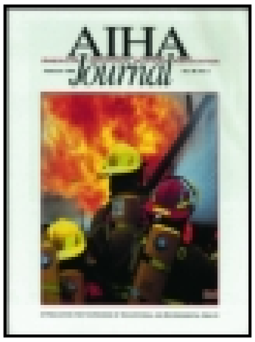

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A New Passive Sampler for Regulated Workplace Ketones

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A new solid sorbent passive air sampler for ketones has a silicone membrane atop a diffusion cylindrical path length of 1.1 cm and diameter 1.3 cm above a pellet of Tenax TA coated with 10% (w/w) O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride. Vapors of known concentrations approximating their workplace permissible exposure limits of Occupational Safety and Health Administration-regulated ketones at a relative humidity (RH) of 3 ± 1% were generated by a syringe pump connected to a dynamic air dilution system connected to an exposure chamber that allowed measurement of face velocities, temperatures, exposing vapor concentrations, and RHs. The O-oxime derivative was desorbed with hexane, and an aliquot injected for gas chromatographic analysis on a nonpolar capillary column by mass spectrometric or electron capture detection. The experimental passive sampler sampling rates in milliliters per minute at 25°C were 4.07 ± 0.49, cyclohexanone; 6.30 ± 0.59, diethyl ketone; 6.31 ± 0.31, ethyl n-butyl ketone; 3.78 ± 0.25, methyl n-amyl ketone; 3.43 ± 0.19, methyl n-butyl ketone; 6.48 ± 0.64, methyl ethyl ketone; 4.37 ± 0.43, methyl isopropyl ketone; and 4.57 ± 0.17, methyl n-propyl ketone. These preliminary data show that sterically unhindered ketones can be sampled by the passive sampler as well as aldehydes.

Keywords: adsorption, gas chromatography, ketone, oxime, passive sampler, personal sampling

Ketones (R_1-(C=O)-R_2, where R_1 and R_2 are alkyl, aromatic, or alicyclic functional groups) are widely used industrial chemicals. They are used as solvents, chemical intermediates, cleaning fluids, dewaxers, and reaction enhancers, as well as in paints, hydraulic fluids, cleaning fluids, inks, pharmaceuticals, cosmetics, and dopes.(1,2) Ketones are also environmental products of photooxidation. For example, methyl ethyl ketone can be produced in outdoor air by the photooxidation of such air pollutants as butane and other hydrocarbons.(3) Methyl ethyl ketone also has been found in drinking water and surface waters.(4) Commercially important ketones include acetone, diacetone, methyl ethyl ketone, methyl n-propyl ketone, and methyl isobutyl ketone.(2) Ketones are mucous membrane irritants, but are not as potent as their closely related aldehyde analogs of the same number of carbon atoms. Ketones dehydrate the skin on contact. Overexposure can cause narcosis, headache, nausea, light-headedness, dizziness, and incoordination. Methyl n-butyl ketone is oxidized to the same neurotoxic metabolite (2,4-hexanedione) as is n-hexane, and peripheral and central neuropathy are caused in rats after 8-hr/d time-weighted average (TWA) exposure to 1300 ppm.(2)

Methods to sample ketone vapors usually involve dynamic air sampling with solid sorbents.(5) The National Institute for Occupational Safety and Health recommends several methods such as charcoal tube sampling for acetone, cyclohexanone, diisobutyl ketone, 2-hexanone, methyl isobutyl ketone, and 2-pentanone.(6) However, CS_2 desorption of the more nonpolar ketones on charcoal tubes is inefficient. A desorbing mixture of 1% methanol in CS_2 improves desorption of camphor, mesityl oxide, 5-methyl-3-heptanone, methyl-(n-amyl) ketone, and ethyl butyl ketone.(7) Methyl ethyl ketone is sampled on beaded carbon before desorption by CS_2.(8) 2-, 3-, and 4- methyl cyclohexanone are sampled on Porapak Q, desorbed with acetone, and analyzed by gas chromatography (GC).(9) Thermal desorption from graphitized carbon and carbon molecular sieves is used for parts-per-billion concentrations of ketone vapors.(10)

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The 2,4-dinitrophenylhydrazine (2,4-DNPH) solid sorbent method is recommended by the U.S. Environmental Protection Agency(3) to determine aldehydes and ketones in ambient air. The 2,4-DNPH method potentially allows relatively selective quantitation of different aldehydes and ketones through high-performance liquid chromatography (HPLC)/ultraviolet (UV) detection of their hydrazones but not by GC, since many hydrazones decompose at high temperatures. 2,4-DNPH does not react quantitatively with conjugated aliphatic aldehydes, can be light sensitive, shows RH dependence, and variable recoveries occur for liquid spiking.(5)

The advantages of passive samplers(11) include lower cost and greater wearer acceptability as no bulky, expensive pumps are required. Some passive samplers have been developed for the lower molecular weight aldehydes and ketones based on liquid systems.(12,13) Passive sampling based on solid sorbents coated with 2,4-DNPH is available.(14–17)

O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) has been used to analyze aldehydes in water because of its fast quantitative reaction to form O-oximes suitable for detection at the picogram (pg) level by GC/mass spectrometry (GC/MS) and GC/electron capture detection (GC/ECD).(18) The PFBHA method also has been used to chemisorb aldehyde vapors by dynamic sampling(19,20) and passive sampling.(21,22) Neither method is influenced by relative humidity (RH), temperature, intermittent sampling, shelf life for at least 3 months, or sample stability for at least 6 months. The aldehyde passive sampling method now has been extended to the major regulated positive interferences, the ketones.

