

# Development of the Personal Aldehydes and Ketones Sampler Based upon DNSH Derivatization on Solid Sorbent

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This paper presents the design and evaluation of a tube-type diffusive sampler, the Personal Aldehydes and Ketones Sampler (PAKS). The sampler employs dansylhydrazine (DNSH)-coated solid sorbent to collect aldehydes and ketones (carbonyls). The DNSH-carbonyl derivatives are analyzed using a sensitive HPLC-fluorescence technique. The PAKS was evaluated using test atmospheres containing eight carbonyls for a range of face velocity, temperature, relative humidity, concentration, and sampling duration. The PAKS was also evaluated in the field by comparing results obtained from the PAKS method to those from a conventional DNPH method. The evaluation results indicate that the PAKS is a valid passive sampler for 24–48-h collection of carbonyls in indoor, outdoor, or personal air. The fluorescence detection of DNSH-carbonyl derivatives substantially enhances the sensitivity of the PAKS method as compared to the DNPH method when the sampling rates for the two methods are comparable. The PAKS exposure detection limits for the eight tested carbonyls of relatively large health risk importance (formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, benzaldehyde, and hexaldehyde) range from 0.4 to 1.6 (ppb) (day).

## Introduction

Aldehydes and ketones (carbonyls) are of increasing concern due to their potential adverse health effects and environmental prevalence (1–4). Carbonyls present in ambient air are produced directly from incomplete combustion of biomass and fossil fuels and indirectly through the atmospheric photooxidation of hydrocarbons (5–10). Some carbonyls are released into occupational and residential indoor air settings from building materials, furniture, consumer products, tobacco smoking, and fuel combustion (5, 11–16). Carbonyls can also be produced indoors through indoor air chemistry involving ozone reactions with unsaturated hydrocarbons (14, 17–19).

Despite the fact that carbonyls are ubiquitous in the ambient atmosphere and indoor microenvironments where people can be potentially exposed, few data are available to understand human exposures to these compounds, especially those carbonyls other than formaldehyde. This is perhaps

due partly to the lack of a convenient method to measure personal exposures.

A passive sampler is generally preferable to an active sampler (i.e., a sampler that involves the use of a pump) for monitoring personal exposures because the use of passive samplers decreases the number of sample losses due to possible pump failure and is more readily accepted by participants, especially small children. Using passive samplers is also of advantage in monitoring indoor concentrations without noises and in outdoor locations without concerns for power supply. However, most of the personal passive samplers currently available from commercial sources or reported in the literature, to our knowledge, are designed primarily for the determination of formaldehyde. These samplers utilize 2,4-dinitrophenylhydrazine (DNPH)-coated filters or solid sorbents as sampling media on which carbonyl compounds are collected as DNPH derivatives (20–24). The DNPH derivatives are subsequently extracted and analyzed using HPLC–UV techniques.

Formaldehyde and acetaldehyde are the most abundant carbonyls in indoor and outdoor air (9, 14, 25). Other carbonyls are typically present at a much lower concentration. To detect low-level carbonyls requires that the subsequent analysis technique associated with a passive sampling method is extremely sensitive. A fluorogenic reagent, 5-dimethylaminonaphthalene-1-sulfohydrazide (DNSH), or dansylhydrazine, has been used to collect carbonyl compounds on solid sorbents. The DNSH-based method has enhanced sensitivity and selectivity as compared to the DNPH-based method because the carbonyl–DNSH derivatives can be determined through fluorescence detection, which is generally more sensitive and selective than UV detection (8, 26–28). Utilizing the DNSH-carbonyl derivatization on C<sub>18</sub>-coated silica gels, we have developed the Personal Aldehydes and Ketones Sampler (PAKS). In this paper, we describe the design of the PAKS and report the results from a set of laboratory and field experiments aimed at evaluating the PAKS performance under various conditions of concentration, temperature, relative humidity, face velocity, and exposure duration.

## Methods

**Preparation of the Sampler.** The PAKS was designed as a tube-type diffusive sampler. The configuration of the sampler was simply achieved by modifying a commercially available C<sub>18</sub> cartridge of syringe shape, i.e., a Supelclean LC-18 Cartridge (6 mL, 0.5 g, Supelco Corporation), as shown in Figure 1. The LC-18 cartridge uses a polypropylene syringe barrel containing silica-based bonded C<sub>18</sub> packing material. The cartridge, placed on a rack, was cleaned by passing through 6 mL of HPLC-grade acetonitrile (ACN) slowly by gravity into a waste reservoir. Then 4 mL of an ACN solution containing 1000 mg/L DNSH (Aldrich Chemical Co.) and 1 mL/L acetic acid was allowed to pass through the cartridge by gravity. Once the solution had stopped flowing through the cartridge, any leftover liquid was squeezed out with a plastic syringe. This procedure leads to 0.5 mg of DNSH being coated onto the cartridge. A batch of DNSH-coated cartridges was dried using a manifold through which high-purity (zero-grade with charcoal scrubbers) nitrogen was passed for 60 min at about 100 mL/min. After being dried, the syringe barrel of a DNSH-coated cartridge was cut off at 1.44 cm from the sorbent surface, and the luer tip of the cartridge was sealed securely. Because only the barrel end of the cartridge would be open during sampling, the length of diffusion gap for the sampler was 1.44 cm. The barrel diameter

