

Evaluation of a Passive Sampler for Volatile Organic Compounds at ppb Concentrations, Varying Temperatures, and Humidities with 24-h Exposures. 1. Description and Characterization of Exposure Chamber System

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A dynamic exposure chamber was constructed to evaluate the performance of the 3M 3520 organic vapor monitor (3520 OVM, 3M Co., St Paul, MN) when exposed during 24 h to combined test atmospheres of benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, methylene chloride, styrene, tetrachloroethylene, and toluene at target concentrations of 10, 20, and 200 $\mu\text{g}/\text{m}^3$ in combination with temperatures of 10, 25, and 40 $^{\circ}\text{C}$ and relative humidities of 12, 50, and 90%. These conditions are generally representative of the range of community air environments, both indoor and outdoor. The system consists of five distinct units: (i) dilution air delivery, (ii) humidification, (iii) VOC generation and delivery, (iv) mixing chamber, and (v) exposure chamber. High-emission permeation tubes were utilized to generate the target VOCs. Both the target temperatures and humidities were achieved and maintained for multiple consecutive days. The variation of the temperature in the exposure chamber was controlled within ± 1 $^{\circ}\text{C}$, while relative humidity was controlled within $\pm 1.5\%$ at 12% RH, $\pm 2\%$ at 50% RH, and $\pm 3\%$ at 90% RH. Under constant preset temperatures and stable nitrogen flow through the VOC generation unit, various temporal patterns of permeation rates were observed over time. The lifetimes and permeation rates of the tubes differed by compound, length of the tube, and manufacturer. For tubes with a long shelf life, an initial conditioning period of up to 50 days in the VOC generation unit was necessary before permeation rates became stable. A minimum of 3 days of reconditioning was required when the tubes were stored in the refrigerator before they were used again. 1,3-Butadiene tubes had a short shelf life, and the permeation rates changed significantly and relatively quickly over time; however, the rates could be estimated by using a best-fit equation for the tube weight loss data for each exposure period. By closely monitoring weight loss over time, the permeation tubes could be used for delivering low and stable concentrations of VOCs over multiple months.

Introduction

Personal monitoring is the most direct and accurate approach to determine personal and population inhalation exposures to air pollutants (1). While active samplers have been most frequently used for this purpose, passive dosimeters offer several advantages including ease of use and lower burden on participants. A few studies (2–10) have or are currently using commercially available charcoal-based passive monitors for personal, indoor, and outdoor sampling of volatile organic compounds (VOCs) in nonindustrial environments. Only five studies (3, 11–14) have attempted to evaluate the performance of these samplers under conditions approaching the VOC concentrations and the range of temperature and humidity levels typically encountered in community settings. The range of these testing conditions, however, was narrower than those targeted by the current study.

This paper describes the components and characterization of a dynamic exposure chamber system for generating controlled atmospheres of benzene, 1,3-butadiene, carbon tetrachloride, chloroform, chloroprene, 1,4-dichlorobenzene, methylene chloride, styrene, tetrachloroethylene, and toluene at 10, 20, and 200 $\mu\text{g}/\text{m}^3$, in combination with temperatures of 10, 25, and 40 $^{\circ}\text{C}$ and 12, 50, and 90% relative humidity. The target VOCs were selected because of their prevalence in the ambient air of Houston, TX, a major petrochemical manufacturing center, and their toxicity (15). The chamber was used to evaluate the performance of the 3520 organic vapor monitor (OVM; 3M Co., St. Paul, MN) at each combination of these conditions; the results of the dosimeter evaluation are presented in the following paper (16).

Controlled test atmosphere systems for the generation of VOCs have been described for various applications, including instrument calibration (17); testing the efficiency of activated carbon filters (18); toxicity studies (19, 20); monitoring method comparison (21); and passive sampler evaluation (11–14, 22, 23). We based our system on Cohen et al. (11) with significant modifications.

VOC generation methods have included diffusion tubes and vials (25), saturation bubblers (17), counter-current volatilizers (20), syringe injection (23), permeation tubes (11–13), sintered spheres of glass beads coated with organic solvents (25), a capillary-effect generation system (26), and dilution of compressed gases (22). Given the ease of use and commercial availability, we selected permeation tubes as the VOC generation devices. There are very limited data on the long-term stability of the permeation rate for organic compounds (27). The results presented here address some of this deficiency.

