Long Term Sampling with Mini Canisters- A Comparison With Sorbent Tubes

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Clarkson UNIVERSITY *defy* convention

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Overall Research Objective

Design and evaluate a sampling system for the collection of long-term (hours to days) personal samples using an evacuated canister.

History of Research

Characterize the flow rate for a novel capillary flow control device. (Rossner, Env. Sci. Tech. Nov. 2002)

Compare the capillary-canister sampling system to sorbent sampling systems using a

- Small exposure chamber. (Rossner, JOEH Jan. 2004)
- Large exposure chamber. (Rossner, JOEH May 2004)

Evaluate the performance of the system in an industrial environment. (Rossner, JOEH Sept 2005)

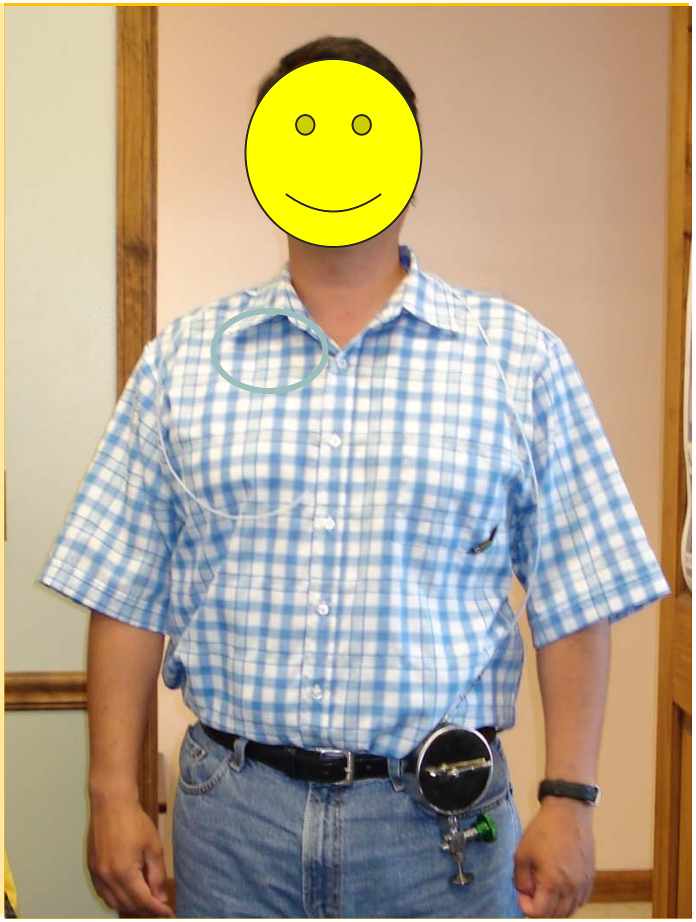
Characterize the sampling bias associated with the diminishing flow rate. (Rossner, JOEH Sept 2005)

Background - Sorbents vs Whole air samples

- Advantages of canisters :
  - Broader array of compounds (C-1 to C10)
  - Possible Semi volatiles
  - Passive sampling
  - Simple to use
  - Multiple analysis of the same sample
  - Not sensitive to RH, Temperature and air velocity

- Disadvantages of canisters :
  - Leaks
  - Size
  - Cost of analysis (in some cases)

Personal sampling with canisters



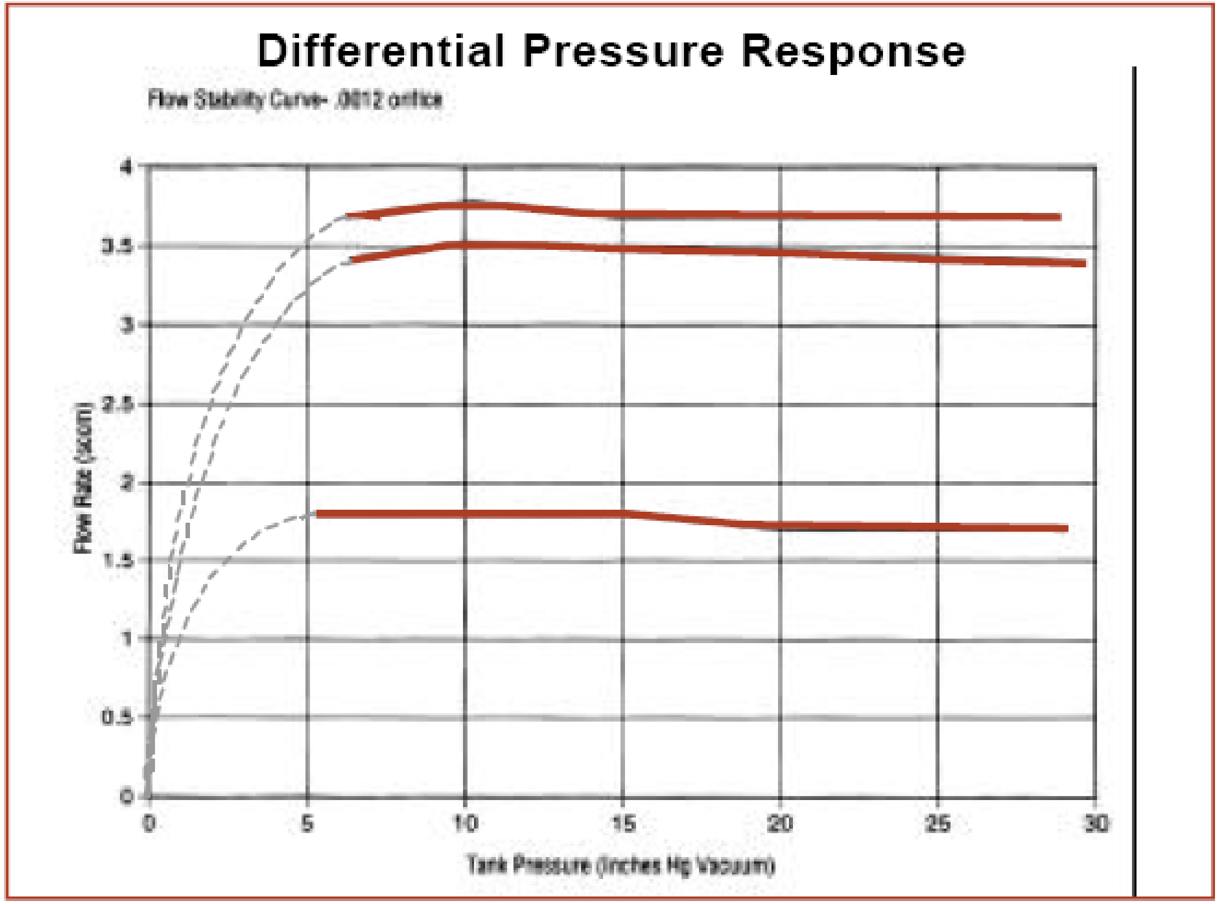
- 300 - 400 mL stainless steel canister (Capillary flow controlled (~0.05 to 1ml/min)
- Collects compounds in breathing zone
- Minutes to days
- Indoor or outdoor sampling

Flow Controllers – How they function and their capabilities.