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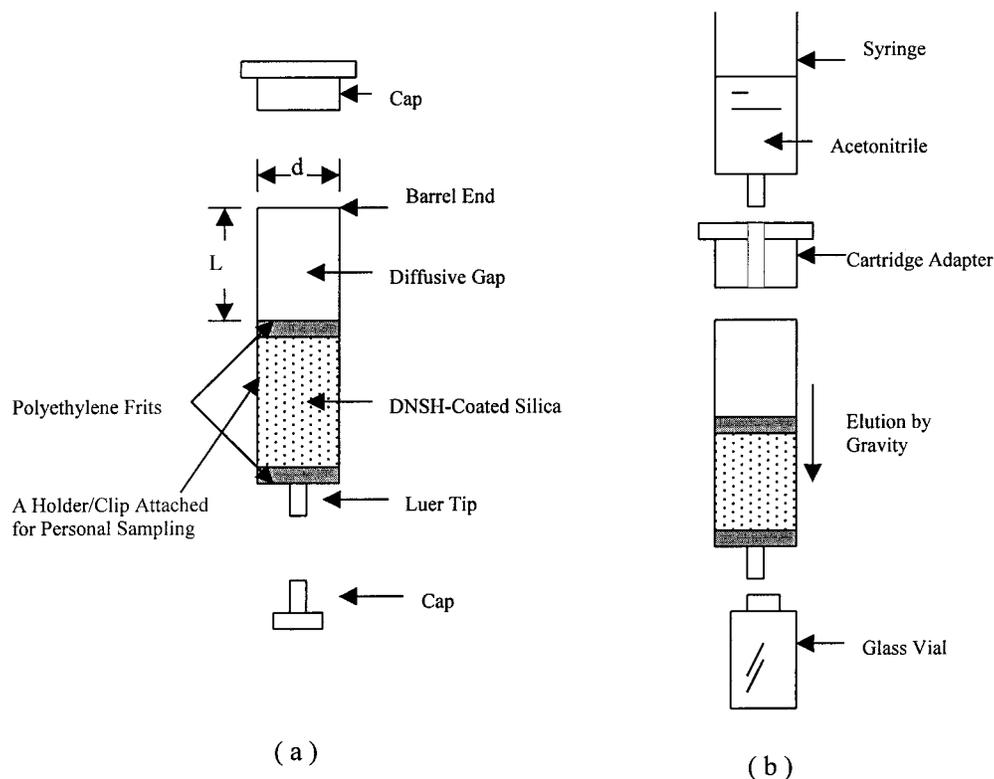


FIGURE 1. (a) Configuration of the PAKS and (b) extraction schematic diagram.

was 1.2 cm. Therefore the ratio of the open area to the length of diffusion gap ( $A/L$ ) was 0.785 cm for the PAKS. Each freshly prepared cartridge had been capped securely at both ends, wrapped in aluminum foil individually, and stored in a freezer before it was deployed for sampling. A replaceable and reusable cartridge holder with a clip was attached to the cartridge during personal sampling. Background carbonyl levels of DNSH coating solution and blank samplers were checked regularly to ensure that there was no contamination during the preparation processes.

**Generation of Test Atmospheres of Carbonyl Compounds.** A dynamic dilution system, as schematically shown in Figure 2, was used to generate test atmospheres of the following eight carbonyls: formaldehyde, acetaldehyde, propionaldehyde, acrolein, acetone, crotonaldehyde, hexaldehyde, and benzaldehyde. These eight carbonyls were selected for testing due to their potential health risk importance. Formaldehyde was generated from a formaldehyde permeation tube, and the other seven carbonyl compounds were from a compressed gas cylinder containing a standard mixture of these compounds. The formaldehyde permeation tube was placed in oven no. 2 that can be set at a desired temperature. The concentration of formaldehyde was determined from formaldehyde permeation rate at a given temperature and the total flow rate of the dynamic dilution system. The gas cylinder, prepared by Scott Specialty Gases, Inc., contained 5.20 ppm of acetaldehyde, 5.22 ppm of acetone, 1.76 ppm of acrolein, 1.78 ppm of propionaldehyde, 2.10 ppm of crotonaldehyde, 1.67 ppm of hexaldehyde, and 2.11 ppm of benzaldehyde in pure nitrogen. This mixture was diluted with high-purity nitrogen and introduced into the mixing ball where all the carbonyls and humidity-controlled nitrogen (using the salt-based humidifier) were well mixed with magnetic stirrers. The humidifier, mixing ball, and passive sampling house were placed in oven no. 2 in which the temperature could be controlled at a precision of  $\pm 1$  °C. A range of desired passive sampling face velocity values were obtained by varying the flow rate of the gas stream

passing the passive sampling house. The face velocity was measured using an anemometer with its probe close to the open end of the PAKS cartridge. The active sampling manifold was used to collect parallel samples using sampling pumps.

