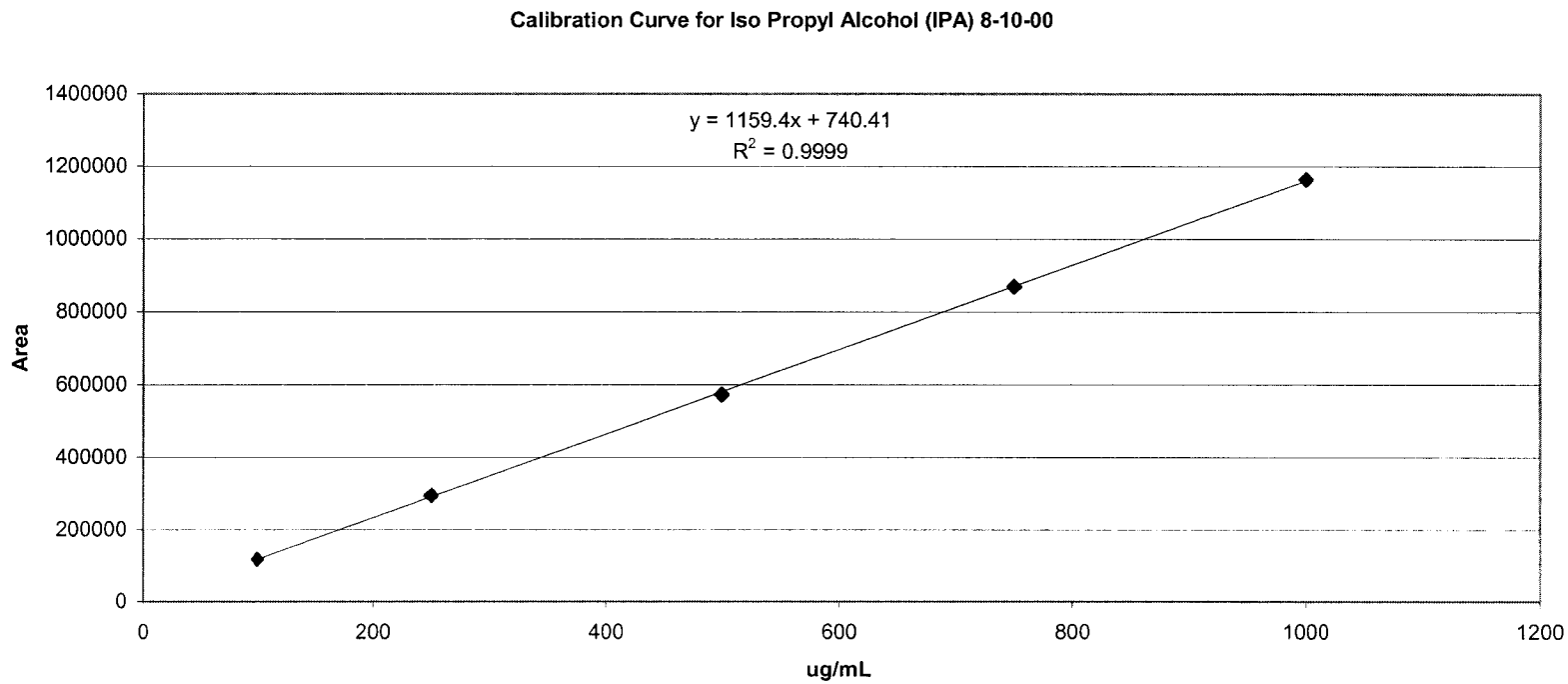
Appendix B – Concentration Calculation Methods for Charcoal tubes, Badges and Capillary-canisters

Table B-1 Example Calculations and Calibration curves for six compounds used in Phase II experiments

Iso propyl Alcohol

X	Y1	Y2	Y3	X	Ave	STD	CV
50	54338	54737	54355	50	54477	225.6	0.004142
100	117950	117887	117975	100	117937	45.3	0.000384
250	293986	295197	294986	250	294723	646.9	0.002195
500	572256	573612	572527	500	572798	717.6	0.001253
750	868925	865897	870964	750	868595	2549.5	0.002935
1000	1160360	1160670	1171080	1000	1164037	6101.7	0.005242

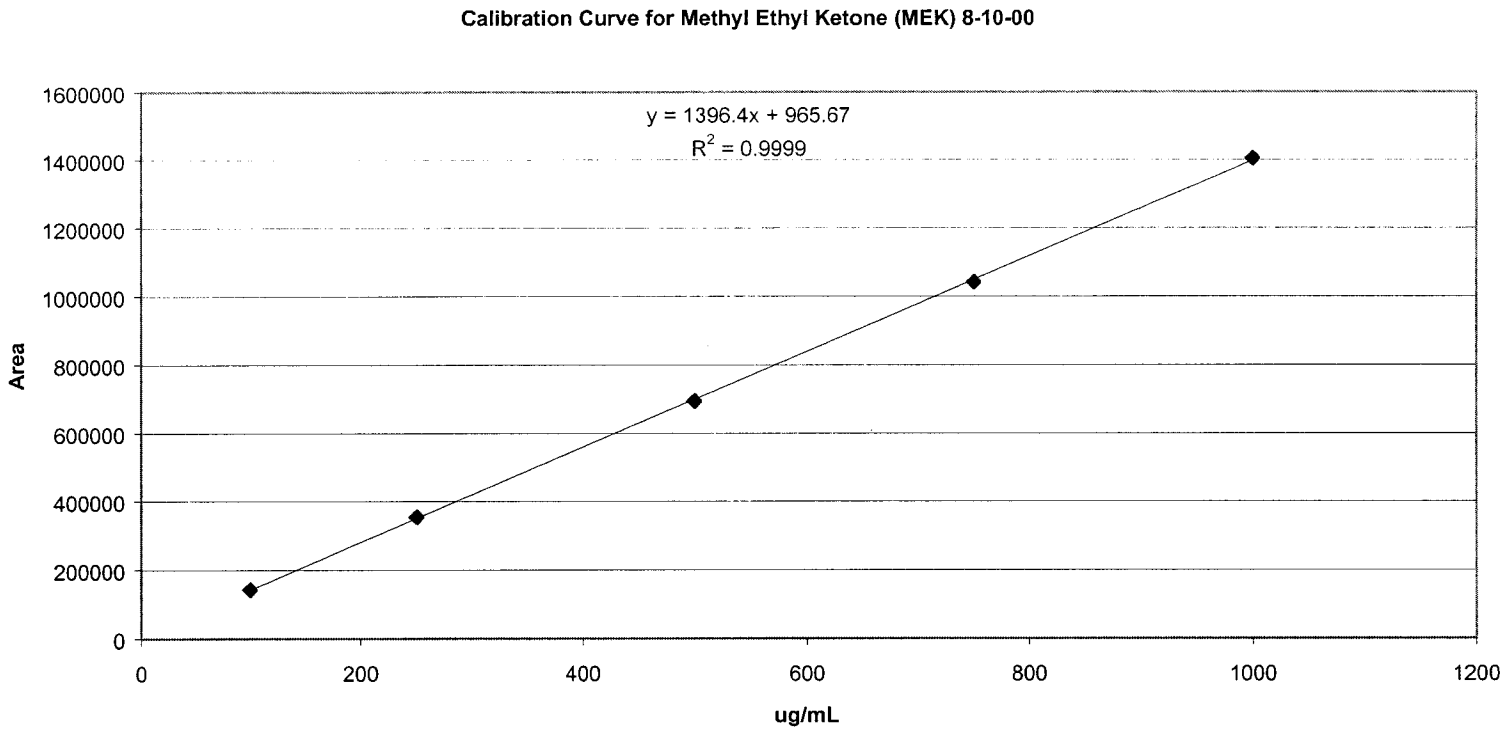
Badges	Area	ug	Flow Rate	Time	C(mg/m3)	Char Tu	Area	BArea	ug	Flow Rate	Time	C(mg/m3)
810-B-1	685654	1183.2	39.4	439	91.21	810-1	425782	0	**734.74**	0.032	405	80.99
810-B-2	655837	1131.7	39.4	443	86.45	810-2	419752	0	**724.33**	0.031	405	82.42
810-B-3	691591	1193.4	39.4	447	90.35	810-3	406975	0	**702.29**	0.033	405	75.07
810-B-4	690632	1191.8	39.4	445	90.63	180-4	572857	0	**988.54**	0.0383	405	91.04
810-B-5	597073	1030.3	39.4	441	79.06	810-5	477382	0	**823.78**	0.0315	405	92.25
810-B-6	697475	1203.6	39.4	440	92.57	810-6	417387	0	**720.25**	0.0295	405	86.12
810-Blank	<DL					810-Blank	<DL					
Mean	**669710**				**88.4**	**Mean**	**453356**					**84.6**
STD	**38497**				**5.00**	**STD**	**63549**					**6.50**
CV	**0.057**				**0.057**	**CV**	**0.140**					**0.077**
OU					**35.1**							**40.7**
Reference					**120.8**							**120.8**


