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A New Passive Sampler for Regulated Workplace Aldehydes

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A new solid sorbent passive air sampler for aldehydes had a silicone membrane atop a cylindrical diffusion path of 1.1 cm length and 1.3 cm diameter above a 10 percent (w/w) O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) Tenax TA pellet. Known vapor concentrations of Occupational Safety and Health Administration (OSHA)-regulated aldehydes near their permissible exposure limits were generated from a syringe pump dynamic air dilution system that was connected to an exposure chamber. The O-oxime derivatives from aldehyde reaction with PFBHA were desorbed with hexane, and quantified by capillary gas chromatography/mass spectrometry (GC/MS) or gas chromatography/electron capture detection (GC/ECD). The capacity for aldehydes with one carbonyl group was 30–35 μmoles, and 15 μmoles for the dialdehyde, glutaraldehyde. The experimental sampling rates in mL/min were 8.86 ± 0.38, acetaldehyde; 11.69 ± 0.32, chloroacetaldehyde; 7.85 ± 0.19, crotonaldehyde; 9.97 ± 0.10, formaldehyde; 6.47 ± 0.42, furfural; and 4.46 ± 0.15, glutaraldehyde. Other data on valeraldehyde and acrolein have shown that the sampling constants were independent of face velocity between 0.1 to 0.35 m/s (20 to 70 fpm), temperatures between 9 to 48°C, RH between 3 to 79 percent, and intermittent sampling exposure pattern.

Keywords Adsorption, Aldehyde, Aldehyde Oxime, Gas Chromatography, Passive Sampler, Personal Sampling

INTRODUCTION

Aldehydes (R-CHO where R is alkyl, aromatic, or alicyclic) are widely used industrial chemicals that are also detected in the environment as products of combustion,[1–6] water disinfection,[7] and biological oxidation.[8] Aldehydes irritate mucous membranes.[9] Formaldehyde, acetaldehyde, furfural, and crotonaldehyde are animal carcinogens.[10] Adverse exposure effects of formaldehyde and glutaraldehyde are documented to embalmers,[11,12] operating theater personnel,[13] and pathologists.[9] The exposure and the health effects of formaldehyde have been reviewed elsewhere.[14,15]

Aldehyde vapors are usually sampled with solid sorbents.[2,16–19] The National Institute for Occupational Safety and Health (NIOSH) method uses XAD-2 resin coated with 2-(hydroxymethyl)piperidine. Nonreactive C_3-C_5 aldehydes are not collected quantitatively,[16] and volatile acids reduce loading capacity. The 2,4-dinitrophenylhydrazine (DNPH) method is used by the Environmental Protection Agency (EPA)[18] and the American Society for Testing and Materials (ASTM).[20] The DNPH methods potentially allow specific quantitation of different aldehydes and ketones through high performance liquid chromatography (HPLC)/ultraviolet (UV) detection of their hydrazones. DNPH does not react quantitatively with conjugated aliphatic aldehydes. The hydrazones are light-sensitive, and their recoveries are variable after liquid aldehyde spiking.[2] Some passive samplers have been developed for the lower molecular weight aldehydes and ketones based on liquid systems,[22–24] and on solid sorbents coated with DNPH.[22,25–28]

O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) has been used to react quickly and quantitatively with aldehydes in water to form O-oximes suitable for picogram (pg) detection by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD).[21] The PFBHA method also has been used to chemisorb aldehydes by dynamic air sampling.[19] We have previously reported[29] on a new passive sampler design for *n*-valeraldehyde and acrolein based on the PFBHA method. We now extend the method to other aldehydes regulated by the Occupational Safety and Health Administration (OSHA).