**Collection of Personal and Stationary Samples.** Personal sampling was achieved by clipping the PAKS to the collar or pocket of a subject and then removing the cap from the barrel end of the sampler. Participant ID, cartridge ID, start date and time, and end date and time were recorded on a sampling sheet accompanying each sampler. Subjects were instructed to wear the samplers whenever they were awake except during showing/bathing/swimming (in these circumstances, the samplers were placed away from getting wet but as close to the breathing zones as possible). During sleeping hours, the samplers were placed near the beds. The open end of each PAKS was never covered with clothing or any objects and was never faced down against any surface. At the end of the sampling period, the PAKS was removed from the subject and securely capped. When a PAKS was used to collect carbonyls in indoor air, in outdoor air, or in the test atmosphere as shown in Figure 2, it was simply placed in the selected sampling location with the barrel end uncapped and completely exposed. At the end of the sampling, the barrel end was recapped. The capped samplers were wrapped individually with aluminum foil, placed in a cooler, and shipped to the lab as soon as possible.

**Sample Treatment and Extraction.** Prior to sample extraction, each exposed PAKS, with both ends securely capped and wrapped in aluminum foil, was placed in an oven at 60 °C for 60 min to drive the reversible DNSH-carbonyl reactions toward the direction of products formation. After being cooled to ambient temperature, the caps were removed from both ends, and the uncapped sampler was placed in a rack and extracted with 2 mL of ACN using a special adapter and a syringe (see Figure 1). The extraction was accomplished by gravity. The extract was collected using a glass vial with a 2-mL mark on it. The mark was lined up with additional ACN when necessary. The extract was stored in a refrigerator

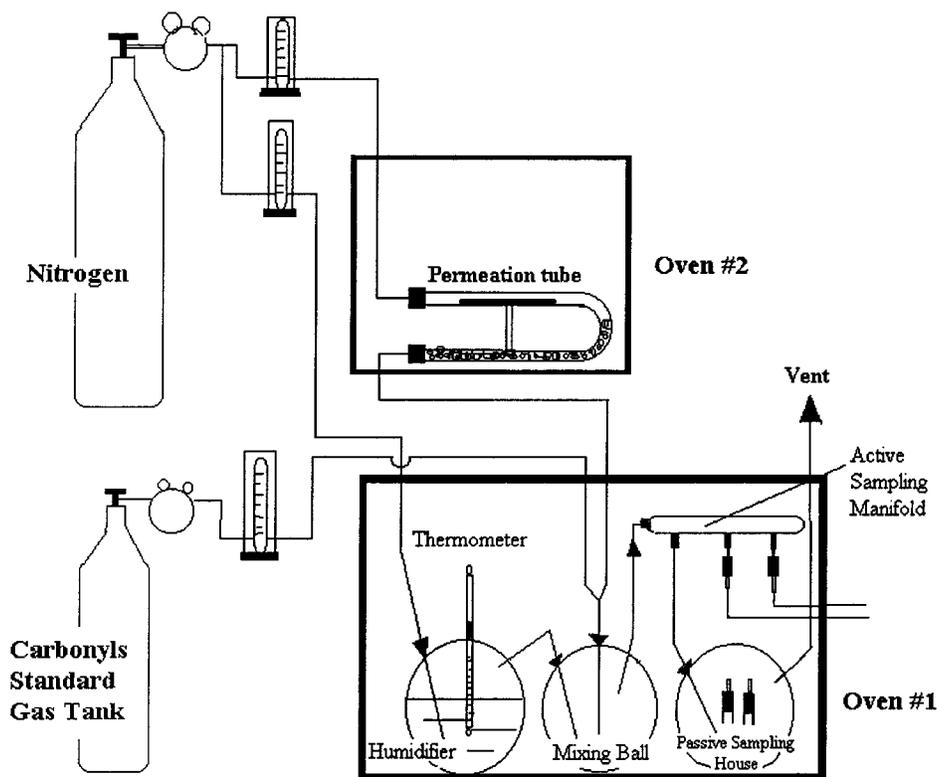


FIGURE 2. Dynamic dilution system for generation of test atmosphere of carbonyl compounds.

if not analyzed immediately. The extracts were stable under refrigeration (4 °C) for at least 7 days. (We have not done tests for beyond 7 days.)

**Sample Analysis.** The sample analysis was performed using an HPLC system [Waters 600E system controller, Waters 712WISP autosampler, 4100 programmable fluorescence detector, and Waters Nova-Pak C<sub>18</sub> column (3.9 × 150 mm) and its guard column]. The mobile phase program used was as follows: solution A = 32% ACN and 68% water containing 1.6 g/L KH<sub>2</sub>PO<sub>4</sub>; solution B = 70% ACN and 30% water containing 1.6 g/L KH<sub>2</sub>PO<sub>4</sub>; linear gradient from 100% A to 100% B in 20 min, then from 100% B back to 100% A in 10 min, and then held at 100% A for 10 min; the mobile phase flow rate = 1.0 mL/min. The injection volume was 20 μL. The fluorescence detector was set at an excitation wavelength of 240 nm and an emission wavelength of 470 nm. By using this analytical program, we were able to well-resolve the eight tested carbonyl compounds.