Calibration Curve for Iso Propyl Alcohol (IPA) 8-10-00
y = 1159.4x + 740.41
R2 = 0.9999
Area
ug/mL
0
200000
400000
600000
800000
1000000
1200000
1400000
0
200
400
600
800
1000
1200

Methyl Ethyl Ketone

X	Y1	Y2	Y3	X	Ave	STD	CV
50	69988	70812	69986	50	70262	476.3	0.001243
100	142496	142160	142326	100	142327	168.0	0.000457
250	352264	354689	354221	250	353725	1286.4	0.00263
500	694617	694886	692770	500	694091	1151.9	0.00166
750	1043156	1037360	1043600	750	1041372	3481.6	0.003343
1000	1402660	1406830	1402730	1000	1404073	2387.6	0.0017

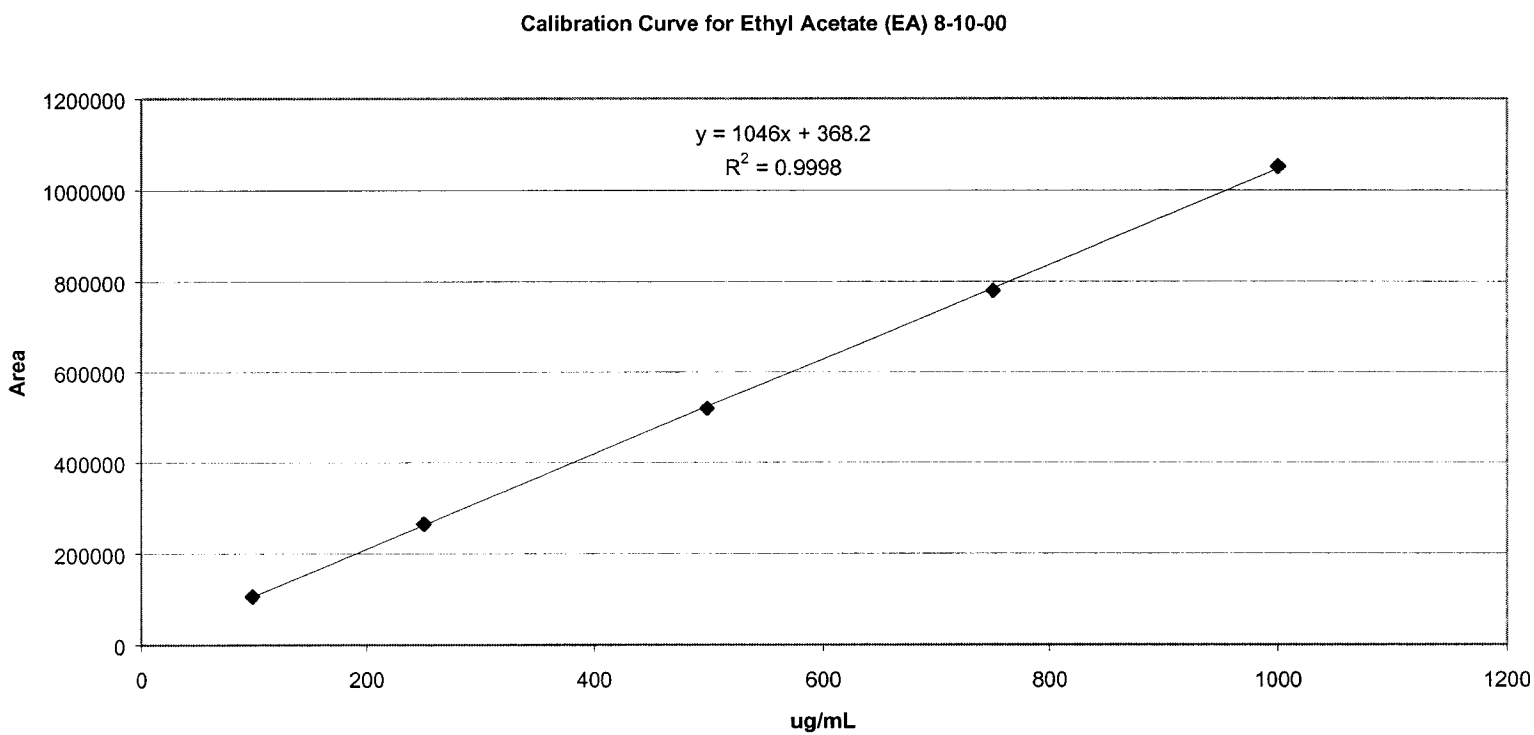
Badges	Area	ug	Flow Rate	Time	C(mg/m3)	Char Tu	Area	BackArea	ug	Flow Rate	Time	C(mg/m3)
810-B-1	877960	1257.8	36.3	439	89.69	810-1	381666	0	**546.80**	0.032	405	47.94
810-B-2	852794	1221.8	36.3	443	86.34	810-2	383302	0	**549.14**	0.031	405	49.70
810-B-3	899890	1289.2	36.3	447	90.29	810-3	367881	0	**527.05**	0.033	405	44.81
810-B-4	882237	1263.9	36.3	445	88.92	180-4	489173	0	**700.82**	0.0383	405	51.34
810-B-5	764882	1095.8	36.3	441	77.79	810-5	400196	0	**573.35**	0.0315	405	51.07
810-B-6	894762	1281.9	36.3	440	91.20	810-6	350475	0	**502.11**	0.0295	405	47.76
810-Blank	<DL					810-Blank						
Mean	**862087**				**86.6**	**Mean**	**398205**					**48.8**
STD	**50378.3**				**4.98**	**STD**	**54080.815**					**2.46**
CV	**0.058**				**0.057**	**CV**	**0.136**					**0.050**
OU					**33.7**							**39.3**
Reference					**72.2**							**72.2**


Calibration Curve for Methyl Ethyl Ketone (MEK) 8-10-00
y = 1396.4x + 965.67
R2 = 0.9999
Area
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
0
200
400
600
800
1000
1200
ug/mL

Ethyl Acetate

X	Y1	Y2	Y3	X	Ave	STD	CV
50	48755	50328	49665	50	49583	789.7	0.015927
100	106670	106517	106606	100	106598	76.8	0.000721
250	263502	265597	265023	250	264707	1082.6	0.00409
500	519168	519302	518070	500	518847	675.9	0.001303
750	780753	776839	781152	750	779581	2383.3	0.003057
1000	1053090	1052590	1049590	1000	1051757	1893.0	0.0018