EXPERIMENTAL METHODS

Materials

The aldehydes investigated were acetaldehyde (99.5 percent w/w), chloroacetaldehyde (50 percent in water), crotonaldehyde (98 percent), formaldehyde (37 percent in water), furfural

(98 percent), and glutaraldehyde (50 percent in water), all from Aldrich, Milwaukee as was the internal standard decachlorobiphenyl. Optima hexane, Optima methanol, nitric acid, activated charcoal, molecular sieves, and Drierite were from Fisher Scientific, Tustin, Los Angeles. PFBHA (Lancaster Laboratories Inc., Lancaster, Pennsylvania), Tenax TA 80/100 mesh (Alltech Associates, Deerfield, Illinois), and 5 percent (v/v) methane/argon (Alphagaz, Los Angeles, California) were also used.

Equipment

Lengths of Pyrex tubing (7 cm × 5-mm ID), Pyrex® glass wool (Soxhlett-extracted in methanol and then hexane), 4-mL Kimble vials (PTFE-lined screw caps), 10-μL Hamilton syringes, gas-tight Hamilton syringes, a Parr 2811 bench manual pellet press, 3M Model 3500 OVM passive sampler, and a Model 11 Harvard syringe pump were from Fisher Scientific. Dupont P30A personal sampling pumps, Tedlar gas bags (SKC Inc., Eighty Four, Pennsylvania), and a Whatman Zero Air generator (Balston Inc., Haverhill, Massachusetts) were also used.

A Hewlett-Packard 5890 gas chromatograph (Hewlett-Packard, Palo Alto, California) equipped with a 30-m × 0.32-mm ID 1-μm film DB-1701 chemically bonded fused-silica capillary column was linked to either a Hewlett-Packard 5988A mass spectrometer or a ^{63}Ni-electron capture detector (ECD). The temperature for the injector, ECD, and GC/MS transfer line was 250°C. The MS ion source temperature was 260°C. The column temperature program for glutaraldehyde was: solvent delay, 5 min at 105°C; 105°C for 0.5 min, 105°C to 220°C at 70°C/min, and holding then for 40 min. The temperature program for other aldehydes was: solvent delay 5 min at 105°C, 105°C for 0.5 min, 105°C to 220°C at 10°C/min, and holding then for 10 min. Selective ion monitoring (SIM) used m/z 181 and total ion monitoring m/z 50-500. Quantitation used both E- and Z-isomer areas. The carrier gas for GC/MS was helium and for GC/ECD 5% methane/argon at 3.0 ± 0.4 mL/min. The ECD signal was displayed with a Hewlett-Packard 3396 integrator.

Methods

A 13-mm-diameter and 0.2-cm-thick pellet of PFBHA-coated Tenax TA (10 percent, w/w) was made by the hand press. The sampler had a silicone membrane and a diffusion path length of 1.1 cm (Figure 1). Figure 2 presents the vapor generator, air dilution system, and exposure chamber.[29] The air generator was connected to the vapor and water generation syringe pumps set at known plunger speeds. Heating tape wrapped around the outside of the stainless steel tubing at the needle exit from the syringe pumps ensured total volatilization of organic vapor or water. The two streams were then routed through a stainless steel T-joint adapter connected by Teflon® tubing to a Greenburg-Smith impinger mixing chamber. Teflon tubing then conveyed the diluted mixed organic vapor into the exposure chamber through a

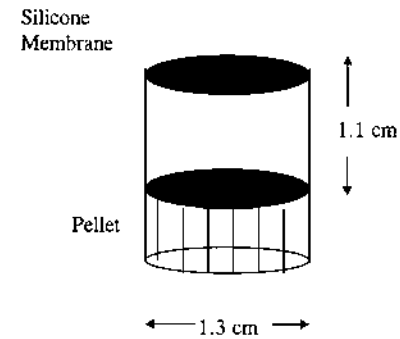

Diagram of Sampler

FIGURE 1
Cross-section of the passive sampler.

leakless hole bored on the side wall near the chamber bottom to just underneath the chamber fan blades under the ceramic metal plate. Six samplers were placed horizontally on the plate, each with a nearby closable hole in the chamber wall for insertion of calibrated probes to measure RH, temperature, organic vapor concentration, and face velocity. For acetaldehyde of boiling point 21°C,[30] the syringe pump was surrounded by ice cubes and blue ice at 4 ± 1°C to stop acetaldehyde liquid evaporation before entering the dilution system.