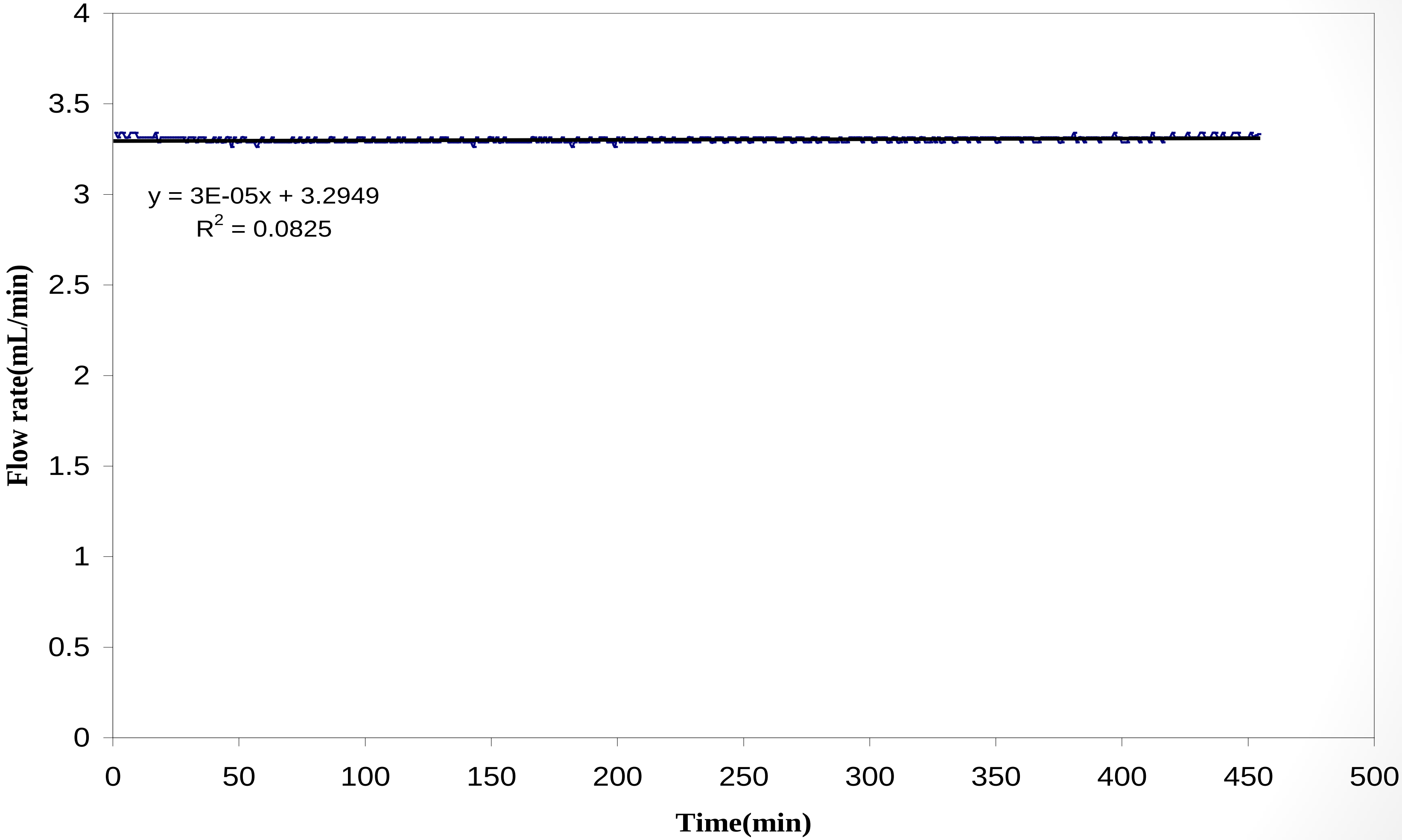
Critical orifice flow controller

Diaphragm flow controller

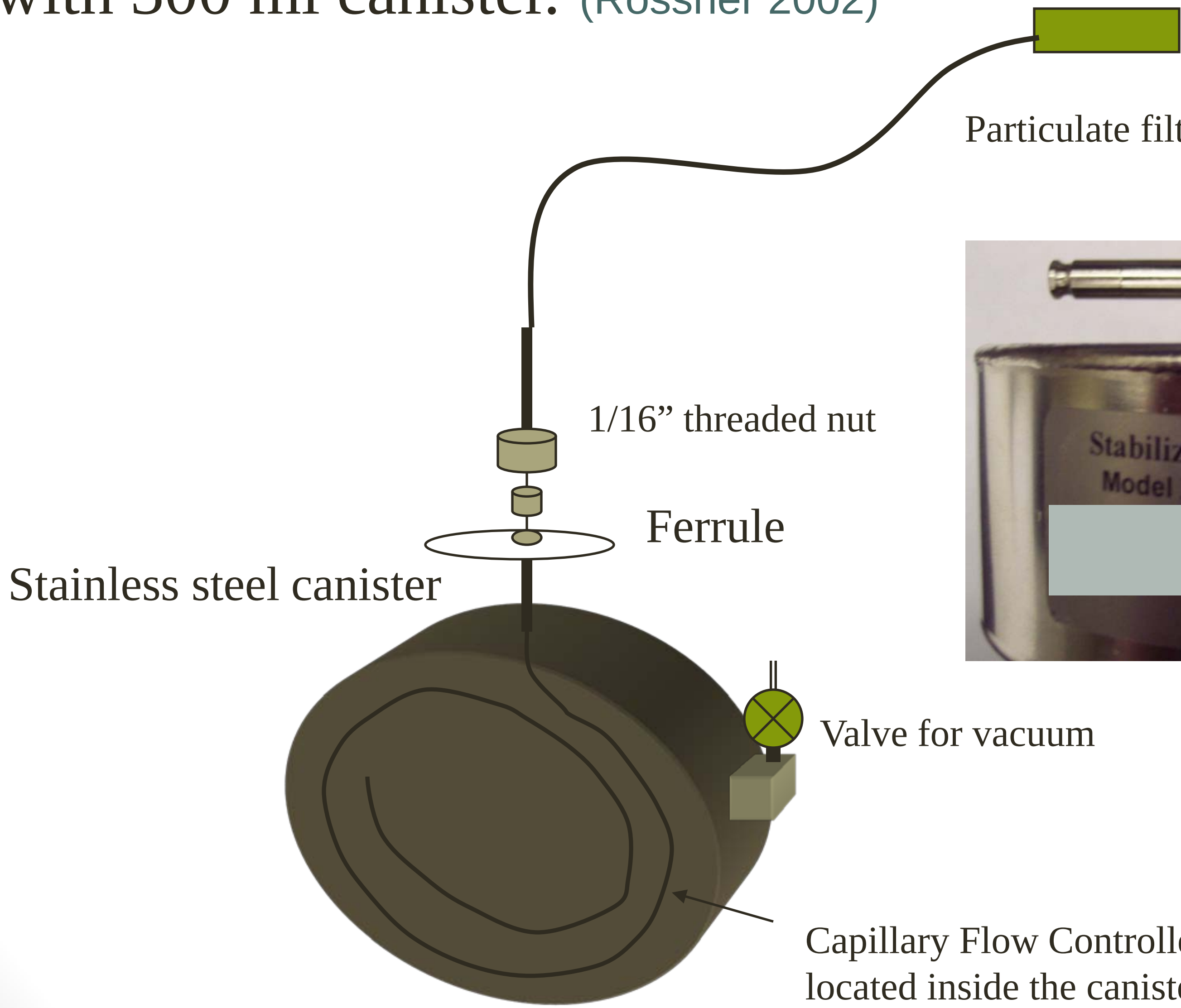
Constant Flow Rate: A flow controller will maintain a constant sample flow until it is unable to maintain a stable pressure differential across the critical orifice.



Example of an experimental flow-rate from an diaphragm constant flow controller



Capillary-Canister Prototype: Capillary flow controller with 300 ml canister. (Rossner 2002)



Characterization of the flow rate for the capillary flow control device.

- The volumetric flow rate in the capillary is related to pressure gradient, viscosity of air, and the dimensions of the capillary (*r* and *L*)
  - *Hagan-Poiseuille*:

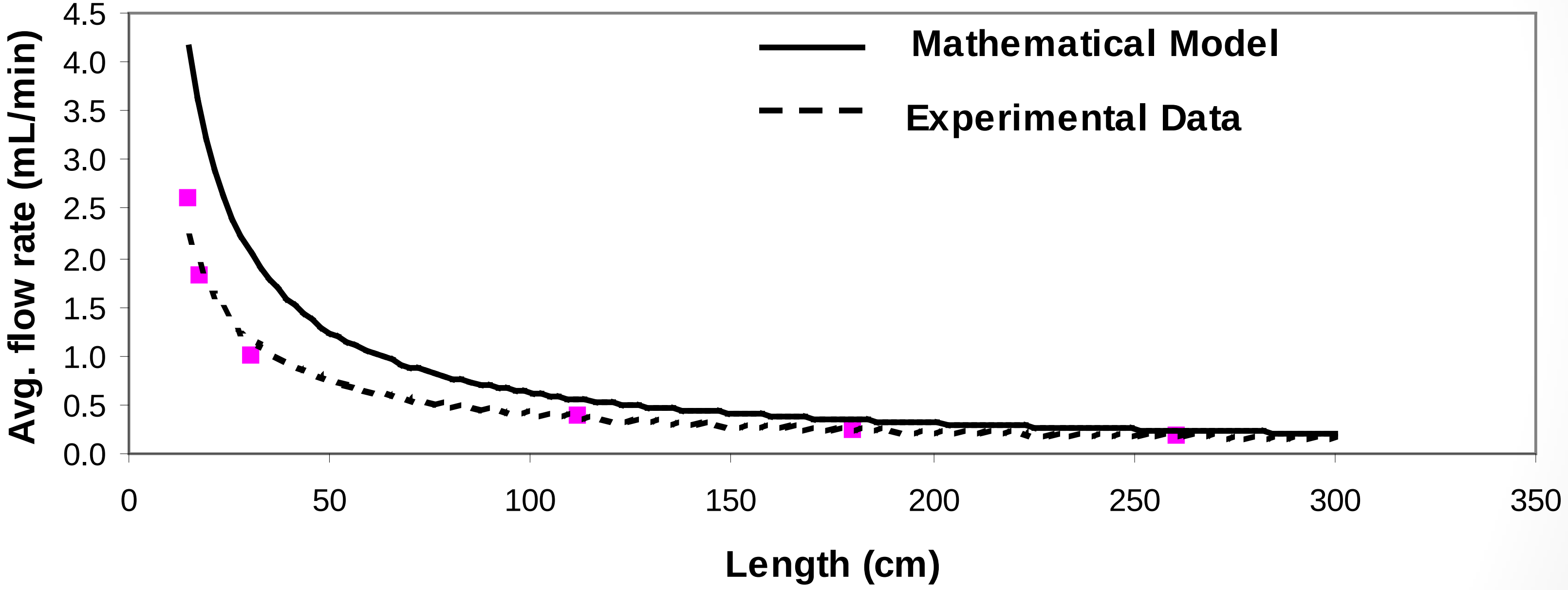
$$Q(t) = \frac{\pi \left(P_{atm} - P(t)\right) r^4}{8 \mu L}$$