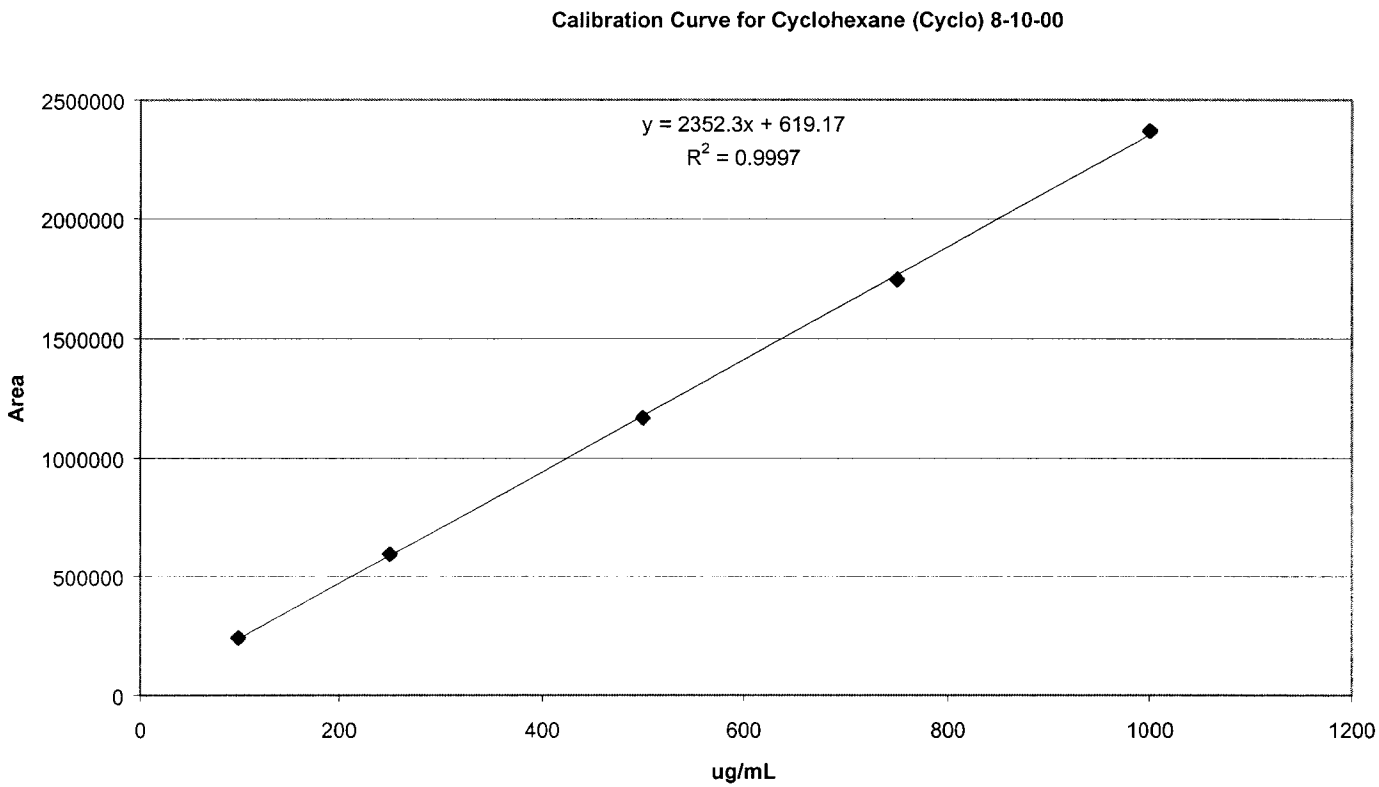
Badges	Area	ug	Flow Rate	Time	C(mg/m3)	Char Tu	Area	Back Area	ug	Flow Rate	Time	C(mg/m3)
810-B-1	1781460	3406.2	**34.5**	439	234.3	810-1	1418230	0	**2711.72**	0.032	405	217.96
810-B-2	1726090	3300.4	**34.5**	443	224.9	810-2	1388390	0	**2654.67**	0.031	405	220.25
810-B-3	1813900	3468.3	**34.5**	447	234.3	810-3	1355640	0	**2592.05**	0.033	405	202.02
810-B-4	1775740	3395.3	**34.5**	445	230.4	810-4	1581350	0	**3023.61**	0.0383	405	203.05
810-B-5	1538240	2941.2	**34.5**	441	201.4	810-5	1339650	0	**2287.93**	0.0315	405	186.81
810-B-6	1825810	3491.0	**34.5**	440	239.6	810-6	1196590	0	**2287.93**	0.0295	405	199.48
810-Blank	<DL					810-Blank						
Mean	**1743540**				**227.5**	**Mean**	**1372324**					**204.9**
STD	**106438.9**				**13.67**	**STD**	**138002.1**					**12.45**
CV	**0.061**				**0.060**	**CV**	**0.101**					**0.06**
OU					**17.1**							**17.3**
Reference					**217.6**							**217.6**


Calibration Curve for Ethyl Acetate (EA) 8-10-00
y = 1046x + 368.2
R2 = 0.9998
Area
ug/mL
0
200000
400000
600000
800000
1000000
1200000
0
200
400
600
800
1000
1200

Cyclohexane

X	Y1	Y2	Y3	X	Ave	STD	CV
50	117545	118818	115619	50	117327	1610.6	0.013727
100	241114	240768	241457	100	241113	344.5	0.001429
250	592262	596070	595395	250	594576	2031.9	0.003417
500	1170430	1169130	1164480	500	1168013	3128.2	0.002678
750	1752450	1736520	1748610	750	1745860	8313.4	0.004762
1000	2375700	2379430	2353680	1000	2369603	13915.6	0.005873

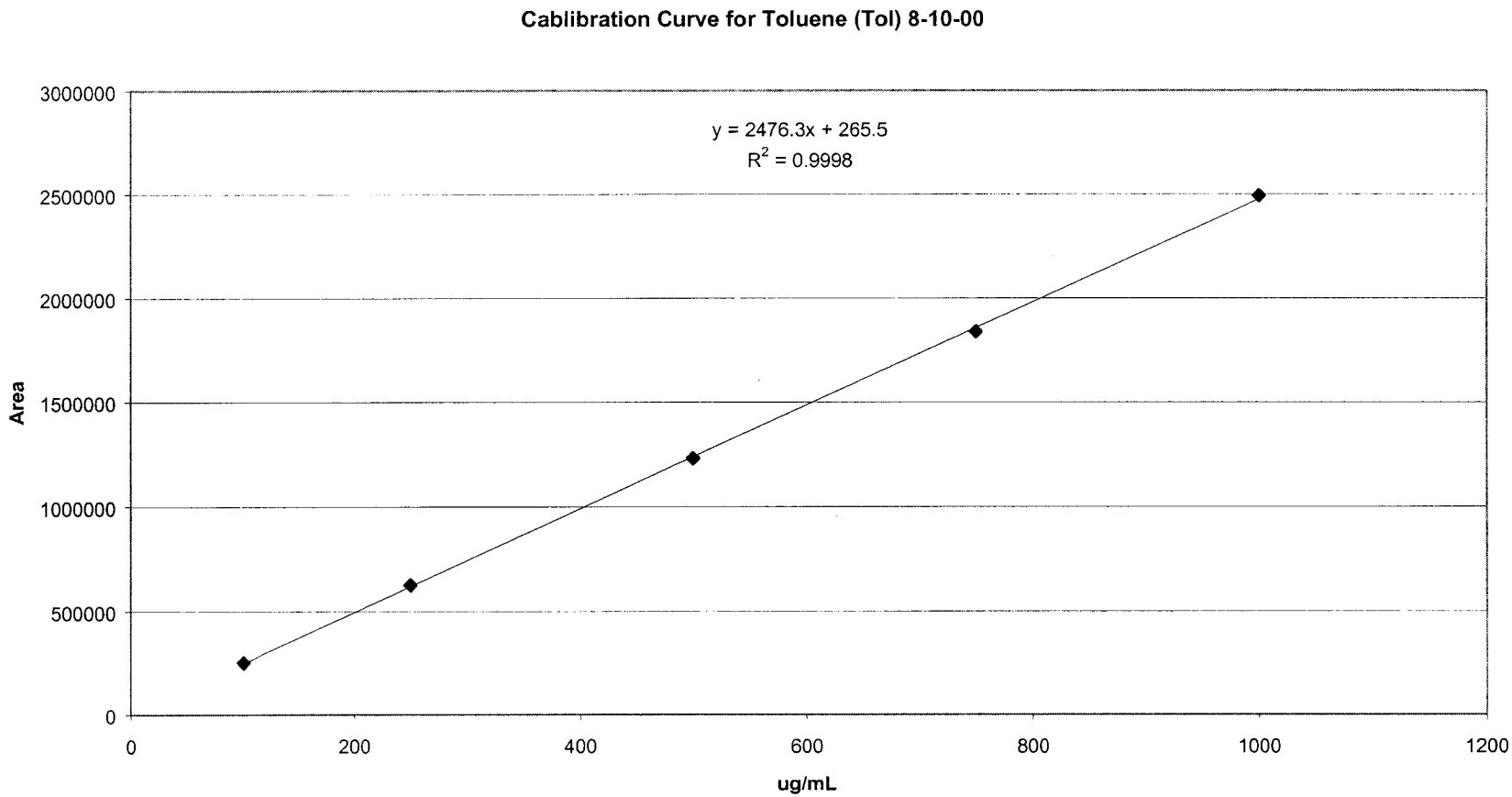
Badges	Area	ug	Flow Rate	Time	C(mg/m3)	Char Tu	Area	Back Area	ug	Flow Rate	Time	C(mg/m3)
810-B-1	2225140	1892.1	32.4	439	133.0	810-1	2129220	0	**1810.56**	0.032	405	139.70
810-B-2	2138660	1818.6	32.4	443	126.7	810-2	2069770	0	**1760.01**	0.031	405	140.18
810-B-3	2265720	1926.6	32.4	447	133.0	810-3	2031670	0	**1727.61**	0.033	405	129.26
810-B-4	2209190	1878.6	32.4	445	130.3	180-4	2211300	0	**1880.36**	0.0383	405	121.22
810-B-5	1916810	1629.9	32.4	441	114.1	810-5	1899780	0	**1615.46**	0.0315	405	126.63
810-B-6	2276300	1935.6	32.4	440	135.8	810-6	1698750	0	**1444.52**	0.0295	405	120.91
810-Blank	<DL					810-Blank	<DL	0				
Mean	**2223002**	1890.3			**128.8**	**Mean**	**2006748**					**129.7**
STD	**54713.8**	46.5			**7.85**	**STD**	**183160**					**8.59**
CV	**0.025**				**0.061**	**CV**	**0.091**					**0.066**
OU					**22.8**							**24.7**
Reference					**117.7**							**117.7**


