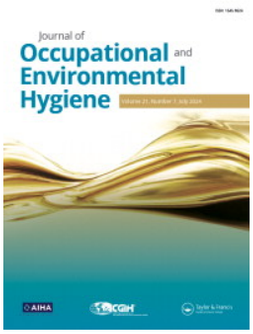

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REPORT

Evaluation of flow controllers used with evacuated canisters to assess VOC exposures in occupational and non-occupational environments

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ABSTRACT

Ideally, measuring exposures to volatile organic compounds should allow for modifying sampling duration without loss in sensitivity. Traditional sorbent-based sampling can vary sampling duration, but sensitivity may be affected when capturing shorter tasks. Diaphragm and capillary flow controllers allow for a range of flow rates and sampling durations for air sampling with evacuated canisters. The goal of this study was to evaluate the extent to which commercialized capillary flow controllers satisfy the bias (±10%) and accuracy (±25%) criteria for air sampling methods as established by the National Institute for Occupational Safety and Health (NIOSH) using the framework of ASTM D6246 *Standard Practice for Evaluating the Performance of Diffusive Samplers* to compare their performance with diaphragm flow controllers in a long-term field study. Phase 1 consisted of a series of laboratory tests to evaluate capillary flow controller flow rates with respect to variations in temperature (−15–24 °C). The results demonstrated a slight increase in flow rate with lower temperatures. In Phase 2, the capillary flow controller was evaluated utilizing a matrix of parameters, including time-weighted average concentration, peak concentration (50–100× base concentration), air velocity across the sampler inlet (0.41–0.5 m/s), relative humidity (20–80%), and temperature (10–32 °C). Comparison of challenge concentrations with reference concentrations revealed the aggregate bias and overall accuracy for four tested compounds to be within the range of criteria for both NIOSH and ASTM standards. Additionally, capillary flow controllers displayed lower variability in flow rate and measured concentration (RSD: 2.4% and 4.3%, respectively) when compared with diaphragm flow controllers (RSD: 6.9% and 7.2%, respectively) for 24-hr laboratory tests. Phase 3 involved further testing of flow rate variability for both diaphragm and capillary flow controllers in a field study. The capillary flow controller displayed a lower level of variability (RSD: 5.2%) than the diaphragm flow controller (RSD: 8.0%) with respect to flow rate, while allowing for longer durations of sampling.

KEYWORDS

Air sampling; bias; capillary flow controller; diaphragm flow controller; diffusive sampling; sensitivity

Introduction

For years, evacuated canisters have been used to assess airborne contaminants in industrial, residential, and community settings (Brymer et al. 1995; Austin et al. 2001; Crawford et al. 2006; Coffey et al. 2011; ASTM 2013; Bari et al. 2015; Duan et al. 2016). Canisters have been utilized for both personal and area sampling to characterize human exposure in various microenvironments when used with the appropriate flow controllers, whether that be through a capillary or diaphragm type. Canisters may be used to measure exposure levels in indoor air quality (IAQ) for homes, hospitals, and buildings impacted by vapor intrusion (VI) or used to study outdoor ambient air (Austin et al. 2001; Liu et al. 2005; Crawford et al. 2006; LeBouf et al. 2012; Li et al. 2012; Kalenge et al. 2013; LeBouf et al. 2014; Duan et al. 2016). All of the aforementioned applications rely on the ability of the flow controller to maintain a relatively constant flow rate of air into the canisters, thus allowing for an accurate reporting of time-weighted average exposures for the compounds of concern.

Sampling procedures and methods of analysis for both ambient and industrial environments have been established and adopted by laboratory and regulatory

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agencies, such as the Environmental Protection Agency with EPA Method TO-15 (EPA 1997) and the National Institute for Occupational Safety and Health with Method 3900 of the NIOSH Manual of Analytical Methods (Andrews and O'Connor 2020). Canisters, regardless of the flow controller employed, are useful for the sampling and analysis of many compounds across a wide range of functional groups and boiling points (C1 to C10) with approved sampling and analytical methods. Canisters have been used to sample concentrations from parts per hundred (percent) down to parts per billion (ppb), or in some cases, as low as parts per trillion (ppt). The lower concentrations for which the EPA TO-15 method is applicable are in the low ppt range. Trace levels (ppt to ppb) of target VOCs can be measured in ambient air to assess for vapor intrusion or indoor air concentrations, while occupational exposures are generally measured in the high ppb to ppm concentrations (EPA 1997).

The application of capillary flow controllers for both individual and area sampling under a variety of environmental conditions has been examined. With recent developments in their use, the maximum duration for canister sampling has been extended from approximately 24 h up to 3 wk (using a 6 L canister), allowing for more expansive and representative exposure characterizations especially for chronic low-level chemical exposures (ppb to ppm) (Rossner et al. 2002; LeBouf et al. 2014). These studies demonstrated that the controller provided a low flow rate that allowed for extended sampling times and, in the latter case, resulted in statistically similar results with respect to other air sampling methods.

With both capillary and diaphragm flow controllers, the flow rate can be affected by variations in temperature and pressure. Such variations may result in over- or under-estimation of concentrations of sampled chemicals. Additionally, the capillary flow rate change, with respect to sampling time, has been characterized by Rossner and Wick (2005) who further demonstrated the importance of significant peaks in concentration occurring very early or very late in the sampling period, also resulting in a potential over- or under-estimation of concentrations, the extent of which is dependent on the peak amplitude. However, their results showed that the capillary flow controller met the NIOSH criterion for sampling method bias for peak concentrations not exceeding 10 times the base concentration (Kennedy et al. 1995).