By combining this with the *Ideal Gas Law*

a model was developed to predict the dimensions of flow controller needed for a particular sampling time:

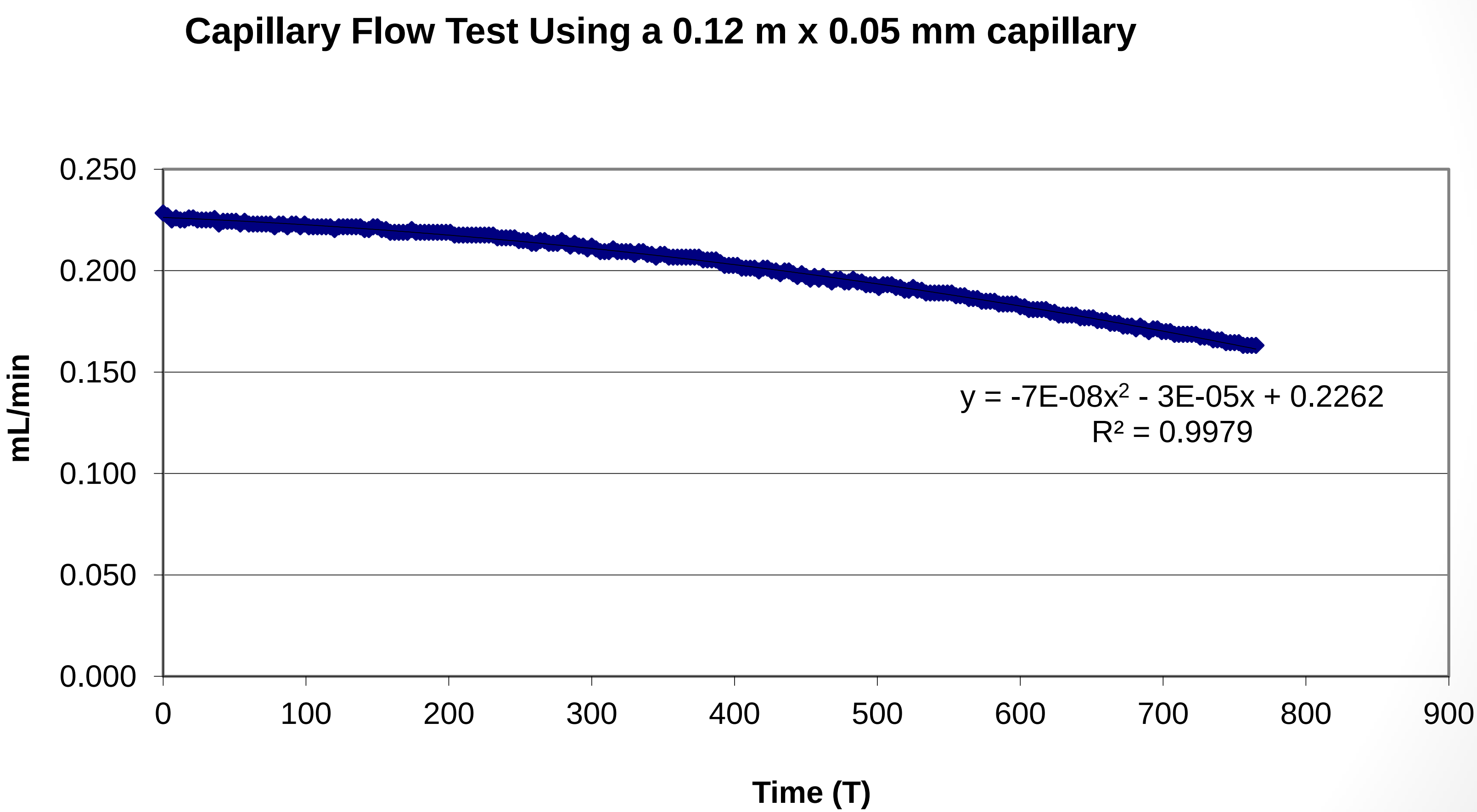
$$L = \frac{K_6 r^4 T}{e^{\frac{V_f}{K_5}} - 1}$$

Mathematical Model vs. Experimental Data

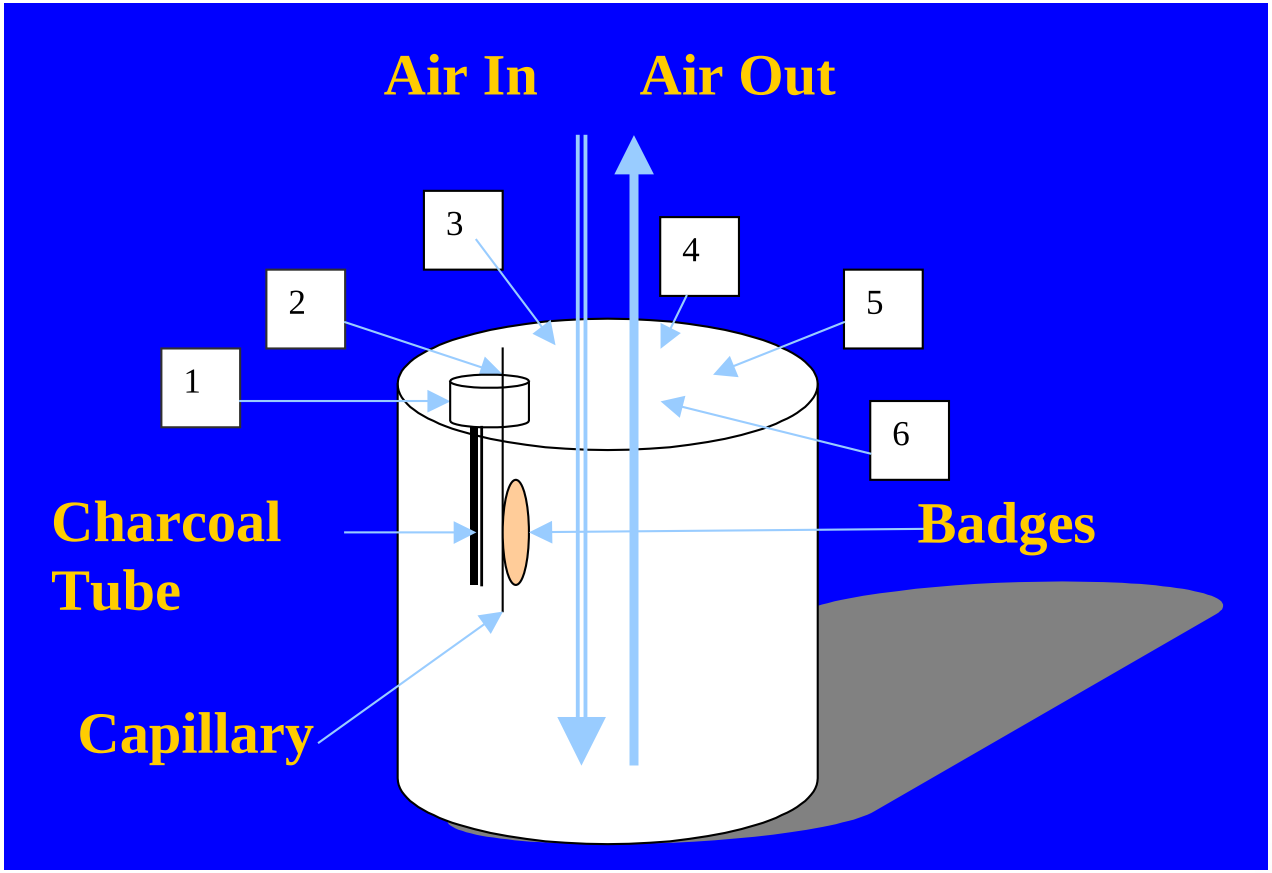


Experimental Flow Rate Data

Linear and *quadratic* fit of these data points are shown.



Comparison of the capillary-canister to sorbent samplers using a *small (8 Liter)* exposure chamber.



Performance Assessment of the Sampling Device

- **NIOSH and OSHA, and European Standard EN 482**, *Workplace atmospheres-General requirements for the performance of procedures for the measurements of chemical agents*.

$$\text{Overall Uncertainty} = \frac{\left| x_i - x_{ref} \right|}{x_{ref}} + 2std$$

- *Provides a measure of **Accuracy and Precision.***
- ***Ref – was an on-line GC.***

Overall Uncertainty (OU)

	Canisters OU %	Std Dev	Char. Tubes OU %	Std Dev
IsoPropyl Alcohol	18.1	7.4	41.3	19.3
Methyl Ethyl Ketone	15.4	5.5	43.3	24.4
Ethyl Acetate	16.5	5.5	23.4	17.2
Cyclohexane	16.1	6.8	16.5	7.2
Toluene	16.8	6.1	20.2	11.4
Perchlorothylene	17.1	8.5	16.3	16.3

- Number of samples (n = 84)
- Overall Uncertainly Should be < 30 % Per EN 482

Comparison of the capillary-canister to sorbent sampler using a *large* (18.1 m^3) exposure chamber.