Calibration Curve for Cyclohexane (Cyclo) 8-10-00
y = 2352.3x + 619.17
R2 = 0.9997
Area
2500000
2000000
1500000
1000000
500000
0
0
200
400
600
800
1000
1200
ug/mL

Toluene

X	Y1	Y2	Y3	X	Ave	STD	CV
50		123294.0	121192	50	122243	1486.3	#DIV/0!
100	252613	252237.0	253245	100	252698	509.4	0.002016
250	623266	626701	625972	250	625313	1809.8	0.002894
500	1232530	1231460	1226900	500	1230297	2989.9	0.00243
750	1846690	1830760	1838520	750	1838657	7965.9	0.004332
1000	2493270	2507540	2477790	1000	2492867	14879.1	0.005969

Badges	Area	ug	Flow Rate	Time	C(mg/m3)	Char Tu	Area	Backarea	ug	Flow Rate	Time	C(mg/m3)
810-B-1	1086040	877.3	31.4	439	63.6	810-1	948059	**0**	765.8	0.032	405	59.1
810-B-2	1063720	859.2	31.4	443	61.8	810-2	936161	**0**	756.2	0.031	405	60.2
810-B-3	1116710	902.0	31.4	447	64.3	810-3	908819	**0**	734.1	0.033	405	54.9
810-B-4	1088660	879.4	31.4	445	62.9	180-4	970517	**0**	783.9	0.0383	405	50.5
810-B-5	955967	772.2	31.4	441	55.8	810-5	832130	**0**	672.2	0.0315	405	52.7
810-B-6	1113220	899.2	31.4	440	65.1	810-6	750487	**0**	606.2	0.0295	405	50.7
810-Blank	<DL					810-Blank						
Mean	**1070720**	864.9			**62.2**		**919137**					**54.7**
STD	**59490**				**3.37**		**53486**					**4.17**
CV	**0.056**				**0.054**		**0.06**					**0.076**
OU					**28.9**							**17.8**
Reference					**53.5**							**53.5**


Cablibration Curve for Toluene (Tol) 8-10-00
y = 2476.3x + 265.5
R2 = 0.9998
Area
ug/mL
3000000
2500000
2000000
1500000
1000000
500000
0
0
200
400
600
800
1000
1200

Percholoroethylene

X	Y1	Y2	Y3	X	Ave	STD	CV
50	21587	23374.0	21593	50	22185	1030.0	0.046428
100	43591	43571.0	43644	100	43602	37.7	0.000865
250	107919	108397	108418	250	108245	282.2	0.002607
500	213414	212896	212011	500	212774	709.5	0.003334
750	320333	317906	318654	750	318964	1242.9	0.003897
1000	431223	433722	428617	1000	431187	2552.7	0.00592

Badges	Area	ug	Flow Rate	Time	C(mg/m3)	Char Tu	Area	B-area	ug	Flow Rate	Time	C(mg/m3)
810-B-1	328360	1531.6	28.3	439	123.3	810-1	315394	0	1471.1	0.032	405	113.5
810-B-2	319502	1490.3	28.3	443	118.9	810-2	312337	0	1456.9	0.031	405	116.0
810-B-3	336107	1567.7	28.3	447	123.9	810-3	302726	0	1412.0	0.033	405	105.7
810-B-4	328824	1533.8	28.3	445	121.8	180-4	324521	0	1513.7	0.0383	405	97.6
810-B-5	289750	1351.5	28.3	441	108.3	810-5	283392	0	1321.9	0.0315	405	103.6
810-B-6	334394	1559.7	28.3	440	125.3	810-6	257792	0	1202.4	0.0295	405	100.6
810-Blank	<DL					810-Blank						
Mean	**322823**				**120.2**	**Mean**	**299360**					**106.2**
STD	**17216**				**6.25**	**STD**	**15647**					**7.24**
CV	**0.053**				**0.052**	**CV**	**0.052**					**0.068**
OU					**31.8**							**19.8**
Reference					**100.7**							**100.7**

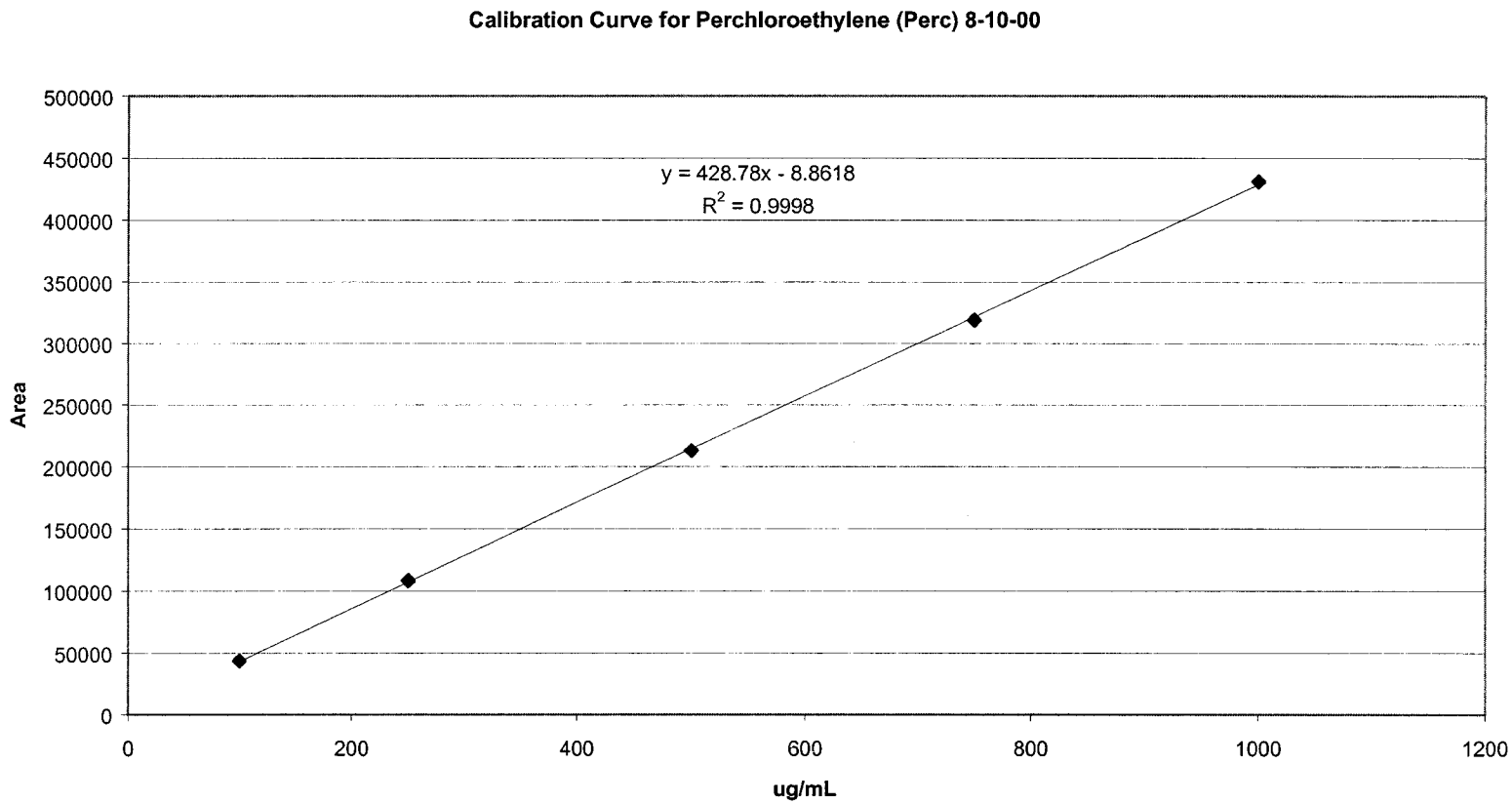

Calibration Curve for Perchloroethylene (Perc) 8-10-00
y = 428.78x - 8.8618
R2 = 0.9998
Area
ug/mL
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0
200
400
600
800
1000
1200