Although the flow rate characteristics of the capillary and diaphragm flow controllers are discussed in significant detail in the literature, a brief review of their functionality is discussed here. The capillary flow control device allows contaminated air to pass into the canister at a low flow rate (0.1 to 0.5 mL/min for full-shift sampling and 10 to 15 mL/min for short-term sampling). A fused-silica capillary column functions as a restricting orifice to control the flow rate of air into an evacuated canister (See Figure S1). The resulting flow rate slowly declines as the canister fills and is a function of the volume of the canister and the selected capillary diameter and length. The capillary flow controller has been tested under controlled laboratory conditions at varying concentrations of numerous volatile organic compounds (VOCs), as well as a variety of temperature and humidity conditions (Rossner et al. 2002).

A diaphragm flow controller maintains a relatively constant flow rate using a critical orifice that acts as a flow restrictor upstream of a metal diaphragm controlled by a mechanical spring. The pressure differential across the diaphragm is a result of the outside atmospheric pressure and the internal canister pressure. Manufacturers of diaphragm flow controllers have released laboratory work that shows a change in flow rate as a function of temperature and pressure (Cardin 2021; Restek Corporation, Bellefonte, PA 2022).

The purpose of this study is to build upon existing work by evaluating the precision and bias performance of a commercialized capillary flow controller for personal and environmental monitoring with evacuated canisters. While several accepted standards guide the use of canisters for air sampling (ASTM D5466 2021; ASTM D7663 2012, and EPA TO-15, 1997), they do not directly address the evaluation of bias associated with variations across a range of environmental parameters, changes in concentration, and the appearance of peak concentrations. However, the ASTM D6246 "Standard Practice for Evaluating the Performance of Diffusive Samplers" is a guideline familiar to air sampling researchers and does provide an evaluation of accuracy and bias, albeit for diffusive samplers. The statistical approach of the ASTM D6246 standard is therefore employed in this study because it provides an analytical framework for evaluating bias across a matrix of experimental parameters, enabling the calculation of a Total Relative Standard Deviation (TRSD) using the individual RSDs for temperature, humidity, air flow rate, concentration, and peak concentration. When testing a passive diffusive sampler, the "pulse" concentration is used to assess reverse diffusion, yet in this study, the "pulse bias" is

an artifact of peak concentrations in combination with the changing flow rate in capillary flow controllers. This research contributes to prior studies by incorporating a multitude of factors in the evaluation of bias, using an established bias evaluation methodology with similar experimental parameters.

This work was completed in three phases. In Phase 1, flow rate performance with respect to temperature (−15 to 24 °C) was studied in laboratory tests. In Phase 2, a series of target concentrations of four volatile organic compounds of diverse chemical classes (aromatic, ester, chlorinated hydrocarbon, and ketone) were generated in a stainless-steel chamber under controlled laboratory conditions. The parameters considered included: time-weighted average concentration, peak concentration, air velocity, humidity, and temperature. In Phase 3, a series of six 14-day field sampling events was conducted over 18 months in two large, non-heated warehouse-style buildings. The varying environmental conditions provided an ideal location to extend Phase 1 to an assessment of flow rate in actual field conditions. The specific aim was to compare the flow rate variability of capillary flow controllers with that of diaphragm flow controllers.

Methods

Phase I: flow rate laboratory experiments

To assess and quantify flow rates for different temperatures, a series of laboratory tests was conducted. Flow rate tests on multiple capillary flow controllers connected to evacuated air sampling canisters were conducted with temperatures ranging from −15 °C–24 °C at 50–60% RH. Multiple 1 L canisters were used to collect samples at three different temperature groupings across this range, denoted as subzero, cool, and moderate. The duration of each test lasted at least 8 hr but no longer than 24 hr to provide a representative average flow rate for an air sample.

The same system was used to connect both flow controllers to their respective canisters. Before sampling, the system was pressure tested to ensure no appreciable leaks occurred over an 8-h period, (< 1% change by volume in the canister). The pressure measurements were taken immediately before the tests after the sample was collected and after the canisters were pressurized before analysis. Once a sample test was completed, the flow controller was detached from the canister to stop the sample collection. The average flow rates were computed for each phase using the volume collected in the canister and the time sampled for each test. Pressures in the canisters were measured for all tests using a pressure transducer (PTU Series UHP transducer, Swagelok Company, West Henrietta, NY, USA). The pressure transducer measurement uncertainty was ± 0.1 Torr. The volume of air collected was calculated using the pre- and post-sampling pressures (EPA 1997). The same method was used for all three phases of this work.

Laboratory testing was performed in laboratory incubators, refrigerators, and freezers. To monitor for changes in temperature as well as percent relative humidity, a Lascar EL-USB-2-LCD probe (Lascar Electronics Inc., Erie, PA, USA) was used. The probe was located nearby (< 0.5 m) to the canisters and set to log data in 5-min intervals.

Phase 2: bias and accuracy as a function of environmental parameters

To evaluate the precision and bias of the capillary flow controller during both steady state and peak concentrations, a series of tests were conducted under different conditions (temperature, humidity, face velocity, and concentration level). Target concentrations of four VOCs were generated in a 32 L stainless steel chamber and sampled with capillary (Aura^{TM}, Restek Corporation, Bellefonte, PA, USA) and diaphragm (CS1200E Passive Canister Sampler, Entech Instruments, Simi Valley, CA, USA) flow controllers as detailed in Figure 1.