Aqueous aldehydes, including formaldehyde, glutaraldehyde, and chloroacetaldehyde are easily polymerized. Therefore, exact purity was determined for generation purposes using the NIOSH back-titration method with 1.13 M sodium sulfite.[16]

Synthesis of PFBHA O-Oximes

The PFBHA O-oximes were synthesized by methods detailed elsewhere[19] except for glutaraldehyde. A molar ratio of 8:1 of PFBHA (90.5 mg; 0.36 mmol) to glutaraldehyde (50 percent solution; density 1.007 ± 0.026 g/ml) was used to synthesize the di-substituted glutaraldehyde PFBHA O-oxime. Attempts were made to make the monosubstituted O-oxime by varying the ratio of aldehyde to PFBHA and reaction times. White precipitates formed immediately in all cases. The mixtures were centrifuged for 5 minutes. Subsequent steps were the same as for other O-oximes.[19]

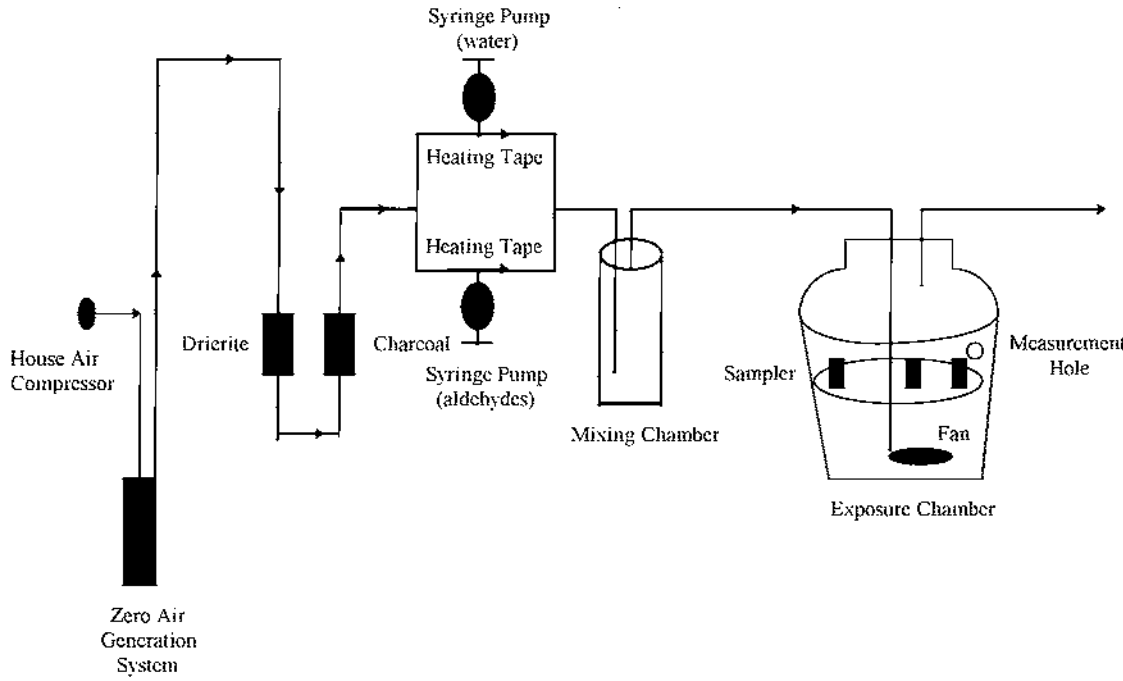

FIGURE 2
Aldehyde vapor generation and exposure chamber system.