Materials and Methods

Exposure Chamber System. A diagram of the exposure system is presented in Figure 1. All components were made of Pyrex glass or Teflon. Specific and complete details about each component of the system are provided in the Supporting Information. Glass components were wrapped with temperature-controlled heating tapes and insulated with multiple layers of Zetex tape to avoid water condensation on interior walls. Briefly, the exposure system consisted of five distinct units: (i) dilution air, (ii) humidification; (iii) VOC generation, (iv) mixing chamber, and (v) exposure chamber. Dilution air

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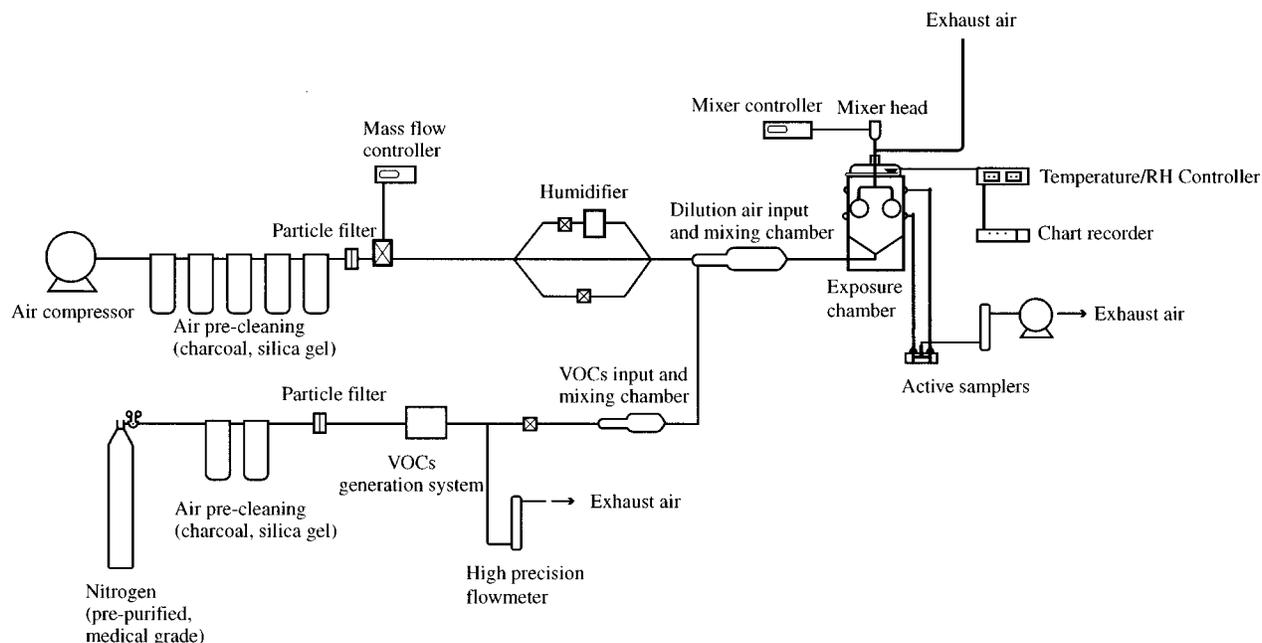


FIGURE 1. Diagram of the exposure chamber system.

was provided by a compressor, predried and cleaned through multiple beds of silica gel and activated charcoal, respectively, and metered through a mass flow controller.

A variable portion of the dilution air stream was saturated with water vapor at preset temperatures and then remixed with the dried dilution air stream in order to obtain the three target relative humidities.

Target VOCs were generated with permeation devices obtained from two different manufacturers and maintained inside custom-made U-tubes placed in two temperature-controlled oil baths, one maintained at 60 °C (i.e., benzene, carbon tetrachloride, tetrachloroethylene, toluene, 1,4-dichlorobenzene, and styrene permeation tubes) and the other maintained at 30 °C (i.e., 1,3-butadiene, chloroform, chloroprene, and methylene chloride permeation tubes). Permeation rates for each tube were verified experimentally as part of the chamber characterization. A constant, controlled flow of medical-grade nitrogen also predried and cleaned with silica gel and activated charcoal was directed with precision flow valves through each of the 10 U-tubes. Downstream of each U-tube, the VOC-laden nitrogen stream was split into two streams. One stream was directed to the mixing unit where it was combined with the humidity-preconditioned dilution air; the second stream was directed to an exhaust fume hood. The permeation tubes were thus maintained at constant conditions and fully equilibrated throughout the duration of the experiments; varying concentrations of VOCs were achieved by adjusting the flow of the exhaust stream. Dilution air flow was adjusted depending on the amount of the VOC-laden stream being introduced in the mixing chamber during each test in order to maintain a total flow of 25.6 L/min. Temperature was monitored with a thermometer placed 10 cm from the exit of this mixing chamber before the air stream entered the exposure chamber.