Details of the canister preparation and experimental design are described as follows. Before sampling, canisters were cleaned by flushing with ultra-high purity nitrogen (UHP-N_2) and evacuating down to 150 mTorr. This cycle was repeated five times, and the final evacuation was taken down to approximately 50 mTorr. The actual pressure in each canister was measured and recorded before starting each test. To validate the canister cleaning procedure, 15% of each set was pressurized with UHP-N_2 and analyzed as

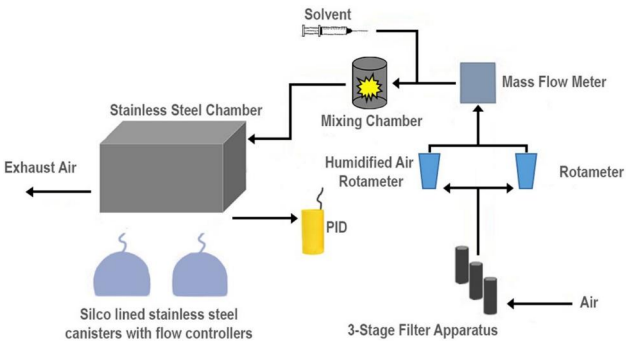

Figure 1. Sampling apparatus with a dynamic dilution system used to generate known concentrations.

described below to ensure canisters were not contaminated with compounds from previous tests.

The dynamic dilution system was designed with a series of valves to control the flow of air and solvent to generate known airborne concentrations while varying the humidity in the test chamber. A known volume of air (5 L/min) was passed through a three-stage particle filtering apparatus (Donaldson Ultrafilter, P0035, S0035, A0035, Donaldson Company Inc., Bloomington, MN, USA) to remove possible contaminants. Four solvents (toluene, perchloroethylene (PCE), ethyl acetate, methyl ethyl ketone (MEK) were delivered at a constant flow rate by a syringe pump (Harvard Apparatus 1 plus, Holliston, MA, USA). These solvents were selected to represent a variety of VOC categories (aromatic, ester, chlorinated hydrocarbon, and ketone). The chemicals were combined in a proportion that was equal to the ratio of their respective threshold limit value (TLVs). Table S1 (see Appendix) displays the physical and chemical properties of the VOCs. All chemicals used were reagent grade (Sigma-Aldrich, St. Louis, MO, USA).

A MiniRae 2000 photoionization detector (PID) (Rae Systems, San Jose, CA, USA) was used to continuously monitor the total VOCs in the chamber to confirm that the concentration was not fluctuating over time. The Teflon sampling tubes (1.6 mm internal diameter) from each flow controller were passed through inlet ports to the center of the chamber (clustered within an 8 cm radius of each other) for all experiments. Swagelok connections with Teflon tubing were connected to each of the diaphragm and capillary flow controllers to allow for easy attachment to the canisters. The diaphragm flow controllers were connected to 1-L canisters, while capillary flow controllers were connected to 400 mL canisters. The diaphragm flow controllers have approximately 10-fold greater flow rate than the capillary flow controls, hence a larger canister was needed.

A matrix of experimental parameters to be tested was established using ASTM D6246 methodology and is displayed in Table 1 (ASTM 2013). Eleven tests were conducted with the capillary flow controller, including reference conditions (Ref) and comparison tests (test 10) using diaphragm flow controllers. The following parameters were evaluated in tests 1–5: time-weighted average concentration, air velocity across the sampler inlet, relative humidity, and temperature.

These conditions were controlled and altered between tests to evaluate the effect on sample collection. Figure 1 shows the testing apparatus with the airflow into the chamber measured using a mass flow meter. An anemometer was used to measure the air velocity at the location of the sampling inlets. The airflow rates tested were relatively high, simulating a setting with local exhaust ventilation (similar to conditions in a spray booth). Temperature and relative humidity were monitored inside the chamber using a Lascar EL-USB-2-LCD probe (Lascar Electronics Inc., Erie, PA, USA). The probe was nearby (10 cm) to the canister inlets.

In pulse concentration tests 6–9, a peak concentration was generated for 0.5 hr of the total sample time of 4 hr to simulate extended peak concentrations that may be observed in field settings. For this study, concentrations that remain elevated for up to 15% of the total sampling time are defined as peaks. The peak concentrations were approximately 50–100× higher than the base concentration of 2 ppm during a typical run. The pulse concentration tests were conducted with the peak occurring at the beginning or end of the sample time to assess the predicted maximum or near-maximum bias associated with a varying concentration in combination with the decreasing flow rate of the capillary flow controller (Rossner and Wick 2005). Five to eight replicate canister samples with individual flow controllers were simultaneously collected for each pulse experiment.

Additional tests were conducted in the dilution chamber to evaluate the capabilities of the capillary flow controllers to function at very low flow rates (0.11 mL/min) for 8 hr, 24 hr, and 21 days. The 8-hr tests were run to simulate an 8-hr time-weighted average (TWA) for a mixture of acetone, ethanol, hexane, and PCE generated using the dynamic dilution system. The 24-hr tests were run to simulate an indoor air quality assessment of a toluene and PCE mixture and directly compare capillary flow controllers to diaphragm flow controllers. Three-week (21-d) sampling was conducted to evaluate the feasibility of an extended sampling campaign for capillary flow controllers used with canisters. A reference concentration for each compound in each test was established with an online GC to provide an estimate of the actual concentration in the chamber. Measured and reference concentrations were compared using two-tailed t-tests where $\alpha = 0.05$.

