A New Air Sampling System for Long Term Sampling.

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Final Report: NIOSH Grant No. R03 OH008130

Grant Funding Period: July 2005 to July 2008
October 31, 2008

Abstract

A continuing challenge in occupational hygiene is that of accurately estimating a worker's exposure to the multitude of airborne chemicals found in the workplace and surrounding community. Hence, the development of new methods that will permit more effective sampling of contaminants in the workplace is essential to ensure that accurate exposure assessments are completed. Over the last five years a capillary flow controller was designed and tested in laboratory and field studies. The very low flow rate provided by the capillary flow controller permits a sample to be collected over an extended period of time when used with a small portable evacuated canister. The initial research focused on the development of the capillary-canister and the evaluation of its ability to collect representative air samples. However, capillary flow controllers exhibit a characteristic drop in flow rate with time. The time dependent flow rate coupled with concentration changes in the sampling environment could result in a sampling bias. The focus of this study was performance evaluation based on field studies and prediction of the sampling bias. As part of this study, the capillary canister system was redesigned to make it less expensive, more compact, and more acceptable to the person wearing the sampler. The performance of the capillary canisters was evaluated by conducting field experiments at two different locations. Twenty-four paired samples were collected using canisters and diffusive badges. The paired t-test performed on the personal samples showed no statistical difference between the two methods. The model developed to predict the sampling bias associated with capillary canisters was experimentally validated. A series of predicted worst-case scenarios involving peak concentrations were experimentally simulated at three sampling time durations: 8 hrs, 24 hrs and 40 hrs. Three canisters, a gas chromatography (GC), and photo ionization detector were used to monitor the concentration profile during the experiments. The bias between the canisters and the GC was calculated from the experimental values. When analytical errors were considered, the experimental values approached the predicted model values.

Highlights/Significant Findings

The overall goal of this work was to validate the effectiveness of 300 mL capillary canisters as personal sampling devices. To accomplish this goal three objectives were developed:

1. To redesign the 300 mL capillary canister to make it more economical and compact.
2. To validate the performance of the redesigned capillary canisters as personal samplers using in-field sampling trials.
3. To experimentally validate the mathematical bias model to predict the bias associated with capillary flow controller, by experimentally simulating positive and negative bias conditions that could be encountered in the field at peak

concentration amplitudes of 10X and 100X for sampling periods of 8 hrs, 24 hrs, and 40 hrs.

The capillary canister was redesigned to improve field performance as a field personal air sampling device. Its performance as a personal sampling device was evaluated by conducting field sampling at two different locations. The new design overcame some of the drawbacks observed in the existing design. The protrusion of the steel shaft from the sides was removed. The use of a micro-valve made the system less susceptible to leak, thus reducing loss of samples. The use of the micro-valve also provided the option of removing the top valve, resulting in a 40% reduction in cost and a significant reduction in weight. The new design was less expensive, weighed less, and was more acceptable to the subjects.

The performance of this personal sampler was evaluated by conducting field sampling at two locations, including a fiberglass lay-up operation and a chandelier coating company. Twenty-four paired samples were collected, including sixteen personal samples and eight area samples. The paired t-test performed on the personal samples showed no statistical difference between the canisters and badges.

A further study looked into the potential sampling bias associated with the diminishing flow-rate of the capillary system when sampling conditions include peak concentrations. Detailed flow characteristics of several lengths of the capillary flow controllers were examined. In particular, flow-rate data was collected for capillaries of length 10 cm, 30 cm, and 50 cm. The characteristic change in flow rate was similar for capillaries irrespective of their length. This allowed for the development of a single bias envelope model for different concentration amplitudes. The worst-case scenario conditions in which the bias was expected to be the largest were tested for three capillary lengths, representing 8 hr, 24hr, and 40 hr sampling periods. Overall, the results from the bias experiments were convincing, showing that the bias canister sampling data did approach the results predicted by the model.

The results from this study demonstrate that the new design was an improvement upon the previous version of the sampling system and that the sampling bias could be accurately predicted and verified by our mathematical model. These results confirm that capillary canisters can be used as personal samplers in many microenvironments.

Translation of Findings

As an industrial hygienist 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.

The variability of sampling data 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 issue of limited resources results in a limited number of samples being collected. Accurately extrapolating that data to a large number of workers will always be a challenge faced by occupational hygienist.

Measurement error is most frequently a small component of the total variation in exposure monitoring. If the sample size (n) is increased then the sampling and analytical error may have diminished importance with respect to the overall error of an air sample. Hence, new air sampling devices that allow for increased sample numbers and increased sample duration should provide additional exposure data that is more representative of the actual workplace exposures. 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. The capillary canister device is accurate, relatively inexpensive, easy to use, and collects multiple chemicals simultaneously. The better the tools we have to characterize exposure, the more effective one can be at minimizing risk in the workplace.

The results of this research have been communicated to the IH community through the publication of one manuscript and several presentations at local and national American Industrial Hygiene Association meetings. A second manuscript is currently in preparation.

Outcomes/Relevance/Impact

Exposure assessment is a corner stone of industrial hygiene (Mulhausen and Damiano, 1998). The outcomes of this research were the development and evaluation of a new tool to help characterize workplace exposures assessments leading to improved risk characterization. While air sampling does not directly reduce workers risk of disease, new technology can often allow us to characterize exposures that we did not previously understand. The primary goal of this research was to validate the effectiveness of the capillary canister and further understand the bias associated with capillary flow controllers used with evacuated canisters. The significance of this work is that it moves canister sampling another step forward in providing a means to collect personal samples for volatile organic compounds (Rossner, 2004). The light weight design, relative to sorbent tubes and air sampling pumps, allows for the collection of integrated samples in many work environments without the problems associated with active sorbents or passive diffusion samplers.

Scientific Report

A. Specific Aims

Aim 1. Hypothesis: No statistical difference exists between capillary-canister devices and passive badges when collecting multi-day personal samples.

Aim 2. Hypothesis: The sample bias associated with the capillary-canister, when peak concentrations are present in the test atmosphere, will remain below 10% for all peaks up to 100 times the base concentration.

The aims of this study were not modified during the course of this investigation.

B. Studies and Results

Aim 1: Extensive field sampling was necessary to provide definitive information for assessing the value of the capillary-canister device as a viable tool for workplace exposure assessment. A series of preliminary activities were necessary to prepare for the field sampling campaign. The actual field testing was designated in our time line for the summer of 2006. However, the redesign and manufacturing of the 11 new prototype canisters took significantly longer than anticipated; the canisters were finally completed in January 2007. The field testing was started in January 2007.

In October of 2005, a gas chromatograph (GC) dedicated to canister analysis was obtained and set up in the research lab. The GC is an HP 5890 series II modified for direct air injection and outfitted with a thermal desorption unit to analyze concentrations in the parts per billion range. The thermal desorption unit (TD-5, Scientific Instruments Services, Inc.) provides for broader analysis capabilities to validate the canisters at low concentrations in industry and for indoor air quality applications. To adequately calibrate the GC for direct injection analysis down to ppb range, a dynamic dilution system using a syringe pump and ultra-pure air was designed and set up. The system includes a relative humidity and temperature meter and mass flow meters to constantly monitor flow. In addition, small environmental chambers were designed and connected directly to the dynamic dilution system allowing for follow-up studies comparing the canister to other types of sampling methods, as shown in previously published manuscripts. These small environmental chambers range in size from 0.001 m^3 to 1.5 m^3 and have been used to evaluate the canister measurement accuracy and as a quality control component to mimic field conditions for the field studies.

Canister Re-design: The capillary-canisters were redesigned to make them more functional in the field and acceptable to the individuals being sampled. The main difficulty with the original design was an awkward protruding (4 cm) shaft that housed the capillary controller and on-off assembly. In the new configuration, the shaft has been moved to the top of the canister and a micro valve (Entech, Inc, Simi Valley, CA) has

been added as a means of turning the canister on and off during field sampling. A conceptual design is displayed below in Figure 1. Lab Commerce, Inc. built the newly designed canisters, shown in Figures 2 and 3.

The micro valve was unique, easy to open and close, and reduced the risk of leaking, thus making field sampling significantly easier. It was possible to vacuum and sample through the micro valve giving us the option to replace the top-valve. The top-valve is a Nupro valve (as shown in Figure 2.) that is used in the existing design to vacuum the canisters. The removal of the top-valve resulted in a 40% reduction in the total cost. This option can be taken into account in future designs. The final dimensions of the canisters used in this research were 4" in diameter, 1 5/8" thick and weighed 562 grams.