Table B-2 Calculation Methods for the Capillary-Canister

0.1mm Cappillary Length : 1 m Flow Rate 0.441 mg/m^3
Time: 7 hrs 22min.= 474
Volume of Canitster: 1
Conc. 50 ul/hr - @ 1.0 Lpm @ 50% RH

						Dilution Factor
Can #	**Po (torr)**	**Ps (torr)**	**Pa (torr)**	**Vs (liters)**	**Va (Liters)**	**Va/Vs**
1	1	170	1651	0.224	2.172	9.712
2	1	153	1283	0.201	1.688	8.386
3	1	165	1652	0.217	2.174	10.012
4	1	160	1285	0.211	1.691	8.031
5	1	147	1289	0.193	1.696	8.769
6	1	219	1135	0.288	1.493	5.183
			mean	0.209		
			Stdev	0.012		
			RSD	0.058		

			GC Area				
Can #	**IPA**	**MEK**	**EA**	**Cyclo**	**Tol**	**Perchloro**	
1a	2666	1555	3117	3849	4969	677	
1b	2833	1409	2821	4021	5066	827	
1c	3308	2181	4525	5525	5613	1056	*
mean	**2936**	**1715**	**3488**	**4465**	**5216**	**853**	
std	333.1	410.1	910.5	922.0	347.2	190.9	
RSD	0.113	0.239	0.261	0.206	0.067	0.224	
2a	3520	2320	4689	5713	5799	1020	
2b	3906	2340	4816	5997	6046	1105	
2c	4045	2438	4888	5923	6053	1110	
mean	**3824**	**2366**	**4798**	**5878**	**5966**	**1078**	
std	272.0	63.2	100.8	147.3	144.7	50.6	
RSD	0.071	0.027	0.021	0.025	0.024	0.047	
3a	2498	1410	2815	3385	5469	720	
3b	2547	1462	2896	3481	5720	807	
3c	2704	1407	2939	3538	5689	658	
mean	**2583**	**1426**	**2883**	**3468**	**5626**	**728**	
std	107.6	30.9	63.0	77.3	136.8	74.8	
RSD	0.042	0.022	0.022	0.022	0.024	0.103	
4a	3815	2258	4768	6130	5196	1043	
4b	3877	2629	5242	6720	6074	1273	*
4c	4155	2717	5549	6713	6279	1244	*
mean	**3949**	**2535**	**5186**	**6521**	**5850**	**1187**	
std	181.1	243.6	393.5	338.6	575.3	125.3	
RSD	0.046	0.096	0.076	0.052	0.098	0.106	

Table B-2 Calculation Methods for the Capillary-Canister (continued)

5a	4277	2738	5525	6786	6196	1209
5b	4604	2716	5577	6859	6243	1311
5c	4533	2708	5427	6770	6157	1306
mean	**4471**	**2721**	**5510**	**6805**	**6199**	**1275**
std	172.0	15.5	76.2	47.4	43.1	57.5
RSD	0.038	0.006	0.014	0.007	0.007	0.045

6d	6108	4017	8079	9972	8401	1739
6b	5737	3774	7741	9855	8057	1753
6c	5909	3867	7929	9690	8218	1789
mean	**5918**	**3886**	**7916**	**9839**	**8225**	**1760**
std	185.7	122.6	169.4	141.7	172.1	25.8
RSD	0.031	0.032	0.021	0.014	0.021	0.015

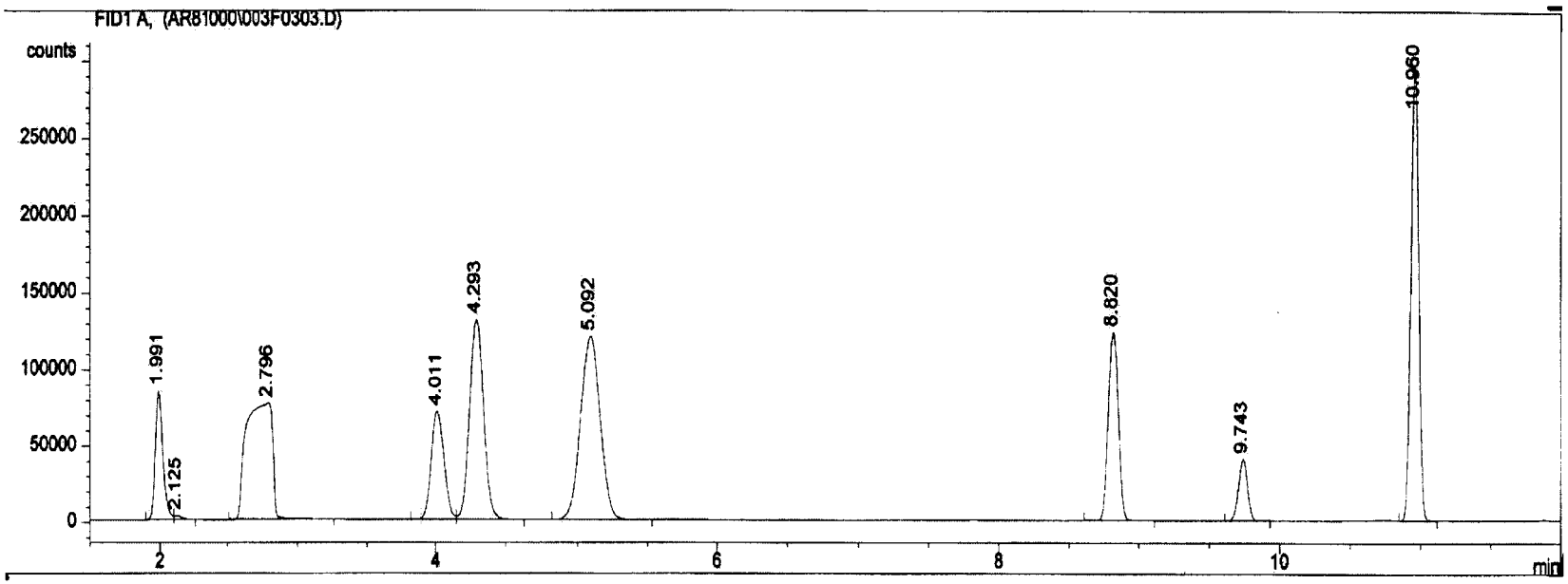
Concentrations for Each Chemical in Each Canister