Phase 3: flow rate field testing

Although laboratory tests allow for an assessment of accuracy and precision for sampling methods, field testing provides additional confirmation of the performance of a sampling method under frequently changing conditions, interferences, and the presence of other analytes, as well as other unanticipated conditions. Hence, to augment the laboratory flow controller testing completed in

Table 1. Experimental design for the sequence of tests with the parameter evaluated.

Test	Parameter	Flow controller type (n)	Sample time (h)	Chemical	Temp (°C)	Face velocity (m/s)	Conc. (ppm)	Relative humidity (%)
Ref	(Reference)	I (8)	4	mixture	23	0.5	20	50
1	High RH	I (8)	4	mixture	23	0.5	20	80
2	Low RH	I (8)	4	mixture	23	0.5	20	35
3	Low Conc	I (8)	4	mixture	23	0.5	10	30
4	High Temp Low RH	I (8)	4	mixture	32	0.5	20	20
5	Low Face Vel. & Low Temp	I (8)	4	mixture	10	0.41	20	40
6	Positive peak Conc	I (8)	4	toluene	23	0.5	Peak	40
7	Positive Peak Conc	I (5)	4	PCE	23	0.5	Peak	40
8	Negative Peak Conc	I (5)	4	ethyl acetate	23	0.5	Peak	40
9	Negative Peak Conc	I (8)	4	MEK	23	0.5	Peak	40
10	Low face Velocity	I, II (6, 6)	24	toluene	23	0.41	20	30

Notes: I - Capillary; II - Diaphragm. Mixture (ratio) – toluene (2/10), PCE (2/10), ethyl acetate (4/10), and MEK (2/10). Test 1 - reference condition, ~23 (+/−1) °C and % RH of 50% (+/−3).

Phase 1, a series of field tests were completed comparing flow rate variability of the diaphragm and capillary flow controllers for 14 consecutive days at four locations and replicated six different times (six sampling events) over 18 months. Two sampling locations in each of two large non-heated warehouse-style buildings (~50,000 ft^2 each) were selected. Each sampling location had two 15-L canisters and one 6-L canister with capillary flow controllers to collect samples continuously for 14 days (see Figure S2). Simultaneously at each location, a single 6-L canister with a diaphragm flow controller was used to collect 24 hr samples each day for 14 consecutive days, during the six sampling events. The flow rates for all diaphragm and capillary flow controllers were calculated using the volume of air collected over each period, 24 hr and 14 d, respectively. Descriptive statistics were used to assess the flow rate variability for each type of controller.

The capillary flow controllers, unlike the diaphragm flow controllers, are not adjustable; as a result, the manufacturer provides a specific flow rate for each of the capillary flow controllers. Eight capillary flow controllers were used with a manufacturer flow rate of approximately 0.32 mL/min (CFC-Type I) and four with a manufacturer flow rate of 0.11 mL/min (CFC-Type II). Flow rates were validated before the field test to confirm the flow rates specified by the manufacturer.

Sample analysis

To prepare for analysis, canisters were pressurized to approximately 1200 Torr with UHP-N_2 (EPA 1997; Andrews and O'Connor 2020). Analysis was conducted using a Hewlett-Packard gas chromatograph flame ionization detector (GC-FID) model 5890 series II. The column was 30 m long with a 0.32 mm inside diameter and a 1.0-µm stationary phase consisting of poly (5% diphenyl/95% dimethyl) siloxane (Phenomenex, Torrance, CA, USA). A 1 mL sample loop was fitted to the GC injection port to allow for direct injection of the samples onto the GC column. For each VOC, gas standards were generated over a series of concentrations to create a five-point calibration curve and injected into the GC in the same manner as the samples. The reference samples for each experiment were analyzed on the same GC using the same temperature profile.

Data analysis

Data were managed using Microsoft Excel (Version 2016, Microsoft Corp., Redmond, WA, USA) and statistical analysis was conducted using IBM SPSS (Version 26, IBM Corp., Armonk, NY, USA) and JMP (Version 16, SAS Institute, Cary, NC, USA).

The performance of capillary flow controllers was assessed using ASTM and NIOSH methodologies. ASTM D6246 provides a systematic statistical approach that can be similarly applied in the computation of canister sampler bias and accuracy. To assess accuracy, the estimated total precision is determined through the propagation of errors (RSD for each variable).

The TRSD is the overall or total relative standard deviation of concentration estimates expressed relative to a reference concentration. To estimate the total precision of the capillary flow controller, in terms of the independent parameters, the TRSD is calculated as follows:

$$TRSD = \sqrt{\frac{dF * RSD^2{}_{LH} + dF * RSD^2{}_{MH} + dF * RSD^2{}_{HH} + dF * RSD^2{}_{LT} + dF * RSD^2{}_{HT} + dF * RSD^2{}_{LC} + dF \ \frac{1}{3} * BIASpulse^2}{Total \ dF}}, \quad (1)$$

with the following nomenclature: degrees of freedom (df), relative (inter-day) standard deviations of low humidity (RSD_{LH}), medium humidity (RSD_{MH}), high humidity (RSD_{HH}), low temperature (RSD_{LT}), high temperature (RSD_{HT}), and low concentration with low wind speed (RSD_{LC}). Additionally, the combined bias associated with concentration peaks occurring early and late in the sampling period is defined as:

$$BIASpulse = \frac{C_1 - C_2}{C_1 + C_2}, \quad (2)$$

where C_1 is the average concentration of the replicates of a "positive" peak and C_2 is the average concentration of the replicates of a "negative" peak. A positive peak is in reference to a pulse in concentration occurring in the beginning half of sample collection leading to an overestimation of sample concentration. A negative peak is in reference to a pulse in concentration occurring in the latter half of sample collection leading to an underestimation of sample concentration.

