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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

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Small, evacuated canisters (300 mL) equipped with a unique capillary flow controller were used to evaluate airborne concentrations of Stoddard solvent. The physical characteristics of the flow controller permitted the collection of air samples for a time period of 40 hours (5 consecutive work days). Long-term sampling (greater than 8 hours) is rarely performed in industrial hygiene due to limitations in current air sampling technology but may provide valuable information in characterizing worker cumulative exposures for some processes. A field study was performed to evaluate the feasibility of collecting a 40-hour area sample using the small canisters. Six canister samplers were used as area monitors to evaluate a cleaning operation for an entire workweek. For comparison, 30 diffusive badges (6 per day) were simultaneously used to monitor the same process. No statistical difference was found between the time-weighted average for the two sampling methods ($p > 0.05$). In addition, the canister samples integrate airborne concentrations for an entire workweek and therefore peak concentrations are not explicitly observed. Thus, an examination of peak exposures using simulated concentrations was conducted. A mathematical model was developed to determine whether a significant sampling bias was associated with long-term canister sampling when peak concentrations are present. The maximum possible bias was determined to be less than 9% for peak amplitudes having 10 times the background concentration and well below that for smaller amplitudes. Long-term sampling with the small, evacuated canisters was found to provide results comparable to sorbent sampling methods but with the added benefit of a significantly increased sampling time.

Keywords air sampling, capillary-canister, evacuated canister, long-term sampling, sampling bias

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To effectively develop and design control strategies for exposures to airborne contaminants, measurements are necessary to characterize worker or community exposures. Air sampling methodologies that allow for cost-effective collection of field samples permit an increased number of samples to be collected, resulting in a more complete characterization of exposure. Such air sampling methods also provide dependable exposure assessment data necessary to assess occupational and community health risks.[1,2] New air sampling techniques that are easy to use and provide accurate results for long-term (>8 hour) average integrated sample collection will supply the occupational hygienist with another tool to refine the exposure assessment process.

BACKGROUND

A novel air sampling device capable of collecting gases and vapors for extended periods was recently designed and tested.[3–6] The device is composed of an evacuated canister equipped with a capillary flow controller and was developed to collect air samples from the breathing zone of an exposed individual for time periods ranging from a few minutes to an entire week. The capillary-canister consists of a 300-mL stainless steel chamber 10 cm in diameter (4 in.), weighing approximaetly 225 g (8 oz). The canister is equipped with a 0.05 mm inside diameter deactivated capillary tube that functions as a flow controller. The capillary restricts the flow of air, causing a slightly diminishing flow rate as the canister fills. Previously, the samples collected with this capillary-canister[4–6] device were compared with those obtained with charcoal tubes and diffusive badges in small (2.0 L) and large exposure chambers (18.3 m^3), where test subjects wore the capillary-canisters as personal samplers.[5,6] Results of the chamber studies showed very good correlation ($R^2 > 0.95$) between measurements made with the capillary-canister and sorbent-based sampling methods for several different chemicals collected over 6- to 8-hour periods.

The long-term sampling capability is unique to the capillary-canister system for the collection of personal samples. Continued validation of this device is desirable as it would be useful for exposure assessment campaigns requiring extended sampling times in light of existing guidelines.

Occupational hygienists frequently use multiple exposure limits, such as action limits, short-term exposure limits, and 8-hour time-weighted averages (TWAs) as guidelines for determining the acceptability of a worker's exposure level.[7–11] Since long-term (>8 hour) sampling of a worker's personal breathing zone has been difficult with current technologies, long-term exposure limits have not been fully established. Such limits would provide useful extensions of the existing exposure limits, supplying the investigator with a more complete set of guidelines for a given exposure scenario. Several authors have explored the concept of long-lerm average-occupational exposure limits (LTA-OEL), where long-term refers to a sampling period of a workweek, several weeks, months, or even years.[8,10]

The American Conference of Governmental Industrial Hygienists (ACGIH®) threshold limit values time-weighted average (TLV®-TWA) definition states that: "In some instances, it may be permissible to calculate the average concentration for a *workweek* rather than a *workday*."[12,p.5] This clearly implies that a LTA-TLV of 40 hours for certain chemicals is acceptable in some circumstances. However, ACGIH does not provide examples or criteria that would define the "instances" in which the TLV should be considered a workweek average, perhaps due in part to the difficulty in collecting such samples. Since occupational hygiene organizations and practitioners have considered LTA-OELs for some agents for a number of years, a sampling device that allows for extended time air sampling may be useful to examine chronic exposures.