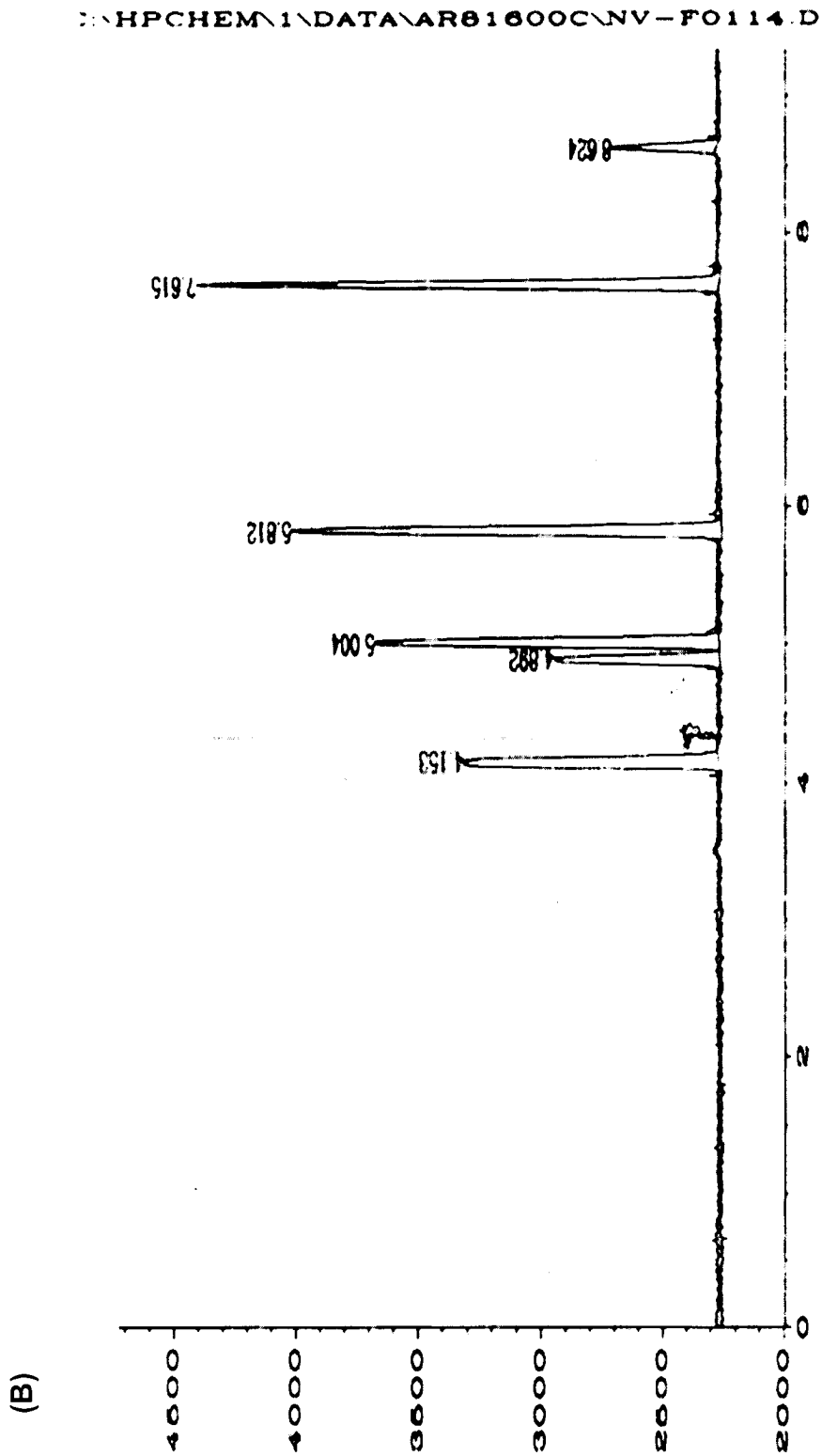
	IPA mg/m^3	**MEK** mg/m^3	**EA** mg/m^3	**Cyclo** mg/m^3	**Tol** mg/m^3	**Perchloro** mg/m^3
1	110.3	59.0	171.0	95.5	48.8	88.0
2	124.1	70.3	203.2	108.6	48.2	96.0
3	100.1	50.6	145.8	76.5	54.3	77.4
4	120.5	74.8	212.6	118.9	47.0	108.5
5	119.4	72.1	207.6	110.3	49.0	95.0
6	118.7	71.3	207.2	112.3	41.1	96.9
Mean	**118.6**	**69.5**	**200.3**	**109.1**	**46.8**	**96.9**
St Dev	**5.1**	**6.1**	**16.7**	**8.5**	**3.3**	**7.4**
RSD	**0.043**	**0.088**	**0.083**	**0.078**	**0.071**	**0.076**
Cknw	120.8	72.2	217.6	117.7	53.5	100.7
Ratio	**0.98**	**0.96**	**0.92**	**0.93**	**0.88**	**0.96**
OU	10.20	20.65	23.30	21.81	24.85	18.52

$$\text{Overall Uncertainty (OU)} = \frac{\text{Mean - Ref (True value) + 2Std dev} * (100)}{\text{Ref value}}$$

Figure B-1 Gas chromatographs: (A) Charcoal tubes Analysis, (B) Canisters Analysis

(A)




C:\HPCHEM\1\DATA\AR81600C\NV-F0114.D
8.624
7.615
5.812
5.004
4.852
4.153
(B)

Appendix C Calculation methods and calibration curves and for styrene experiments

Table C-1 Styrene concentration calculations

Morning

Badges	Area	ug	Cont	Flow Rat	Time	C(mg/m3)	Char Tu	Area	BArea	ug	Flow Ra	Time	C(mg/m3)
1124B-1m	927711	628.1	34.6	28.9	155	159.33	1124-1m	2272030	0	**1538.27**	0.0641	155	175.94
1124-2m	972323	658.3	34.6	28.9	155	166.99	1124-2m	1607960	0	**1088.67**	0.0449	155	177.76
1124-3m	1029280	696.9	34.6	28.9	155	176.77	1124-3m	1229860	0	**832.67**	0.036	155	169.57
1124-4m	887578	600.9	34.6	28.9	155	152.44	1124-4m	2419260	0	**1637.96**	0.0601	155	199.81
1124-5m	874721	592.2	34.6	28.9	155	150.23	1124-5m	2008330	0	**1359.74**	0.0569	155	175.20
1124-6m	938085	635.1	34.6	28.9	155	161.11	1124-6m		0	**0.00**	0.076	155	0.00
1124-7m	920536	623.2	34.6	28.9	155	158.10	1124-7m		0	**0.00**	0.0763	155	0.00
Mean	**938283**					**161.1**	**Mean**	**1907488**					**179.7**
STD	**56854.39**					**9.76**	**STD**	**892856**					**11.67**
CV	**0.06**					**0.06**	**CV**	**0.47**					**0.06**
OU						**25.8**							**18.1**
Reference						**190.8**							**190.8**
ppm						**37.83**							**42.17**

Afternoon

1124-1a	1395830	945.0	34.6	28.9	190	195.57	1124-1a	4001260	0	**2709.05**	0.0641	190	252.77
1124-2a	1439060	974.3	34.6	28.9	180	212.82	1124-2a	2601860	0	**1761.58**	0.0449	180	247.69
1124-3a	1522990	1031.1	34.6	28.9	180	225.24	1124-3a	1720440	0	**1164.82**	0.036	180	204.27
1124-4a	1409320	954.2	34.6	28.9	180	208.43	1124-4a	2701950	0	**1829.35**	0.0601	180	192.16
1124-5a	1292710	875.2	34.6	28.9	180	191.18	1124-5a	3614960	0	**2447.50**	0.075	180	206.02
1124-6a	1269080	859.2	34.6	28.9	180	187.68	1124-6a		0	**0.00**	0.076	180	0.00
1124-7a	1364370	923.7	34.6	28.9	180	201.78	1124-7a		0	**0.00**	0.0763	180	0.00
1124-BLA <DL							1124-Blank <DL		0				
Mean	**992148**					**203.5**	**Mean**	**2075250**					**220.6**
STD	**438655.23**					**14.48**	**STD**	**1068630**					**27.64**
CV	**0.44**					**0.07**	**CV**	**0.51**					**0.13**
OU						**26.6**							**30.5**
Reference						**237.8**							**237.8**
ppm						**47.77**							**51.78**