Bias, Accuracy, and Accuracy 95% were calculated using the method discussed in the NIOSH Manual of Analytical Methods (Andrews and O'Connor 2020). A measure of accuracy that accounts for systematic error (bias) and precision to quantify the closeness of estimates to the reference values can be approximated as follows (Bartley 2001):

$$bias = \frac{C_{Measued} - C_{Reference}}{C_{Reference}} \quad (3)$$

$$Accuracy = \begin{cases} u_{(1+\alpha)/2} * [bias^2 + TRSD^2]^{\frac{1}{2}}, |bias| < \dfrac{TRSD}{u_\alpha}; \\ |bias| + u_\alpha * TRSD, otherwise. \end{cases} \quad (4)$$

$$Accuracy_{95} = |average\ bias| + u_\alpha * \tau * TRSD, \quad (5)$$

where the unit normal quantile u_α =1.645 (α = 95%), $u_{(1+\alpha)/2}$ = 1.96 (α = 95%), and τ = t-Quantile/(1.645*SQRT(df)). Acceptable bias and accuracy criteria for air sampling methods established by NIOSH and ASTM are bias = ±10%, Accuracy = ±25% (95% CI) (Kennedy et al. 1995; ASTM 2013).

Results

Phase I: flow rate Laboratory testing

Figure 2 displays capillary flow rate data in three relevant temperature ranges: subzero (-15 to 0 °C), cool (3 to 8 °C), and moderate (10 to 24 °C). The average flow rate shows an inverse relationship with temperature, likely related to decreased dynamic viscosity at lower temperatures (Kadoya et al. 1985). Respectively,

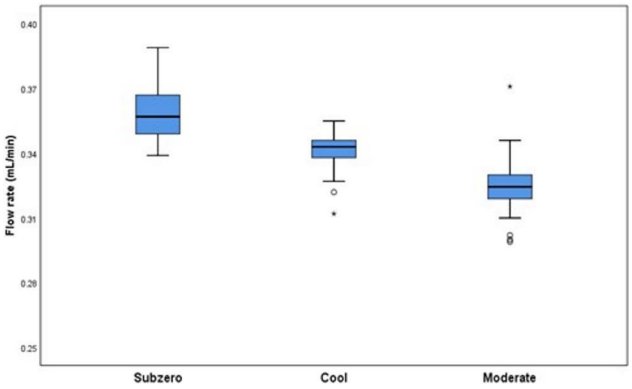

Figure 2. Capillary flow rate at different temperature ranges. The box and whisker plot displays median (50%), minimum values, maximum values, lower quartile values, and upper quartile values. Outliers are identified by ° for mild outliers (1.5 x interquartile range) and * for extreme outliers (3.0 x interquartile range).

the mean and standard deviation of the flow rates for each category are subzero: 0.353 ± 0.016 mL/min (RSD 4.5%), cool: 0.342 ± 0.009 mL/min (RSD 2.6%), and moderate: 0.326 ± 0.015 mL/min (RSD 4.5%). While flow rates vary somewhat with respect to temperature, the volume of air collected can be estimated for any given sample, because before and after pressure measurements are collected. Hence, a time-weighted average calculation of the airborne concentration can be completed.

Phase 2: bias and accuracy as a function of environmental parameters

A total of five tests were conducted with varying environmental parameters using a solvent mixture. Tests were performed to investigate the extent to which environmental parameters influenced the capillary flow controller's performance for the collection of selected VOCs. Figure 3 summarizes the calculated bias associated with the following conditions: low and high humidity, high temperature, low concentration, and low face velocity (tests 1 through 5). The reference concentration (Ref) was collected under the following conditions: relative humidity 40%, temperature 25 °C, and flow rate 0.5 mL/min.

The data shown in Table 2 is of particular interest because it displays how the capillary flow controller performs when peak concentrations of approximately 50 to 100x the baseline concentration (~2 ppm) were introduced to the chamber during a 4-hr test. The peaks were introduced very early (tests 6 and 7) or very late (tests 8 and 9) in the sampling period. Environmental parameters were kept constant at 40% RH, 23 °C, and 0.5 m/s air speed with the

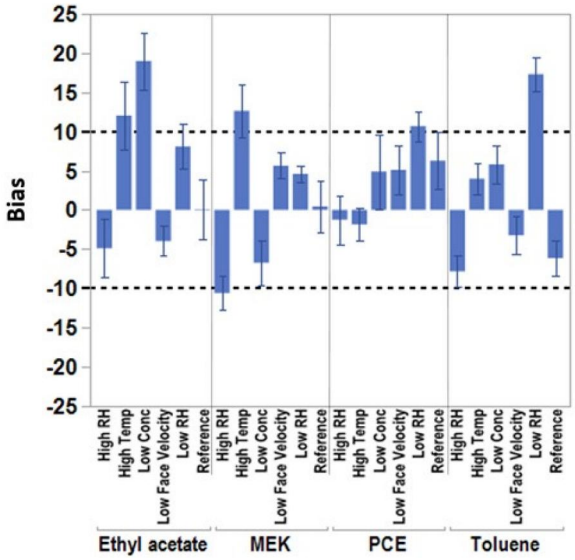

Figure 3. Bias results for tests 1–5. The horizontal dashed lines indicate the acceptable ASTM and NIOSH criterion for method bias.

Table 2. Pulse bias related to positive and negative peak concentrations during the sampling period for four compounds.