The implementation of a monitoring technique that will allow for the collection of a workweek (40-hour) sample or a full week (168-hour) indoor air quality sample, could lead to new exposure assessment strategies and improved characterization of exposure. Long-term sampling is very difficult to perform using current sorbent methods, and the sampling and analysis have the potential to be cost and time prohibitive for most organizations. The use of the capillary-canister device would result in significantly reduced labor and analysis costs, since the analysis is only necessary at the end of the total sampling period.

While the capillary-canister device does not utilize an external air-sampling pump that would require calibration and maintenance, typical of a sorbent tube sampling system, it does operate with a slightly changing flow rate. The primary component of the flow control mechanism is a long capillary tube. This small tube is a variation of a sharp-edge orifice flow controller, which controls the velocity of the fluid (air) as a function of the fluid properties; pressure, tube diameter, and length. As the initially evacuated canister fills, the chamber pressure decreases. Hence, the flow controller always exhibits a slowly diminishing flow rate, as shown in Figure 1 for a typical sampling case.[4–6] A measurement bias may exist with the capillary canister device if significant concentration fluctuations exist during the sampling period due to the diminishing sampling rate of the device. For example, a peak concentration occurring at the beginning of the sampling period would be collected at a higher flow rate than a similar peak collected toward the end of the sampling period, resulting in a bias in the predicted concentration.

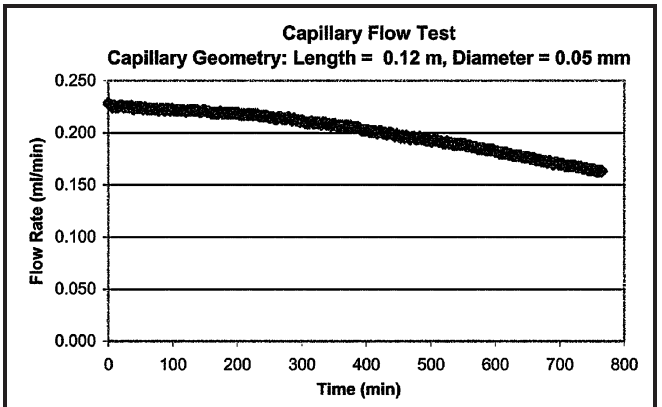

FIGURE 1. Change in flow rate over time for a typical capillary-canister flow controller

As a follow-up to the chamber evaluations previously conducted, this research focuses on field testing and sampling validation. The primary objective of this article is to explore the relationship between the capillary-canister and diffusive badges during a long-term air sampling campaign (40 hours). A secondary objective is to assess the potential influence of peak concentrations on the predicted final sampled concentration, using a series of mathematically modeled exposure scenarios.

METHODS

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

A solvent cleaning operation in an aluminum fabrication facility was selected to evaluate the performance of the capillary-canister device over a 40-hour workweek in an actual industrial environment. A location that had a relatively uniform use of solvents with low concentrations of airborne vapors was of interest.

At the facility, aluminum wire and bar are cold extruded through dies of various shapes and sizes. The dies are coated with a heavy oil to aid the extrusion process. After a series of extrusions, the dies must be removed from the extrusion machine and cleaned. Workers remove the heavy oil from the dies with Stoddard solvent. The cleaning operation is performed 5 days per week throughout the year in a small room adjacent to the extrusion room. One worker cleans approximately 40 dies per day. The die is washed with the Stoddard solvent using a hose in a washbasin. The worker

then removes the small amounts of aluminum with abrasive paper and small hand tools. Each die requires approximately 8–10 min to clean, resulting in exposures that are characterized by fluctuating airborne concentrations. The dies range in size from 10 cm in diameter, weighing 10 kg, to 40 cm in diameter, weighing 50 kg. The actual number and type of dies that are cleaned is dependent on the production cycles and the type of product being extruded.

Six capillary-canisters were used in this study. The number of canisters selected for the sampling was based on National Institute for Occupational Safety and Health (NIOSH) guidelines for the development and evaluation of air sampling methods and the European Committee for Standardization CEN 838.[13,14] Each canister was sampled for an entire 40-hour workweek. Simultaneously, 6 diffusive charcoal badges were used each day, for a total of 30 badges for the entire workweek. The two methods were co-located on a ring stand and positioned adjacent to a die-cleaning washbasin. All samplers were located within 10 cm of each other and within 20 cm of the lip of the washbasin.