Styrene Exposure (Sample No.)	Badges (mg/m^3)	Canisters (mg/m^3)	Reference (GC/FID) (mg/m^3)	(ppm)
1	18.3	16.5		
2	18.6	19.7		
3	16.9	18.0		
4	16.9	17.1		
5	16.9	19.7		
6	16.9	20.0		
Mean	17.4 ± 0.8	18.5 ± 1.5	21.0 ± 2.0	4.1

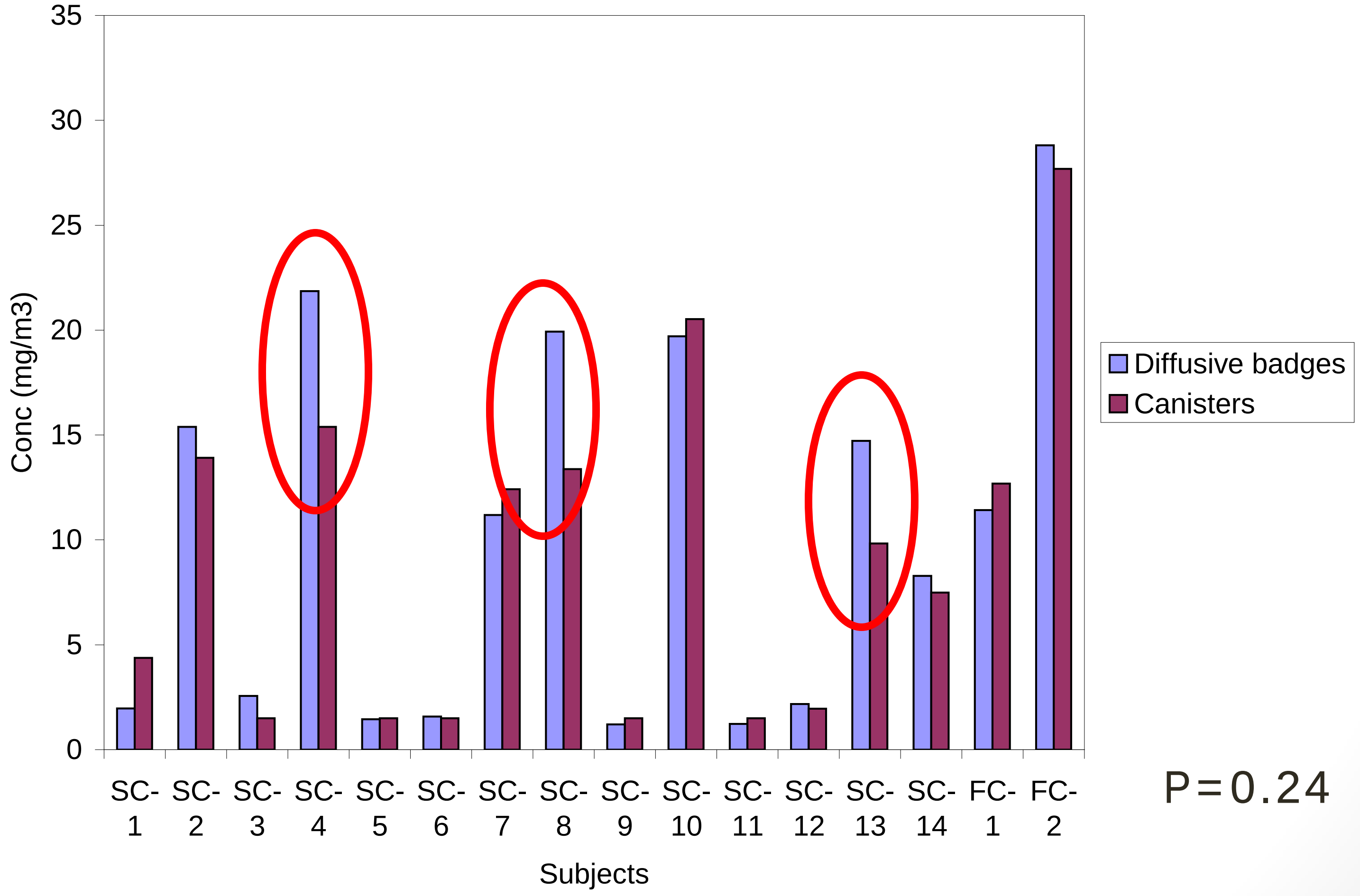
Evaluation of the capillary canister in an industrial environment –Long-term sampling. (Stoddard Solvent)

Diffusion Badges (8 h)	(mg/m3)
Monday	30.2 ± 2.1
Tuesday	42.7 ± 1.8
Wednesday	38.0 ± 5.9
Thursday	31.1 ± 3.6
Friday	35.7 ± 3.7
(n = 6 per day)	
Mean value (40 h)	**35.3 ± 5.4**

Capillary-Canister (40 h)	(mg/m3)
1	34.7
2	38.5
3	28.7
4	30.0
5	30.3
6	36.8
Mean value (40 h)	**33.2 ± 4.1**

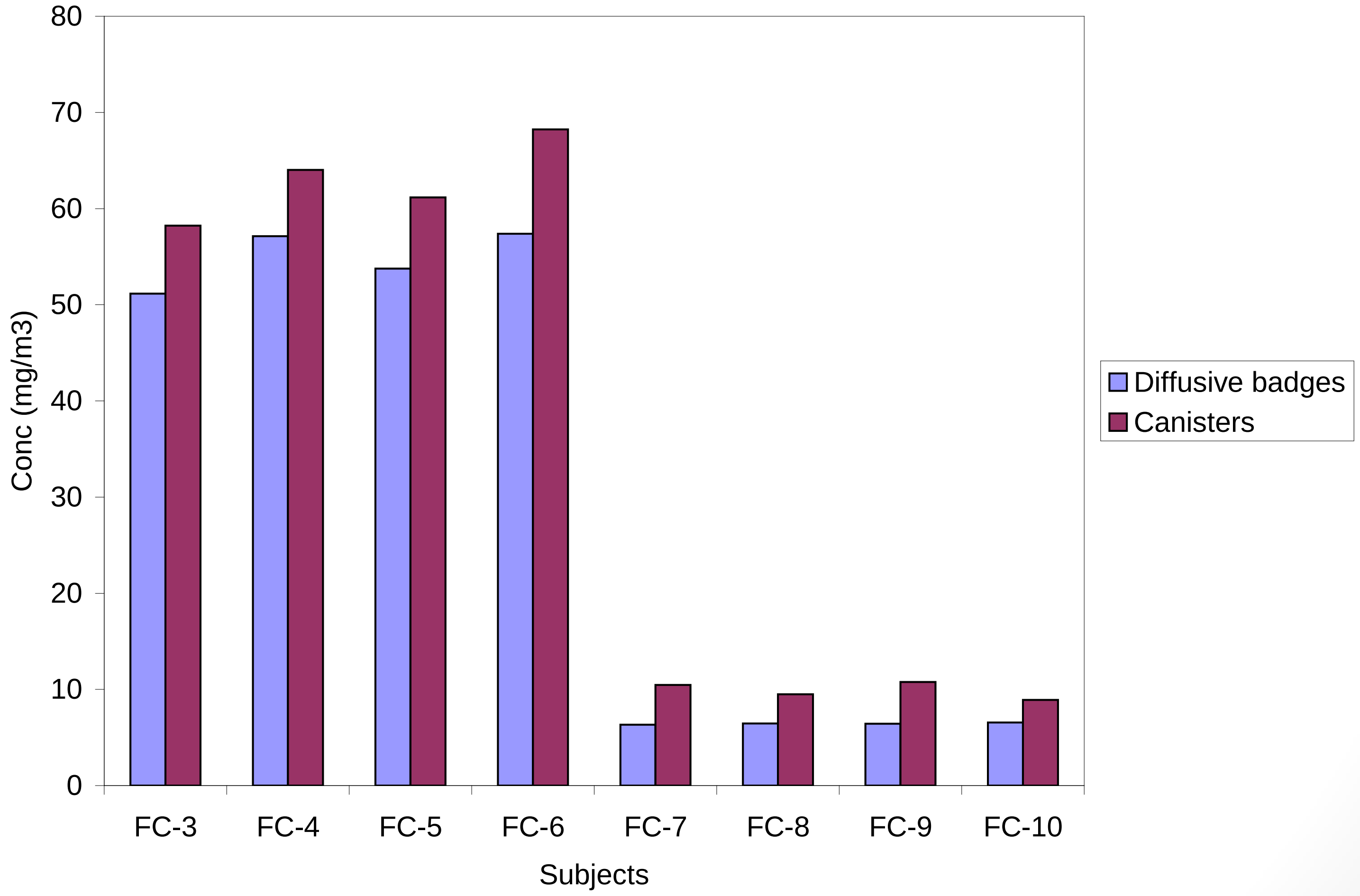
(Stoddard Solvent)

Field Comparison of capillary canisters personal samples and Diffusion Badges for Xylene in a Lacquer coating.