Compound	Positive bias		Negative bias		Pulse bias	|% Pulse bias|
Ethyl Acetate	0.053	$n=4$	−0.048	$n=4$	−0.050	5.0
MEK	0.039	$n=8$	−0.068	$n=7$	−0.054	5.4
PCE	−0.015	$n=5$	−0.116	$n=5$	−0.053	5.3
Toluene	0.002	$n=6$	−0.030	$n=6$	−0.016	1.6

Table 3. Average bias, inter-sampler relative standard deviation (RSDs), total relative standard deviation (TRSD), overall accuracy, and accuracy at the 95th percentile for ethyl acetate, MEK, PCE, and toluene.

	Ethyl acetate ($n=53$)	MEK ($n=63$)	PCE ($n=57$)	Toluene ($n=56$)
Avg Bias (%)	3.1	−3.1	−1.3	2.6
RSDs (%)	6.0	4.6	4.1	2.9
TRSD (%)	6.5	4.0	3.5	4.9
Accuracy (%)	14.1	9.8	7.3	10.9
Accuracy$_{95}$ (%)	17.1	11.7	8.8	13.1

concentration elevated (peak) for the first 30 min or the last 30 min depending upon the test. This testing protocol allowed for an assessment of the impact of the pulse in concentration on the bias while holding the other parameters fixed. Peaks occurring at either the beginning or end of a sampling period can result in the largest potential bias (worst-case) for a capillary flow controller because the flow rate will be at its highest or lowest. The data displayed in Table 2 shows that the absolute value of the measured pulse bias ranged from 1.6 to 5.4% when a pulse concentration was present during the sampling of the four compounds.

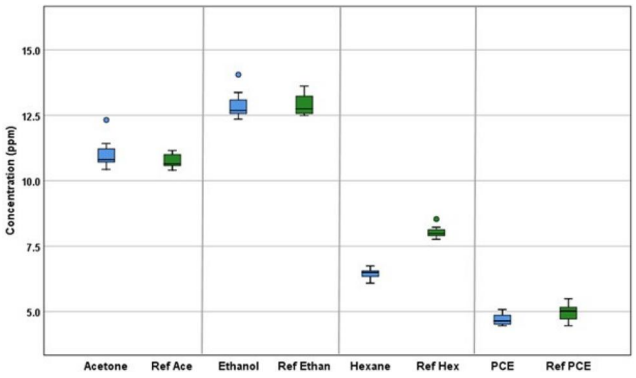

Figure 4. The 8 h time-weighted average (TWA) concentrations of each compound collected with capillary flow controllers ($n=8$) were compared to reference concentrations (denoted as ref) using a two-tailed t-test ($\alpha=0.05$) with the following results: Acetone ($p=0.21$), ethanol ($p=0.44$), hexane ($p=2$ x 10^{-5}), and perchloroethylene (PCE) ($p=0.16$). An online GC was used to monitor the concentration in the chamber to provide the reference values.

Table 3 summarizes the average bias, inter-sampler relative standard deviation (RSDs), total relative standard deviation (TRSD), overall accuracy, and accuracy at the 95th percentile for all compounds throughout tests 1 through 10. The results demonstrate that the capillary flow controller consistently performed within the criteria set by ASTM with respect to bias and accuracy.

To further examine the performance and capabilities of the capillary flow controller for a typical workday, full day (indoor air quality sampling), and extended or long-term sampling campaign, time-weighted average sampling of 8 hr, 24 hr, and 3-week periods was conducted in a laboratory setting. Different VOC concentrations were generated in the ppm range (low of 3 ppm, high of 15 ppm) for each experiment at 50% RH and 23 °C.

Figure 4 displays the result of four different VOCs (acetone, ethanol, hexane, and perchloroethylene) that were generated in a chamber and sampled with the capillary flow controller over an 8-hr period. Reference concentrations were obtained using an online GC. A relatively good comparison between the capillary canister systems and reference values was found for three of the four compounds (acetone, ethanol, and PCE) using two-tailed *t*-tests for statistical significance ($\alpha=0.05$), as noted in the figure caption. While the difference in the hexane data with respect to the reference values was statistically significant, the mean sample value was observed to be within 20% of the reference. The reason behind the greater difference observed in the hexane tests, in comparison to other compounds, remained somewhat ambiguous.

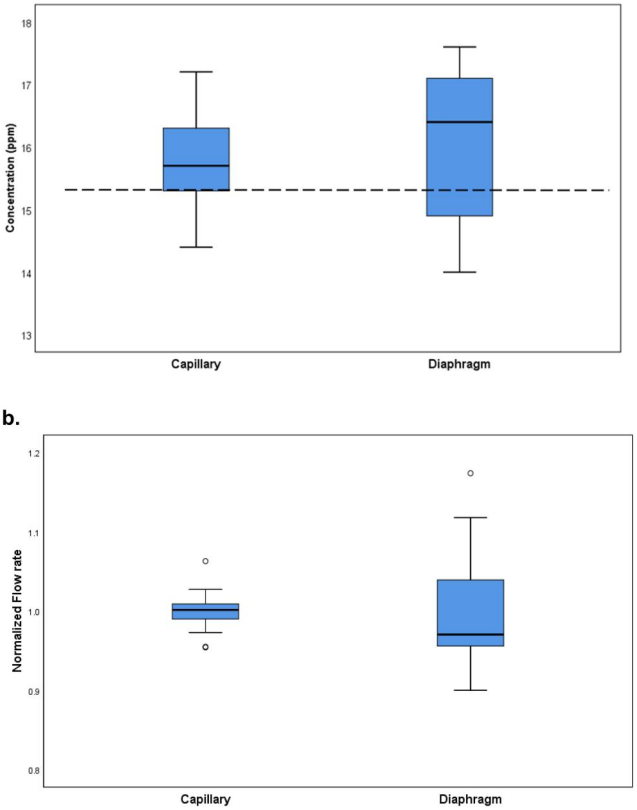

Figure 5. (a) Three 24 h tests were completed collecting toluene with six replicates per test ($n = 18$). The dashed line shows the reference concentration of 15.4 ppm using data from an online GC. **(b)** Normalized flow rate demonstrating comparative variability of the capillary and diaphragm flow controllers.