EXPERIMENTAL METHODS

Materials

The ketones (from Aldrich, Milwaukee, Wis.) were cyclohexanone (99.8%); diethyl ketone or 3-pentanone (99+%); n-butyl ethyl ketone or 3-heptanone (98%); methyl n-amyl ketone or 2-heptanone (98%); methyl n-butyl ketone or 2-hexanone (98%); methyl ethyl ketone or 2-butanone (99+%); methyl isopropyl ketone or 3-methyl 2-butanone (99%); and methyl n-propyl ketone or 2-pentanone (99.5%). The internal standard, decafluorobiphenyl (99%), was also from Aldrich. Hexane (Optima), methanol (Optima), nitric acid, activated charcoal, molecular sieves, and indicating Drierite were from Fisher Scientific (Tustin, Calif.). PFBHA was from Lancaster Laboratories (Lancaster, Pa.). Tenax TA (80/100 mesh) was from Alltech Associates (Deerfield, Ill.). Helium, nitrogen, and 5% methane/argon, all chromatographic grade, were from Alphagaz (Los Angeles, Calif.).

Equipment

Pyrex tubing; Pyrex glass wool; 4-mL Kimble vials with PTFE-lined screw caps; 10-μL Hamilton syringes; gas-tight Hamilton syringes; Soxlett-extraction apparatus; a Parr 2811 bench manual pellet press; 3M Model 3500 OVM passive sampler; Bel-Art clear polycarbonate vacuum desiccator that served as exposure chamber; calibrated temperature/RH meter/recorder; hot/cold hair dryer; a Thermolyne Series 5000 carbon dioxide incubator for elevated temperature experiments; and Harvard syringe pumps (model 11) were from Fisher Scientific. Personal sampling pumps, rotameters, and Tedlar gas bags were from SKC West (Fullerton, Calif.). A Whatman Zero Air generator was from Balston (Haverhill, Mass.). A M-5 Mini-Buck calibrator for flow rate measurement was from Buck Scientific (East Norwalk, Conn.). A Goldstar Multiwave shelf microwave oven for O-oxime syntheses was from Circuit City (Westwood, Calif.). A small box desk air fan connected to a variac to generate constant face velocities in the exposure chamber was from Tekna Design (Rockford Mich.).

GC/MS was done with a Hewlett-Packard 5890 gas chromatograph (Hewlett-Packard, Palo Alto, Calif.) equipped with a 30-m × 0.32-mm i.d. 1 μm film DB-1701 chemically bonded fused-silica capillary column. The temperature for the injector and link was 250°C. The column temperature program 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. The Hewlett-Packard 5988A quadrupole mass spectrometer had an electron multiplier detector, and the 70 eV ion source temperature was 260°C. Selective ion monitoring (SIM) used m/z 181 and total ion monitoring (TIC) m/z utilized 50–500. The areas of both E- and Z-isomers were utilized for quantitations for asymmetric ketones.

The same column and temperature conditions were used for Hewlett-Packard 5890 capillary GC/^{63}Ni ECD with 5% methane/argon flow of 3.0 ± 0.4 mL/min. The detector temperature was 250°C. The signal was visualized with a Hewlett-Packard 3396 integrator.

Methods

A 13 mm diameter and 0.3 cm thick pellet of PFBHA coated Tenax GC (10%, w/w) was made by the hand press, after the coating and drying procedure described elsewhere.(21) The sampler utilized the silicone membrane, badge body, and badge clip unchanged from the 3M Model 3500 OVM sampler.(21) The pellet was placed into a Teflon-lined screw cap of dimensions 18-mm o.d., 14-mm i.d., internal depth 14 mm, and outer height 16 mm. The three-pronged inner stay of the 3M sampler was cut to allow the pellet to be held securely by one of its prongs. The 3M silicone membrane and then a 10-μm Teflon filter of the same diameter were placed over it and both fixed tightly over the cap with an aluminum seal via a crimper. The screw cap was secured centrally to the bottom of the empty 3M badge body by a small piece of duct tape. The whole sampler was wrapped in aluminum foil (shiny side out) until sampling, which was initiated by removing the foil. The diffusion path length was 1.1 cm (Figure 1). The vapor generator, air dilution system, and exposure chamber (Figure 2) are described in detail elsewhere.(21,22) The air generator was connected to the vapor and water generation sites to provide constant defined flow rates. Vapor generators were syringe pumps set at known plunger velocities to produce the desired concentration of organic vapor for dilution, or water vapor for RH. 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, and the outlet connected by Teflon tubing to a Greenburg-Smith impinger, which acted as a mixing chamber. Teflon tubing then conveyed the diluted organic vapor into the exposure chamber through a hole bored on the side near the chamber bottom to just underneath the fan blades, the fan resting at the bottom of the chamber and under the ceramic metal plate. Six samplers were set horizontally on the plate each with a nearby closable hole in the chamber wall for probe insertion for measurement of RH, temperature, organic vapor concentration, simultaneous dynamic sampling(23) using Tenax TA coated with 20% PFBHA,(19) and face velocity.