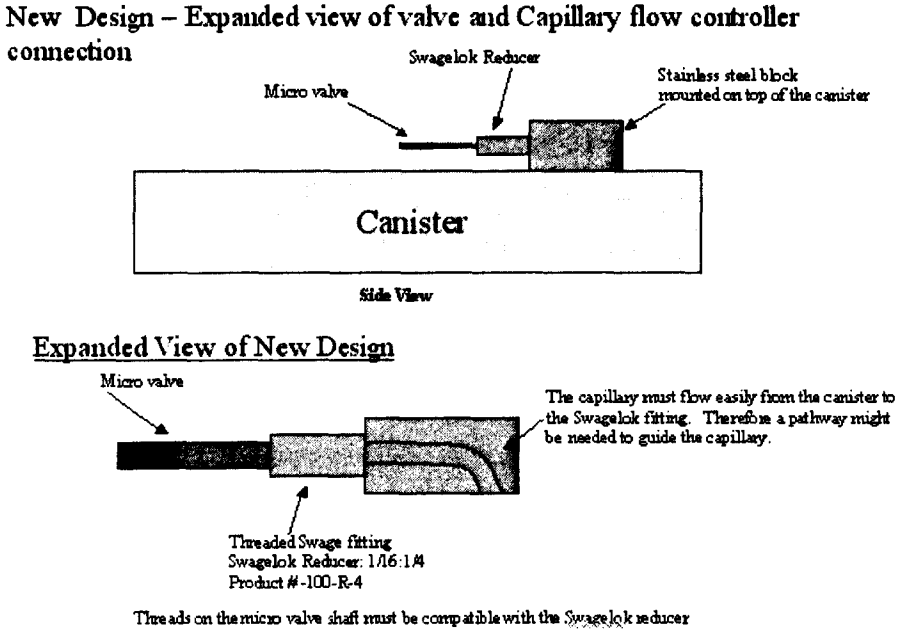


Figure 1. New Design for Capillary-Canister. The new design has incorporated a unique, easy to open and close, micro valve, that makes field sampling significantly easier, reduces the risk of leakage during sampling, and should be more acceptable to workers.

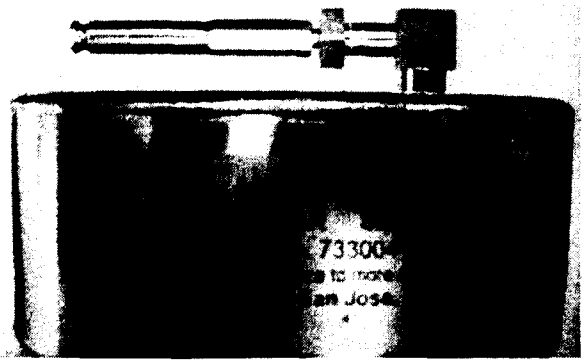


Figure 2. Photogragh (Side view) of the Capillary Canister with micro valve attached to the flat top surface of the canister.

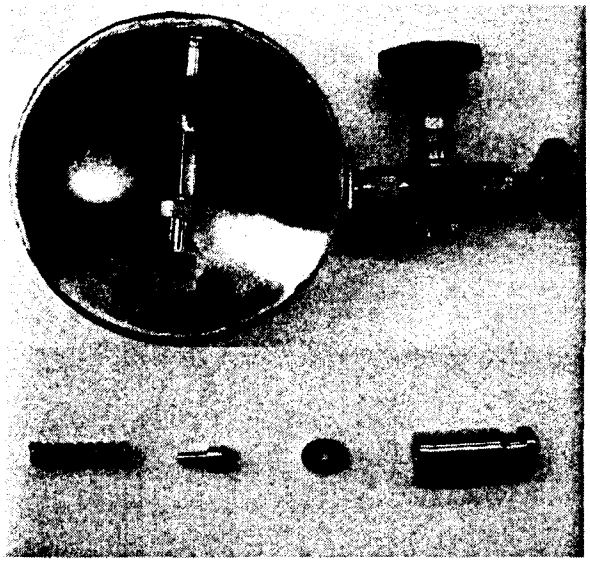


Figure 3. Top view of the Capillary Canister with micro valve and the nupro valve attached to the top of the surface. The lower left corner shows an expanded version of the valve.

Field Sampling

To evaluate the performance of capillary canisters, field sampling was performed at two different facilities including a fiberglass lay up operation and chandelier manufacturing operation. A series of personal and area paired canister and badge samples were collected. Ten samples were obtained from the fiberglass lay up operation and fourteen samples from the chandelier coating operation.

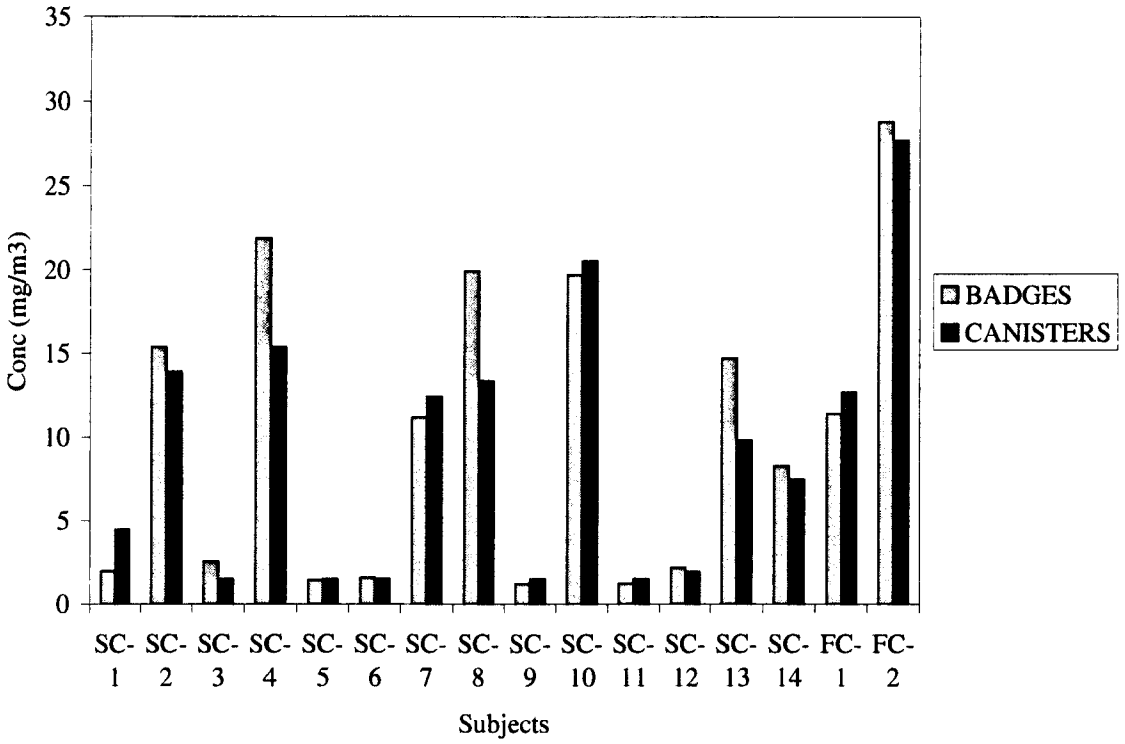


Figure 4. Airborne concentration of Xylene for personal samples.

Figure 4 shows the comparison of diffusive badges and canisters from the personal samples. The measured concentrations (mg/m^3) are displayed for each of the subjects. The subjects with prefix SC are from the chandelier coating operation and represent xylene concentrations while the data with the prefix FC are from the fiberglass lay up operation and represent styrene concentrations. There was good correlation between the canisters and the badges, except for samples SC-4, SC-8, and SC-13. In these cases, the diffusive badges had a higher concentration compared to the canisters. During analysis it was observed that drops of lacquer (containing xylene) were located on the surface of badges SC-4, SC-8, and SC-13, which could have altered the diffusion of the xylene on to the badge, resulting in concentrations being significantly higher than expected when compared to their respective canisters. A similar effect was observed by Eriksson et al., 2005. The lowest detection limit for xylene was 1.5 mg/m^3. Canister concentrations for samples SC-3, SC-5, SC-6, SC-9 and SC-11 were found to be below the detection limit.