However, the box plots for hexane (sample and reference, as shown in Figure 4) show similar variability to the other compounds, indicating the observed difference is mostly likely due to a systematic error as opposed to an error associated with the flow controllers. Lacking definitive evidence, the authors felt it necessary to include the hexane data.

Figure 5a displays the results of test 10 from Table 1, comparing measured TWA concentrations collected by capillary and diaphragm flow controllers over a 24-hr sampling period for toluene. The reference concentration of 15.4 ppm for toluene was established using an online GC and is denoted with a dashed line in the figure. A smaller relative standard deviation (RSD 4.3%) was observed for the capillary-flow controller when compared to the diaphragm (RSD 7.2%) demonstrating a somewhat lower variability. However, a t-test performed between the capillary and diaphragm for all measurements shows that the difference between the means is not statistically significant ($p = 0.076$).

Figure 5b shows the flow rate variability for each flow controller. Since the flow rates vary by approximately an order of magnitude, they were normalized

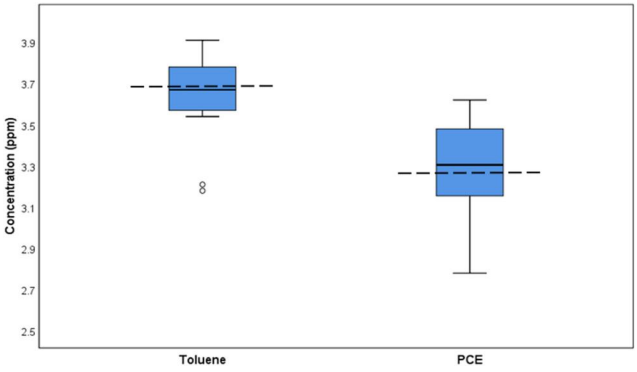

Figure 6. Toluene and PCE were each measured in a chamber for 3 wk using capillary flow controllers connected to six canisters. An online GC was used to monitor the concentration in the chamber approximately five times per day ($n = 103$). Reference values are shown for each compound using dashed lines.

using their respective mean values to allow for direct comparison. Similar to the measured concentration, a smaller relative standard deviation (RSD 2.4%) was observed for the capillary-flow controller when compared to the diaphragm (RSD 6.9%).

The capillary-flow controller data presented in Figure 6 shows good agreement between measured and reference concentrations. No statistically significant difference was found between the 3-wk sampling canisters and the reference concentration established using the online GC for either toluene or perchloroethylene ($p = 0.43$ and $p = 0.48$, respectively).

Phase 3: flow rate field testing

Capillary flow controllers were utilized to collect 14 d samples in the same location as the diaphragm flow controllers and the average flow rates for each flow controller over the sampling periods were computed. The total number of samples collected was 385 for all locations, approximately 16 per location. The relative standard deviations (RSD) of the flow rates of each flow controller are shown in Table 4, where capillary and diaphragm flow controllers are abbreviated as CFC and DFC, respectively. The 14 d average flow rates for CFC–Type I and II were 0.298 mL/min (RSD 5.1%) and 0.104 mL/min (RSD 5.2%) with $n = 43$ and 19, respectively. The overall RSD for all of the diaphragm flow controllers was 8.0% and the overall RSD for all capillary flow controllers was 5.2%.

Discussion

While in use for over two decades, diaphragm flow controllers used with evacuated canisters are

Table 4. Flow rate variability field test for nine diaphragm flow controllers (DFC, labeled as A–I) for multiple 24-hr tests ($n = 385$) and 12 capillary flow controllers (CFC, labeled J to U) for 14-d tests. The CFC devices are referenced as Type I (~0.31 mL/min) and Type II (~0.11 mL/min) to distinguish between manufacturer-specified flow rates.

Diaphragm flow controller (DFC)			Capillary flow controller (CFC)					
DFC ID (n)	Flow Rate (mL/min)	RSD (%)	CFC Type I ID (n)	Flow Rate (mL/min)	RSD (%)	CFC Type II ID (n)	Flow Rate (mL/min)	RSD (%)
A ($n = 61$)	2.98	6.59	J ($n = 5$)	0.297	4.91	R ($n = 5$)	0.103	4.28
B ($n = 29$)	2.44	11.02	K ($n = 6$)	0.307	7.20	S* ($n = 4$)	0.104	7.28
C ($n = 52$)	2.77	3.70	L ($n = 6$)	0.298	5.69	T ($n = 5$)	0.105	4.27
D ($n = 43$)	3.13	5.71	M ($n = 6$)	0.310	4.11	U ($n = 5$)	0.105	4.24
E ($n = 19$)	3.99	3.40	N ($n = 6$)	0.300	3.60			
F ($n = 45$)	2.89	7.64	O ($n = 4$)	0.304	4.67			
G ($n = 60$)	2.94	6.46	P ($n = 4$)	0.296	7.08			
H ($n = 25$)	2.67	14.15	Q ($n = 6$)	0.302	4.11			
I ($n = 51$)	3.03	13.03						

*One of the flow rates for CFC Type II was considered an outlier based on the results of Grubb's test (Kennedy et al. 1995). This data point was not used in the final statistics. The CRC Type I and DFC flow controllers did not have any outliers that were removed.

considered by many practitioners to be the established standard for whole air sampling. This research aimed to evaluate capillary flow controllers relative to the criteria established by NIOSH and ASTM. Although the evaluation was primarily focused on accuracy and bias, a comparison with diaphragm flow controllers was also incorporated into the study. Different environmental conditions in a controlled laboratory setting and a field study provided evidence of the flow controllers' performance capabilities. The design of the study was intended to assess both occupational and non-occupational environmental exposure scenarios.