Figure C-1 Calibration Curve for Styrene

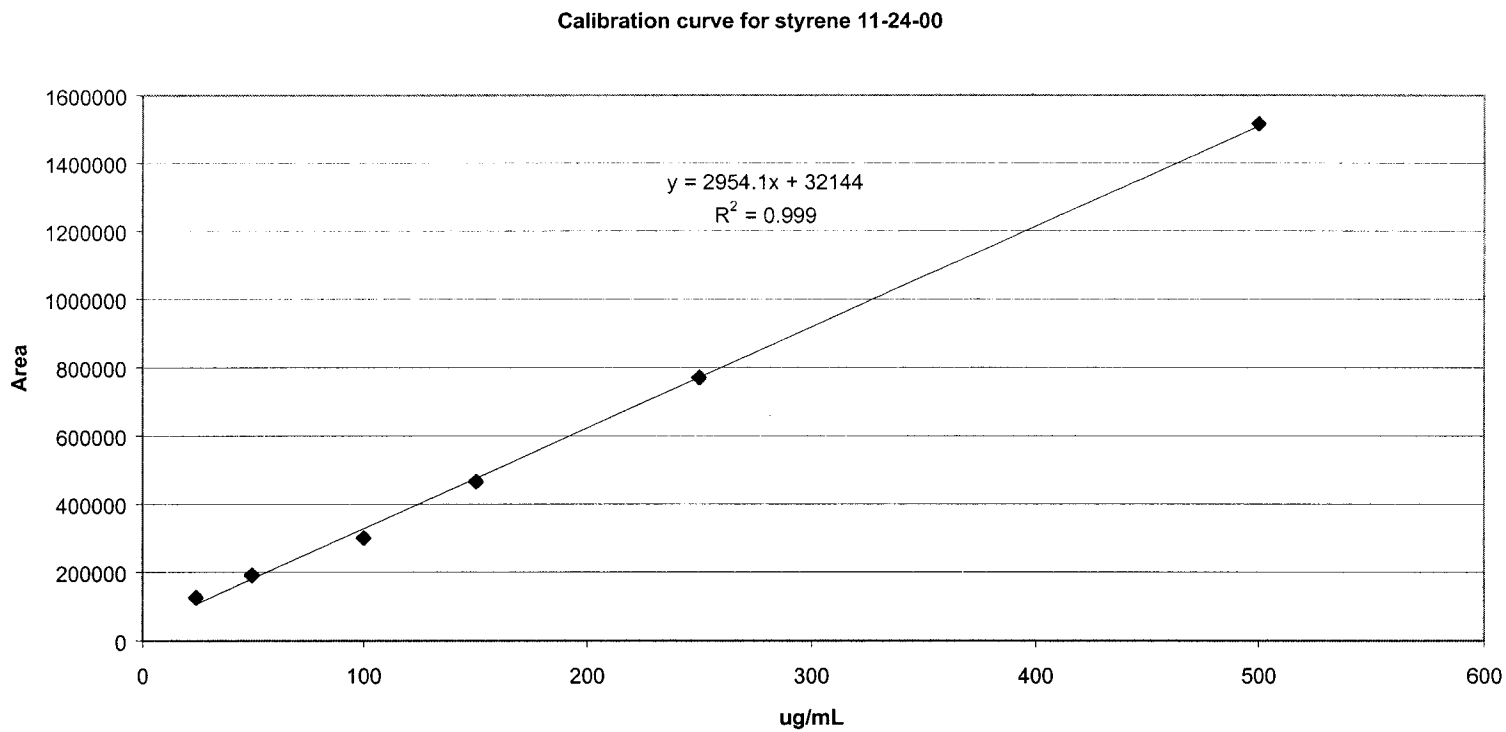


Table C-2 Capillary-canister calculations for the styrene experiments

Experiment 11-24-00 Styrene 300ml Canister

Scenerio # 6 - 40ppm w/4 - 100ppm peaks

Cappillary Length : 10 cm of 0.05 mm ID

Time: 6 hours = 362 Flow Rate 0.261 mL/min

Volume of Canitster: 300

GC Reference value 213.8 mg/m^3 (50 ppm)

Can #	Po (torr)	Ps (torr)	Pa (torr)	Vs (mls)	Va (mls)	Dil Factor Va/Vs
1	1	283	1448	111.7	571.579	5.117
2	1	220	1590	86.8	627.632	7.227
3	1	228	1018	90.0	401.842	4.465
4	1	227	1523	89.6	601.184	6.709
5	1	239	1448	94.3	571.579	6.059
6	1	224	1505	88.4	594.079	6.719

mean	94.5
Stdev	9.272
RSD	0.098

	Styrene						Conc	
Can #	a	b	c	Mean	Std	RSD	mg/m3	ppm
1	23668	23477		**23573**			213.7	50.2
2	14114	14261		**14188**			180.0	42.2
3	27300	27040		**27170**			215.1	50.5
4	16888	16624		**16756**			199.9	46.9
5	17420	17370		**17370**			186.2	43.7
6	15481	15407		**15447**			183.5	43.1
mean	**19145**	**19754**				Mean	196.4	46.1
std	5423.5	5305.7				Std Dev	15.81	3.71
RSD	0.283	0.269				**RSD**	**8.0**	**8.0**
						OU	**22.9**	**23.0**

* Note: Styrene recovery rates from the capillary-canisters - 97.8 ± 3.2 %, n=12

Appendix D Example of 40 hour capillary-canister test, Peak simulation model and Summary of statistical methods used for all experiments.

Table D-1 Example of the calculations for a 40-hour capillary-canister

Capillary Length : 40 cm @ 0.05mm
Time: 38 hrs 26min.= 2306
Volume of Canitster: 300
Conc. 20 ul/hr - @ 1.-0 Lpm @ 50% RH

Can #	Po (torr)	Ps (torr)	Pa (torr)	$V_{s\ (liters)}$	$V_{a\ (Liters)}$	Dil Factor Va/Vs
1	1	386.8	1293	152.7	510.4	3.34
2	1	378.4	1293	149.4	510.4	3.42
3	1	369.7	1302	145.9	513.9	3.52
4	1	382.1	1298	150.8	512.4	3.40
5	1	388.8	1295	153.5	511.2	3.33
6	1	390.3	1035	154.1	408.6	2.65
*7	1	780.7	1193	308.2	470.9	1.53
			mean	151.1	**Flow Rate**	**0.066**
* Blank			Stdev	3.056		
			RSD	0.020		

	Area					
Can #	**IPA**	**MEK**	**EA**	**Cyclo**	**Tol**	**Perchloro**
1a	3463	2498	5198	9127	3324	1032
1b	4141	2909	5991	9378	3471	1091
1c	386	450	1259	1363	1657	457
mean	**3802**	**2704**	**5595**	**9253**	**3398**	**1062**
std	479.4	290.6	560.7	177.5	103.9	41.7
RSD	0.126	0.107	0.100	0.019	0.031	0.039
2a	4000	2744	5584	8996	3231	1014
2b	4521	2872	5867	9027	3285	1005
2c	391	526	1190	1120	1413	432
mean	**4261**	**2808**	**5726**	**9012**	**3258**	**1010**
std	368.4	90.5	200.1	21.9	38.2	6.4
RSD	0.086	0.032	0.035	0.002	0.012	0.006
3a	4379	2888	5876	8893	3252	983
3b	4728	2920	5925	8870	3293	1007
3c	402	507	1135	1054	1320	392
mean	**4554**	**2904**	**5901**	**8882**	**3273**	**995**
std	246.8	22.6	34.6	16.3	29.0	17.0
RSD	0.054	0.008	0.006	0.002	0.009	0.017

test

4a	4699	2992	6150	9155	3385	1063
4b	4711	2960	6108	9144	3353	1083
4c						
mean	**4705**	**2976**	**6129**	**9150**	**3369**	**1073**
std	8.5	22.6	29.7	7.8	22.6	14.1
RSD	0.002	0.008	0.005	0.001	0.007	0.013

5a	4896	3015	6184	9209	3402	1044
5b	4900	3060	6245	9162	3386	1054
5c						
mean	**4898**	**3038**	**6215**	**9186**	**3394**	**1049**
std	2.8	31.8	43.1	33.2	11.3	7.1
RSD	0.001	0.010	0.007	0.004	0.003	0.007

6a	5063	3518	7398	9415	4337	1682
6b	5300	3575	7506	9453	4426	1719
6c						
mean	**5182**	**3547**	**7452**	**9434**	**4382**	**1701**
std	167.6	40.3	76.4	26.9	62.9	26.2
RSD	0.032	0.011	0.010	0.003	0.014	0.015

Concentration (mg/m^3)

1	50.4	29.7	85.1	58.9	21.78	41.29
2	53.0	29.3	83.2	57.9	20.90	39.05
3	58.4	31.2	88.3	58.8	21.63	39.67
4	58.2	30.8	88.5	58.4	21.48	41.26
5	59.4	30.9	88.0	57.5	21.22	39.55
*6	50.0	39.5	115.5	64.7	29.99	70.19
Mean	**55.9**	**30.4**	**86.6**	**58.3**	**21.40**	**40.17**
Std	3.9	0.8	2.4	0.6	0.35	1.04
% RSD	7.1	2.8	2.7	1.0	1.64	2.6

Actual	**52.34**	**32.2**	**94.14**	**51.87**	**23.09**	**43.54**
Ratio	**1.07**	**0.94**	**0.92**	**1.12**	**0.93**	**0.92**

* not included in average

Calculations used to develop the simulation model to show the relationship between concentration variability as a function of flow rate change

Summary of the scenario - An industrial process that has a theoretical air concentration of 20 mg/m^3 with a series of peak concentrations of 100 and 200 mg/m^3 occurring at different periods during the workweek were examined. A 33 hour sampling period was used. The entire 33 hours was sampled using the capillary-canister. If the flow rate was constant during the sampling period, the sampled concentration would be equal to the actual atmospheric concentration. However, because the flow rate slowly decreases slightly during the sampling period, the timing of the peak will change the sampled concentration. Sets of simulations were run to evaluate the degree to which the sampled concentration deviated from the actual concentration. The following procedure was used to develop the simulation.