In addition to personal samples, a series of area samples were collected during the fiberglass layup operation. The measured concentrations of the chemicals are displayed in mg/m^3 in Figure 5. Sampling was performed on two different days, with four samples collected each day for a total of eight samples.

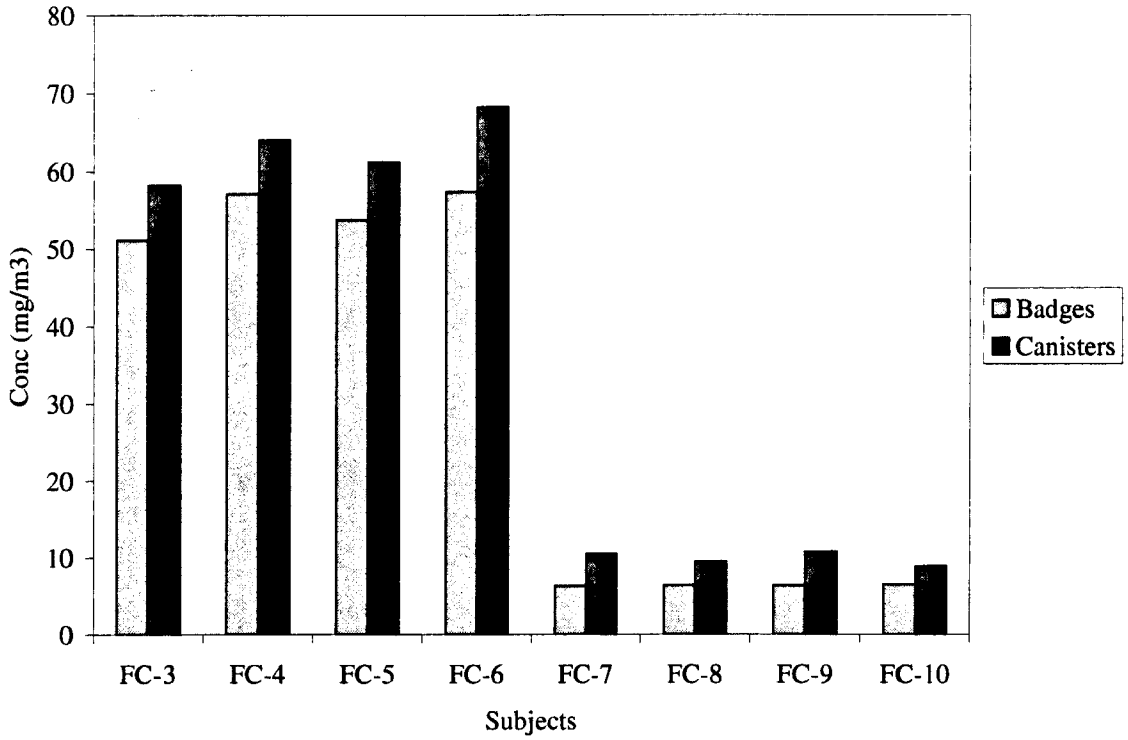


Figure 5: Airborne concentration of Styrene for area samples collected during a fiberglass layup operation.

Samples FC-3 to FC-6 were collected on day-1, and samples FC-7 to FC-10 were collected on day-2. Figure 5 shows that the concentration of styrene was approximately six times higher on day-1 compared to day-2. All eight badge concentrations for the area samples were lower than the measurements made with the canisters. Low badge concentration could have been due to limited airflow across the surface of the badge. Badges require a minimum of ~ 0.13 m/s (25 fpm) for effective sampling. When the air movement in the room was measured, the airflow rate was observed to be less than 0.1 m/s (20 fpm) which could have resulted in the badges under estimating the airborne concentrations in the room.

Paired comparison of badges and canisters was performed to evaluate the collection efficiency of the canister with respect to the badges. A paired t-test was performed on both the area samples and the personal samples using 95% confidence level to assess whether the mean was significantly different from zero. Samples SC-3, SC-5, SC-6, SC-9 and SC-11 were not taken into consideration as their concentrations were found to be below the detection limit.

The p-value for the personal samples was found to be 0.344 (greater than the required 0.05 for our confidence level). Hence we concluded that there was no statistically significant difference between the canisters and badges.

The canisters and badges were found to be statistically different for the area samples (p = 0.001). The lower p-value was likely the result of the low velocity air movement in the room at the time of sampling, thus resulting in an under-estimate of the styrene concentration by the badges.

Figures 6 and 7 show the data for the canisters and the badges for the personal and area samples, respectively. A linear regression analysis was performed to compare the measured concentrations from the badges and canisters. The R^2 value for the personal samples was 0.92 and for the area samples was observed to be greater than 0.99. Both the area and personal samples from the canisters show a very good correlation with the badges, further supporting the capillary canisters as effective industrial hygiene sampling devices.

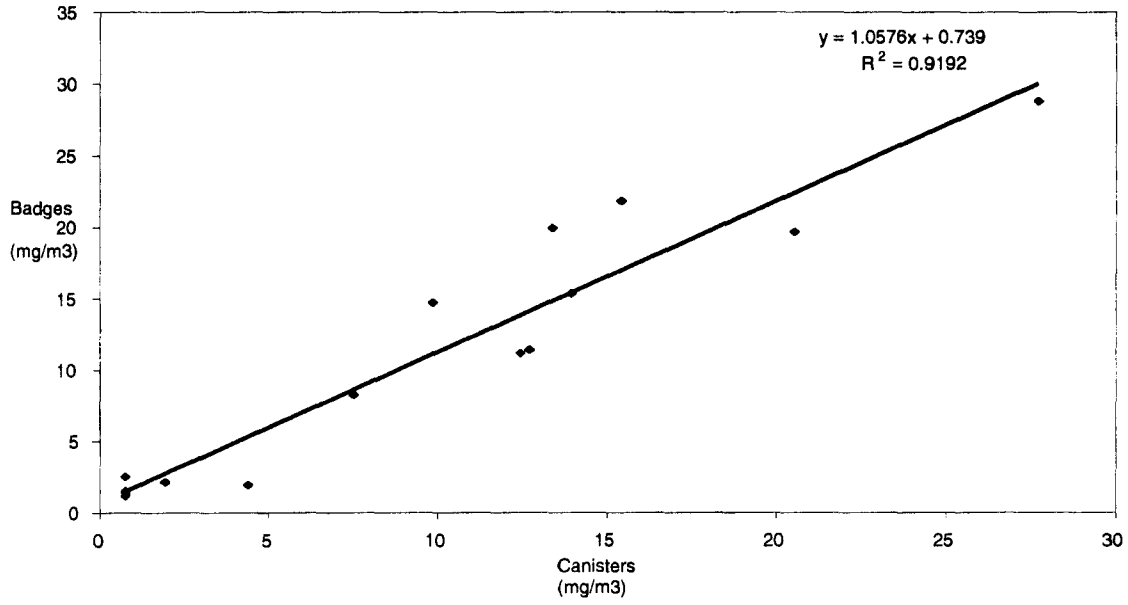


Figure 6. Linear Regression analysis on the data from the personal samples.