DNSH-carbonyl derivatives were prepared in situ by spiking a known amount of carbonyls into the DNSH-coated C<sub>18</sub> cartridges. The spiked cartridges, treated and extracted in the exact same manner as the samples, served as external standards for qualification and quantification of the carbonyl compounds.

**Calculation of Concentrations.** The concentration ( $C_{\text{air}}$ , in μg/m<sup>3</sup>) of an airborne carbonyl was calculated from

$$C_{\text{air}} = \frac{C_{\text{ex}} V_{\text{ex}}}{Qt} \times 10^6 \quad (1)$$

where  $C_{\text{ex}}$  is the carbonyl concentration in the extracts determined by HPLC-fluorescence detector, in μg/mL;  $V_{\text{ex}}$  is the extraction volume, in mL;  $Q$  is the sampling rate, in mL/min; and  $t$  is the sampling time or exposure duration, in min.

The PAKS sampling rate for each tested carbonyls was determined from a series of experiments. In these experiments, we have collected carbonyls in the test atmosphere with DNSH-coated cartridges placed in the passive sampling

house and with DNSH-coated cartridges placed in the active sampling manifold (see Figure 2). Since the paired passive and active cartridges were exposed to the same concentrations for the same duration, the sampling rate ( $Q$ ) of the passive cartridge (PAKS) should be

$$Q = \frac{M_p}{M_a} Q_a \quad (2)$$

where  $M_p$  is the carbonyl mass collected with the passively exposed cartridge (PAKS),  $M_a$  is the carbonyl mass collected with the actively exposed cartridge, and  $Q_a$  is the sampling rate for the actively exposed cartridge. All actively exposed DNSH-coated cartridges were temperature treated, extracted, and analyzed using the same procedures for the passively exposed PAKS samples.

**DNPH Active Sampling and Analysis Method.** The PAKS was further evaluated using results derived from actively exposed DNPH-coated cartridges that were co-located with the PAKS cartridges. The DNPH method used in our laboratory has been reported in detail earlier (5, 14). Briefly, DNPH-coated Sep-Pak C<sub>18</sub> cartridges (Waters Corp.), freshly prepared in our laboratory, were used to collect carbonyls samples at a sampling flow rate of < 1 L/min. The DNPH-carbonyl derivatives were then extracted with ACN and analyzed using the following HPLC program: Nova-Pak C<sub>18</sub> column (Waters, 3.9 × 150 mm) was used as the analytical column; after holding 100% of solvent A (water/ACN/THF 60/30/10) for 2 min, the mobile phase was linearly changed to 100% solvent B (ACN/water 60/40) in 10 min, then held at 100% B for 13 min, and then changed back to 100% A in 5 min. The flow rate of the mobile phase was constant at 1 mL/min. The sample injection volume was 20 μL. The UV detector was set at 365 nm. The concentrations of carbonyls were determined through calibration curves prepared daily using standard solutions of DNPH-carbonyl derivatives.

**TABLE 1. Analytical Detection Limits (pg) for Carbonyl Compounds**

carbonyl compds	detection limits (pg)		
	DNPH method (reported)	DNSH method (reported)	DNSH method (this study)
formaldehyde	91–1100 <sup>a-d</sup>	2–81 <sup>e,f</sup>	5
acetaldehyde	31–2000 <sup>a-d</sup>	25–56 <sup>e,f</sup>	18
acetone	102–239 <sup>a,b</sup>	10 <sup>g</sup>	13
acrolein	466 <sup>a</sup>	22 <sup>e</sup>	26
propionaldehyde	42–2300 <sup>a,c,d</sup>	2–50 <sup>e,f,h</sup>	7
crotonaldehyde	577 <sup>a</sup>	18 <sup>e</sup>	13
benzaldehyde	660–5900 <sup>a,d</sup>	7–12 <sup>e,f</sup>	23
hexaldehyde	674 <sup>a</sup>	12–100 <sup>e,h</sup>	13

<sup>a</sup> Test in our laboratory. <sup>b</sup> Ref 32. <sup>c</sup> Ref 33. <sup>d</sup> Ref 34. <sup>e</sup> Ref 8. <sup>f</sup> Ref 28. <sup>g</sup> Ref 14. <sup>h</sup> Ref 26.

**TABLE 2. Effect of Temperature on the Sampling Rates**

carbonyl compds	sampling rate (mL/min)				max difference (%) <sup>a</sup>
	temperature (°C)			mean	
	20	30	40		
formaldehyde	7.41	7.69	7.74	7.61	4.3
Acetaldehyde	5.15	5.02	5.41	5.19	7.5
acetone	4.67	4.99	4.97	4.88	6.6
acrolein	3.87	4.07	4.12	4.02	6.2
propionaldehyde	4.75	5.23	5.32	5.10	11.2
crotonaldehyde	3.33	3.54	3.36	3.41	6.2
benzaldehyde	3.20	3.26	3.41	3.29	6.4
hexaldehyde	3.68	3.85	4.02	3.85	8.8