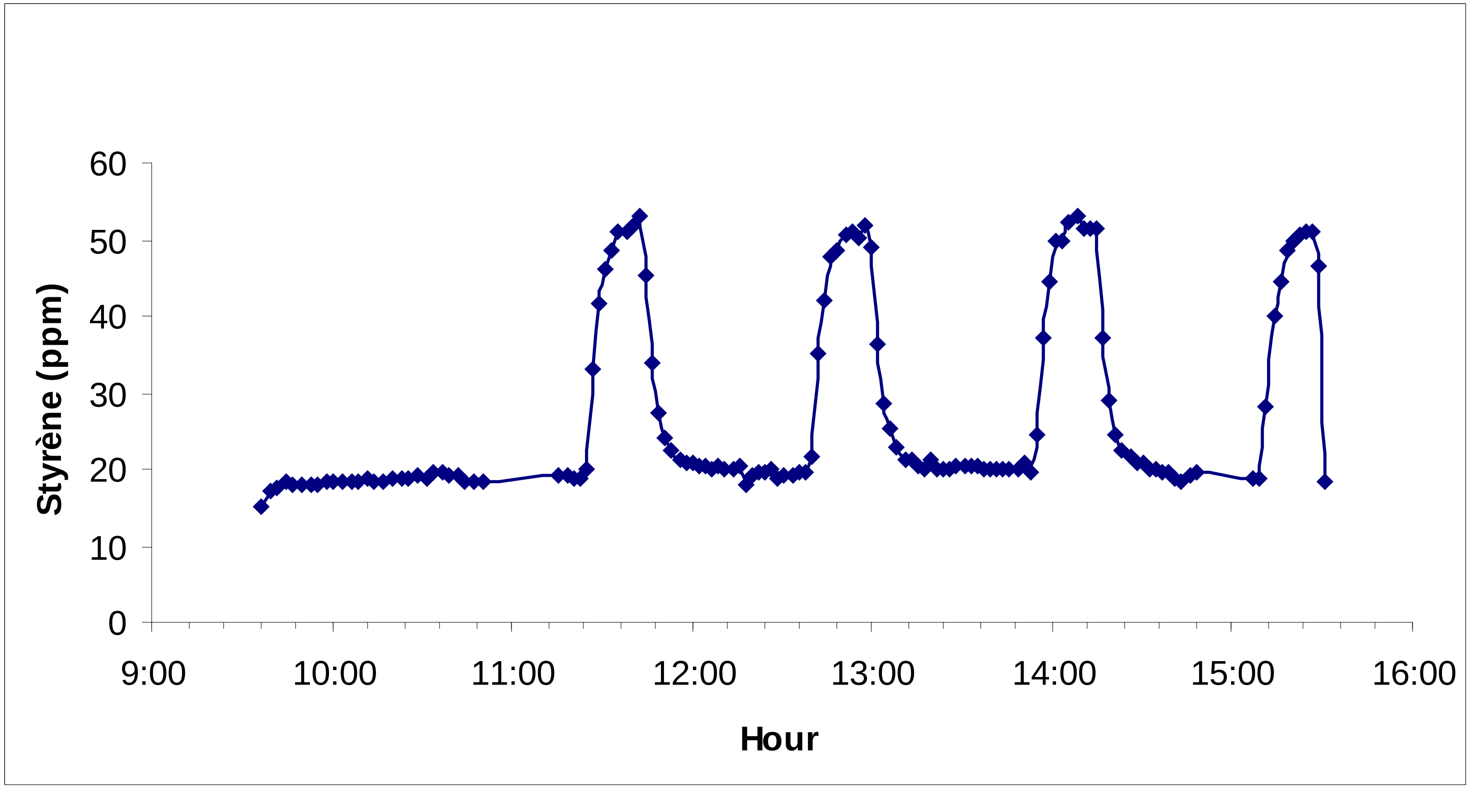
P=0.24

Comparison of Capillary canisters and diffusion badges for Area samples in a Fiberglass lay-up operation

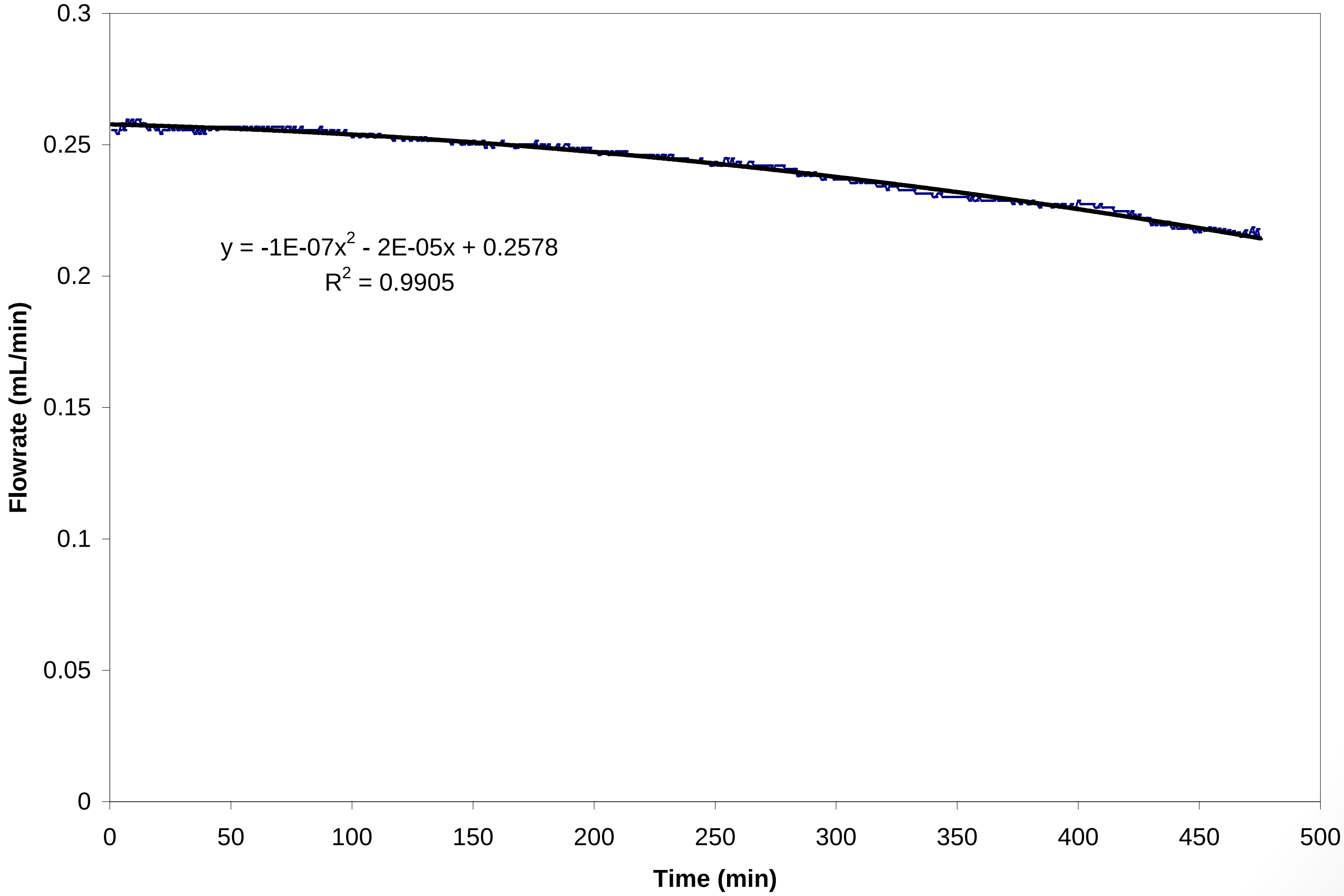


Air flow Rate in Room < 25 fpm in the work area for this set of data

Work Place Atmosphere with Peak values



Example of change in flow rate over time with a capillary flow controller. (10cm capillary flow controller of 0.05mm diameter)



Characterization of the sampling bias associated with the diminishing flow rate.