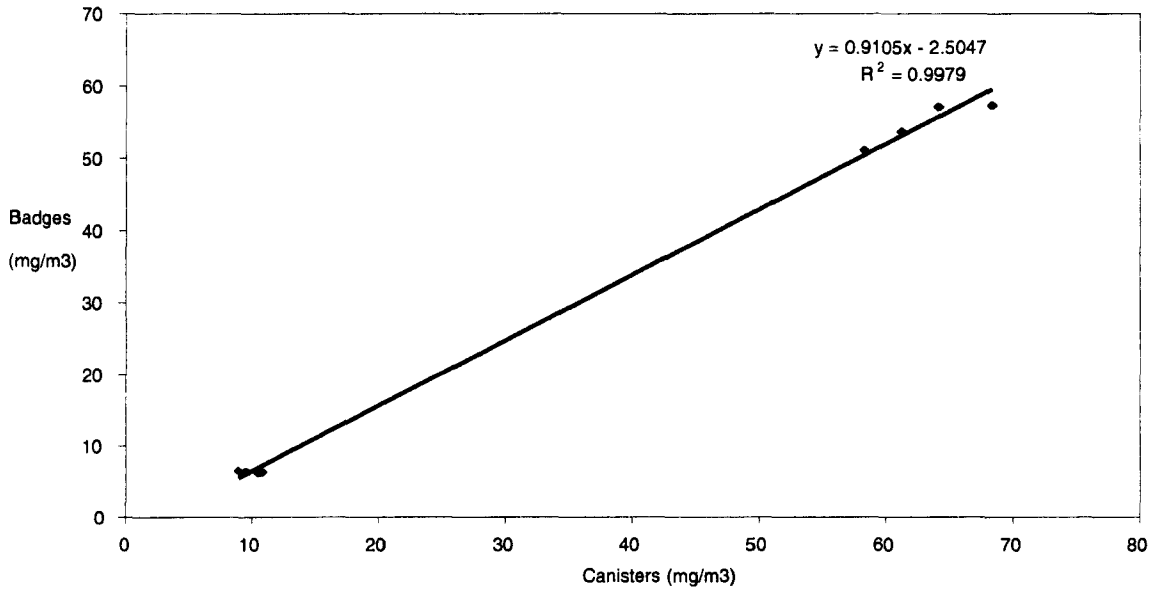


Figure 7. Linear Regression analysis on the data from the area samples.

Aim 2: The study of the potential sampling bias associated with capillary canisters involved three stages: 1) flow rate measurement, 2) model development, and 3) experimental validation of the model.

We began this part of the study by quantifying the bias associated with the diminishing flow rate using extensive computer simulations of varying peak concentrations. The simulations were based on the original development of the mathematical model and tested through comparison with measured data. The model and the validation data supported our hypothesis showing a < 10% bias when peak concentrations were less than 10 times the base concentration. The initial results were formulated into a manuscript and submitted for publication. The manuscript was accepted and published in ***Journal of Occupational and Environmental Hygiene*, Rossner, A., and Wick, D. P.,: A field Study to Assess the Long-Term Sampling Feasibility of Evacuated Canisters and the Development of a Mathematical Model to Analyze Potential Sampling Bias., J. Occup. And Environ. Hyg. 2 (9) 474-480 (2005).** While this manuscript supported our hypothesis and displayed a solid endorsement of the effectiveness of the flow controller, additional work was needed to further examine the details of the model and validate its bias envelope predictions experimentally.

Mathematical Model

A mathematical model was developed to predict the magnitude of the measurement bias associated with the diminishing flow rate over time and to further understand the relationship between the bias and three separate characteristics of peak concentrations,

including peak amplitude, duration, and time of occurrence. The overall flow rate for the capillary-canister system diminishes by approximately 20 - 25% during a typical sampling period, depending on the geometry of the capillary used. The rate of accumulation of a contaminant in the canister was modeled as

$$V_C \frac{dC(t)}{dt} = Q_{in}(t)\, C_{in}(t) \qquad (1)$$

assuming it depends on the time-dependent incoming flow rate (Q_{in}) and incoming concentration (C_{in}), where V_c represents the volume of the canister. The sampling bias is then calculated using the following relationship

$$Bias = \frac{C(T) - \tilde{C}(T)}{\tilde{C}(T)} \times 100 \qquad (2)$$

where $\tilde{C}(T)$ represents the final canister concentration assuming a *constant flow rate* (as would be achieved with a mechanical pump), *C(T)* represents the final concentration for a *diminishing flow rate*, and *T* is the total sampling time.

The mathematical model was constructed to examine the bias associated with the characteristic parameters that define a single-peak concentration profile, including the relative peak amplitude (*A*), peak duration (τ), and peak time of occurrence (τ_i), as illustrated in Figure 8. The amplitude is defined as a ratio of the peak concentration (C_p) to the background or baseline concentration (C_b). The model was developed using MATLAB® (MathWorks, Natick, MA) and has been used to analyze simulated exposure scenarios that include peak amplitudes of up to 100 times the background concentration, with peak durations lasting from a few minutes to the entire sampling time. For each amplitude and peak duration combination, the bias was calculated for peaks occurring every 0.1 minutes. For comparison, the average flow rate associated with each capillary was used to represent the constant flow rate that would be achieved with a mechanical pump.

Simulation of Peak Concentrations

The flow rate of the capillary flow controller slowly decreases over the sampling time, which could result in inaccurate estimation of exposure depending upon concentration fluctuations in the sampled atmosphere and the temporal characteristic of the peaks. It is important to remember that although the flow rate changes, the total amount of air collected is known for canister samples. Total volume can be determined by measuring the initial and final canister pressures. 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 over estimating exposure when compared to peaks in concentration occurring toward the end of the sampling period.

The specific simulated conditions evaluated included a constant background atmospheric concentration (C_b) (mg/m^3) superimposed with peak values occurring throughout the sampling period for a range of relative amplitudes (A) from 1 to 100, where an amplitude of 1 indicates that no peak is present. In addition to varying the amplitude, the model also simulated different peak durations (τ). The duration was analyzed in comparison to the total sampling time (T). It is important to recognize that our definition of a "peak" is much broader than what one typically thinks of as a "peak concentration". The bias in the measured concentration is influenced by the amplitude, timing, and duration (width) of the peak. Therefore, a "peak" includes an elevated concentration that could range from a small fraction (minutes) to 50% of the sampling period.

The timing of the occurrence of each peak was changed from scenario to scenario to observe how the sampled concentration was affected. The model varied each parameter simultaneously to provide an envelope of bias (worst-case scenario) associated with a particular capillary dimension. Figure 9 shows the envelope of bias for several relative peak amplitudes (1, 3, 5, and 10) for a 0.05 mm diameter capillary of length 40 cm. The relative bias is plotted versus a ratio of the peak duration to the total sampling time (τ/T). The amount of bias observed ranged from 0% to 9% for the peak amplitudes as large as 10 times the base concentration. For an amplitude factor of 10, the bias should never exceed 9% for the scenario shown, and in most cases is well below this value.

The greatest measurement error results when a concentration spike occurs at the very beginning or end of the sampling period, as the canister has the potential to over or under sample due to its transient flow rate. Furthermore, the bias increases with peaks of increasing amplitude. All individual bias measurements for a given set of peak duration and occurrence characteristics reside within this envelope. The envelope increases in size with increasing amplitude, where the zero-bias line represents no relative peak concentration (A = 1). The *positive* bias values correspond to over-sampling scenarios associated with concentration peaks that occur early in the sampling process. The *negative* bias values correspond to under-sampling scenarios associated with peaks that occur late. Note that transient decreases in the concentration, as described by negative values of the amplitude, would result in bias values that are opposite in sign to the ones shown in Figure 9.

The non-symmetric nature of the bias envelope directly reflects the nonlinear characteristics of the flow rate. A linearly decreasing flow rate would have resulted in a symmetric envelope. The model approximates the actual flow rate change as a quadratic decay, to match experimentally observed flow rate data originally documented by Rossner et al (ES&T 2002). As expected, the bias is greatest when a peak occurs late in the sampling period when the flow rate is most diminished.

The magnitude of the bias is heavily influenced by the amplitude of the peak, but is also affected by the timing and duration of the peak. For an amplitude factor of 10, the maximum over sampling bias occurs when the duration of the peak is approximately 35% of the total sampling time, while the maximum under sampling occurs when the duration is close to 20% of the total sampling time. With this model one can estimate the

maximum possible bias associated with a particular sampling campaign, even if the details of the peak occurrences are not explicitly known. The envelope of bias is of great interest because it defines the sampling error associated with the diminishing flow rate, and more importantly, when combined with the analytical bias, defines the under or over estimation of exposure.