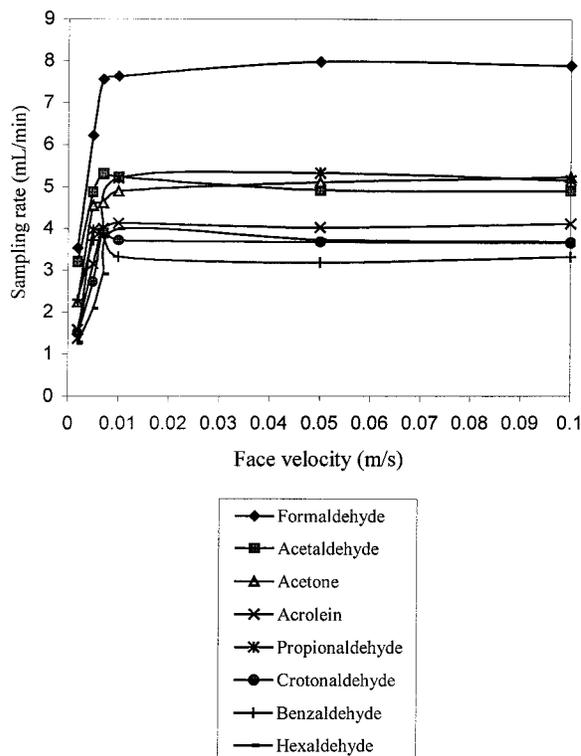
<sup>a</sup> Maximum difference (%) = (maximum – minimum)/(mean) × 100%, based on 9 tests with relative humidity = 10%; face velocity = 0.05m/s; and exposure duration = 24 h.

## Results and Discussion

**Analytical Detection Limits.** The analytical detection limits (ADLs) for DNSH-carbonyl derivatives using HPLC-fluorescence methods (DNSH methods) have been reported to be lower than those for DNPH-carbonyl derivatives using HPLC–UV methods (DNPH methods), as shown in Table 1. In the present study, we have determined the ADLs for the eight carbonyls under the analytical conditions described above. The ADL was determined as 3 times the standard deviation that was derived from ACN extracts of six randomly selected blank PAKS cartridges. (To get near-baseline lowest detectable responses, a trace amount of some tested carbonyl compounds was added to the “blank” solutions.) The results are shown in Table 1. Our results agreed in that the DNSH method for determining the eight carbonyl compounds was substantially more sensitive than the DNPH method.

**Effects of Temperature on the Sampling Rates.** The PAKS sampling rates for the eight carbonyl compounds were determined experimentally at three levels of temperature using the dynamic dilution system shown in Figure 2. The relative humidity of the test atmosphere was set at 10% for all the experiments. In these experiments, all PAKS cartridges were exposed for 24 h in the passive sampling house at a face velocity of 0.05 m/s. The results, as shown in Table 2, indicate that the PAKS sampling rates were not significantly affected by ambient temperature in the range of 20–40 °C. These experimental results are not in contradiction with the theoretical temperature dependence of the PAKS sampling rates. The calculated theoretical values of the PAKS sampling rates, as shown in Table 5, increase <10% from 20 to 40 °C.

**Effects of Relative Humidity on the Sampling Rates.** The effects of relative humidity (RH) on the PAKS sampling rates were determined using the dynamic dilution system with



**FIGURE 3. Effect of face velocity on the sampling rates, based on 12 tests with temperature = 30 °C, relative humidity = 10%, and exposure duration = 24 h.**

**TABLE 3. Effect of Humidity on the Sampling Rates**

carbonyl compds	sampling rate (mL/min)				max difference (%) <sup>a</sup>
	relative humidity (%)			mean	
	10	50	90		
formaldehyde	7.69	7.32	7.23	7.41	6.2
acetaldehyde	5.02	4.83	4.67	4.84	7.2
acetone	4.99	5.21	5.12	5.11	4.3
acrolein	4.07	4.22	4.27	4.19	4.8
propionaldehyde	5.23	5.44	5.39	5.35	3.9
crotonaldehyde	3.54	3.68	3.47	3.56	5.9
benzaldehyde	3.26	3.34	3.16	3.25	5.5
hexaldehyde	3.85	3.71	3.55	3.70	8.1

<sup>a</sup> Maximum difference (%) = (maximum – minimum)/(mean) × 100%, based on 9 tests with temperature = 30 °C, face velocity = 0.05m/s, and exposure duration = 24 h.

three RH levels: 10%, 50%, and 90%. Two PAKS cartridges were exposed in the passive sampling house for 24 h at a face velocity of 0.05 m/s for each tested RH level. The temperature of the test atmosphere was kept constant at 30 °C for all the experiments. The results from these experiments are shown in Table 3, indicating that the changes in the PAKS sampling rates for the eight carbonyl compounds were within 8% for a wide range of RH (10–90%). This suggests no significant effects of RH on the PAKS sampling rates.