Area sampling was chosen over personal sampling to ensure replicates could be obtained for each sampling method, as it was impractical to consider attaching all 12 samplers to a single worker. The area sampling was considered to be somewhat representative of the worker exposure because of the location of the solvent washbasin with respect to the worker's breathing zone. The primary focus of the sampling was not to characterize worker exposures but to evaluate how the capillary canister performed with respect to the diffusive badges over the entire workweek. Based on information obtained from the company, the concentration of the airborne Stoddard solvent was expected to be low, at approximately 5% of the TLV (TLV-TWA = 572.6 mg/m^3).[12]

The solvent used to clean the dies was Safety-Kleen Premium Solvent (Safety-Kleen Corp. Columbia, S.C.). This is a light petroleum distillate consisting of a mixture of C_9 to C_{11} compounds, (CAS # 84742-47-8). Common synonyms are Stoddard solvent and petroleum naphtha. The molecular weight and density of decane (C_{10}) are suggested by the manufacturer for use in approximating concentrations. Analytical standards were prepared using the bulk solvent and neat decane (J.T. Baker, Phillipsburg, N.J.).

Capillary-Canisters

The canisters used in this study were built by Meriter, Inc. (San Jose, Calif.) The canisters and valves were made of a high purity stainless steel to reduce the possibility of contamination or sample loss. All samples were collected in 300-mL canisters. A deactivated, fused silica capillary 0.05 mm in diameter and 40 cm long (J&W Scientific, Folsom, Calif.) was connected to each canister. During the sampling period, this configuration provides an average flow rate of 0.062 Ll/min, where the driving pressure arises from the difference between atmospheric pressure and the pressure inside the evacuated canister. The procedure used to prepare the canisters and sample was a modified version of the U.S. Environmental Protection Agency (EPA) TO-15.[15,16]

Prior to collection, canisters were cleaned by evacuating them to 0.05 mmHg absolute pressure and flushed with high purity humidified nitrogen three times. The vacuum-pressure cleaning system consisted of a vacuum pump, a stainless steel manifold with stainless steel connections, and a pressure transducer with digital meter (PX 615, DP 3002; Omega, Inc. Stamford, Conn.). After each canister was evacuated to a pressure of $<$0.05 mmHg absolute, high purity nitrogen gas was passed through water to humidify it as it entered the canister. The canisters were then pressurized to approximately 1550 mmHg absolute. To further insure the canisters were clean prior to testing, they were analyzed before the start of each experiment. No contamination was found during the testing of any of the blanks. Canisters were then evacuated to 0.05 mmHg and leak tested for at least 24 hours prior to the next round of sampling.

The sampling was performed for 5 consecutive days for 2 consecutive weeks. The sampling was initiated at approximately 7:00 each morning and terminated at 3:00 each afternoon, Monday through Friday. Each day, the canister flow was stopped at the end of the shift until the beginning of the next shift. The canisters were pressurized at the end of the sampling period (40 hours) to approximately 1000 mmHg absolute, with humidified pure nitrogen.

The pressurized canisters were allowed to stand for 12 hours, and then analyzed with a Hewlett-Packard gas chromatograph (GC), model 5890 Series II, equipped with FID.[16] A HP-5 capillary column (0.32 mm diameter, 50 m long, and (5%-Phenyl)-methylpolysiloxane stationary phase thickness of 1.05 μm) was used in this analysis. The concentrations of solvent collected in the canisters were in the ppm range. As a result, pre-concentration was not necessary, and samples could be analyzed by direct injection into the GC. A special fitting was designed to allow the capillary-canister to be connected directly to a 6-position valve that was connected to the GC injection port. The 6-position value was fitted with a 1.0-mL gas sample loop. A rotameter was connected to the exit port of the 6-position valve to monitor the flow rate of sample through the loop. The sample was injected into the GC after allowing the canister's contents to flow through the sample loop a minimum of 1 min at flowrate of 30 mL/min. This approach ensured that the gas sample loop was purged of any residual solvent before the sample was injected.