- Rate of accumulation in the canister depends on flow rate (Q_{in}) and incoming concentration (C_{in})

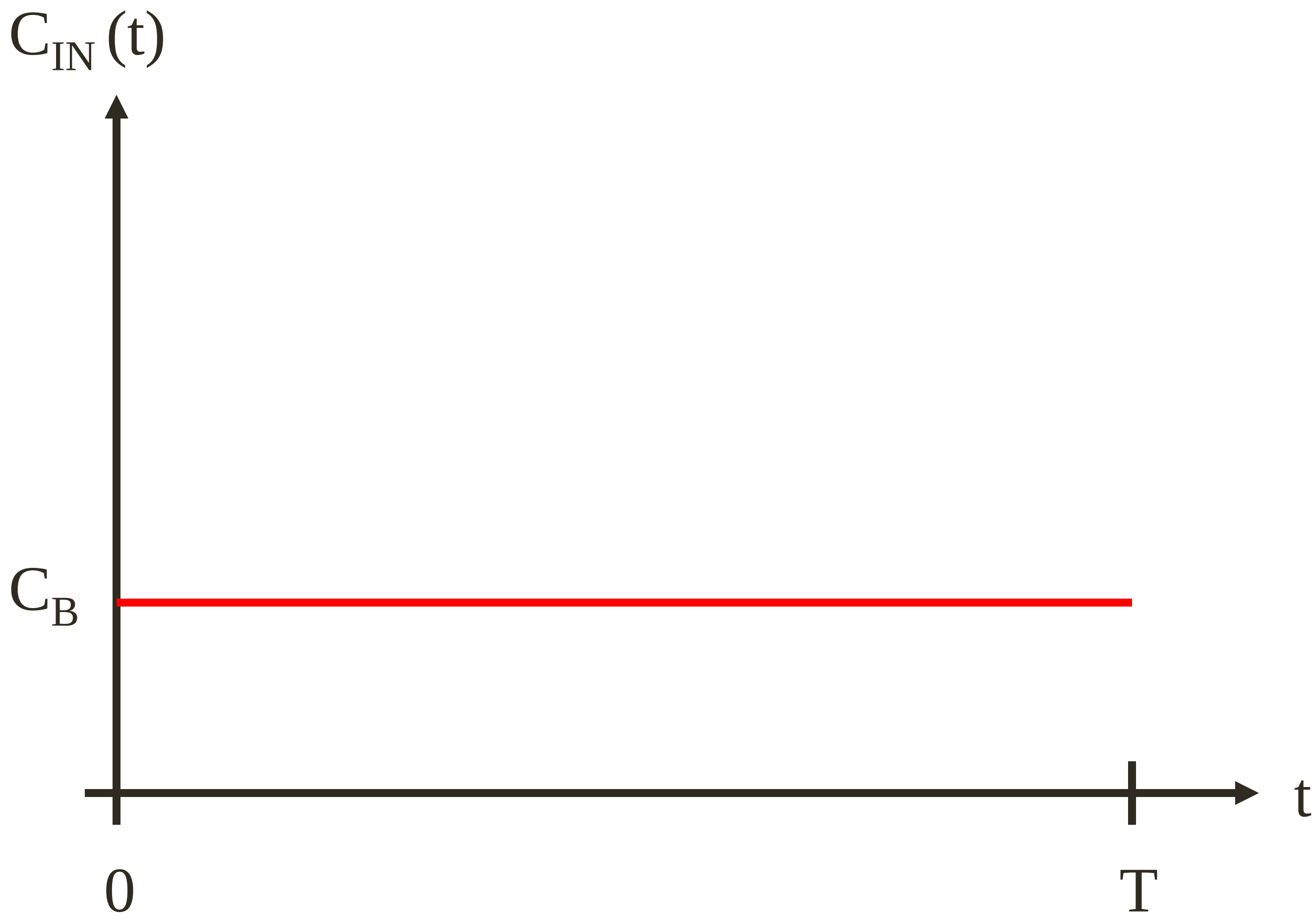
$$V_c \frac{d\,C(t)}{dt} = Q_{in}(t)\,C_{in}(t)$$

where V_c is the canister volume.

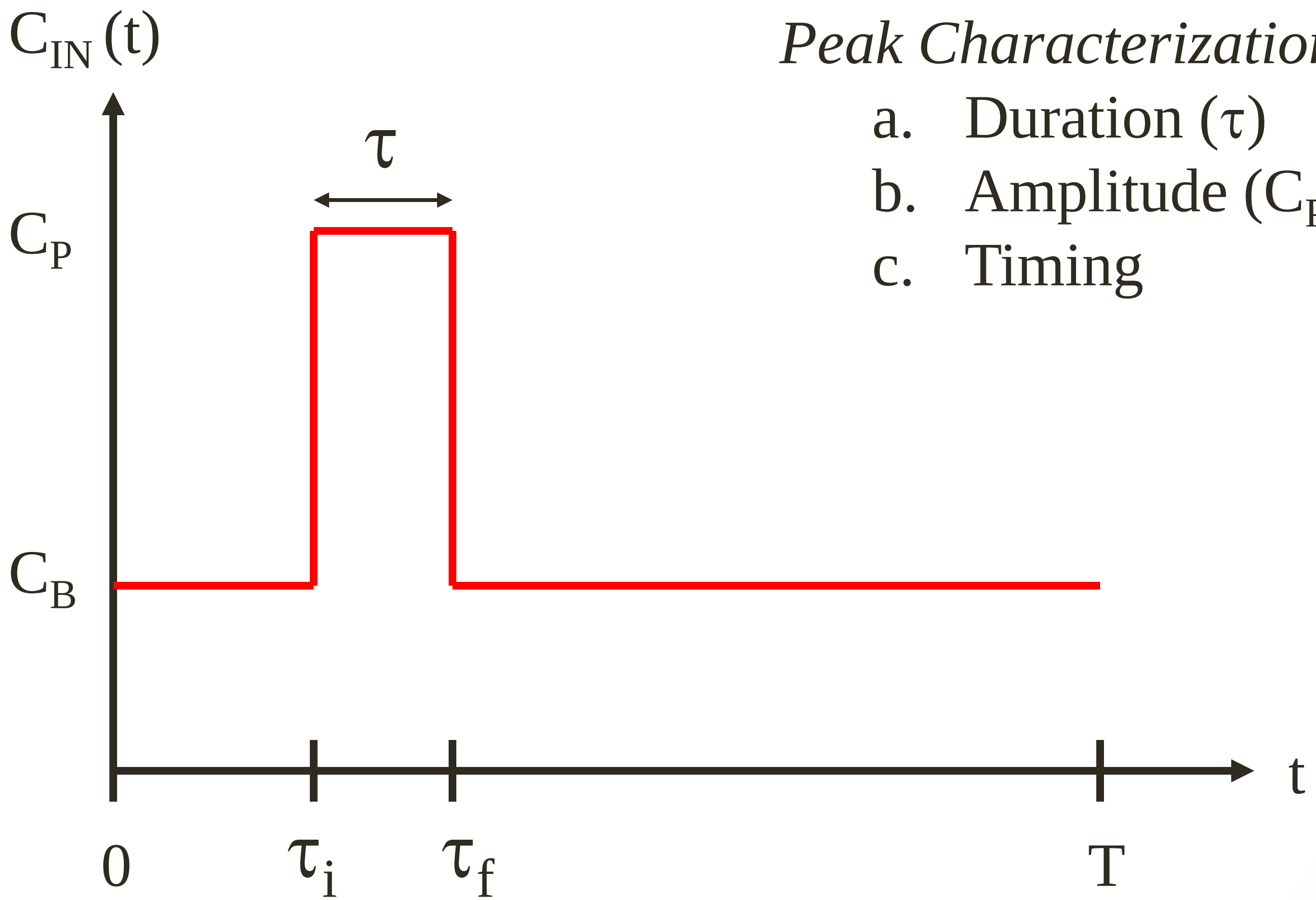
- Sampling bias: $$Bias = \frac{C(T) - \tilde{C}(T)}{\tilde{C}(T)} \times 100$$

Where $\tilde{C}(T)$ e final concentration for constant flow rate.
And $C(T)$ is the final concentration for diminishing flow rate.

Incoming Concentration Profile: *Constant*



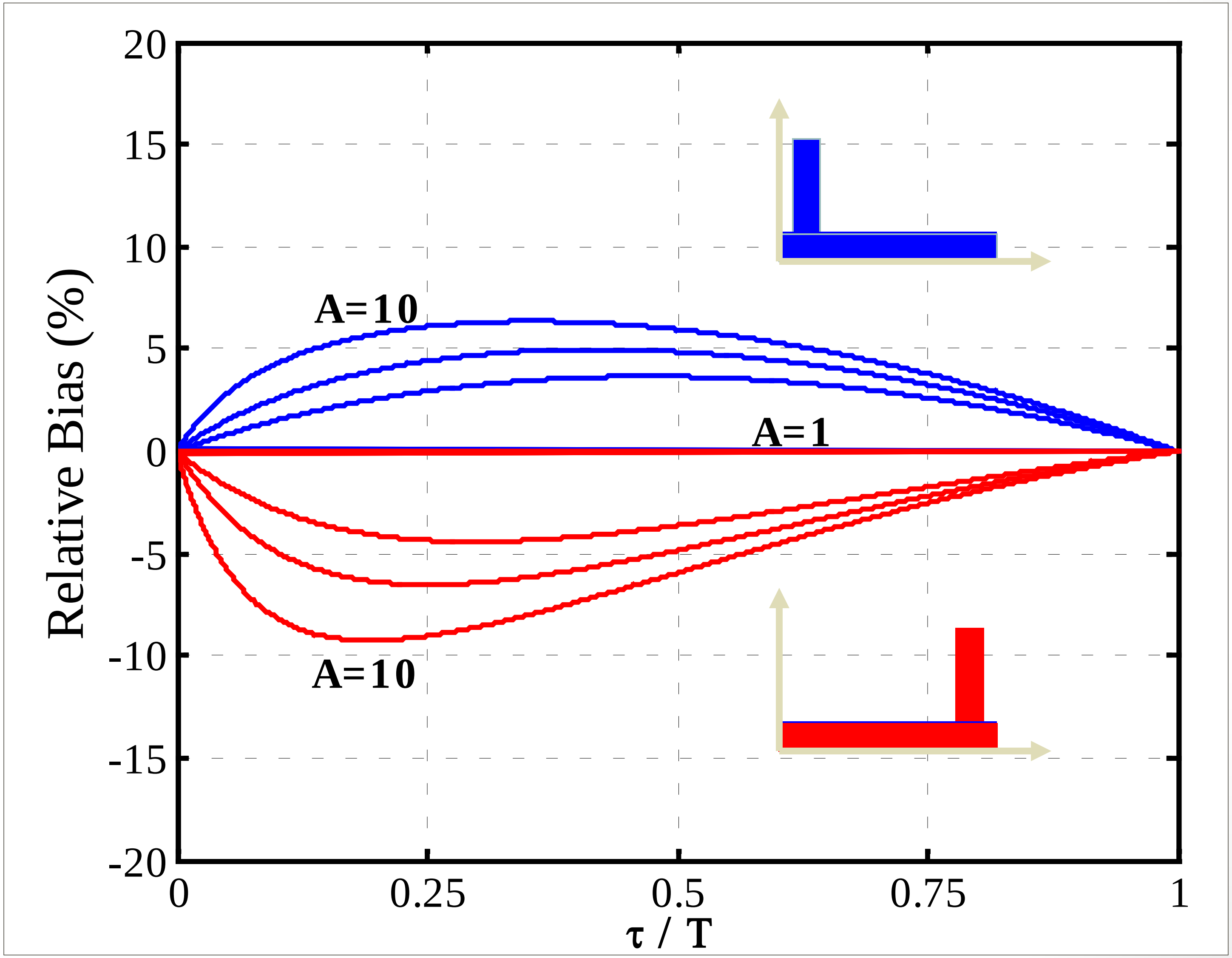
Incoming Concentration Profile: *with peak*