**Effects of Face Velocity on the Sampling Rates.** Face velocity is an important factor to consider in developing a personal sampler due to a relatively large variation in face velocity during personal sampling than during stationary sampling. The effects of face velocity on the PAKS sampling rates are shown in Figure 3. In all the experiments testing face velocity effects, the temperature of the test atmosphere was 30 °C, relative humidity was 10%, the exposure duration was 24 h, and the tested range of face velocity was from 0.002 to 0.10 m/s. The results show that when the face velocity was

**TABLE 4. Effect of Carbonyls Concentration on the Sampling Rates**

carbonyl compds	concn range (ppb)	mean of sampling rate (mL/min)	max difference (%) <sup>a</sup>
formaldehyde	7.89–201	7.52	6.2
acetaldehyde	3.00–95.4	5.14	7.6
acetone	3.01–95.8	4.89	4.0
acrolein	1.02–32.3	4.12	3.2
propionaldehyde	1.03–32.7	5.13	4.8
crotonaldehyde	1.22–38.5	3.61	6.0
benzaldehyde	1.22–38.7	3.04	8.2
hexaldehyde	0.96–30.6	3.77	8.1

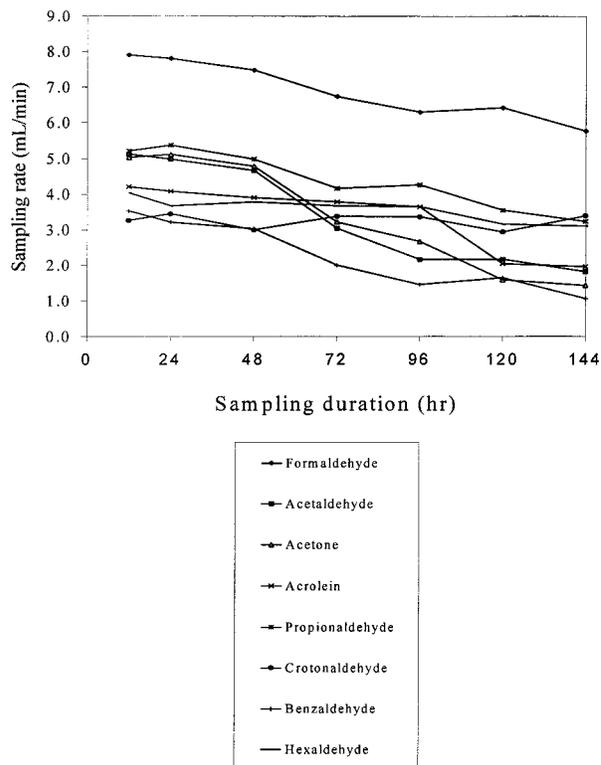
<sup>a</sup> Maximum difference (%) = (maximum – minimum)/(mean) × 100%, based on 12 tests with temperature = 30 °C, face velocity = 0.05m/s, relative humidity = 10%, and exposure duration = 24 h.

0.01 m/s or greater, the PAKS sampling rates were constant for all the eight tested carbonyl compounds. This indicates that the PAKS can be properly used not only for personal sampling conditions (air velocity typically around 0.1 m/s) but also for most indoor and outdoor sampling conditions (air velocity typically above 0.01 m/s) (21, 29).

**Effects of Carbonyl Concentrations on the Sampling Rates.** The effects of carbonyl concentrations on the PAKS sampling rates were determined using the dynamic dilution system with a range of concentrations of the eight carbonyl compounds. These experiments were all conducted at a constant temperature (30 °C) and relative humidity (10%) for an exposure duration of 24 h and a face velocity of 0.01 m/s. The results, shown in Table 4, indicate there were no influences of the carbonyl concentrations on the PAKS sampling rates. However, we realize that the lower end of the concentration range for most of the eight carbonyls may still be higher than the typical air concentrations. Due to the experimental limitation, we were unable to further lower the carbonyl concentrations in the tested atmosphere.

**Effects of Sampling Duration on the Sampling Rates.** The effects of sampling duration were determined by varying the exposure duration of the PAKS cartridges in the passive sampling house from 12 to 144 h (6 days). In all the experiments, the temperature was 30 °C, relative humidity was 10%, and face velocity was 0.01 m/s. The results from this set of experiments show that the sampling rates for all the tested carbonyl compounds appeared not stable over 6 days, especially after 48 h (see Figure 4). The observed decrease in the sampling rates with sampling time was perhaps due to the increased distance of diffusion of the carbonyls through the solid sorbent that was necessary as DNSH was successively depleted at the front interfaces of the cartridge. The decrease, however, was less likely due to the negligible decrease in DNSH capacity with sampling time because the DNSH coated on the PAKS was in great excess and also stable over the tested period. Nevertheless, within a smaller time window, from 24 to 48 h, the largest variation in the sampling rates was within 10%. We have also found that a 12-h exposure was not adequate to detect many carbonyl compounds present in the air. Therefore, the recommended exposure duration for the PAKS would be from 24 to 48 h.

**The Sampling Rates.** As discussed above, the PAKS sampling rates for the eight tested carbonyl compounds were insignificantly affected by temperature, relative humidity, face velocity, carbonyl concentration, and exposure duration (24–48 h). Therefore, we have calculated the means of the sampling rates from 48 experiments. These mean values, shown as *measured mean value* in Table 5, should be used as PAKS sampling rates to calculate airborne concentrations of the eight tested carbonyl compounds using eq 1.



**FIGURE 4.** Effects of sampling duration on the sampling rates, based on 12 tests with temperature = 30 °C, relative humidity = 10%, and face velocity = 0.05 m/s.