Badges

The diffusive badges used in this study were 3M organic vapor monitors (3M Company, Minneapolis, Minn.). At the end of the shift, they were removed from the ring stand, then capped and stored in a freezer until the end of the week, when all sets of badges were analyzed. The *NIOSH Manual of Analytical Methods (NMAM)* method 1550 and a 3M sampling and analysis guide for OVM 3500 were followed for the 3M badges.[17] The manufacturer's established sampling rate of 24.3 mL/min was used to calculate sample concentrations.[18]

Using diffusive badges as area samplers can result in an underestimation of exposure if the airflow across the badge is too low (<0.13 m/sec or 25 ft/min).[17] The airflow in the shop was measured prior to selecting the area for sampling and several times during the 2 weeks of sampling. In each case, the average airflow in the sampling area ranged from 0.18 to 0.25 m/sec (35 to 50 ft/min) above the required minimum. The air currents in the room were a result of the air exchange between the die cleaning room and the factory where the extrusion process was performed.

The charcoal was desorbed in 2 mL carbon disulfide for 60 min, and 1.0 μL of eluate was injected into a gas chromatograph. Analysis was performed using a Hewlett Packard 5890 Series II gas chromatograph (Hewlett Packard, Palo Alto, Calif.) equipped with FID. A Supelco VOCOL capillary column, 30 m × 0.53 mm inside diameter and a 3.0 μm film thickness was used to analyze the sorbent samples. The column temperature program for all analyses provided an initial temperature of 138°C increasing to 153°C at 1.5°C per min. Helium was used as a carrier gas.[16] Five calibration standards were prepared and run with each set of samples for the diffusive badges.

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

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

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

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

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 2. 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, Mass.) and has been used to analyze simulated exposure scenarios that include peak amplitudes of up to 10 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 min. 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.

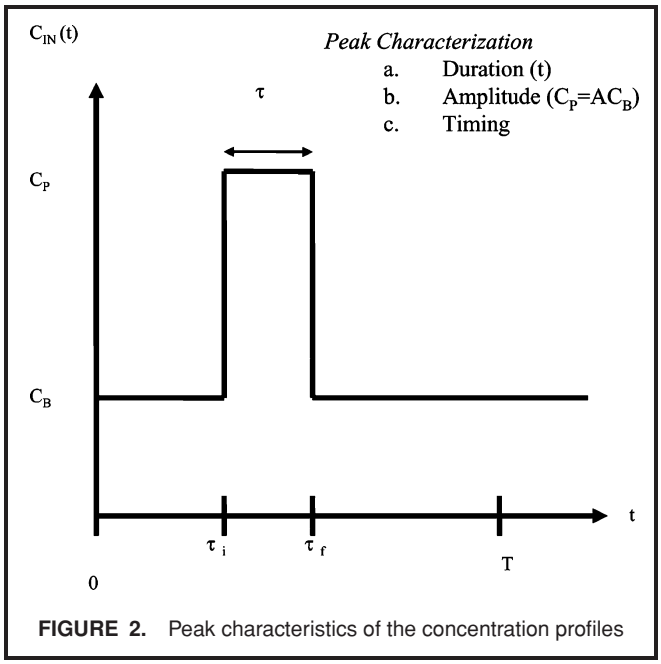

FIGURE 2. Peak characteristics of the concentration profiles

RESULTS AND DISCUSSION

Field Sampling Data

Table I displays the airborne concentrations determined from both sampling devices, where the mean value of all 30

TABLE I. Summary of Diffusive Badges and Capillary-Canister Data

Badges	Mean Week 1 mg/m³	RSD	Mean Week 2 mg/m³	RSD
Monday	16.40	11.4	30.20	7.1
Tuesday	29.10	11.4	42.70	4.3
Wednesday	15.20	14.6	38.00	15.2
Thursday	21.60	16.3	31.10	11.6
Friday	21.30	14.4	35.70	10.4
Week long Mean (n = 30)	20.72[A]	26.4	35.54[A]	14.5
Canisters				
Week long Mean	18.71[A]	43.8	33.16[A]	12.4

Note: Six badges were collected each day.
[A]No statistically significant difference between the two sampling methods for weeklong means ($p > 0.05$), where t-statistic for Week 1 = 0.73 and Week 2 = 0.95, compared with a t critical value of 2.03.

badges was compared with the average concentration collected by the six capillary-canisters. The relative standard deviations for the badge data sets ranged from 4% to 16%, with a mean value of 11.5% ± 3.8%. The badge method was used as a reference for comparison with the results of the capillary-canister samplers.