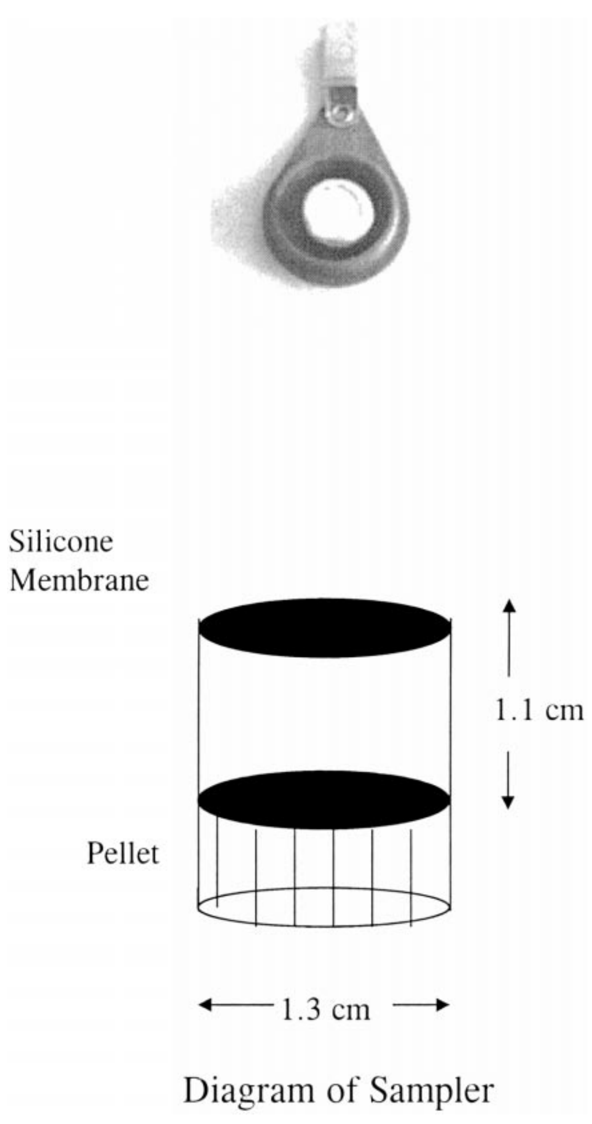

FIGURE 1. Cross section of the PFBHA passive sampler

Synthesis of PFBHA O-Oximes

The PFBHA O-oximes are not commercially available. They were synthesized by methods detailed elsewhere.(24) The major difference in the synthetic method for the ketones relative to the aldehydes(19,22,23) was to allow the reacted solution to cool to room temperature gradually rather than by ice bath cooling. This procedure increased ketone O-oxime yields.(24)

Ketone Diffusion Coefficients and Sampling Constants

The dependence of the diffusion constant on molecular weight and temperature is expressed through Equation 1:(25)

$$D_{AB} = \frac{0.00143 \times T^{1.75}}{PM_{AB}^{1/2} \cdot \left[\left(\sum_{V}\right)_{A}^{1/3} + \left(\sum_{V}\right)_{B}^{1/3}\right]^{2}} \tag{1}$$

where D_{AB} is the binary diffusion coefficient of analyte in air in cm²/sec 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

Σ_v is the summation of atomic diffusion volumes, unitless

i is all the contributing species

A is air

B is the analyte.