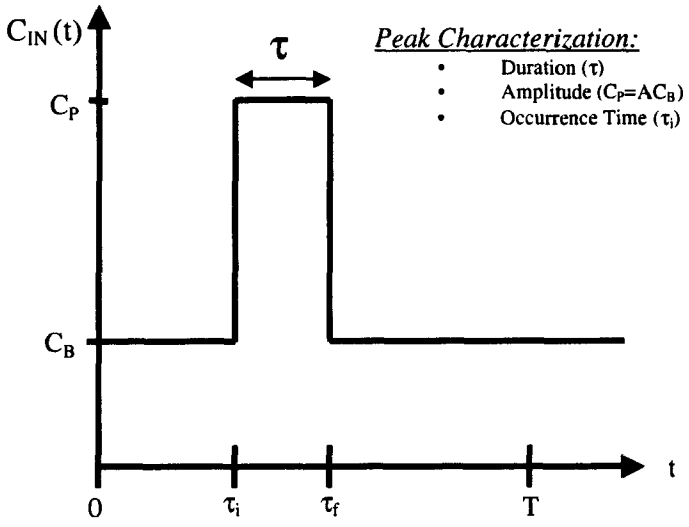


Figure 8. Peak characteristics of the concentration profiles

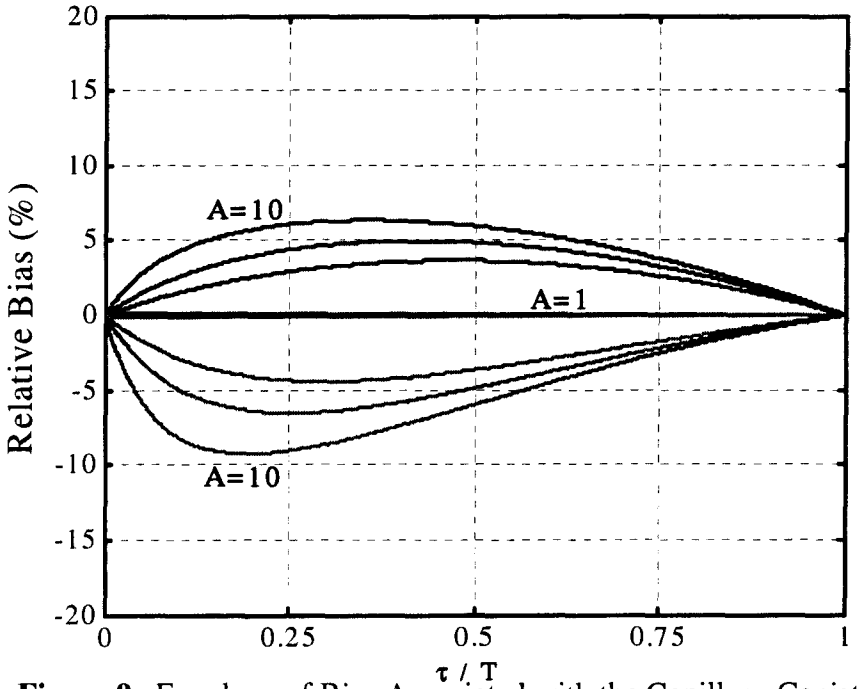


Figure 9. Envelope of Bias Associated with the Capillary-Canister Sampler where Peak Concentration Amplitudes are A = 1, 3, 5, and 10, respectively. Note that a positive bias is associated with an early occurring concentration peak as depicted in the upper inset

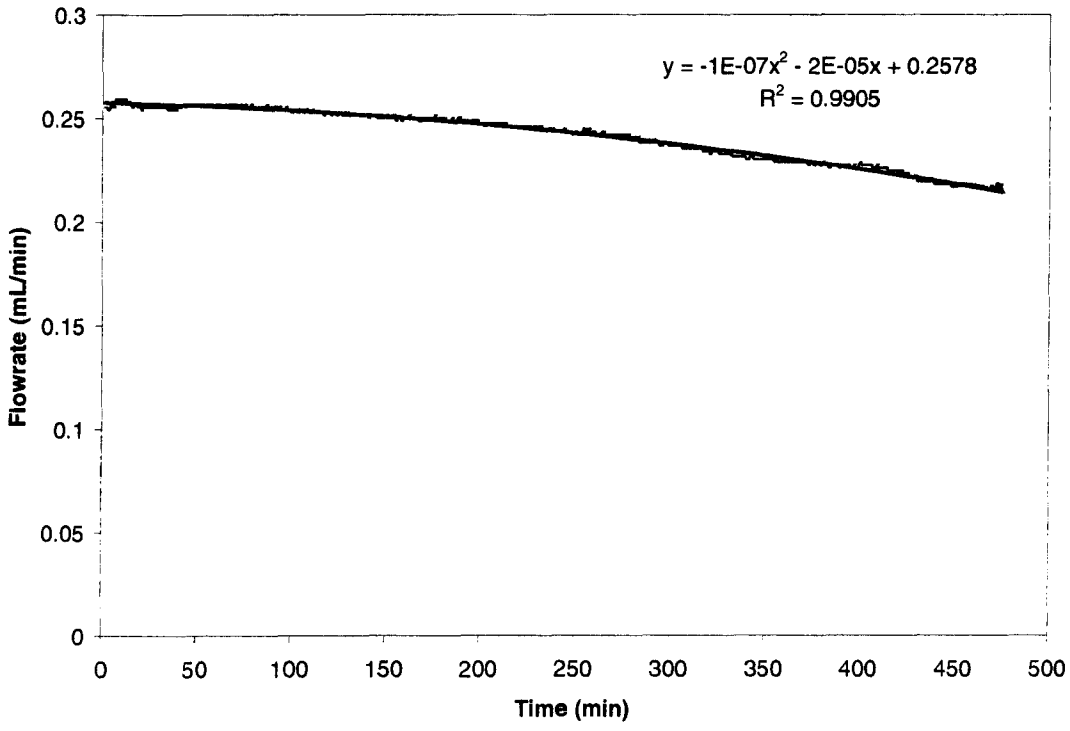
figure, while a negative bias is associated with a late occurring concentration peak as depicted in the lower inset figure.

Flow-rate measurements

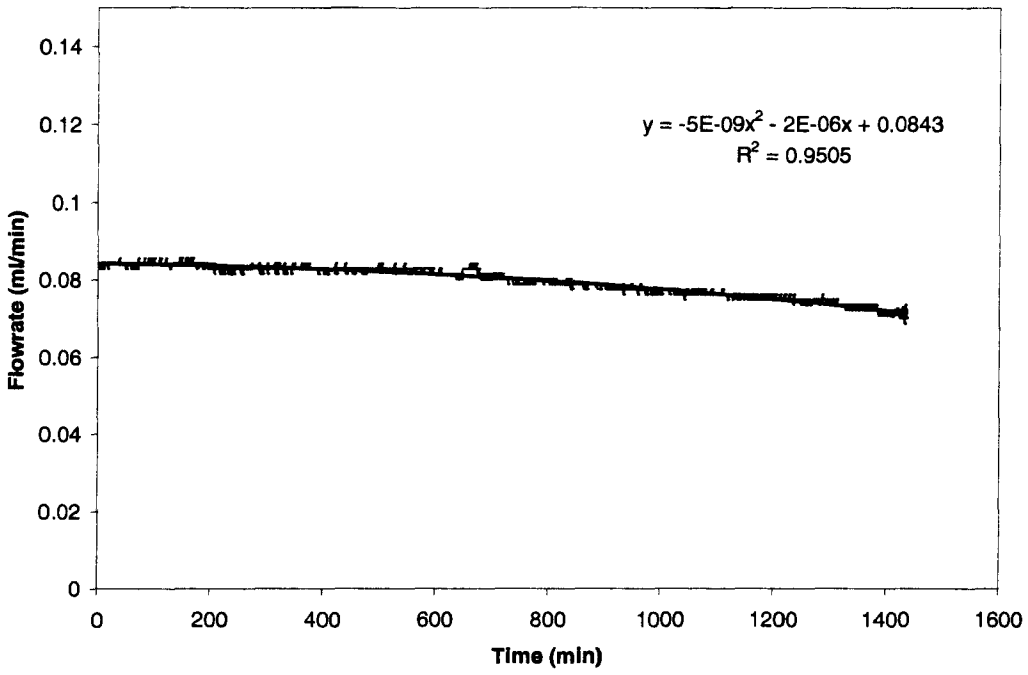
The air flow rates through capillaries of length 10 cm, 30 cm, and 50 cm were tested using a meter connected to the pressure transducer, where the output was continuously downloaded to a personal computer. The data collected provided a flow-rate profile for the entire sampling period for three capillary flow controllers. Each capillary was experimentally tested three to five times. The mean flow rates are listed in Table 1 for three different 0.05 mm diameter capillaries, while sample temporal flow-rate characteristics are documented in Figure 10 for the respective capillary lengths listed.

