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Evaluation of a Passive Sampler for Volatile Organic Compounds at ppb Concentrations, Varying Temperatures, and Humidities with 24-h Exposures. 2. Sampler Performance

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The performance of the 3M 3520 organic vapor monitor (OVM) as a tool for monitoring inhalation exposures to volatile organic compounds (VOCs) in nonoccupational community environments was evaluated by using combined controlled test atmospheres of benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, methylene chloride, styrene, tetrachloroethylene, and toluene. Eight OVMs were simultaneously exposed to concentrations of 10, 20, and 200 μg/m^3 in combination with temperatures of 10, 25, and 40 °C and relative humidities of 12, 50, and 90% for 24 h. The results of this study indicate that the performance of the 3520 OVM is compound-specific and depends on concentration, temperature, and humidity. With the exception of 1,3-butadiene under most conditions and styrene and methylene chloride at very high relative humidities, recoveries showed a negative bias as compared to calculated chamber concentrations but were generally within ±25% of theory, indicating that the 3520 OVM can be effectively used over the range of concentrations and environmental conditions tested with a 24-h sampling period. Increasing humidities resulted in increasing negative bias from full recovery. Reverse diffusion experiments conducted at 200 μg/m^3 and five temperature/humidity combinations indicated diffusion losses only for 1,3-butadiene, methylene chloride, and styrene under increased humidity conditions. The recovery rates reported in this study can be used for estimating measurement biases when using OVMs for indoor, outdoor, and personal air monitoring of VOCs in community environments.

Introduction

Because of their ease of use, passive dosimeters are attractive alternatives to active samplers for monitoring personal exposures to air contaminants in both occupational and community environments (*1*). Charcoal-based passive air samplers were originally developed for measuring worker exposure to volatile organic compounds (VOCs) at ppm concentrations with sampling times of 15 min−8 h. More recently, these samplers have been used for personal, indoor, and outdoor air monitoring of VOCs at ppb concentrations in community and office environments with sampling times ranging from 1 day to eight weeks (*2*−*10*).

There has been limited evaluation of the performance of passive air samplers at ppb concentrations of VOCs and the range of temperature and humidities found in community settings. Seifert et al. (*3*) tested two types of passive samplers, including the 3500 organic vapor monitor (OVM; 3M Company, St Paul, MN) in a dynamic chamber with a 2-week period of exposure to mixed atmospheres of benzene, toluene, *p*-xylene, *n*-hexane, *n*-heptane, and 1,1,1-trichloroethane but at a single concentration (temperature and humidty not reported), showing good recoveries. Cohen et al. (*11*) performed a chamber evaluation of the 3500 OVM with atmospheres of benzene, chloroform, 1,4-dichlorobenzene, heptane, and tetrachloroethylene at 10 and 100 μg/m^3 with 25% and 75% relative humidity (RH) and room temperature (actual temperature not reported) over a 21-day sampling period. The results indicated variable recoveries down to 20% depending on compound, concentration, and RH with no clearly interpretable patterns. Otson et al. (*12*) evaluated the 3500 OVM and the Pro-Tek model G-AA (E. I. Dupont de Nemours & Co., Wilmington, DE; no longer manufactured) in controlled test atmospheres of 10 VOCs at 50−5000 μg/m^3; 23−28 °C; 30−26%, 51−53%, and 90% RH; and 0.01, 0.05, and 1.8 m/s face velocities with 24-h exposure duration, reporting good agreement with parallel charcoal sampling independent of concentration, humidity, temperature, or face velocity, although some significant differences between experimentally derived sampling rates and those provided by 3M were noted. A later evaluation of the 3500 OVM by the same investigators using 16 other VOCs at 50, 250, 1000, and 5000 μg/m^3 in combination with 10, 25, and 36 °C and 20 and 90% RH also indicated recoveries of 90−110% as compared to charcoal tube sampling, with good precision. There were no effects observed from varying face velocity, while increasing temperature resulted in slightly increased sampling rates, and increasing humidity decreased them to some extent. Ullrich and Nagel (*14*) also tested the 3500 OVM for six VOCs with sampling periods from 2 days to 3 weeks at mixed concentrations of ∼1 to ∼20 μg/m^3 (no temperature or humidity were reported). The results indicated negative biases of −4 to −19% as compared with parallel active charcoal tube samples, except for benzene.