**TABLE 5. Sampling Rates of the PAKS**

carbonyl compds	sampling rate (mL/min)		
	theoretical value <sup>a</sup>		measured mean value <sup>b</sup>
	20 °C	40 °C	
formaldehyde	6.85	7.57	7.48
acetaldehyde	5.20	5.74	5.02
acetone	4.38	4.84	4.99
acrolein	4.53	5.00	4.11
propionaldehyde	4.33	4.78	5.23
crotonaldehyde	3.92	4.33	3.48
benzaldehyde	3.33	3.67	3.27
hexaldehyde	3.12	3.44	3.72

<sup>a</sup> Theoretical value of sampling rate is equal to  $D(A/L)$ , where  $D$  denotes the diffusion coefficient that can be calculated from Gilliland's approximation (see ref 35). <sup>b</sup> The test temperature ranged from 20 to 40 °C, relative humidity ranged from 10 to 90%, face velocity ranged from 0.01 to 0.10m/s, exposure duration ranged from 24 to 48 h, concentrations of the test carbonyls ranged from 1 to 200 ppb, and the number of experiments was 48.

For a tube-type diffusive sampler such as the PAKS, the Fick's law can be approximated to the following form if the rate-limiting step for the sample collection is molecular diffusion (30):

$$M = D \frac{A}{L} t C_{\text{air}} \quad (3)$$

where  $M$  is the mass uptake (g),  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $A$  is the cross sectional area of diffusion path ( $\text{cm}^2$ ),  $L$  is the length of diffusion path (cm),  $C_{\text{air}}$  is the concentration at the end of gas gap chamber ( $\text{g}/\text{cm}^3$ ), and  $t$  is the time of sampling (s).

The term  $D(A/L)$  has a unit of cubic centimeters per second and therefore represents what can be considered as the "sampling rate" of the passive sampler when comparing to

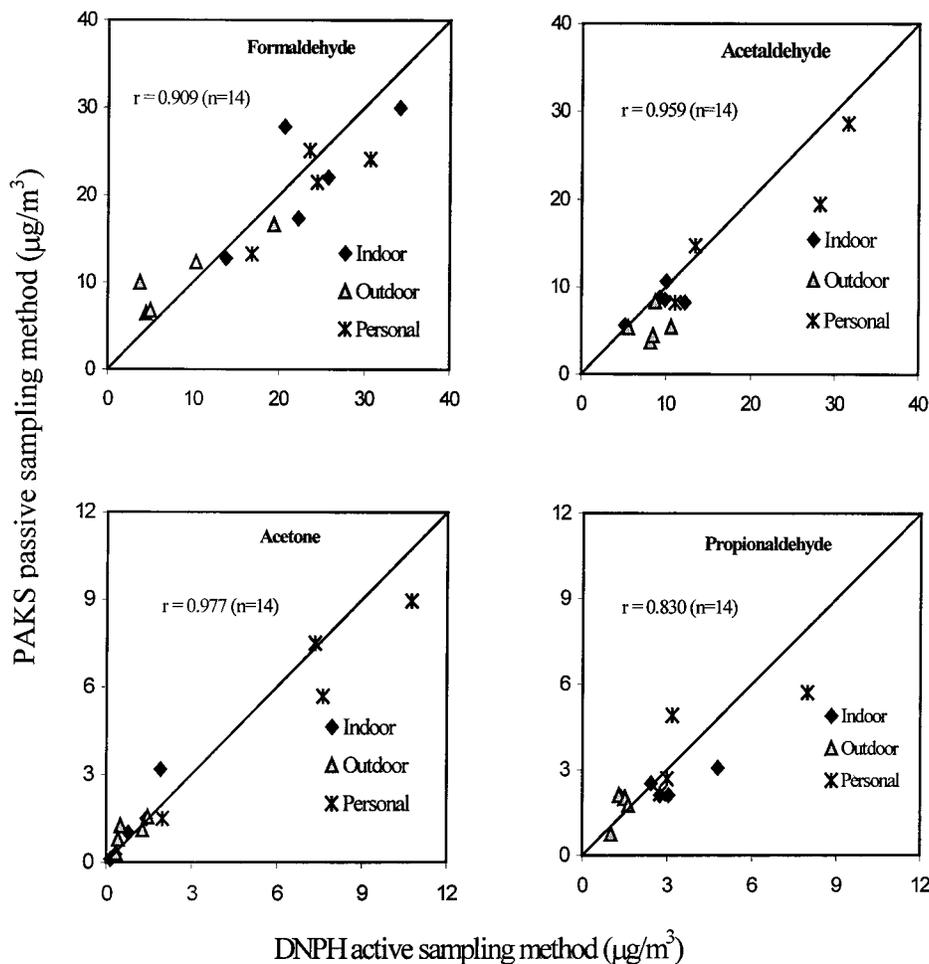


FIGURE 5. Comparison between the PAKS method and the DNP active sampling method. The correlation coefficient ( $r$ ) between the two methods is also shown in the figure. The results were derived from 48-h indoor, outdoor, and personal samples, all collected using co-located pairs of PAKS cartridges and DNP cartridges.

an active sampling system. This simple use of the sampling rate concept has proven to be of considerable value to users of the devices and is most often expressed in units of milliliters per minute.