Table 1. Mean flow-rates for capillaries of length 10 cm, 30 cm, and 50 cm

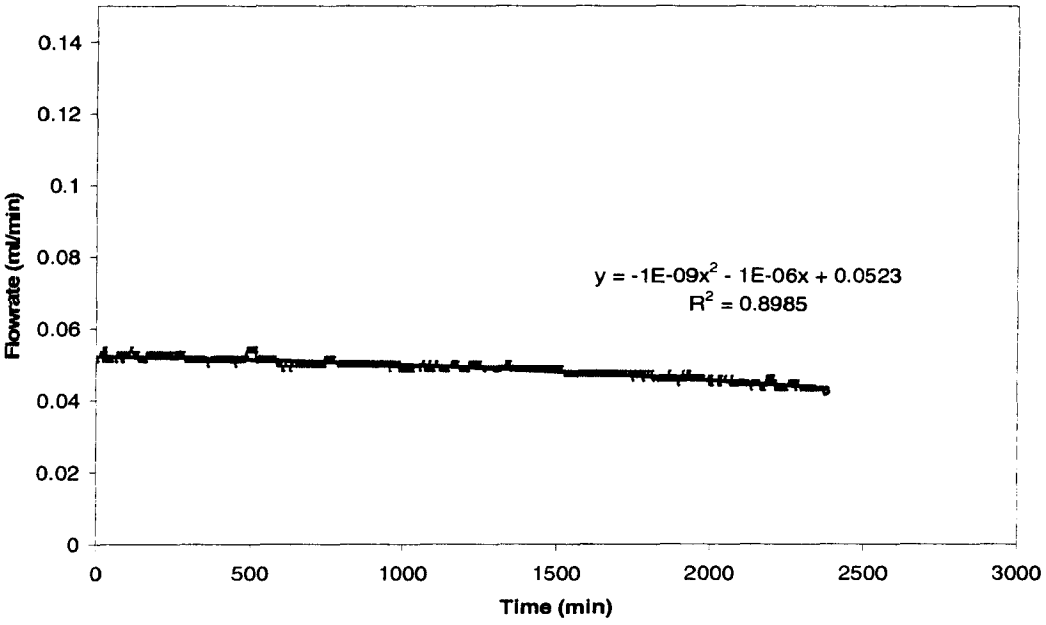
Capillary Length (cm)	Mean flow-rate (mL/min)
10	0.24
30	0.07
50	0.04



a) 10 cm capillary



b) 30 cm capillary



c) 50 cm capillary

Figure 10. Typical graphs of the experimental change in flow-rate for 10 cm, 30 cm and 50 cm capillary flow controllers of 0.05 mm diameter.

The flow-rate patterns for these capillaries were compared by normalizing the flow rate data. Figure 11 displays the plot of the flow rate (Q) divided by the initial flow rate (Qo) vs. normalized time (time divided by the total time of the experiment (t/T)).

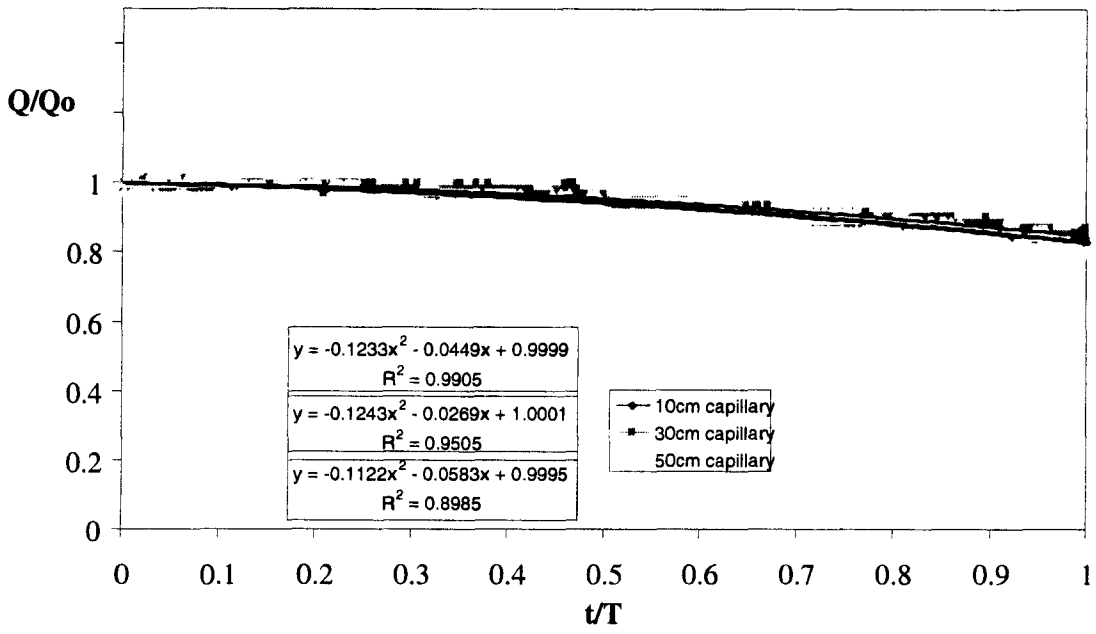


Figure 11. Normalized plot of Q/Qo vs t/T for capillaries of length 10 cm, 30 cm, and 50 cm of diameter 0.05 mm.

This normalized data shows that the flow-rate pattern was very similar for all three capillaries, demonstrating that the characteristic change in flow rate is independent of the length of the capillary. This allowed us to justify the development a single analysis to predict the sampling bias independent of capillary length.

Using the model previously discussed, a bias envelope (positive and negative bias) at concentration amplitudes of 10X and 100X the base concentration was generated for our experimental investigation by varying the ratio of peak width to the total sampling time (Tau/T). The percentage relative bias was calculated and plotted against Tau/T as shown in Figure 12. The maximum bias for the worst-case situations (conditions at which the percentage relative bias was maximum) for the positive and negative bias conditions at

these amplitudes were identified and are marked in the figure. Table 2 also displays the maximum bias for the worst-case scenarios identified in the simulations.

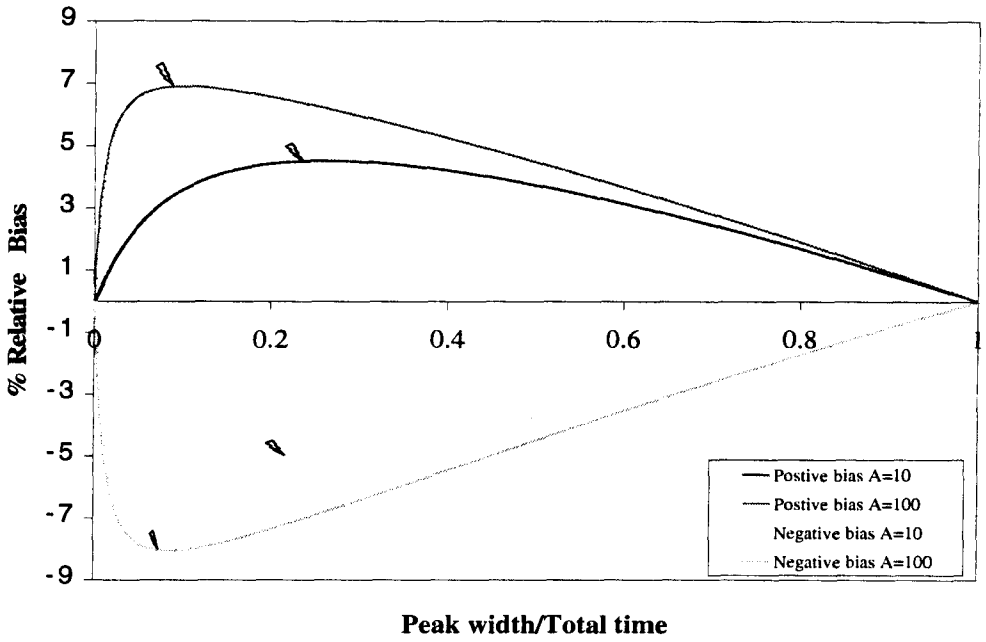


Figure 12. Bias envelope for concentration amplitudes of 10X and 100X. Maximum bias for worst-case peak concentration scenarios are marked.

Table 2. Maximum bias for the worst-case scenarios identified in simulations.