Aldehyde Diffusion Coefficients and Sampling Constants

The dependence of the diffusion constant on molecular weight and temperature is expressed through equation (1):[31]

$$D_{AB} = \frac{0.00143 \times T^{1.75}}{P M_{AB}^{1/2}\left[\left(\sum_V\right)_A^{1/3} + \left(\sum_v\right)_B^{1/3}\right]^2} \qquad [1]$$

where D_{AB} is the binary diffusion coefficient of analyte in air in cm^2/s at T; T is temperature, K; M_A and M_B are molecular weight, g/mol; $M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$; P is the external pressure, bar; $\sum_V$ is the summation of atomic diffusion volumes, unitless; i is all the contributing species; A is air; B is the analyte; $(\sum_V)_A$ is 19.7.[31] For acetaldehyde H_4C_2O, the $\sum_V$ is:[31]

$$\left(\sum_V\right)_{H_4C_2O} = 4 \times 2.31^H + 2 \times 15.9^C + 1 \times 6.11^O = 47.2 \qquad [2]$$

where[31] H = 2.31 is the atomic diffusion volume increment for hydrogen; C = 15.9 is the atomic diffusion volume increment for carbon; O = 6.11 is the atomic diffusion volume increment for oxygen.

The method does not distinguish between keto and enol isomers. The diffusion coefficient of acetaldehyde at 25°C and 1 atm (1.01 bar) is:

$$D_{Air\text{-}Acetaldehyde} = \frac{0.00143 \times 298^{1.75}}{1.01 \times [2 \times (1/29.0 + 1/44.1)^{-1}]^{1/2} \times [19.7^{1/3} + 47.2^{1/3}]^2}$$

$$= \frac{30.56}{1.01 \times 5.92 \times 39.8} = \frac{30.56}{238.02} = 0.128\ (cm^2/sec) \qquad [3]$$

The theoretical sampling constant k is implicated in Fick's first law of diffusion as shown in equation (4) in its form for a cylindrical open tube:[32]

$$dm/dt = (D_{AB}\ A/L)(c_{air} - c_{surf}) = k(c_{air} - c_{surf}) \qquad [4]$$

where dm/dt is the steady state mass sampling rate or mass transfer rate, weight/time; A is the effective cross-sectional area of the sampling element, cm^2; L is the effective path length where diffusion control prevails to the sampling element from the exposing atmosphere, cm; c_{air} is the air concentration of the analyte, weight/cm^3; c_{surf} is the air concentration of analyte just above the sampling surface in the same units as c_{air}; k is the sampling constant of the analyte equal to $(D_{AB}\ A/L)$, cm^3/time.

For the present sampler, A/L is $(\frac{1.3}{2})^2 \times \pi \times \frac{1}{1.1} = 1.2$ cm.

Reaction Efficiency/O-Oxime Recovery for Wet Spiking of Aldehyde

Liquid aldehydes equivalent to two times the PEL-8 hour mass as determined from the theoretical sampling constant (or

two times the STEL-15 min) were spiked on methanol on to the pellets. The spiked pellet was held overnight in a desiccator containing Drierite to allow the methanol to evaporate before desorption with 2.0 mL hexane at room temperature over 2 hours with 30 seconds of ultrasonication at every half-hour before analysis by GC/MS or GC/ECD using synthesized aldehyde oximes of known purity.

Face Velocity, Relative Humidity, Temperature, and Capacity

For all experiments, the face velocities were above 0.10 m/s (20 fpm), the critical face velocity of the sampler[29] while the range of face velocities encountered in a typical workplace is above 0.10 m/s.[22] The relative humidity (RH) was 3 ± 1%, that is, no humidification was done. The temperature was 22 ± 1°C. All data were corrected to 25°C and 1 atmosphere pressure. All saturation capacities were determined through liquid aldehyde spiking in methanol, the O-oxime desorbed by hexane, and quantification by GC/MS or GC/ECD. The vapor capacities were not done here since liquid spiking and vapor spiking had the same aldehyde saturation capacity.[29]

Vapor Exposures

The ppm-hour levels of exposure were equivalent to 0, 0.5,1 and 2 times the PEL for 8 hours, or 15 min for the STEL. Dynamic sampling at 50 mL/min flow rate was utilized as a reference method after its sampling efficiency was evaluated for each aldehyde using the static gas bag method.[19] The O-oxime was desorbed with hexane, and quantified by GC/MS or GC/ECD. The moles desorbed was plotted against (μmole/mL) × min.