As shown in eq 3, the sampling rate of a diffusive sampler is proportional to the  $A/L$  value. Therefore, a larger  $A/L$  value would increase the sampling rate and thus the method sensitivity. However, the larger the  $A/L$  is, the greater the face velocity effects may be. For this reason, we have carefully selected through experimental tests an optimized ( $A/L$ ) value for the PAKS, i.e., the largest ( $A/L$ ) at which face velocity had no significant effects on the sampling rates (see Figure 3). The  $A/L$  value for the PAKS is 0.785 cm.

We have calculated the sampling rates (*theoretical value*) of the PAKS for the eight tested carbonyl compounds using  $D$  values given in the literature and the  $A/L$  value of the sampler (Table 5). The results, shown in Table 5, indicate that the calculated theoretical values and experimentally determined values of sampling rate were in good agreement. This implies that the PAKS sampling rate for a carbonyl compound may be reasonably predicted using the  $D$  value of the carbonyl compound.

**Recovery Rates.** We have conducted a set of experiments in which the PAKS cartridges were exposed to known concentrations of the eight carbonyl compounds in the passive sampling house (see Figure 2). The concentrations of the eight carbonyls in the passive sampling house were known from the concentrations of the carbonyl standards and the dilution factors. The values of recovery rate, defined

TABLE 6. Recovery Rates of the PAKS

comps	concentration (ppb)		recovery rates (%) <sup>b</sup>
	generated in the chamber	mean value measured with PAKS <sup>a</sup>	
formaldehyde	27.8	28.1	101.1
acetaldehyde	28.9	25.2	87.2
acetone	28.9	23.2	80.3
acrolein	17.4	10.5	60.3
propionaldehyde	17.4	18.7	107.5
crotonaldehyde	17.3	13.2	76.3
benzaldehyde	17.4	17.1	98.3
hexaldehyde	17.3	16.3	94.2

<sup>a</sup> Based on 4 tests with temperature = 30 °C, face velocity = 0.05m/s, relative humidity = 10%, and sampling duration = 24 h. <sup>b</sup> Recovery rate (%) = (mean value measured)/(generated in the chamber) × 100%.

as the ratio of the carbonyl concentration determined using the PAKS to the known concentration present in the passive sampling house, are shown in Table 6. The recovery rates for six of the eight tested carbonyl compounds were within 100 ± 20%. The recovery rates for acrolein and crotonaldehyde were low (60.3% and 76.3%, respectively), perhaps because the DNSH derivatives of acrolein and crotonaldehyde were not stable (31).

**Field Evaluation.** The performance of the PAKS was further evaluated in the field by comparing results from co-located passively exposed PAKS cartridges and actively exposed DNPH cartridges. All co-located field samples were taken on a 48-h basis. Some of these co-located cartridges were placed inside of homes (indoor samples); some were placed outside of homes (outdoor samples); and some were worn by people (personal samples). All the DNPH active sampling was done using constant-flow sampling pumps at a flow rate between 50 and 100 mL/min. The comparison between the PAKS results and the DNPH results, as shown in Figure 5, indicates that the two methods agree reasonably well for at least the following four compounds: formaldehyde, acetaldehyde, acetone, and propionaldehyde. On average, the difference between the two methods was within 40% for these four carbonyls. The field evaluation of the PAKS for other carbonyls was not reported here either due to the presence of many nondetects or due to the lack of appropriate standards in our laboratory at this point.

**Applications.** The PAKS, on the basis of our laboratory and field evaluation, has proven to be a valid passive sampler for 24–48-h collection of carbonyls present in indoor, outdoor, or personal air. Because of its tube-like design with an  $A/L$  of 0.785 cm, the PAKS only requires a minimum face velocity of 0.01 m/s to achieve constant sampling rates as compared to a typical minimum face velocity of 0.10 m/s for a badge-type diffusive sampler (29). Therefore, the PAKS can be used even under situations when the air movement is very steady (e.g., some indoor locations). It is expected that the sampler can also be properly used for outdoor locations where ozone concentration is high on the basis of the results from a previous study of evaluating ozone interference in the derivatization of atmospheric carbonyls with DNSH on  $C_{18}$  sorbents (27). The study found that ozone (up to 300 ppb) is not a significant interference as long as DNSH is in substantial excess over the carbonyls being derivatized, because ozone appeared to only cause partial oxidation of the DNSH reagent but had no effect on carbonyl-DNSH derivatives (27). All PAKS cartridges were coated with amount of DNSH in a large excess of total amount of all possible carbonyl compounds. The results from our laboratory tests indicate that there is no significant ozone interference when the PAKS is exposed for 24–48 h to up to 300 ppb ozone (The details in the experiments and results will be reported in a separate paper). Therefore, the DNSH-based PAKS method is of no concern of ozone interference in addition to its high sensitivity. The PAKS exposure detection limits for the eight carbonyl compounds tested (formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, benzaldehyde, and hexaldehyde) ranged from 0.4 to 1.6 (ppb) (day).

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