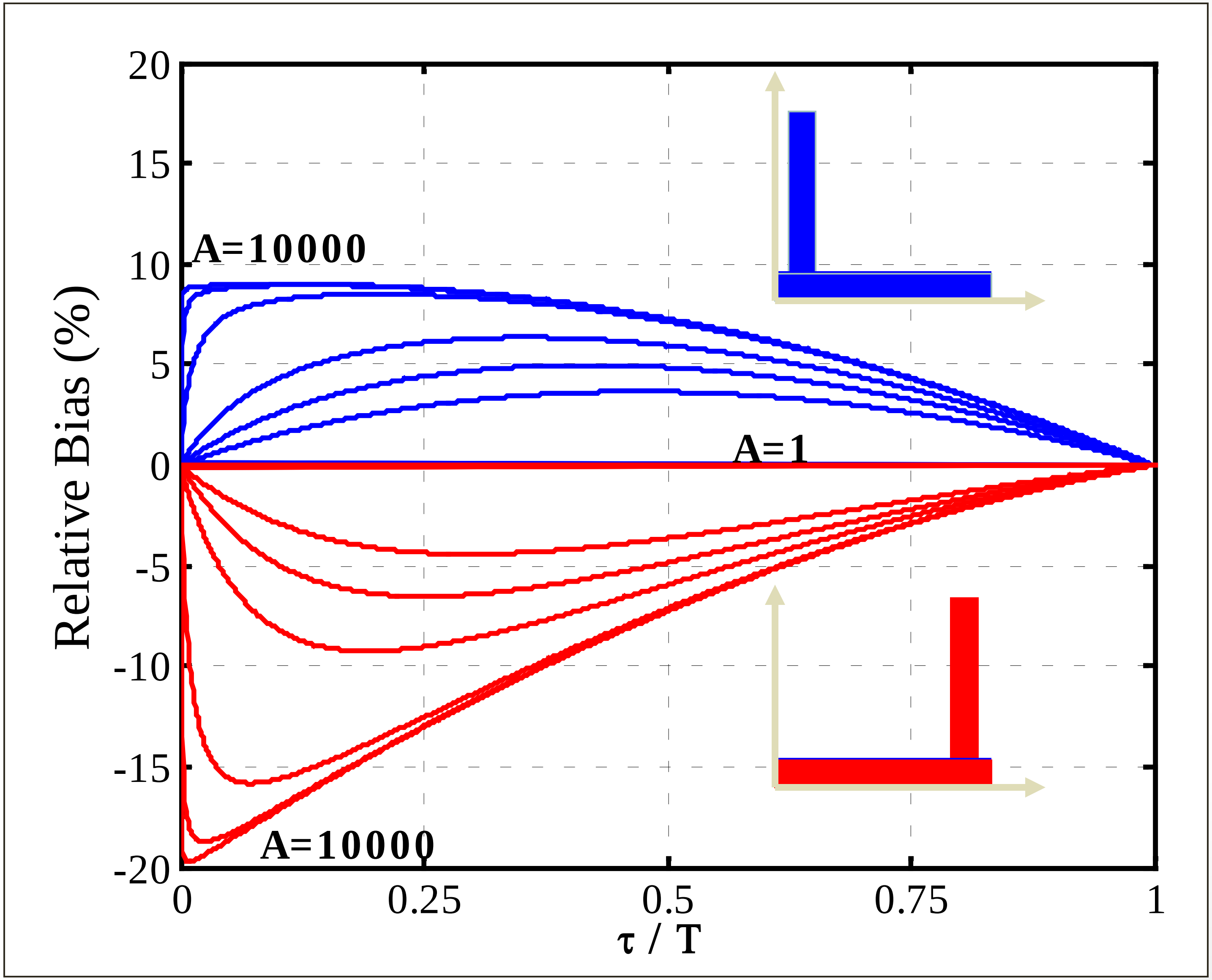
Peak Characterization

a. Duration (τ)
b. Amplitude ($C_P = AC_B$)
c. Timing

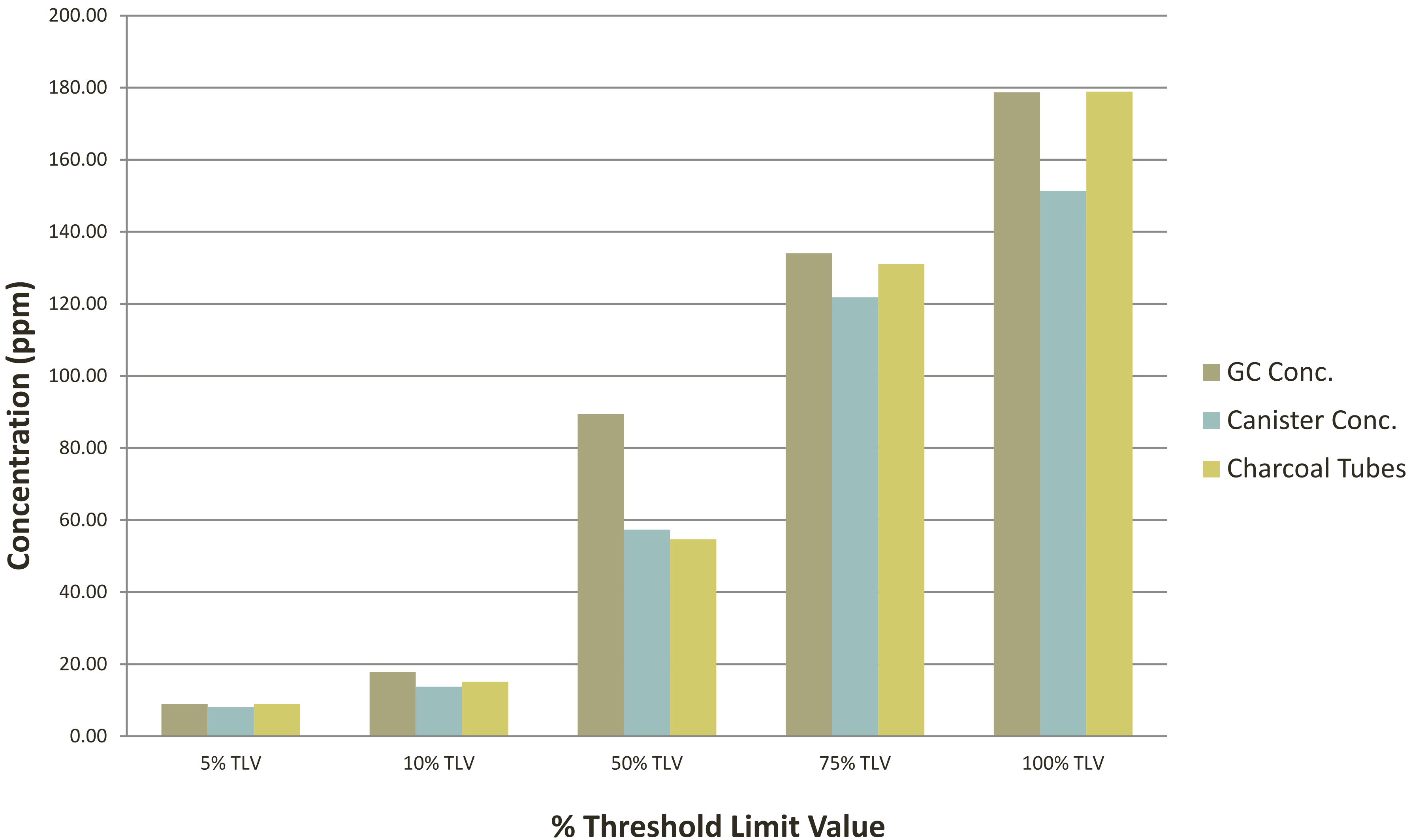
Predicted Bias associated with Peak Concentration Profile
Peak Amplitude (A = 1, 3, 5, 10)