Statistics

All internal comparisons were subjected to analysis of variance (ANOVA) types I and II to detect significant differences at $p < 0.05$ and significant interactions.[33]

RESULTS

Table I shows the results of O-oxime syntheses in terms of GC/MS purities, raw reaction yields, and yields corrected for purities. GC/MS purities correct for the presence of pentafluorobenzaldehyde, pentafluorobenzyl alcohol, and excess PFBHA in the O-oximes.[34] All purities exceeded 92 percent. The corrected reaction yields are based on the assumed 1:1 stoichiometry except for glutaraldehyde (1:2). All yields exceeded 81 percent. Average percent purities/reaction yields were 95.8 ± 2.5/91.1 ± 2.3, respectively. The E- and Z-isomers had the same molecular ion and fragmentation pattern, though different retention times.[34] No monoaldehyde derivative was isolatable for glutaraldehyde even when aldehyde was rate limiting.

Table II shows the results of reaction efficiency/O-oxime recovery for wet spiking of aldehydes, quantifying by pure O-oxime standards. The results for acrolein and valeraldehyde are also included for comparison.[19] Desorption efficiencies for spiked O-oximes were not done because there was no significant difference between O-oxime spiking desorption efficiencies and wet aldehyde spiking recoveries from previous work.[29] The results of dynamic sampling for known gas bag vapor concentrations are also shown in Table II relative to pure O-oxime standards. Although the wet spiking recoveries always exceeded 89 percent for all compounds (mean ± SD: 99.8 ± 6.5 percent), only the monoaldehydes had vapor sampling efficiencies > 85 percent.

TABLE I
GC/MS purity and yield results for aldehyde O-oxime syntheses

	GC/MS purity (%)	Raw yield (%)	Yield corrected for purity (%)
Acetaldehyde	99.5 ± 2.5	90.0 ± 2.0	89.6 ± 2.3
Chloroacetaldehyde	96.0 ± 1.2	91.7 ± 1.2	88.0 ± 1.1
Crotonaldehyde	96.6 ± 2.2	91.2 ± 2.6	88.1 ± 2.0
Formaldehyde	93.2 ± 1.4	90.5 ± 2.3	84.3 ± 1.3
Furfural	97.0 ± 1.2	95.0 ± 2.1	92.2 ± 1.1
Glutaraldehyde	92.7 ± 3.2[a]	88.0 ± 2.5[a]	81.6 ± 2.8
Average	95.8 ± 2.5	91.1 ± 2.3	87.3 ± 3.8

[a] Di-substituted glutaraldehyde-PFBHA oxime.

Figures 3 and 4 show the saturation profiles of the collection element in terms of moles of aldehyde collected backcalculated from moles of O-oximes quantified versus moles of aldehydes expected (equation [4]). As for valeraldehyde and acrolein,[29] the capacities for monoaldehydes were 30–40 μmol. Glutaraldehyde capacity was 10–15 μmol. Thus, the moles of exposure to aldehyde that the sampler accommodated must not approach 30 μmol for $30 \times 10^{-6} \times 6.0234 \times 10^{23} = 1.8 \times 10^{19}$ total carbonyl groups.