The previous studies show varying results in terms of OVM performance. In part, this may be due to the variability in experimental protocols. The present study reports the results of a comprehensive evaluation of the 3520 OVM (3M Company) with 24-h sampling. The 3520 OVM has two adsorbing charcoal pads, separated in the front and back sections of the dosimeter, with the back pad designed as a backup when the capacity of the front pad may be exceeded.

Methods

The target compounds were benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene (*p*-dichlorobenzene), methylene chloride (dichloromethane), styrene, tetrachloroethylene (perchloroethylene), and toluene. The experimental design of the evaluation was based on the National Institute for Occupational Safety and Health (NIOSH) protocol and criteria for evaluating the reliability of diffusion samplers (*15*). The rationale for selection of the target compounds and a detailed description of the dynamic chamber system especially constructed for this evaluation is

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presented in an accompanying paper (*16*). A summary of the testing protocol is presented here.

Eight OVMs were exposed simultaneously during 24-h periods at nominal concentrations of 10, 20, and 200 $\mu g/m^3$ of each VOC in combination. The VOCs were generated in a dynamic chamber using permeation tubes; actual concentrations were calculated based on experimentally determined permeation rates for each of the compounds (*16*). Total flow rate through the exposure chamber coupled with rotation of a platform to which the samplers were attached resulted in an OVM face velocity of 23.4 cm/s for all experiments (*16*). At each concentration, exposures were conducted at 10, 25, and 40 °C in combination with 12, 50, and 90% RH. A set of eight dynamic blanks (i.e., OVMs exposed to clean air) was obtained at each of the nine temperature/humidity combinations. Parallel active sampling using 4 SKC 200 mg/400 mg charcoal tubes (SKC Inc., Eighty Four, PA) was performed at 200 $\mu g/m^3$ and at 10 °C (12, 50, and 90% RH), 25 °C (12 and 50% RH), and 40 °C (12% RH). The sampling flow rate was approximately 20 mL/min controlled by an SKC adjustable flow tube holder (SKC 224-4, SKC Inc.). Pre- and postsampling rates were measured with an Accuflow film calibrator (SKC Inc.). The low sampling flow was necessary to avoid water condensation inside the charcoal tubes during the 24-h sampling time, and it precluded measurements at the two lowest target concentrations. Water condensation was also apparent at absolute humidities greater than 20 mg/L, precluding active sampling at these conditions also.

Additional tests included reverse diffusion experiments in which VOC recoveries following 12-h exposure to 200 $\mu g/m^3$ were compared with recoveries after a 12-h exposure to 200 $\mu g/m^3$ was followed by 12 h of exposure to clean air flow at the same temperature and humidity as the VOC exposure to determine if losses of adsorbed target VOCs could occur as a result of large decreases in concentrations during an exposure period. The temperature/humidity conditions studied were as follows: 10 °C with 12% and 90% RH, 25 °C with 50% RH, and 40 °C with 12% and 90% RH.

The general approach for handling the OVMs and calculating analyte concentrations followed the procedures recommended by the 3M Company (*17*, *18*) but with modifications to the extraction and analysis methods to allow for measurement of the target analytes at low concentrations. Specific modifications are described below.

Extraction and Analysis Protocol. Instead of CS_2 alone (or methylene chloride, one of the target compounds, recommended by 3M for 1,3-butadiene extraction), the extraction solvent consisted of a 2:1 v/v mix of acetone (glass distilled, Catalog No. AX0116-1; EM Science, Gibbstown, NJ) and CS_2 (99.9+% redistilled, Catalog No. 42464-1; Sigma-Aldrich Chemical Co. Inc., Milwaukee, WI). Both these specific solvents were found to have a very low background of target analytes. In addition, 1.0 mL of extraction solvent instead of the recommended 1.5 mL was used. Initial recommendations on the extraction solvent composition and volume were made by Pellizzari (*19*). For charcoal tube samples, 2.5 and 1.0 mL were used for the front and back portions, respectively. A 200 μg/mL solution of 4-bromofluorobenzene prepared from a 25 000 μg/mL standard (Supelco, Inc., Bellefonte, PA) in the mixed solvent was added to the extraction solvent as a surrogate to a final concentration of 5 μg/mL. The extraction solvent was prepared fresh for each set of samples analyzed (usually one experimental run).