A time weighted average (TWA) is normally used to calculated the average concentration workers are exposed to in a given environment (equation D-1).

$$TWA = \sum_1^n T_{n1} C_n \frac{\sum_1^n T_{n1} C_n}{T_n} \qquad \text{(D-1)}$$

The decrease in flow rate provided by the capillary-canister requires that some adjustment be made to calculate the TWA if peak concentrations are present in the sampled atmosphere. Equation D-2 describes the slow reduction in flow rate for a capillary of 40 cm in length and 0.05 mm in diameter.

$$Q(t) = \frac{1}{379}\int_{1}^{380} -3E-07x^2 + 5E-5x + 0.0843 \qquad \text{(D-2)}$$

where the equation is integrated from a pressure of 1 to 380 mm Hg (380 is the pressure at which the canister is half full). Equation D-3 represents the integrated form of equation D-2. If the boundaries of the sampling period are used as limits for both the peak concentration and the steady state concentration one can calculate the time weighted average that would be sampled by the capillary canister.

$$Q = \frac{-3E-7x^3}{3} + \frac{5E-5x^2}{2} + \frac{0.0834\,x}{1} \qquad \text{(D-3)}$$

where Q is the flow rate and x is the pressure in the cansiter.

Using equation D-3, one can calculate the flow rate for the peak concentration and the steady state concentration. The respective flow rates multiplied by the duration of the peak and the steady state concentration provide a volume that can be used to calculate the mass of contaminant collected during the sampling period. Because the peak and steady state concentrations were established in the hypothetical scenario, the variation due to the change in flow rate can be found by comparing the actual TWA to the concentration that would be collected by the capillary-canister for the peak at a given time. To obtain the concentration sampled by the capillary-canister these calculations were performed using an excel spreadsheet. The final calculations are shown in equations D-4 and D-5.

$$\text{Actual TWA} = \underline{(1\text{ hour} * 100\text{ mg/m}^3) + (32\text{ hours} * 20\text{ mg/m}^3)} \qquad \text{(D-4)}$$

33 hours

$$\text{Sampled TWA} = \frac{(1\ \text{hour} * 78.7\ \text{mg/m}^3) + (32\ \text{hours} * 20\ \text{mg/m}^3)}{33\ \text{hours}} \quad \text{(D-5)}$$

where for this calculation the peak occurs within the last hour of the sampling period. Resulting in:

$$\text{Actual TWA} = 22.4\ \text{mg/m}^3$$

$$\text{Sampled TWA} = 21.9\ \text{mg/m}^3$$

In for this example, a 60 minute peak at the end of a 33 hour sampling period, it is estimated that the canister would collect **97.2 %** of the contaminant or under sample by **2.8 %** due to the change in flow rate.

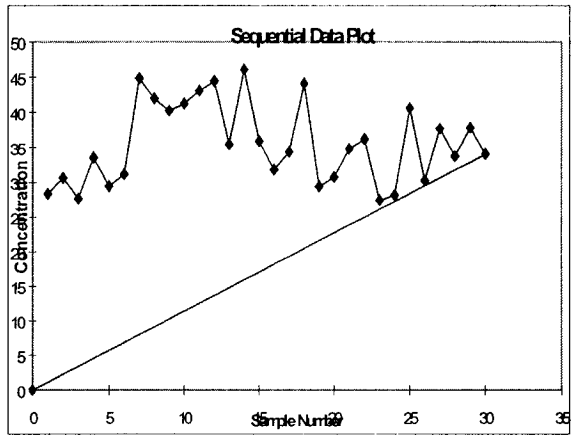
Table D-2 Example of the statistical evaluation of the field data

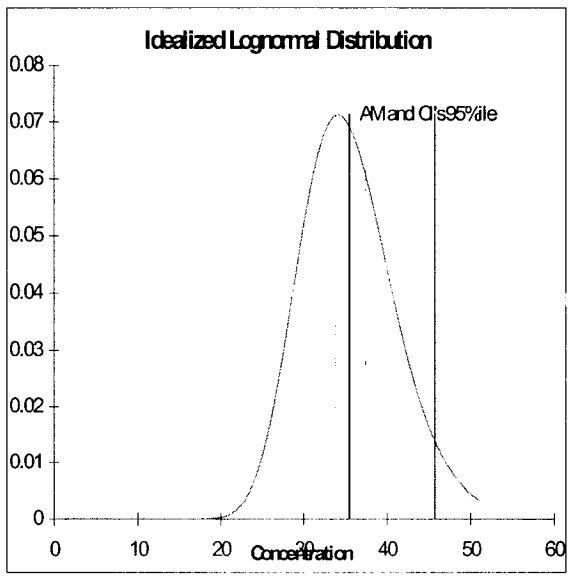
Data Description: Alcoa 40 hour - Badge samples 2-12-00

OEL
572.6

Sample Data (max n = 50) No less-than (<) or greater-than (>)
28.33
30.67
27.69
33.57
29.49
31.16
44.90
42.02
40.31
41.28
43.14
44.51
35.44
46.13
35.90
31.82
34.39
44.16
29.41
30.72
34.81
36.20
27.43
28.20
40.67
30.25
37.70
33.80
37.84
34.08

DESCRIPTIVE STATISTICS	
Number of samples (n)	30
Maximum (max)	46.133072
Minimum (min)	27.434994
Range	18.698078
Percent above OEL (%>OEL)	0.000
Mean	35.534
Median	34.599
Standard deviation (s)	5.793
Mean of logtransformed data (LN)	3.558
Std. deviation of logtransformed data (LN)	0.162
Geometric mean (GM)	35.086
Geometric standard deviation (GSD)	1.175
TEST FOR DISTRIBUTION FIT	
Wtest of logtransformed data (LN)	0.940
Lognormal (a = 0.05)?	Yes
Wtest of data	0.931
Normal (a = 0.05)?	Yes
LOGNORMAL PARAMETRIC STATISTICS	
Estimated Arithmetic Mean - MVUE	35.532
$LCL_{1,95\%}$ - Land's "Exact"	33.840
$UCL_{1,95\%}$ - Land's "Exact"	37.424
95th Percentile	45.776
$UTL_{95\%,95\%}$	50.235
Percent above OEL (%>OEL)	0.000
$LCL_{1,95\%}$ %>OEL	<0.1
$UCL_{1,95\%}$ %>OEL	<0.000
NORMAL PARAMETRIC STATISTICS	
Mean	35.534
$LCL_{1,95\%}$ - t statistics	33.737
$UCL_{1,95\%}$ - t statistics	37.331
95th Percentile - Z	45.064
$UTL_{95\%,95\%}$	48.39
Percent above OEL (%>OEL)	0.000





(Adopted from Mulhausen 1998)

W - Test Value (Shapiro Wilk)

"Goodness of Fit" refers to how well a particular distribution and the data "fit" each other. Exposure data can be lognormal or normal.

It is beneficial to be able to fit a distribution since a distributional assumption (making a judgment that your data fits a particular distribution) enables the user to use lognormal or normal statistics (which are only valid if the data is lognormally or normally distributed).

The "Shapiro-Wilk W-Test," developed by Samuel Shapiro and Wilk in 1965, is a way to determine the goodness of fit of a distribution. It is a mathematically intensive test, yet the information gathered from the test is extremely useful in performing a distributional fit test.

It is important to note that this test can not accept a distributional hypothesis, it can only reject one. This is useful, however, since it can show that the data is lognormal and not normal, or vice-versa, or even that the data set does not fit either distribution (which would indicate that either the data is not a true homogenous exposure group or that a non-parametric analysis must be performed).

In simple terms, the test is performed by using an equation given below to calculate the "w-test value." This value is then compared to a percentage point that is read off of a chart. If the test value is greater than the chart's percentage point, then the distribution is not rejected. However, if the value is less than the percentage point, then the particular distribution is rejected as a possible fit.

As a technical definition, it is based on equations using the slope of the regression line in addition to a generalized least squares technique to correct for observations being ordered and not uncorrelated. To facilitate this process, Shapiro and Wilk have developed several tables of "percentage points" against which one compares values that are calculated using the "w-test value" equation.

The main equations are as follows:

$$S^2 = \left(\sum_{i=1}^{n} \chi_i^2 \right) - \left(\frac{\left(\sum_{i=1}^{n} \chi_i^2 \right)^2}{n} \right)$$

$$b = \sum_{i=1}^{k} (a_{n-i+1})(\chi_{n-i+1} - \chi)$$

$$W = \frac{b^2}{S^2}$$

(Adopted from LogNorm2, version 2.9, Industrial Software Solutions is a d.b.a. as Intech Software Corp.)