Predicted Bias associated with Peak Concentration Profile
Peak Amplitude (A = 1 - 10000)

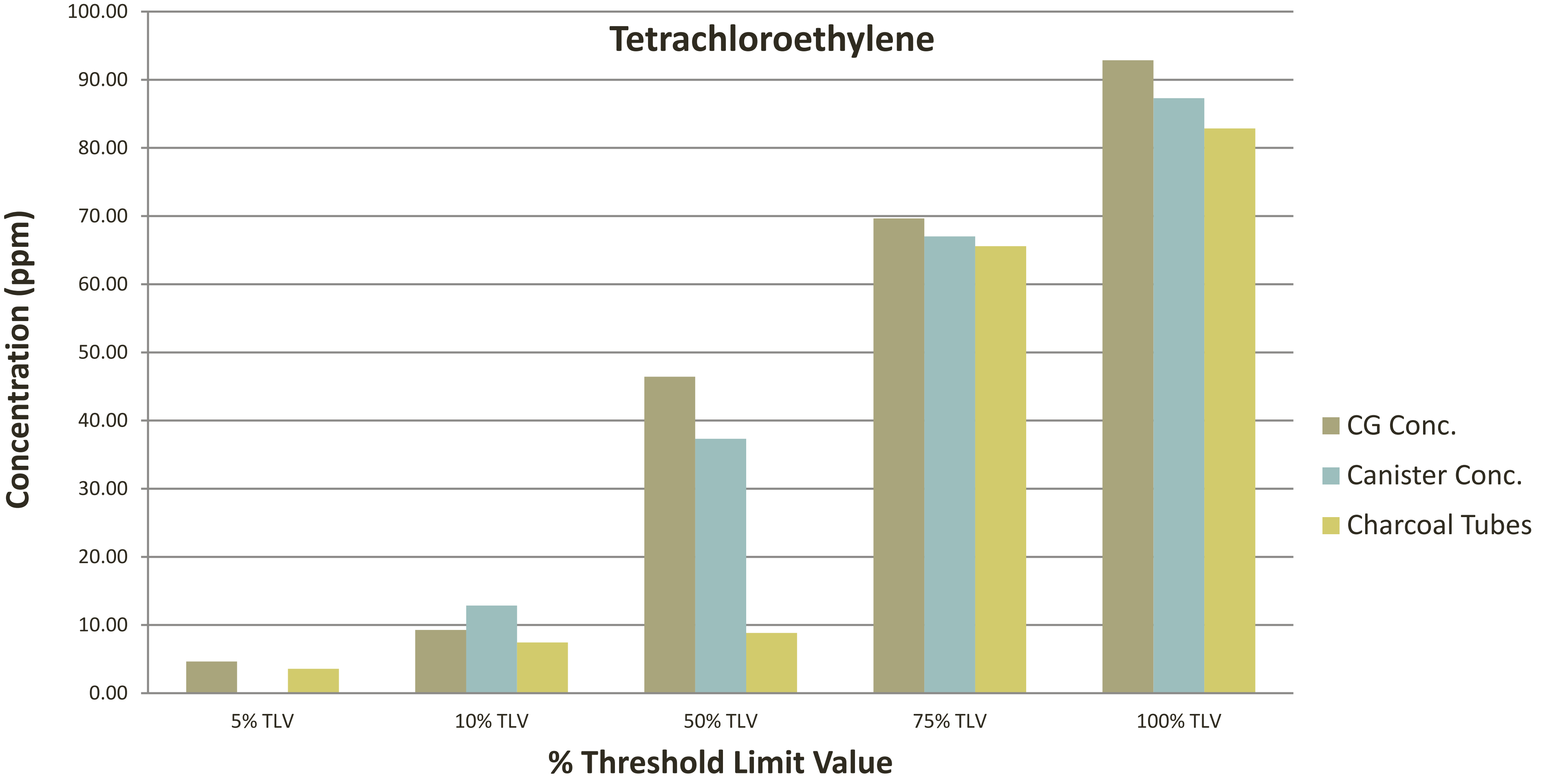


Toluene

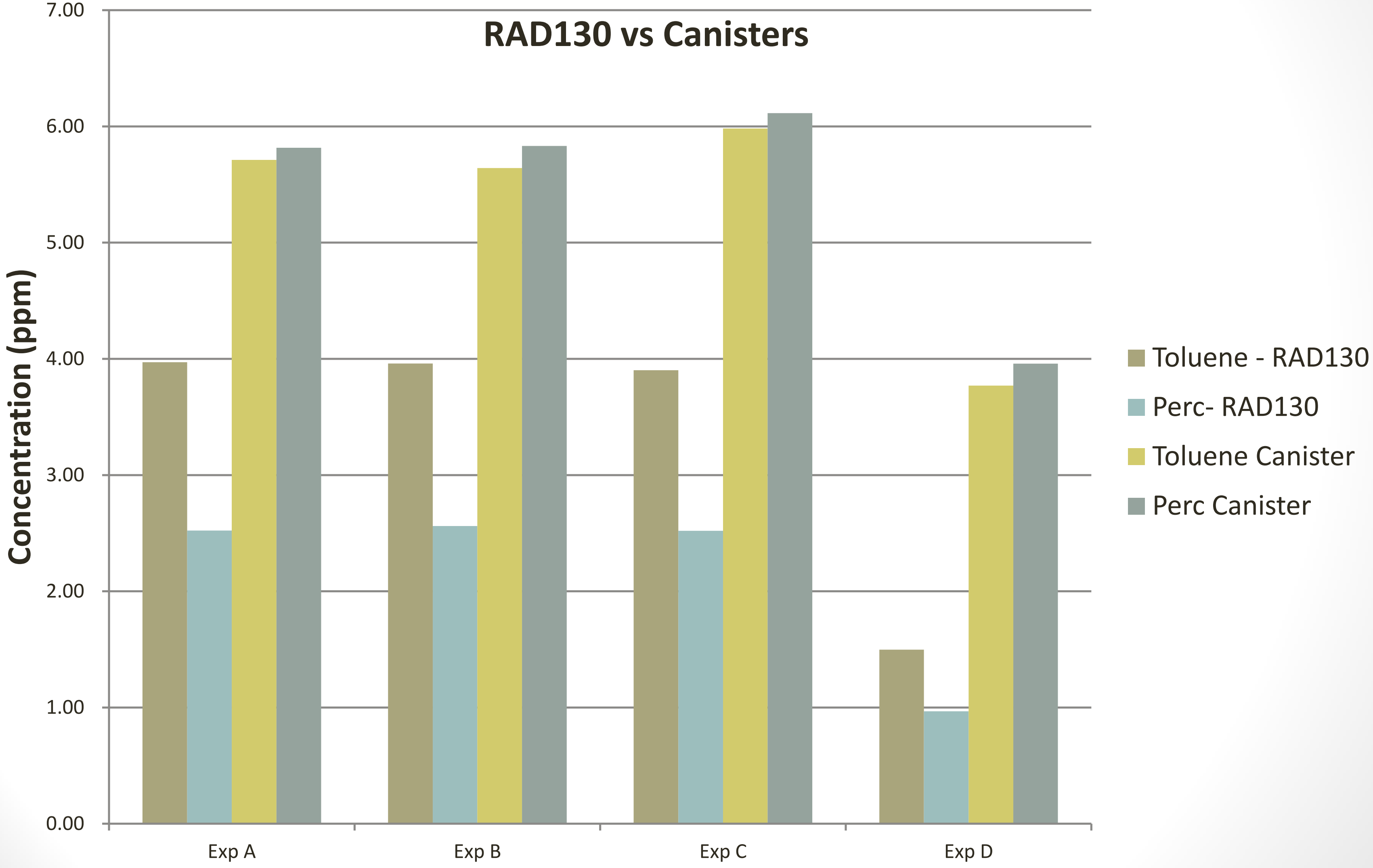


200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Concentration (ppm)
5% TLV
10% TLV
50% TLV
75% TLV
100% TLV
% Threshold Limit Value
GC Conc.
Canister Conc.
Charcoal Tubes

Charcoal tubes vs Canister at Occupational concentrations



7-day sampling



Conclusions

- Low flow rates allow for long-term sampling and enable the use of small canisters for personal sampling or area sampling
- No field calibration and no mechanical parts reduces the risk of failure in field environments
- The capillary flow controller is inexpensive and easy to replace
- Durable light weight design improves user acceptability
- Bias associated with the diminishing flow rate has been quantified and is within acceptable ranges and is predictable
- Long-term sampling of indoor environments is possible for a **broader array** of compounds.
- Multiple analysis of the same sample is easily accomplished.
- No significant problems with high Relative Humidity and Temperature.

Questions