Working analytical standards in the range of 0.1−10 μg/mL were prepared using the mixed solvent for dilution of two separate commercial standard solutions, one containing all analytes except 1,3-butadiene in low-benzene CS_2 (certified concentration 2000 μg/mL, EM Science, Gibbstown, NJ) and the other containing 1,3-butadiene in methanol (certified concentration 2000 μg/mL, Accustandard, Inc., New Haven, CT). An internal standard solution of 200 μg/mL 1,4-difluorobenzene and chlorobenzene-d_5 was also prepared in the mixed solvent from a 1000 μg/mL commercial standard in methanol (Supelco, Inc., Bellefonte, PA).

Each of the two charcoal pads inside the 3520 OVM were separately placed in 2-mL amber glass vials, 1.0 mL of extraction solvent was added, and the vials were closed with Teflon-lined septum caps. The pads were desorbed during 40 min in an ultrasonic bath with water maintained at 15−18 °C by adding small amounts of ice. After sonication, a 200-mL aliquot of the extract was withdrawn through the septum with a gas-tight syringe and transferred to another labeled amber glass autosampler vial fitted with clear glass inserts. After adding 20 mL of the internal standard mix, the vial was capped, and the extract was analyzed by GC/MS. The front and back sections of each charcoal tube were placed in 4- and 2-mL glass vials, respectively, and extracted as described above. The extracts were prefiltered through a Teflon syringe filter (0.45 mm pore size) to eliminate any residual charcoal particles, and analytical samples were then prepared the same way as for the OVM extracts. Two OVM and one charcoal tube blanks were extracted and analyzed for each 24-h experiment.

All extracts were analyzed by GC/MS with a Hewlett-Packard 5890 series II Plus GC with an HP 5972 MS detector, HP 18593B autosampler, Vectra 486 computer with EnvironQuant ChemStation Software and NBS75K Spectra Library (Hewlett-Packard, Palo Alto, CA) using an RTX-1/60 m/0.25 mm i.d./1 mm film thickness capillary column (Restek Corp., Bellefonte, PA). The instrumental analysis conditions included: SCAN or SIM mode; 1 mL injection volume splitless during the first 0.5 min followed by 40:1 split; 180 °C injection port temperature; 3.0 psi initial inlet pressure with 2-min hold and a ramp rate of 10 psi/min to 25 psi; initial oven temperature of 35 °C with 8-min hold followed by a ramp of 8 °C/min to 180 °C then 20° C/min and 280 °C with a 0.6 min hold; detector off between 0 and 4.5 min and again from 7.8 to 9.75 min.

Extraction Efficiencies. OVM extraction efficiencies, i.e., the fraction of mass applied to an OVM that is measured after solvent extraction, for the combined target VOCs at mass loadings ranging from 0.1 to 10 μg per compound per badge were determined at room temperature following the 3M-recommended procedure (*18*), which involves spiking known amounts of a target compound mixture onto a virgin OVM and allowing the capped badge to equilibrate at room temperature for 24 h before extracting and analyzing. Efficiencies were also determined after preconditioning OVMs during 24 h in the dynamic chamber using clean air at 25 and 40 °C in combination with 90% RH to determine the effects from humidity on desorption. A set of extraction experiments were also performed using methylene chloride in order to compare the efficiency of the mixed solvent for 1,3-butadiene extraction.

Method Detection Limits. Benzene, chloroform, methylene chloride, styrene, tetrachloroethylene, and toluene were found to be present at detectable concentrations in either the mixed extraction solvent or the blank OVMs. Mass method detection limits (MDLs) for these compounds were estimated as

$$\mathrm{MDL} = X + \mathrm{SD}t_{(0.01,n-1)}$$

where X is the mean analyte mass in the front or back pads (separate), SD is the standard deviation of each analyte load in blanks, $t_{(0.01,n-1)}$ is the 99th percentile of the Student t distribution, and n is the number of blanks.