The molecular diffusion volume of air is 19.7.(26)

For example, the Σ_v, for cyclohexanone, $H_{10}C_6O$, is calculated as:

$$\left(\sum_{V}\right)_{H_{10}C_6O} = 10 \times 2.31^{H} + 6 \times 15.9^{C} + 1 \times 6.11^{O} = 124.61 \tag{2}$$

where 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

Then, the diffusion coefficient of cyclohexanone at 25°C and 1 atm (1.01 bar) is

$$\begin{aligned} D_{\text{Air-Cyclohexanone}} &= 0.00143 \times 298^{1.75} \\ &\quad \div \{1.01 \times [2 \times (1/28.8 + 1/98.14)^{-1}]^{1/2} \\ &\quad \times [19.7^{1/3} + 124.61^{1/3}]^{2}\} \\ &= 0.0766 \text{ cm}^2/\text{sec} \end{aligned} \tag{3}$$

The theoretical sampling constant k is in Fick's first law of diffusion as shown in Equation 4 in its form for a cylindrical open tube:(26)

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

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, cm²

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/cm³

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, (D_{AB} A/L), cm³/time

For the sampler, A/L is $(1.3/2)^2 \times \pi \times 1/1.1 = 1.2$ cm. Therefore, the sampling constant k for cyclohexanone is

$$k = D_{AB}A/L = 1.2\, D_{AB} = 0.092 \text{ cm}^3/\text{sec}$$

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

Liquid ketone equivalent to two times the permissible exposure level (PEL)-8 hour mass as determined from the theoretical sampling constant was spiked with 50 μL of methanol solution. The spiked pellet was held overnight in a desiccator containing Drierite to allow the methanol to dry before desorption with 2.0 mL hexane at room temperature over 2 hours with 30 sec of ultrasonication at every half-hour before analysis by GC/MS or GC/ECD using synthesized aldehyde O-oximes of known purity.

Face Velocity, RH, and Temperature

For all experiments, the face velocities were above 20 ft/min (0.10 m/sec), the critical face velocity.(21) The range of face velocities in

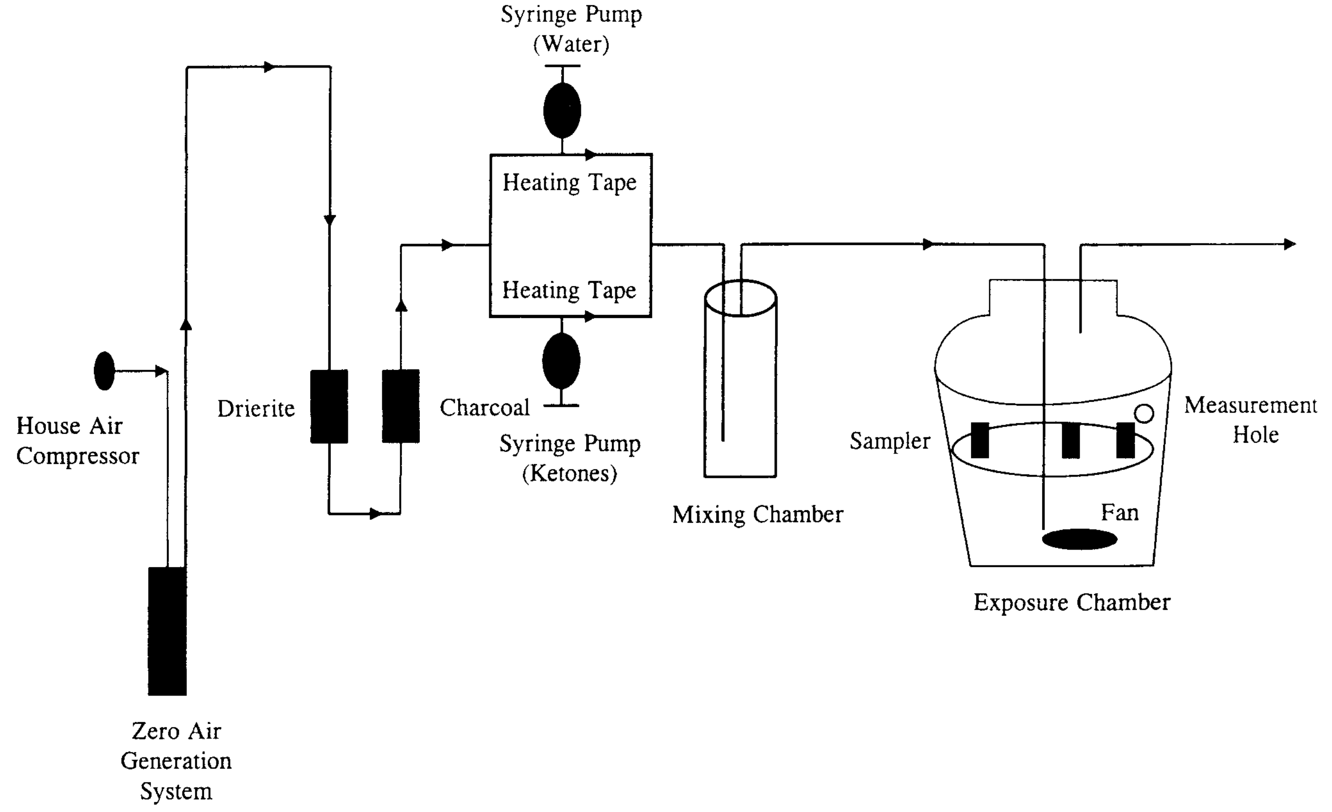

FIGURE 2. Ketone vapor generation and exposure chamber system

a typical workplace is from 20–30 ft/min.(11) The RH was 3 ±1%, and the temperature was 22 ± 1°C. The low RH and the single temperature were selected because previous work with the aldehydes acrolein and n-valeraldehyde had shown no dependence of sampling constants on RH and temperature.(21) All data were corrected to 25°C and 1 atmosphere pressure using the ideal gas law and observed temperatures and atmospheric pressures.