Positive bias		
Amplitude	Percentage relative bias	τ/T
10	4.52	0.26
100	6.91	0.10
Negative bias		
Amplitude	Percentage relative bias	τ/T
10	-4.98	0.22
100	-8.05	0.08

As mentioned previously, the bias envelope is not symmetric because the reduction in flow rate follows a quadratic decay as the canister fills to about 50% capacity. The bias envelope would have been symmetric if the drop in flow rate was linear. The maximum bias for amplitudes of 10X and 100X were then experimentally simulated at three different time conditions to check the model predictions.

Experimental simulation - Bias experiments at amplitude of 10X and 100X

Experiments were performed at three different time periods including 8 hrs - a typical workday, 24 hrs - a full day, and 40 hrs - a typical workweek. Table 3 summarizes the background and peak concentrations for each experiment.

Table 3: Background and peak concentrations

Time Conditions	10X (ppm)	100X (ppm)
8 hours	5-50	2-200
24 hours	2-20	2-200
40hours	2-20	2-200

At the conclusion of the bias experiments, the results from the GC and PID were plotted against time to fingerprint the concentration profile during the course of the experiments. As an example, Figure 13 displays the plot of GC and PID values for the negative bias condition at a concentration amplitude of 10X.

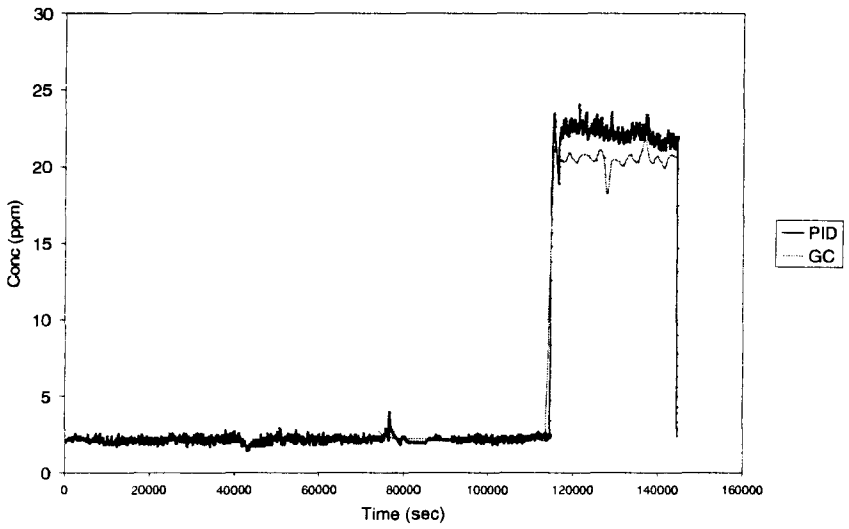


Figure 13. Plot of the GC and PID concentration measurements vs. time for negative bias condition at an amplitude of 10X.

From Figure 13, one can see that there was a better correlation between the GC and PID values at the background concentration compared to the peak concentration. This was because the PID was not responding linearly across the entire range of concentrations. A high and low calibration curve was developed to allow for the comparison of the PID to the online GC. The PID values at peak concentrations were adjusted in accordance to the calibration curve created for the higher concentrations. This correction factor was applied to the raw data generated by the PID.

Figure 4. displays the relationship between the GC and PID values both at background and peak concentrations. The time weighted average concentrations for the canisters, GC and PID were calculated. It was observed from Table 4 that the TWA concentration of canister 1 was always lower when compared to the other two canisters.

Table 4: TWA concentrations of Canisters, GC and PID for bias experiments

a) Summary of 8-hr bias experiments

Canister #	TWA Canister conc (ppm)	TWA GC conc (ppm)	% relative bias (Canister vs GC)	TWA PID conc (ppm)	% relative bias (Canister vs PID)
(+) bias 5-50 ppm					
1	18.21	18.39	-0.98	18.55	-1.83
2	18.68	18.39	1.58	18.55	0.70
3	18.70	18.39	1.69	18.55	0.81
Average	18.53	18.39	0.76	18.55	-0.11
(-) bias 5-50 ppm					
1	12.05	13.48	-10.61	13.66	-11.79
2	13.14	13.48	-2.52	13.66	-3.81
3	13.02	13.48	-3.41	13.66	-4.69
Average	12.74	13.48	-5.49	13.66	-6.73
(+) bias 2-200 ppm					
1	28.76	28.69	0.24	28.61	0.52
2	28.92	28.69	0.80	28.61	1.08
3	28.95	28.69	0.91	28.61	1.19
Average	28.86	28.69	0.58	28.61	0.89
(-) bias 2-200 ppm					
1	15.62	16.96	-7.90	16.78	-6.91
2	15.89	16.96	-6.31	16.78	-5.30
3	15.82	16.96	-6.72	16.78	-5.72
Average	15.78	16.96	-6.98	16.78	-5.98

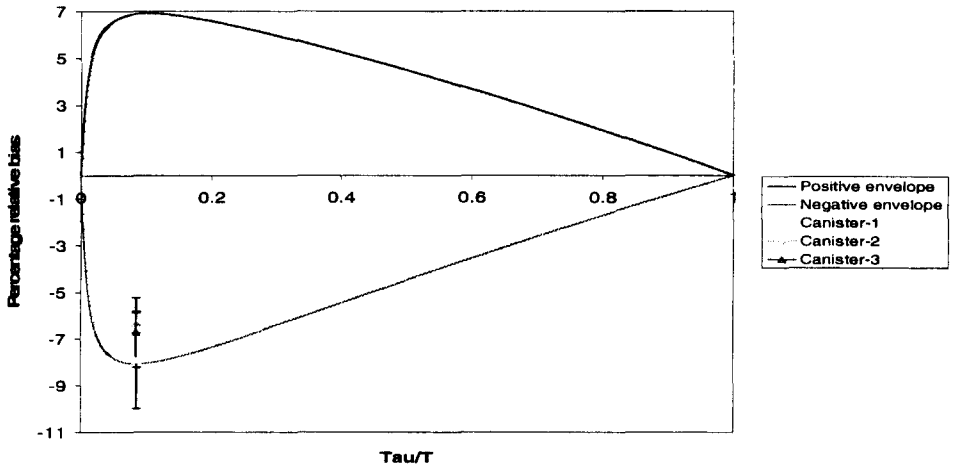
b) Summary of 24 hour bias experiments

Canister #	TWA Canister conc (ppm)	TWA GC conc (ppm)	% relative bias (Canister vs GC)	TWA PID conc (ppm)	% relative bias (Canister vs PID)
(+) bias 2-20 ppm					
1	7.31	7.76	-5.80	7.67	-4.67
2	8.09	7.76	4.25	7.67	5.48
3	7.96	7.76	2.28	7.67	3.78
Average	7.79	7.76	0.34	7.67	1.52
(-) bias 2-20 ppm					
1	5.03	5.98	-15.89	5.88	-14.46
2	5.66	5.98	-5.35	5.88	-3.74
3	5.85	5.98	-2.17	5.88	-0.51
Average	5.51	5.98	-7.80	5.88	-6.24
(+) bias 2-200 ppm					
1	26.46	27.80	-4.82	27.80	-4.82
2	29.96	27.80	7.77	27.80	7.77
3	29.03	27.80	4.42	27.80	4.42
Average	28.43	27.80	2.46	27.80	2.46
(-) bias 2-200 ppm					
1	16.38	17.38	-5.75	17.16	-4.55
2	17.43	17.38	0.29	17.16	-1.57
3	16.79	17.38	-3.39	17.16	-2.16
Average	16.87	17.38	-2.95	17.16	-1.71