For target compounds that were not present in the blanks (i.e., 1,3-butadiene, carbon tetrachloride, chloroprene, and

TABLE 1. OVM Extraction Coefficients for Each Target VOC with and without Temperature/Humidity Preconditioning

compound	preconditioning chamber conditions: 40 °C/90% RH ($n = 6$)	25 °C/90% RH[a] ($n = 6$)	no preconditioning ($n = 17$)
benzene	0.95	0.92	0.94
1,3-butadiene	0.35	0.32	0.73
carbon tetrachloride	0.96	0.93	0.98
chloroform	1.04	1.03	1.02
1,4-dichlorobenzene	0.74	0.68	0.67
methlyene chloride	1.01	1.01	1.05
styrene	0.52	0.48	0.56
tetrachloroethylene	0.89	0.84	0.91
toluene	0.91	0.93	0.91

[a] Also used for samples at 40 °C/50% RH.

TABLE 2. MDL (μg/m^3) of Each Target VOC for Different Temperature and Humidity Conditions

condition									
temperature (°C)	10	10	10	25	25	25	40	40	40
RH (%)	12	50	90	12	50	90	12	50	90
sampling time (min)	1440	1440	1440	1440	1440	1440	1440	1440	1440
target VOC									
benzene	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
1,3-butadiene[a]	5.4	5.4	5.4	5.2	5.2	11.8	5.1	11.6	10.5
carbon tetrachloride[a]	1.2	1.2	1.2	1.2	1.2	1.3	1.2	1.2	1.2
chloroform	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
1,4-dichlorobenzene[a]	4.4	4.4	4.4	4.3	4.3	4.3	4.2	4.2	3.8
methylene chloride	0.9	0.9	0.9	0.9	0.9	1.0	0.9	0.9	0.9
styrene	0.9	0.9	0.9	0.9	0.9	1.0	0.9	1.0	0.9
tetrachloroethylene	2.2	2.2	2.2	2.1	2.1	2.3	2.1	2.2	2.1
toluene	11.2	11.2	11.2	10.9	10.9	10.6	10.6	10.4	10.6

[a] Estimation is based on lowest standard.

1,4-dichlorobenzene), a similar approach was applied using the distribution of seven repeated injections of the lowest standard.

VOC concentrations were calculated as described by 3M (*18*) using their published sampling rates with one modification. If the target compound mass in the back charcoal pad was lower than the corresponding MDL load estimated from the back pad blanks, the contribution of this mass was neglected in the calculation of concentration.

Results

Extraction Efficiencies. Mean extraction coefficients (1.00 = 100% efficiency) for the range of mass loadings corresponding to the chamber exposures (i.e., 0.1−10.0 μg per compound per OVM) are presented in Table 1. These values were obtained from the slopes of linear regressions (intercept = 0) of the extracted mass against the spiked mass loading. Within this mass range, no dependence of extraction efficiency on mass loading was apparent. The extraction efficiency for 1,3-butadiene was similar when using either the mixed solvent or methylene chloride for extraction and was strongly affected by humidity. For the OVMs preconditioned at 40 °C/90% RH and 25 °C/90% RH, 1,3-butadiene extraction efficiencies were about half the value determined for the nonpreconditioned OVMs. The extraction efficiency for styrene was slightly lower at elevated humidities. For the rest of the target VOCs, extraction efficiencies were similar across the different experimental conditions with lower values for 1,3-butadiene, 1,4-dichlorobenzene, and styrene. Extraction efficiencies determined for preconditioned OVMs at 40 °C/90% RH were applied to exposures performed at that condition. Efficiencies determined for OVMs preconditioned at 25 °C/90% RH were applied to exposures at 25 °C/90% RH and 40 °C/50% RH since the absolute humidities at these conditions are similar. Efficiency determinations performed without preconditioning were applied to samples exposed to all other conditions.