A diagram of the exposure chamber is presented in Figure S-1 (Supporting Information). It consisted of a Pyrex glass cylinder with 16 lateral ports, a conical inlet bottom, and a removable dome-shaped cover with six ports fitted with a Teflon gasket. The mixed contaminant stream entered through the bottom inlet. The temperatures at the wall and flow centerline in the exposure chamber were continuously monitored through two lateral ports. A side port on the cover was fitted with a continuously recording temperature/

humidity sensor. The center port in the cover was used for fitting the Teflon rod of a mixer head that supported a 15-cm-diameter Teflon platform from which the eight OVMs were suspended at each experimental condition. The mixer head was connected to a controller that allowed for setting the rotational speed of the platform as a means for controlling the face velocity across the OVMs.

Results and Discussion

Temperature and Humidity Stability. Temperatures of 25 and 40 °C were reached and maintained throughout the exposure chamber by just using the heating tapes with insulation. At 40 °C and 90% RH, a portable heater was needed to avoid potential condensation on the inside front surface of the exposure chamber due to the cooling effect of the hood's in-flowing air (hood face velocity of 54.9 m/min). The temperature of the main mixing chamber was maintained 2–3 °C higher than that of the exposure chamber. This facilitated temperature control in the exposure chamber, and it also avoided condensation of water vapor inside the premixing chamber at 90% RH. The temperature at the center of the exposure chamber was approximately 0.5 °C higher than that in the peripheral region. For the experimental conditions of 25 and 40 °C, the temperature of the chamber was maintained within ± 0.5 °C in the OVM exposure area during the 24-h experiments. Exposures at 10 °C were achieved by using an enclosure filled with dry ice (see details under Supporting Information) that allowed the temperature to be controlled at 10 ± 1 °C. Relative humidities were maintained within $\pm 1.5\%$ at 12% RH, $\pm 2\%$ at 50% RH, and $\pm 3\%$ at 90% RH across all temperatures during each 24-h exposure experiment.

Dynamic blank tests were performed by placing eight OVMs in the exposure chamber for each 24-h sampling with only clean air and N₂ flowing through the chamber. A total of 10 dynamic blank experiments were conducted: at room temperature (21 °C) with 0% RH and at each combination of 10, 25, and 40 °C with 12, 50, and 90% RH. No detectable background concentrations of target VOCs were found at any of these conditions.

Face Velocities. The minimal face velocity across the dosimeters that could be achieved in the chamber was

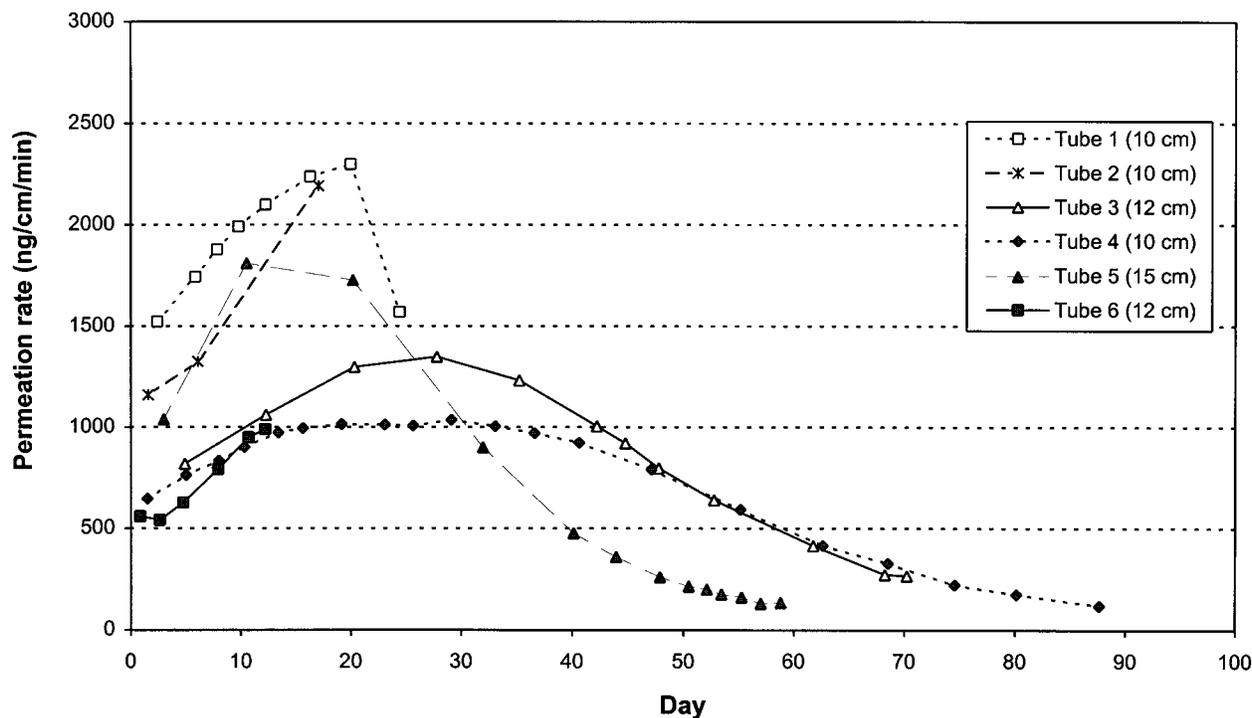


FIGURE 2. Change in permeation rate over time for 1,3-butadiene tubes.