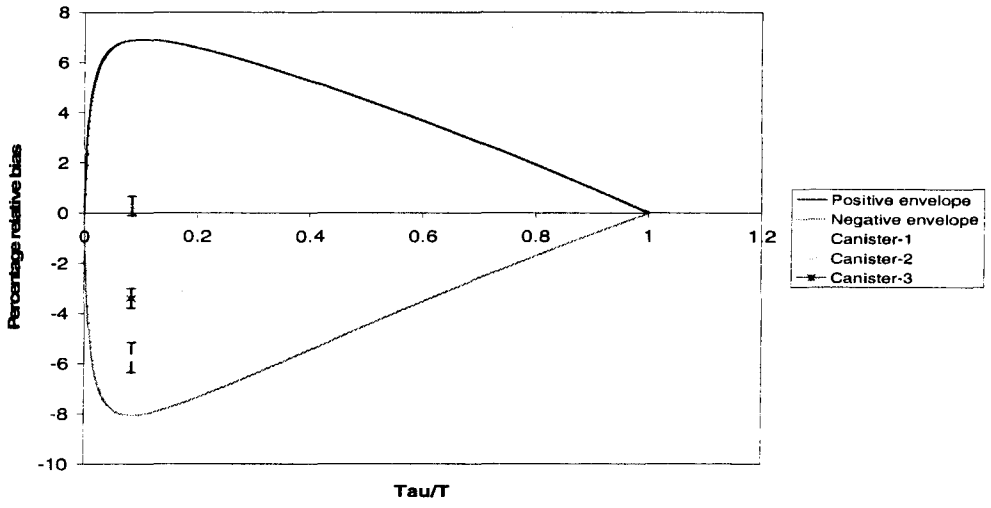
c) Summary of 40 hours bias experiments

Canister #	TWA Canister conc (ppm)	TWA GC conc (ppm)	% relative bias (Canister vs GC)	TWA PID conc (ppm)	% relative bias (Canister vs PID)
(+) bias 2-20 ppm					
1	6.77	7.58	-10.69	7.64	-11.39
2	7.82	7.58	3.17	7.64	2.36
3	7.93	7.58	4.62	7.64	3.80
Average	7.51	7.58	-0.93	7.64	-1.75
(-) bias 2-20 ppm					
1	5.09	5.95	-14.14	5.97	-14.57
2	5.47	5.95	-7.91	5.97	-8.38
3	5.65	5.95	-4.88	5.97	-5.36
Average	5.40	5.95	-8.98	5.97	-9.44
(+) bias 2-200 ppm					
1	25.02	27.37	-8.49	27.48	-8.95
2	28.60	27.37	4.46	27.48	4.04
3	28.83	27.37	5.33	27.48	4.91
Average	26.80	27.37	-2.06	27.48	-2.46
(-) bias 2-200 ppm					
1	14.66	17.27	-15.11	17.30	-15.26
2	16.07	17.27	-6.95	17.30	-7.11
3	15.93	17.27	-7.76	17.30	-7.92
Average	15.53	17.27	-9.94	17.30	-10.10

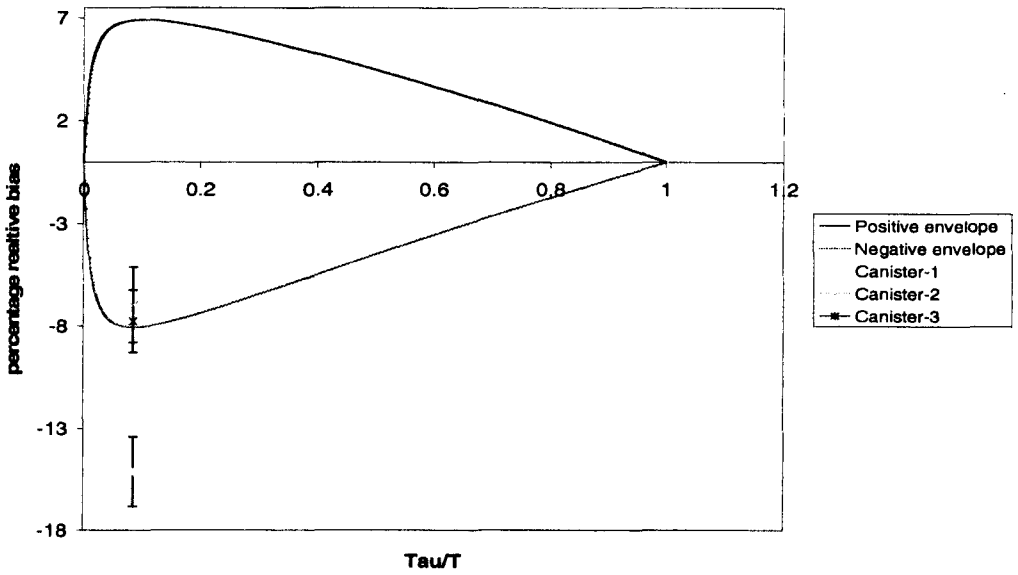
Bias is the difference between the amounts of chemical (mass) that a canister would collect using a theoretical constant flow controller (experimentally measured in this study with a GC) and the actual capillary flow controller. The percentage relative bias between the GC and capillary canisters values were calculated. The experimental results were compared to the results predicted by the model. Figure 14 displays representative plots comparing the experimental results to model predictions, in this case, for a negative bias condition with a concentration peak of 2-200 ppm. A complete set of plots is provided in Ravikumar 2007.



a) Negative Bias at 2-200 ppm (8-hrs)



b) Negative Bias at 2-200 ppm (24-hrs)



c) Negative Bias at 2-200ppm (40-hrs)

Figure 14. Plot of relative percentage bias against Tau/T for Negative bias condition with concentration peak of 2-200ppm for 8-hrs, 24-hrs, and 40-hrs bias experiments (Error bars represent %RSD).

The bias determined from the experimental results was found to be lower then the model predictions. The average percent difference between the experimental measurements and model predictions were a very good fit of less than 3%. Where and average peak amplitude of 10X was 1.54% and 0.55% for positive and negative bias, respectively and average peak amplitude of 100X was 2.95% and 2.84% for positive and negative bias, respectively. However, the range of the bias values for all tests was rather high exceeding 10% for some test. The principle source of the variability was canister 1 which demonstrated elevated levels of bias due to a slow leak in the canister. When the estimated leak rate was considered for canister 1, the bias levels approached the same bias levels as Canisters 2 and 3.

The experimental results from canister 2 and 3 were within the predicted bias envelope. When analytical error (±3%) associated with GC was considered, the experimental values approached the model's predications. Random errors associated with pressurizing the canisters were considered to be minor and did not influence the overall trend of the data.

Conclusions

The capillary canister was redesigned to improve field performance as a field personal air sampling device. Its performance as a personal sampling device was evaluated by conducting sampling at different facilities. The mathematical model developed to predict the sampling bias associated with capillary canisters was experimentally validated.

The new design overcame some of the drawbacks observed in the existing design. The protrusion of the steel shaft from the sides was removed. The use of a micro valve made the system less susceptible to leak, thus reducing loss of samples. The ability to vacuum and pressurize the canister through the micro valve permits removal of the top valve. Replacement of the top valve results in a 40% reduction in cost. The new design was less expensive, weighed less, and was more acceptable to the subjects.

The performance of this personal sampler was evaluated by conducting field sampling at two locations; a fiberglass lay-up operation and a chandelier coating company. Twenty-four paired samples were collected, including sixteen personal samples and eight area samples. The paired t-test performed on the personal samples showed there was no statistical difference between the canisters and badges.

Time dependent flow rate data was collected for capillaries of length 10 cm, 30 cm, and 50 cm. The characteristic change in flow rate was similar for all capillaries irrespective of their length. This allowed the development of a single bias envelope model for particular concentration peak amplitudes. The maximum bias for the worst-case scenarios was identified with the model and experimentally simulated at three different sampling times; 8-hrs, 24-hrs, and 40-hrs. Overall, the results from the bias experiments were convincing. When the errors associated with the analytical procedure were taken into account, the results from the canister did approach the results predicted by the model.

The results from this study suggest that the new design provided an improvement over the previous design and the field results satisfied the requirements of BS EN 838-workplace atmosphere sampling requirements, thus showing that capillary canisters can be used as reliable personal samplers in microenvironments.

Journal Articles

Rossner, A., and Wick, D. P.: A Field Study to Assess the Long-Term Sampling Feasibility of Evacuated Canisters and the Development of a Mathematical Model to Analyze Potential Sampling Bias. *J. Occup. And Environ. Hyg.* 2 (9) 474-480 (2005).

Masters Thesis

Ravikumar, Karthikeyan.: Evaluation of the Performance of Cnaistes as Persoanl Samplers and Experimental Validation of the Bias Model., M.S. Environmental Engineering, Clarkson University, December 2007. Advisors Rossner, A. and Wick, D.P.

Conference Presentations

Rossner, A., and David Wick.: A field Study to Assess the Long-Term Sampling Feasibility of Evacuated Canisters and the Development of a Mathematical Model to Analyze Potential Sampling Bias., Northwest Occupational Health Conference, October 18, 2007.

Rossner, A. Exposure Monitoring for Low Level Volatile Organic Compounds Using Evacuated Canisters, Civil and Environmental Engineering Seminar, Clarkson University, October 27, 2006.

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