Method Detection Limits. A total of 101 OVM blanks were analyzed as part of the chamber evaluation together with 52 blank charcoal tubes. The estimated mass loading MDLs for the front charcoal pads of the OVMs, determined as described above and using the extraction efficiencies determined as a function of temperature and humidity as appropriate, were used to estimate the corresponding 24-h concentration MDLs. These MDLs (Table 2) ranged from 0.56 to 4.43 μg/m^3 for benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, methylene chloride, styrene, and tetrachloroethylene. The MDL for toluene was higher (10.38−11.18 μg/m^3) and was similar to the lowest test concentration (10 μg/m^3). The higher MDL was mainly due to the relatively high and variable background toluene levels measured in the charcoal pads. The MDL for 1,3-butadiene ranged from 5.09 to 11.84 μg/m^3 due to the strong effect of humidity on extraction efficiency.

Recoveries. The actual delivered concentrations were calculated from experimentally determined permeation tube emission rates and chamber air flow rates. VOC percent recoveries (i.e., 100 × measured concentration/delivered concentration) were determined for each chamber experiment at the target concentrations of 10, 20, and 200 μg/m^3 and all temperature−relative humidity combinations. Since there is no standard criterion for acceptable accuracy of passive air samplers when used in nonoccupational settings, recoveries were considered satisfactory if the 95% confidence interval for the mean of each set of eight OVMs was within ±25% of the delivered concentration. This value is consistent with the NIOSH criterion for acceptable performance of passive dosimeters used to evaluate compliance with occupational permissible exposure levels (*15*) and was also used by Cohen et al. (*11*) in their limited chamber evaluation of the 3500 OVM.

The estimated mean recoveries, 95% confidence intervals for the means, temperatures, relative humidities, and absolute humidities for the 10, 20, and 200 μg/m^3 target concentrations are summarized in Tables 3−5, respectively. Corresponding

TABLE 3. Mean (with 95% Confidence Interval) of the Percent Recovery of the OVMs ($n = 8$) for Each Target VOC with Respect to Delivered Concentration in the 10 μg/m^3 Target Range at Different Combinations of Temperature and Humidity

condition									
temperature (°C)	10	10	10	25	25	25	40	40	40
relative humidity (%)	12	50	90	12	50	90	12	50	90
absolute humidity (mg/L)	1	5	8	3	11	21	6	25	46
target VOC									
benzene	93 ± 4	95 ± 5	88 ± 5	75 ± 3	62 ± 4	76 ± 7	82 ± 6	83 ± 3	70 ± 3
1,3-butadiene	152 ± 5	74 ± 11	ND[a]	149 ± 9	67 ± 5	ND	121 ± 5	291 ± 18	ND
carbon tetrachloride	100 ± 4	92 ± 5	77 ± 4	65 ± 2	62 ± 2	63 ± 4	73 ± 4	79 ± 4	62 ± 2
chloroform	106 ± 3	92 ± 6	90 ± 3	49 ± 2	42 ± 2	41 ± 3	81 ± 4	81 ± 3	62 ± 2
1,4-dichlorobenzene	85 ± 6	100 ± 7	88 ± 6	65 ± 2	63 ± 3	60 ± 3	68 ± 4	75 ± 2	63 ± 2
methylene chloride	97 ± 3	80 ± 14	74 ± 12	80 ± 2	79 ± 10	*b*	105 ± 4	109 ± 3	*b*
styrene	107 ± 14	69 ± 4	27 ± 1	85 ± 3	47 ± 3	25 ± 2	78 ± 5	101 ± 3	36 ± 2
tetrachloroethylene	92 ± 7	94 ± 4	80 ± 2	69 ± 1	60 ± 2	65 ± 4	72 ± 4	79 ± 2	63 ± 3
toluene	93 ± 5	77 ± 13	75 ± 8	56 ± 9	45 ± 9	52 ± 13	59 ± 13	66 ± 15	42 ± 6

[a] ND, not detected. [b] Back pad load > 50% front pad load.