Vapor Exposures

The ppm-hour levels of exposure for dynamic and passive sampling were equivalent to 0, 0.5, 1.0, and 2.0 times the PEL for 8 hours. Previous work showed that the absolute recovery for valeraldehyde vapor in the dynamic method varied with flow rate, 10 mL/min being better (efficiency of about 100%) than 50 mL/min (efficiency 71–85%).(19–21) Therefore, the flow rate for sampling pumps in the dynamic sampling method was set at 10 mL/min because the contact and reaction times were expected to be important for the dynamic sampler for ketones. The dynamic sampling technique was utilized as the reference method after its sampling efficiency was determined for each ketone using the static gas bag method. This entailed injecting a known volume of liquid ketone into the Tedlar gas bag containing a known volume of pure or prehumidified air, desorbing with hexane, and then GC/ECD or GC/MS analysis, as described at length in Reference 19.

Previous passive sampling work with the aldehydes acrolein and n-valeraldehyde had shown that exposures to threshold limit value-TWA concentrations for 8 hours were equivalent to parts-per-million/hour exposures for 1-hour exposures using three different intermittent exposure regimens over 8 hours (eight times the target concentration for 1 hour, the same followed by 7 hours of exposure to pure air, or three 1-hour exposures separated by two 1-hour exposures to pure air). Thus, the concentrations used for each ketone were at 0, 4, 8, and 16 times the appropriate PEL for 1-hour exposures to obtain the desired parts-per-million/hour exposure doses and to obtain K values.

The O-oxime in the pellet was desorbed with 2 mL hexane for 2 hours, and analyzed by GC/MS or GC/ECD on injection of 2 μL. The μmoles desorbed corrected for desorption efficiency were plotted against (μmole/mL) × min to provide k as the slope of the linear regression line from the four concentrations generated for each ketone.

Statistics

All internal comparisons were subjected to analysis of variance types I and II to detect significant differences at $p \leq 0.05$ and significant interactions.(27) Linear regression analyses included calculation of standard deviations of the slopes and intercepts.

RESULTS

Table I shows the yields for O-oxime syntheses corrected for GC/MS purities. The latter correct for the presence of pentafluorobenzaldehyde, pentafluorobenzyl alcohol, excess PFBHA in the O-oximes, any other aldehydes, and other peaks not attributable to the reagents and solvents.(23) All yields are greater than 97.8%, based on the 1:1 stoichiometry. The average purity was 98.40 ± 0.36%. Methyl isopropyl ketone yield exceeded 75% though that for diisobutyl ketone did not.(24)

Table I also shows the results of reaction efficiency/O-oxime

TABLE I. Efficiencies from Wet Syntheses, Wet Spikings, and Dynamic Sampling in Terms of O-Oxime Recovered

Ketone (OSHA PEL in ppm, Yield ± SD)	Wet Spiking (%)	Dynamic Sampling* (%) [ppm Sampled in 1 hr]
Cyclohexanone (50, 98.4 ± 1.6)	87.2 ± 7.0	95.5 ± 0.11 [198]
Deithyl ketone (200,[A] 98.91 ± 0.17)	91.1 ± 3.9	95.6 ± 8.5 [199]
Ethyl n-butyl ketone (50, 98.3 ± 2.8)	98.0 ± 3.2	97.9 ± 3.2 [51]
Methyl n-amyl ketone (100, 98.7 ± 1.1)	93.3 ± 2.7	93.5 ± 4.5 [50]
Methyl n-butyl ketone (100, 98.67 ± 0.14)	107.0 ± 0.14	83.8 ± 4.1 [42]
Methyl ethyl ketone (200, 97.8 ±1.4)	90.0 ± 4.0	100.1 ± 6.7 [197]
Methyl isopropyl ketone (200, 98.33 ± 0.36)	92.8 ± 5.6	78.9 ± 4.8 [200]
Methyl n-propyl ketone (200, 98.1 ± 1.3)	92.5 ± 2.6	83.8 ± 4.3 [198]
Average (NA, 98.4 ± 0.36)	93.9 ± 6.1	91.1 ± 7.8

Source: Reference 34.

[A] No OSHA PEL: 1998 ACGIH TLV-TWA.

Notes: NA = not applicable. The ± quantities are standard deviations for n = 3. Yields are relative to 1:1 stoichiometry, and correct for GC/MS purities.

recovery for wet and vapor spiking of ketones relative to pure PFBHA-ketone standards. The lowest wet spiking efficiency was shown by cyclohexanone at 87%, which also had the highest coefficient of variation of 8.0%. The results are similar to those previously observed for aldehydes, in which no significant statistical difference at $p \leq 0.05$ was observed between O-oxime standard curve analysis and wet aldehyde spiking.(21) The detection limits for each O-oxime were between 110–200 pg at two times the background for ECD.