TABLE II
Efficiencies from wet spiking and dynamic sampling in terms of O-oxime recovered relative to pure O-oxime standards

	Wet spiking (%)	Dynamic sampling (%)
Acetaldehyde	96.3 ± 3.2	93.0 ± 3.6
Acrolein[a]	99.0 ± 6.0	86.0 ± 5.0
Chloroacetaldehyde	112.7 ± 4.6	114.6 ± 2.5
Crotonaldehyde	101.3 ± 7.9	115.8 ± 3.6
Formaldehyde	99.9 ± 9.8	107.5 ± 4.6
Furfural	89.3 ± 3.4	94.4 ± 7.9
Glutaraldehyde	100.9 ± 1.7	23.3 ± 2.6
Valeraldehyde[a]	99.0 ± 3.0	85.0 ± 2.0
Average ± SD	99.8 ± 6.5[b]	100.0 ± 13[b]

[a] Reference 19.
[b] Without glutaraldehyde.

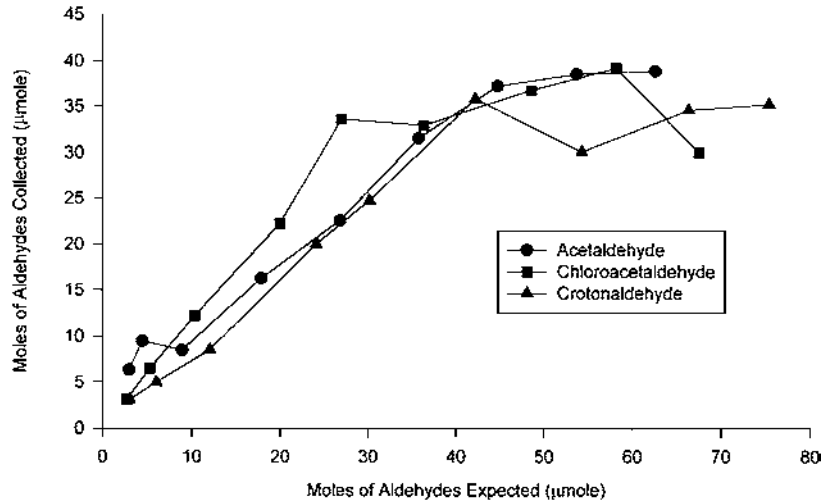

FIGURE 3
Wet spiking capacity tests for acetaldehyde, chloroacetaldehyde, and crotonaldehyde.

Table III shows the results of linear regressions of the aldehyde vapor moles collected versus aldehyde concentration × time curves. The slope is the experimental sampling sampler constant k (equation [4]). Table IV gives the theoretical D and the theoretical k at 25°C and 1 atmosphere from equations (1) and (4). Table IV also shows the experimental k, the experimental D, and sampling efficiencies relative to theoretical.

DISCUSSION

Face velocity, intermittent exposure, temperature, and RH are all important factors which might affect passive sampler performance. These factors were not tested in this research because valeraldehyde and acrolein sampling, which represents the opposite extremes of the PELs, was not affected.[29]

Previous dynamic sampling showed that the absolute recovery for valeraldehyde vapor varied with flow rate, 10 mL/min being better (100 percent) than 50 mL/min (71–85 percent).[19] Flow rate dependence may explain why the sampling efficiency of the passive sampler (79.1 percent relative to equation [4]) was much higher than that for dynamic sampling (23.3 percent at 35 mL/min) for glutaraldehyde. The contact and reaction times were important for the dynamic sampler but not for the passive sampler.

The efficiencies relative to the theoretical sampling constants in Table IV were within ± 25% except for chloroacetaldehyde. Why the latter has a higher relative efficiency is unknown. There is no available experimental D for chloroacetaldehyde. Therefore, experimental sampling rates have to be determined for all