TABLE 4. Mean (with 95% Confidence Interval) of the Percent Recovery of the OVMs ($n = 8$) for Each Target VOC with Respect to Delivered Concentration in the 20 μg/m^3 Target Range at Different Combinations of Temperature and Humidity

condition									
temperature (°C)	10	10	10	25	25	25	40	40	40
relative humidity (%)	12	50	90	12	50	90	12	50	90
absolute humidity (mg/L)	1	5	8	3	11	21	6	25	46
target VOC									
benzene	90 ± 4	96 ± 4	93 ± 3	92 ± 5	92 ± 5	91 ± 7	95 ± 4	93 ± 5	87 ± 2
1,3-butadiene	98 ± 9	93 ± 5	17 ± 4	146 ± 9	61 ± 6	ND[a]	117 ± 23	231 ± 25	ND
carbon tetrachloride	92 ± 4	90 ± 4	83 ± 3	88 ± 5	90 ± 4	86 ± 6	91 ± 3	94 ± 6	81 ± 3
chloroform	81 ± 3	84 ± 3	79 ± 3	103 ± 5	101 ± 5	87 ± 7	103 ± 4	92 ± 5	75 ± 2
1,4-dichlorobenzene	87 ± 3	77 ± 7	100 ± 6	90 ± 3	85 ± 4	90 ± 7	89 ± 3	86 ± 4	80 ± 2
methylene chloride	91 ± 5	98 ± 5	94 ± 3	114 ± 6	112 ± 4	*b*	112 ± 5	106 ± 5	19[c]
styrene	108 ± 3	83 ± 6	50 ± 4	98 ± 3	56 ± 5	43 ± 5	104 ± 2	95 ± 6	35 ± 3
tetrachloroethylene	92 ± 4	91 ± 4	94 ± 7	81 ± 4	82 ± 4	88 ± 7	88 ± 2	90 ± 6	83 ± 2
toluene	92 ± 19	79 ± 3	76 ± 4	79 ± 7	75 ± 4	75 ± 9	84 ± 6	77 ± 6	79 ± 8

[a] ND, not detected. [b] Back pad load > 50% front pad load. [c] Only one valid case.

TABLE 5. Mean (with 95% Confidence Interval) of the Percent Recovery of the OVMs ($n = 8$) for Each Target VOC with Respect to Delivered Concentration in the 200 μg/m^3 Target Range at Different Combinations of Temperature and Humidity

condition									
temperature (°C)	10	10	10	25	25	25	40	40	40
relative humidity (%)	12	50	90	12	50	90	12	50	90
absolute humidity (mg/L)	1	5	8	3	11	21	6	25	46
target VOC									
benzene	94 ± 3	91 ± 3	93 ± 3	82 ± 2	80 ± 4	80 ± 2	88 ± 5	109 ± 5	103 ± 2
1,3-butadiene	89 ± 13	96 ± 4	60 ± 6	130 ± 2	57 ± 8	126 ± 8	127 ± 9	317 ± 36	36 ± 6
carbon tetrachloride	90 ± 3	85 ± 3	89 ± 3	76 ± 2	72 ± 4	89 ± 2	87 ± 5	109 ± 5	96 ± 3
chloroform	91 ± 3	90 ± 3	94 ± 4	91 ± 2	86 ± 4	66 ± 1	87 ± 6	102 ± 5	96 ± 2
1,4-dichlorobenzene	93 ± 3	90 ± 3	91 ± 5	79 ± 2	76 ± 5	90 ± 2	88 ± 5	107 ± 5	95 ± 2
methylene chloride	105 ± 4	102 ± 4	101 ± 2	101 ± 2	98 ± 3	*a*	100 ± 5	110 ± 3	*a*
styrene	95 ± 4	95 ± 3	86 ± 5	91 ± 2	59 ± 4	96 ± 4	106 ± 6	133 ± 8	80 ± 5
tetrachloroethylene	87 ± 3	88 ± 2	89 ± 3	76 ± 1	69 ± 4	83 ± 1	85 ± 5	108 ± 7	98 ± 2
toluene	95 ± 3	97 ± 4	100 ± 2	82 ± 2	77 ± 4	78 ± 2	92 ± 6	116 ± 13	107 ± 6

[a] Back pad load > 50% front pad load.

to the data presented in these tables, compound-specific plots of mean percent recovery vs absolute humidity are available as Supporting Information (Figures S-1 to S-10). Each of these figures shows nine plots, each representing one of the concentration/temperature conditions. In general, the OVMs underestimated the delivered concentration to various degrees for the majority of the VOCs and under most exposure conditions of concentration, temperature, and humidity. The extent of negative recovery bias appeared to be a function of these exposure conditions although not necessarily in a clear pattern. Standard deviations were typically well within ±10% of the mean recoveries but increased significantly in some cases as the OVMs' performance was affected by the temperature and humidity exposure conditions.

Benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, tetrachloroethylene, and toluene had similar recovery patterns (Figures S-1 to S-6 in the Supporting Information). Recoveries for these compounds were generally within the ±25% recovery criterion except at the lowest delivered concentration for all humidities at 25 °C and for 90% RH at 40 °C. A general trend of lower recoveries at the lowest concentration was observed except for experiments at 10 °C. There was a slight trend of decreased recoveries with increasing absolute humidity. Similar patterns were found at 40 °C for all three concentrations, indicating that water content did affect the recovery, although not in a straightforward manner.

Recoveries for 1,3-butadiene (Figure S-7 in the Supporting Information) were strongly affected by humidity, also not in

a consistent manner. Recoveries were within the ±25% criterion only for 10 °C/50% RH and 40 °C/12% RH at all concentrations and 10 °C/12% RH at 20 and 200 $\mu g/m^3$. The very high recoveries at 40 °C/50% RH are certainly related to the use of very low extraction efficiencies determined under these high humidity conditions (see Table 1). Such low extraction efficiencies are typically unreliable and may result in an artificially high positive correction being applied to the measured masses. If the extraction coefficients obtained at room temperature conditions were used instead, recoveries at 40 °C/50% RH would have been more reasonable. Styrene (Figure S-8 in the Supporting Information) exhibited a similar but less extreme recovery pattern than butadiene with a steep decrease in recovery with increasing humidity at 10 and 20 $\mu g/m^3$.

Recoveries for methylene chloride (Figures S-9 and S-10 in the Supporting Information; S-10 includes invalid samples) were within the ±25% criterion except at 25 and 40 °C with 90% RH. The reason for the poorer performance was the increased diffusion of this compound to the back charcoal pad resulting in invalidated samples according to 3M's concentration calculation procedures (*18*) for the 3520 OVM (i.e., the compound load on the back pad exceeded 0.5 of the mass collected on the front pad). Figure S-11 in the Supporting Information, which includes invalid samples, clearly shows the increasing back/front pad mass loading ratio as absolute humidity increases with ratios of 0.75−0.95 and 0.82−1.05 for 90% RH at 25 and 40 °C, respectively. There was a decrease in the overall recovery at high RH despite the increased mass loading on the back pad. It appears that the relatively low binding affinity of methylene chloride for activated charcoal in the presence of high concentrations of water vapor negates the apparent benefit of the backup pad.

As previously indicated, active charcoal sampling was used in parallel with passive monitoring at the 200 $\mu g/m^3$ target concentration and combinations of temperature and relative humidity that did not result in the appearance of condensed water inside the charcoal tubes. With the exception of 1,3-butadiene and styrene (for which the OVM appeared to perform better), the recoveries (Table S-1 in the Supporting Information) for the active sampler and the OVM were similar at the conditions tested. The general similarity in recovery patterns observed for both active and passive samplers suggests that these results are reproducible and reflect a general behavior of activated charcoal under the test conditions.

The results of the reverse diffusion experiments are summarized in Table S-2 in the Supporting Information. In general, the recoveries both with and without exposure to clean air agreed within 10%. Reverse diffusion effects were apparent only for 1,3-butadiene at 25 °C and 40 °C, for methylene chloride at 10 °C/90% RH, and for styrene at 40 °C/90% RH.