The results of dynamic sampling for known gas bag vapor concentrations at a flow rate 10 mL/min also are shown in Table I. Vapor sampling efficiencies all exceeded 78.9%. The vapor spiking recoveries lower than for wet spiking at $p \leq 0.05$ were for n-butyl ketone, methyl isopropyl ketone, and methyl n-propyl ketone, with the lowest recovery being for methyl isopropyl ketone. Acetone, with its PEL of 1000 ppm, exceeded the capacity of the sampler, though it produced O-oxime derivatives efficiently by wet chemistry.(24)

Table II shows the passive sampling constants k in Equation 4 from the results of linear regressions of the ketone vapor moles collected for four concentrations versus the ketone concentration × time curves. The coefficient of variation of the slope was $<10\%$ for all ketones except cyclohexanone, for which it was 12%. No intercepts were significantly different from zero at $p \leq 0.05$ except for diethyl- and methyl ethyl-ketones. Thus, only the latter two ketones do not obey a Henry-type law over the parts-per-million/hour range investigated.

Table II also provides the theoretical D and k values at 25°C and 1 atm from Equations 2 and 4, respectively, in addition to the experimental D, and to the sampling efficiencies relative to theoretical efficiencies (Equations 2 and 4). Whereas diethyl-, ethyl n-butyl-, and methyl ethyl-ketones did not give D values different from theoretical values, those for cyclohexanone and methyl n-amyl-, methyl isopropyl-, and methyl n-propyl-ketones gave experimental values between 73–77% of those predicted. The experimental value for methyl n-butyl ketone was about 63% of that predicted. Except for methyl n-butyl ketone, all the experimental sampling constants for ketones tested were within ±25% of the theoretical sampling constants. Why ethyl n-butyl ketone has a higher relative efficiency is unknown. Therefore, D values must be verified experimentally.

DISCUSSION AND CONCLUSION

The average experimental D relative to theoretical D from Equation 4 (Table II) for all the eight ketones studied was 86 ± 21%, compared with 102 ± 28% for aldehydes.(22) This probably reflects steric effects in ketones during reaction because the aldehyde hydrogen is small relative to the second ketone alkyl group.

For example, diethyl ketone, methyl isopropyl ketone, and methyl n-propyl ketone were all $C_5H_{10}O$ with different carbon chain structures but with the same theoretical D. The propyl group caused lower relative efficiencies of between 74–77% (Table II), whereas diethyl ketone did not. The same behavior was observed in the dynamic sampling results. The methyl n-butyl ketone also had low relative efficiencies in dynamic (Table I) and passive sampling (Table II).

Ethyl n-butyl ketone and methyl n-amyl ketone were both $C_7H_{14}O$ with the latter causing a lower relative efficiency of 73–75% for passive sampling, which was not observed for dynamic sampling, the same being so for cyclohexanone.

The ketones selected here were relatively sterically unhindered, since it is known that when chain branching occurs at both carbons β- to the carbonyl carbon, even the wet chemistry synthesis is drastically inhibited for diisobutylketone and 2,4-hexanedione.(24) Nevertheless, the gas phase/solid phase recoveries are sufficiently high and precise to show that the PFBHA passive and dynamic samplers developed for aldehydes also will function well for these sterically unhindered ketones, and also confirms that the ketones may potentially act as positive interferences to aldehydes for this PFBHA air sampling method. Further work is required to assess the sampler for more sterically hindered ketones, and to confirm whether RH, temperature, and intermittent sampling effects are negligible as found for the aldehydes.

The major alternative passive air sampler based on DNPH has been validated for formaldehyde, acetaldehyde, and glutaraldehyde.(14,15,28,29) Little attention has been paid to the factors that affect 2,4-dinitrophenylhydrazone HPLC analysis until recently.(30) Ozone also is known to interfere with the DNPH-coated silica gel air sampler reaction with formaldehyde(31) in ambient air sampling. This remains to be tested for the present passive sampler. More sensitivity (110–200 pg) and selectivity (selective ion monitoring by GC/MS with m/z 181) are possible for GC/MS and GC/ECD using PFBHA O-oxime derivatives than with HPLC/UVD or liquid chromatography/mass spectrometry (LC/MS) for the DNPH method,(18,32,33) thus allowing unknowns to be better assigned and quantified. The five fluorine atoms in the PFBHA O-oximes allow sensitive screening GC/ECD.(18)

The advantages of a predominantly GC method over HPLC are many: There are many laboratories equipped with flame ionization detectors and ECD GCs, whereas HPLC entails much waste disposal, and LC/MS is still not as available as GC/MS. GC/MS allows for specific identification of carbonyl (e.g., aldehydes and ketones) derivatives within 30 min, whereas HPLC separation of O-oximes takes up to 120 min.(24)