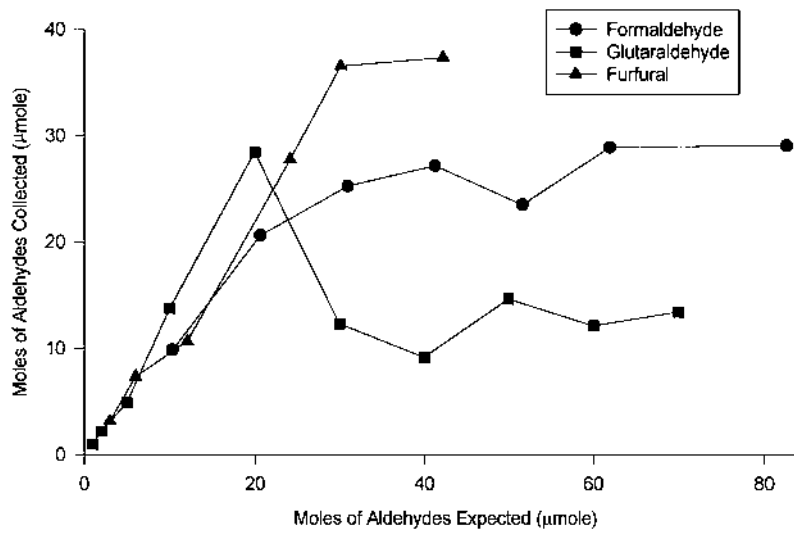

FIGURE 4
Wet spiking capacity tests for formaldehyde, furfural, and glutaraldehyde.

TABLE III
Experimental sampling rates for aldehyde vapor exposures

$$\underset{(\mu\text{mole/mL})\times\text{ min}}{\text{Conc.}\times\text{ time}} = \text{k}\times\underset{\mu\text{mole}}{\text{moles collected}}^{a,b} + \text{B}$$

	k[d] Sampling rate (mL/min)	B (intercept) (μmole/mL) × min	R^2	P
Acetaldhehyde	8.86 ± 0.38	0.02 ± 0.19	0.9963	< 0.005
Acrolein[c]	7.73 ± 0.57	0.04 ± 0.12	0.9936	< 0.005
Chloroacetaldehyde	11.69 ± 0.32	− 0.00036 ± 0.00060	0.9985	< 0.001
Crotonaldehyde	7.85 ± 0.19	0.0074 ± 0.0094	0.9988	< 0.001
Formaldehyde	9.97 ± 0.055	0.05 ± 0.20	0.9999	< 0.001
Furfural	6.47 ± 0.42	0.003 ± 0.011	0.9918	< 0.005
Glutaraldehyde	4.46 ± 0.15	0.15 ± 0.16	0.9978	< 0.005
Valeraldehyde[c]	4.43 ± 0.19	0.047 ± 0.077	0.9992	< 0.001

[a] Moles.
[b] Assumed 100 percent reaction efficiency.
[c] Data from reference 29.
[d] k is defined in equation (4).

vapors of interest because theoretical results are not completely predictive.

The major alternative passive air sampler based on DNPH has been validated for formaldehyde, acetaldehyde, and glutaraldehyde.[25,35,36] The experimental D from the DNPH method and the present PFBHA method for formaldehyde, acetaldehyde, and glutaraldehyde are compared in Table V. There were two different sampler designs for the DNPH method. GMD standard samplers (Hendersonville, Pennsylvania) were used for glutaraldehyde and acetaldehyde sampling, and a filter cassette with a coated 37-mm-diameter filter was used for formaldehyde. The latter accounts for why the theoretical sampling constant for formaldehyde was much higher than the DNPH sampling constants for acetaldehyde and glutaraldehyde. There was no statistical difference at $\alpha = 0.005$ between experimental D values of the same aldehydes for the DNPH and PFBHA methods. This confers credibility to the D values of the other aldehydes.

The DNPH method requires HPLC for analysis which does not distinguish α-hydroxy-carbonyls and the corresponding dicarbonyls like glycolaldehyde/glyoxal, and hydroxyacetone/methylglyoxal, and similar carbonyls such as acrolein, acetone, and propanal. Little attention had been paid to the factors that affect HPLC hydrazone analysis until recently.[37] The absorption spectra vary with pH. Stopped flow HPLC spectra often differ from those of acidified or basic standards, the spectra also varying with the amount of DPNH in standards.[37] There is a pronounced temperature dependence.[37] In addition, the DNPH passive sampler for glutaraldehyde showed a significant temperature effect (lower uptake rate at 12°C and a significantly higher