Discussion

Overall, the results from the performance evaluation studies indicate that the 3520 OVM can be effectively used to sample most of the target compounds at realistic concentrations under a wide range of temperature and humidity conditions. Generally, performance was better at the lowest test temperature (10 °C) while at higher temperatures it decreased as humidity increased. The exceptions to these conclusions are styrene at the highest conditions of temperature and humidity and, especially, 1,3-butadiene, which had highly variable recovery rates. The precision of each sample set and mean biases with respect to delivered concentrations and/or parallel active sampling recoveries were consistent with those reported by Cohen et al. (*11*) and Ullrich and Nagel (*14*) from more limited testing experiments of the 3500 OVM with variable and typically longer exposure periods, varying from 1 day to several weeks. In both these studies there were generally negative recovery biases for those compounds also tested in the current evaluation. Cohen et al. (*11*) also showed effects from temperature and humidity that did not follow clear patterns with some of these effects also apparent in charcoal tube samples. Direct comparison between Cohen's or Ullrich and Nagel's recovery rates and the corresponding values for the current study cannot be made because they used different (and a much narrower range of) conditions. The ranges of concentration, temperatures, and humidities tested by Otson et al. (*12*) were also different than those for the current study. For compounds tested in both studies, their average data for 50−5000 $\mu g/m^3$ concentrations (results were not reported by concentration) indicate negative biases of 10−11% for methylene chloride, benzene, and toluene and positive biases of 6−16% for chloroform, tetrachloroethylene, and 1,4-dichlorobenzene. Otson et al. (*12*) reported small effects from humidity, but tests were done only at 23−28 °C; no extraction efficiencies were determined for the high relative humidity conditions; and the report only presented average data. Styrene was the only compound common to the current study and the second chamber evaluation reported by Otson et al. (*13*) at 10, 25, and 36 °C temperatures with 20 and 90% RH. Their results indicate a positive bias of 25%, independent of concentration, with a poorer recovery at 90% RH as compared to 20% RH. For the most comparable concentration, temperatures and humidity in the current study, i.e, 200 $\mu g/m^3$ at 10, 25, and 40 °C with 90% RH, we found negative biases of 14, 4, and 20%, respectively. Otson et al. (*12*) indicated that the charcoal tube concentration measurements used by them to estimate sampling rates were, on average, 20% lower than chamber concentrations calculated based on permeation tube weight loss. This explains the differences with our results. Cohen et al. (*11*) and our study also found negative biases, although not consistent, for charcoal tube measurements as compared with calculated concentrations in the chamber that varied depending on temperature and humidity. Both Cohen et al. (*11*) and Ullrich and Nagel (*14*) also showed a small to moderate negative bias for the OVMs as compared to charcoal sampling. Our results clearly show that charcoal tube measurements are comparable to OVM sampling results for most compounds, but they have lower precision than the OVMs. Charcoal tube performance is worse than the OVM's for styrene and butadiene at higher humidities and, therefore, should not be used for monitoring concentrations at such conditions. None of the previous evaluation studies included the range of concentrations, temperatures, humidities, and the number of dosimeters tested here. Only the two studies by Otson et al. used 24-h exposures but did not utilize concentrations lower than 50 $\mu g/m^3$. All the previous evaluations tested the 3500 OVM but not the 3520.

With the exception of 1,3-butadiene under most conditions, styrene and methylene chloride at very high relative humidites, and toluene at the 10 $\mu g/m^3$ target concentration, the 3520 OVM can be effectively used over the range of concentrations and environmental conditions tested with exposure durations of 24 h. The experimentally determined recoveries presented in this study can be used to estimate biases in concentration when interpreting measurements obtained under different conditions of temperature and humidity using these passive samplers.

From these results, there appears to be limited advantage to employing a double-layer sampler, such as the 3520 OVM in lieu of a single absorbent pad variety, such as the 3500 OVM, under the conditions employed for these evaluations. For most target compounds, the entire sampled mass was found on the front charcoal pad, except for the conditions of highest concentration, temperature, and humidity (i.e., 200 $\mu g/m^3$ at 40 °C and 90% RH) where a relatively small

proportion of the total collected mass was sometimes found on the back pad. For methylene chloride, high humidity conditions caused significant mass migration to the back pad, resulting in invalid samples. Of course, without the use of a double-layer sampler, assessment of sample validity would be impossible.

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Supporting Information Available

Mean percent recovery vs absolute humidity results (2 tables and 11 figures). This material is available free of charge via the Internet at http://pubs.acs.org.

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