TABLE II. Theoretical and Experimental Passive Sampling Constants

Ketone	Theoretical Diffusion Coefficient (cm^2/sec)	Theoretical Sampling Constant (cm^3/min)	Experimental Diffusion Coefficient (cm^2/sec)	Experimental Sampling Constant cm^3/min(r^2)	Relative Efficiency[A] (%)
Cyclohexanone	0.077	5.59 ± 0.43	0.0562 ± 0.0067	4.07 ± 0.49 (0.972)	73.1 ± 9.1
Diethyl ketone	0.082	5.97 ± 0.46	0.0869 ± 0.0081	6.30 ± 0.59 (0.983)	106 ± 11
Ethyl n-butyl ketone	0.069	5.03 ± 0.39	0.087 ± 0.0043	6.31 ± 0.31 (0.995)	126 ± 10
Methyl n-amyl ketone	0.069	5.03 ± 0.39	0.0521 ± 0.0034	3.78 ± 0.25 (0.992)	75.4 ± 6.7
Methyl n-butyl ketone	0.075	5.46 ± 0.42	0.0472 ± 0.0026	3.43 ± 0.19 (0.994)	63.1 ± 5.2
Methyl ethyl ketone	0.092	6.68 ± 0.51	0.0892 ± 0.0088	6.48 ± 0.64 (0.981)	97 ± 10
Methyl isopropyl ketone	0.082	5.97 ± 0.46	0.0601 ± 0.0059	4.37 ± 0.43 (0.981)	73.5 ± 7.9
Methyl n-propyl ketone	0.082	5.97 ± 0.46	0.0628 ± 0.0023	4.57 ± 0.17 (0.997)	76.8 ± 5.7

[A] Relative Efficiency (%) = [Experimental Sampling Constant/Theoretical Sampling Constant from equation (4)] × 100%.

The present study has shown that a passive sampler and a dynamic sampler at a flow rate of 10 mL/min for 1 hour designed for aldehydes with PELs up to 50 ppm also is adequate for sterically unhindered ketones with PELs up to 200 ppm. The results imply that acetone vapor TWA sampling is possible up to 200 ppm for 1 hour, though at 1000 ppm the capacity is exceeded.