TABLE IV
Theoretical and experimental sampling constants, diffusion coefficients and relative efficiencies

	Theoretical diffusion coefficient cm^2/sec	Theoretical sampling constant cm^3/min	Experimental diffusion coefficient cm^2/sec	Experimental sampling constant cm^3/min	Relative efficiency[a] (%)
Acetaldehyde	0.128	9.27 ± 0.70	0.1224 ± 0.0052	8.86 ± 0.38	95.6 ± 4.1
Acrolein[b]	0.108	7.84 ± 0.61	0.1067 ± 0.0079	7.73 ± 0.57	98.6 ± 7.3
Chloroacetaldehyde	0.101	7.31 ± 0.55	0.1614 ± 0.0044	11.69 ± 0.32	159.9 ± 4.4
Crotonaldehyde	0.092	6.66 ± 0.50	0.1084 ± 0.0026	7.85 ± 0.19	117.9 ± 2.9
Formaldehyde	0.168	12.16 ± 0.91	0.1377 ± 0.0076	9.97 ± 0.055	81.99 ± 0.45
Furfural	0.083	6.01 ± 0.45	0.0894 ± 0.0058	6.47 ± 0.42	107.7 ± 7.0
Glutaraldehyde	0.078	5.64 ± 0.42	0.0616 ± 0.0079	4.46 ± 0.15	79.1 ± 2.7
Valeraldehyde[b]	0.083	5.95 ± 0.39	0.0612 ± 0.0026	4.43 ± 0.19	74.5 ± 3.2

[a] Relative efficiency (%) = $\frac{\text{experimental sampling constant}}{\text{theoretical sampling constant from equation (4)}} \times 100\%$.
[b] Data from reference 19.

TABLE V
Experimental diffusion coefficients for DNPH and PFBHA methods

	Acetaldehyde		Formaldehyde		Glutaraldehyde	
	DNPH[a]	PFBHA	DNPH[b]	PFBHA	DNPH[c]	PFBHA
Theoretical D[d] (cm^2/sec)	0.123	0.128	0.16	0.168	0.0718	0.078
Theoretical k[e] (cm^3/min)	19.4	9.27 ± 0.70	68	12.16 ± 0.91	13.4	5.64 ± 0.42
Experimental D (cm^2/sec)	0.1084 ± 0.0069	0.1224 ± 0.0052	0.1435 ± 0.0071	0.1377 ± 0.0076	0.0647 ± 0.0082	0.0616 ± 0.0079
Experimental k (cm^3/min)	17.1 ± 1.1	8.86 ± 0.38	61 ± 3	9.970 ± 0.055	11.8 ± 1.5	4.46 ± 0.15

[a] Data from reference 35.
[b] Data from reference 25.
[c] Data from reference 36.
[d] Diffusion coefficient.
[e] Sampling constant.

uptake at 40°C, about 1.5%/°C),[36] even though temperature has no effect on the PFBHA method.[29]

Ozone also interferes with the DNPH-coated silica gel air sampler reaction with air formaldehyde.[38] In contrast, greater sensitivity and resolution are possible for GC/MS and GC/ECD using PFBHA O-oxime derivatives because of the five fluorine atoms in the molecule,[39] thus allowing unknowns to be identified more easily than through the less sensitive liquid chromatography/MS method.[21,40] In addition, reaction efficiencies decrease for dry air relative to humid air for the dynamic DNPH sampling method using coated C_{18} reverse phase cartridges.[26] The latter effect is not shown by Tenax GC- or Tenax TA-coated solid sorbents used in the dynamic[19] or passive sampling modes.[29] Another advantage is the lower detection limit for the PFBHA method (110–200 pg for oxime derivatives)[19] relative to the DNPH method (about 400 ng).[41]

More research should be done on the effects of mixtures for the PFBHA method. In addition, effects of ketones, compounds that also contain a carbonyl group, should be understood because ketones might interfere.

ACKNOWLEDGMENTS

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