By comparing the mean values for each day, as measured by the badges, one can examine the variability of the day-to-day airborne concentrations. The Shapiro-Wilk W-test failed to reject the hypothesis that the data fit a normal distribution and therefore no transformation was used in evaluating the data sets. No statistically significant difference was observed between the two methods for the mean concentrations for each week sampled, as determined using a t-test ($p > 0.05$). The capillary-canisters were found to measure a slightly lower concentration than the badges, with differences of 9.7% and 6.7%, respectively, for the two weeklong averages. However, since the relative standard deviations were approximately 11% percent for both methods for the weeklong mean values, one cannot decisively conclude that the canisters were actually under sampling. Further, since the actual temporal characteristics of the airborne concentrations were not explicitly known, the environment may have contained numerous peaks during the sampling week, leading to a potential bias in the canister sampling. Daily airborne concentrations observed over the 10 days of sampling with the diffusive badges varied from 16.4 to 42.7 mg/m^3.

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 on 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 overestimating exposure when compared with 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 10, 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 with 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.

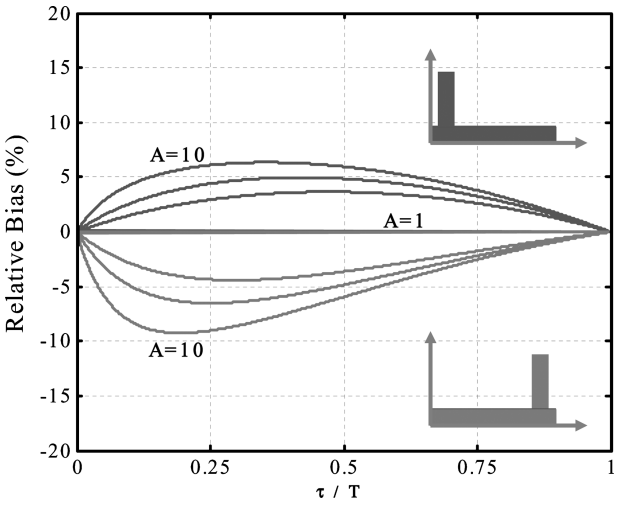

FIGURE 3. Envelope of bias associated with the capillary-canister sampler where peak concentration amplitudes are A = 1, 3, 5, and 10, respectively. Note that a positive bias is associated with an early occurring concentration peak as depicted in the upper inset figure, while a negative bias is associated with a late occurring concentration peak as depicted in the lower inset figure.

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 3 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 because the canister has the potential to over- or undersample 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 oversampling scenarios associated with concentration peaks that occur early in the sampling process. The *negative* bias values correspond to undersampling 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 3.

The nonsymmetric 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.[4] 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 oversampling bias occurs when the duration of the peak is approximately 35% of the total sampling time, while the maximum undersampling 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 overestimation of exposure.

Capillary-Canister and Long-Term Sampling

The ability to accurately collect an air sample over an extended sampling period would be beneficial for industrial and nonindustrial exposure assessments. Long-term sampling data will provide a better estimate of a cumulative exposure to assess long-term health effects. Whether the sampling environment is a traditional production factory, an office environment, the perimeter of a hazardous waste site, or the community down wind of industrial emissions, the ability to assess airborne contamination over periods greater than 8 hours would be a prudent sampling strategy in some instances.

In addition, the advantages of reduced sampling and analytical costs are an important factor in considering the usefulness of the capillary-canister device. The 2 weeks of sampling resulted in 60 charcoal badges and 12 canister samples, a fivefold reduction in samplers and a fivefold reduction in sample analysis. The cost savings associated with the collection and analysis of capillary-canister samples can be appreciable. While a life cycle cost analysis comparing the capillary-canister with the charocal badge sampling and analysis system has not been preformed, it was the experience of the authors that the capillary-canister afforded a reduction in resources. For this technology to fully evolve, a detailed cost anlysis will need to be performed in the future.

CONCLUSIONS

The 40-hour capillary-canister sampling compared favorably with traditional 8-hour badge sampling in a factory environment. No statistically significant difference was observed between the two types of samplers employed in the study, indicating that the capillary-canister device can effectively collect field samples for extended sampling periods. The capillary-canister integrates the peak concentrations into the weeklong concentration, resulting in a long-term average. The sampling bias predicted by the model can be used to establish guidelines for the capillary-canister in a broad range of sampling environments. Since environmental variability is almost always much greater than the error of the measurements, lower levels of sampling and analytical precision can be acceptable to increase the sample size. The field data coupled with the bias model further supports the capillary-canister's effectiveness in collecting long-term air samples.

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

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