REFERENCES

1. **Budavari, S. (ed.):** *The Merck Index,* 11th ed. Rahway, N.J.: Merck & Co., 1989.
2. **U.S. Department of Health, Education, and Welfare:** *Occupational Diseases: A Guide to Their Recognition*. Washington D.C.: U.S. Government Printing Office, 1977. pp. 185–193.
3. **U.S. Environmental Protection Agency (EPA):** *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* 2nd edition. Method TO-11A, EPA/625/R-96/010b. Cincinnati, Ohio: Center for Environmental Risk Information, Office of Research and Development, 1999.
4. **U.S. Environmental Protection Agency (EPA):** *Health Advisory for Methyl Ethyl Ketone*. Washington, D.C.: EPA, 1987.
5. **Otson, R., and Fellin, P.:** A review of techniques for measurement of airborne aldehydes. *Sci. Tot. Environ. 77*:95–131 (1988).
6. **National Institute for Occupational Safety and Health (NIOSH):** Ketones I (Method 1300). In *NIOSH Manual of Analytical Methods,* 4th ed. Cincinnati, Ohio: NIOSH, 1994.
7. **National Institute for Occupational Safety and Health (NIOSH):** Ketones II (Method 1301). In *NIOSH Manual of Analytical Methods,* 4th ed. Cincinnati, Ohio: NIOSH, 1994.
8. **National Institute for Occupational Safety and Health (NIOSH):** Methyl ethyl ketone (Method 2500). In *NIOSH Manual of Analytical Methods,* 4th ed. Cincinnati, Ohio: NIOSH, 1994.
9. **National Institute for Occupational Safety and Health (NIOSH):** Methylcyclohexanone (Method 2521). *NIOSH Manual of Analytical Methods,* 4th ed. Cincinnati, Ohio: NIOSH, 1994.
10. **National Institute for Occupational Safety and Health (NIOSH):** Volatile Organic Compounds (Screening) (Method 2549). *NIOSH Manual of Analytical Methods,* 4th ed. Cincinnati, Ohio: NIOSH, 1994.
11. **Cassinelli, M.E., R.D. Hull, J.V. Crable, et al.:** Protocol for the evaluation of passive monitors. In *Diffusive Sampling: An Alternative Approach to Workplace Air Sampling*. London: Royal Society of Chemistry, 1987. pp. 190–202.
12. **Kawai, T., T. Yasugi, Y. Uchida, et al.:** A personal diffusive sampler for occupational acetone vapor exposure monitoring. *Toxicol. Lett. 55*: 295–302 (1991).
13. **Kollman, J.R.:** Field evaluation of a diffusive sampler for monitoring formaldehyde in air: a comparison of methods. *Appl. Occup. Environ. Hyg. 9*:262–266 (1994).
14. **Levin, J.-O., K. Andersson, R. Lindahl, et al.:** Determination of sub-part-per-million levels of formaldehyde in air using active or passive sampling on 2,4-dinitrophenylhydrazine-coated glass fiber filters and high-performance liquid chromatography. *Anal. Chem. 57*:1032–1035 (1985).
15. **Levin, J.-O., and R. Lindahl:** Diffusive air sampling of reactive compounds: A review. *Analyst 119*:79–83 (1994).
16. **Mulik, J.D., R.G. Lewis, and W.A. McClenny:** Modification of a high efficiency passive sampler to determine nitrogen dioxide or formaldehyde in air. *Anal. Chem. 61*:187–189 (1989).
17. **Noble, J.S., C.R. Strang, and P.R. Michael:** A comparison of active and passive sampling devices for full-shift and short-term monitoring of formaldehyde. *Am. Ind. Hyg. Assoc. J. 54*:723–732 (1993).
18. **Cancilla, D.A., and S.S. Que Hee:** O-(2,3,4,5,6-pentafluorophenyl)methylhydroxylamine hydrochloride: a versatile reagent for the determination of carbonyl-containing compounds. *J. Chromatogr. 627*: 1–16 (1992).
19. **Wu, L.-J., and S.S. Que Hee:** A solid sorbent personal air sampling method for aldehydes. *Am Ind. Hyg. Assoc. J. 56*:362–367 (1995).
20. **Shen, Y., and S.S. Que Hee:** Optimization of a solid sorbent dynamic personal air sampling method for aldehydes. *Appl. Occup. Environ. Hyg. 15*:228–234 (2000).
21. **Tsai, S.W., and S.S. Que Hee:** A new passive sampler for aldehydes. *Am. Ind. Hyg. Assoc. J. 60*:463–473 (1999).
22. **Tsai, S.W., and S.S. Que Hee:** A new passive sampler for regulated workplace aldehydes. *Appl. Occup. Environ. Hyg. 14*:255–262 (1999).
23. **Cancilla, D.A., C.C. Chou, R. Barthel, and S.S. Que Hee:** Characterization of the O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBOA) derivatives of some aliphatic mono- and dialdehydes and quantitative water analysis of these aldehydes. *J. Assoc. Offic. Anal. Chem. Int. 75*:842–854 (1992).
24. **Wiesenthal, K., A. Jehlar, and S.S. Que Hee:** Synthesis of the O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine oximes of selected carbonyl compounds and their determination by liquid chromatography with ultraviolet detection. *J. Assoc. Offic. Anal. Chem. Int.* (Submitted)
25. **Reid, R.C., J.M. Prausnitz, and B.E. Poling:** Diffusion coefficients for binary gas systems at low pressures: Empirical correlations. In *The Properties of Gases and Liquids,* 4th ed. London: McGraw-Hill, 1988. pp. 586–589.
26. **Tompkins, F.C., Jr., and R.L. Goldsmith:** A new personal dosimeter for the monitoring of industrial pollutants. *Am. Ind. Hyg. Assoc. J. 38*:371–377 (1977).
27. **Snedecor, G.W., and W.G. Cochran:** *Statistical Methods,* 8th ed. Ames, Iowa: Iowa University Press, 1989.
28. **Lindahl, R., and J.-O. Levin:** Laboratory validation of a diffusive sampler for the determination of glutaraldehyde in air. *J. Chromatogr. A. 710*:175–180 (1995).
29. **Lindahl, R., J.-O. Levin, and M. Martensson:** Validation of a diffusive sampler for the determination of acetaldehyde in air. *Analyst 121*:1177–1181 (1996).

30. **Dasgupta, P.K., G. Zhang, S. Schulze, et al.:** Measurement of carbonyl compounds as the 2,4-dinitrophenylhydrazonate anion. Reaction mechanism and an automated measurement system. *Anal. Chem. 66*:1965–1970 (1994).
31. **Arnts, R.R., and S.B. Tejada:** 2,4-Dinitrophenylhydrazine-coated silica gel cartridge method for determination of formaldehyde in air: Identification of an ozone interference. *Environ. Sci. Technol. 23:* 1428–1430 (1989).
32. **Lacheur, R.M. et al.:** Identification of carbonyl compounds in environmental samples. Environ. Sci. Technol. *27*:2745–2753 (1993).
33. **Vairavamurthy, A., J.M. Roberts, and L. Newman:** Methods for determination of low molecular weight carbonyl compounds in the atmosphere: A review. *Atmos. Environ. 26A*:1965–1993 (1992).
34. **Lin, Y.-W, and S.S. Que Hee:** Regulated workplace ketones and their interference in the PFBHA method for aldehydes. *Appl. Occup. Environ. Hyg.* (In press)