Capillary flow controllers provide a range of flow rates to allow for extended sampling times (minutes to weeks) and consequently the use of various-size canisters. The longer-term sampling periods improve exposure assessments because they are representative of longer-term exposures and can be applied to many microenvironments (i.e., VI or IAQ) (Odencrantz et al. 2008). Additionally, Rappaport (1991) makes a compelling argument for long-term monitoring to assess chronic risk.

This study demonstrated that the measured bias associated with several of the individual environmental parameters exceeded the ±10% bias criterion as shown in Figure 3. However, when an aggregate of all the parameters was calculated (Table 3) for each chemical, the average bias fell well within the acceptable guidelines per ASTM D6246 and NIOSH 95-117 (Kennedy et al. 1995; Bartley 2001; ASTM 2013). Additionally, the capillary flow controller consistently performed within the Accuracy criterion of ±25%. Note that the NIOSH and ASTM criteria are more stringent guidelines than the EPA's criteria of bias = ±25% and Accuracy = ±30%.

Pulse bias can be an important component of accuracy based on the amplitude, duration, and timing of a pulse (peak) in concentration. The observed negative pulse bias for all four of the compounds tested, as shown in Table 2, is expected due to the asymmetric bias predicted by Rossner and Wick (2005), demonstrating that late peaks ("negative peaks") contribute more to the overall bias than early peaks ("positive peaks"). Figures 4 through 6 demonstrate an effective sampling capability of capillary flow controllers for periods ranging from 8 hr to 3 wk. The ability to sample for extended periods can be useful to characterize VOC concentrations in both occupational and non-occupational environments. Sampling for 24 hr up to a period of 2 wk is not common for most exposure assessments, however, indoor environments impacted by vapor intrusion or other indoor pollutants can benefit from longer-term sampling to characterize exposures of building occupants.

Field data presented in Table 4 compares the flow rate variability of diaphragm and capillary flow controllers under actual field conditions. Although no statistically significant difference in flow rate variability was observed between Type I (0.11 mL/min) and Type II (0.32 mL/min) ($p = 0.43$) capillary flow controllers, a significant difference ($p = 0.0325$) was observed in flow rate variability between the diaphragm and capillary flow controllers (both Type I and type II). This suggests that the capillary flow controller displayed less variability for the field sampling periods that included variable temperature, humidity, and fluctuations in concentrations.

In this study, seven VOCs were evaluated. However, it is important to note that evacuated canisters have been extensively validated for the collection of numerous VOCs as demonstrated by EPA TO-15 (EPA 1997) and NIOSH 3900 (Andrews and O'Connor 2020) methods. Additionally, the flow controllers in this study would be expected to effectively collect a similar multitude of VOCs in occupational or non-occupational environments (Pate et al. 1992;

EPA 1997; Ochiai et al. 2002). Finally, the capillary flow controllers demonstrated an expanded temporal capability of up to 3 wk, which may be useful for exposure assessments in several microenvironments.

Limitations

As with many laboratory and field studies, researchers are restricted to a limited range of environmental parameters. Laboratory testing in this study was limited to three temperature ranges, noted as subzero, cool, and moderate (−15 °C to 24 °C), and could be extended to include a high-temperature range (25 °C to 40 °C) that would simulate warmer environments. Similarly, this study would benefit from additional evaluation at the high humidity range, as high relative humidity (RH >75%) often accompanies warmer temperatures.

While this study includes low ppm concentrations, it is somewhat limited in that it does not include concentrations in the ppb range. While a range of compound classes was considered, the total number of VOCs was limited. Additionally, this study could be expanded to include compounds, such as organic sulfur, that have been historically challenging to collect with canister sampling systems that utilize flow controllers.

Conclusion

This study demonstrated that the capillary flow controller met NIOSH and ASTM criteria for bias and accuracy across variations in a variety of environmental conditions (temperature, humidity, face velocity, concentration level, peaks in concentration). Although some laboratory trials showed variable mean bias and accuracy for specific compounds, the aggregate results were acceptable when compared to the established standards, even for scenarios with peak concentrations of 100 times the base concentrations. A slight decrease in flow rate concerning temperature was observed in the subzero to moderate temperature range (∼8% decrease in flow rate across a 25 °C increase in temperature). Because the flow rate change is small with respect to temperature, this is unlikely to be a constraint even when sampling scenarios include somewhat extreme temperature variations.

Diaphragm flow controllers have a more established history of use with canisters and were consequently used as a comparison with respect to flow rate variability and concentration. The capillary flow controllers displayed low variability in flow rate and measured concentration for the 24-hr laboratory tests. Similarly, observations of low flow rate variability for capillary flow controllers were observed in the field study, where environmental parameters were not controlled. This study underscores the accuracy and precision achieved when using evacuated canisters with flow controllers to measure short-term and long-term exposures in both occupational and non-occupational environments.

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Disclaimer

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Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availablilty statement

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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