approximately 1.4 cm/s as estimated based on the chamber total flow of 25.6 L/min and without platform rotation. Most experiments were conducted with a platform rotation velocity of 30 rpm that produced a total face velocity of 23.4 cm/s.

Characterization of VOC Generation. Permeation tubes were purchased from VICI Metronics Inc. (Santa Clara, CA) and Kin-Tek Laboratories Inc. (La Marque, TX). Maximum length was 20 cm for VICI tubes, and 10 cm for Kin-Tek tubes; Kin-Tek tubes were smaller in diameter. Determination of the required number of tubes was based on the highest targeted experimental concentration ($200 \mu\text{g}/\text{m}^3$) and the permeation rates provided by the manufacturers. Benzene, 1,3-butadiene, carbon tetrachloride, methylene chloride, and tetrachloroethylene required the use of only one tube; chloroform, 1,4-dichlorobenzene, and toluene required two tubes; and styrene required four tubes. At the lowest experimental concentration ($10 \mu\text{g}/\text{m}^3$), a single tube was needed for each compound. Of the 10 VOCs initially targeted by the study, only chloroprene could not be generated. Analysis of the contents of new chloroprene tubes by GC/MS indicated that the compound was not present.

The temperature of one oil bath was uniformly maintained at 30 °C, while the second oil bath ranged from 60 to 60.5 °C from one side of the bath to the other. The stability of the temperature inside each U-tube was confirmed by placing a thermometer in each U-tube. Prior to the exposures, permeation rates for each tube were experimentally verified by weighing the tubes every 2–7 days for 1 month of continuous use. These experiments demonstrated that initial permeation rates could vary significantly over relatively short periods of time, particularly for compounds such as 1,3-butadiene. As a result, the effective shelf life of the permeation tubes was determined in advance of the OVM evaluation study so that new permeation tubes could be ordered on a timely basis.

Over the length of the evaluation study of approximately 1 year, the permeation tubes were weighed approximately once a week using an analytical balance (Ohaus Analytical Plus, Bel-Art Products, Pequannock, NJ), except during two

periods of 2 and 1 month, respectively, when exposure experiments were not conducted and the tubes were stored in a refrigerator. The net weight loss of the tubes was used for calculating permeation rates for each specific exposure experiment during the corresponding period. A minimum of 3 days of equilibration time was allowed between tube weighings and chamber exposures.

Examples of the variability in tube permeation rates over time are presented in Figures 2–4. The permeation rates are given as mass emitted per minute per centimeter of length of the tube. Day one in each graph corresponds to the first time any given tube was weighed, typically after a conditioning period of at least 2 days in the VOC generation/delivery unit of the chamber system. The breaks between consecutive weighings for the tubes at 200–250 and 315–340 days correspond to periods of storage in a refrigerator when experimental exposures were not being conducted.

The permeation rates of 1,3-butadiene (Figure 2) tubes were quite variable over time and decayed rapidly. Butadiene permeation rates followed generally bell-shaped patterns that differed among tubes of different lengths and from different vendors. For the first two tubes (nos. 1 and 2) purchased from Kin-Tek, the permeation rates increased rapidly and the contents were exhausted within 3 weeks. VICI 1,3-butadiene permeation tube (nos. 3–5) rates were also not constant but could be approximated by best-fit equations so that the concentration in the chamber could be calculated during each exposure experiment. Tube 6 was used only for a few exposures at the end of the study, and the complete temporal permeation rate pattern for it could not be determined. From the patterns of tubes 3–5, it can be seen that the peak permeation rate was highest for the longest tube (no. 5) and lowest for the shortest tube (no. 4). The shortest tube had the longest useful life, around 3 months, while the longest had around a 2-month useful life.

Benzene, carbon tetrachloride, methylene chloride, and tetrachloroethylene tubes showed relatively stable behavior over a period of 1 year, with permeation rates ranging from 400 to 700 $\text{ng min}^{-1} \text{cm}^{-1}$ depending on the VOCs. Methylene chloride (Figure 3) had a relatively steady permeation rate

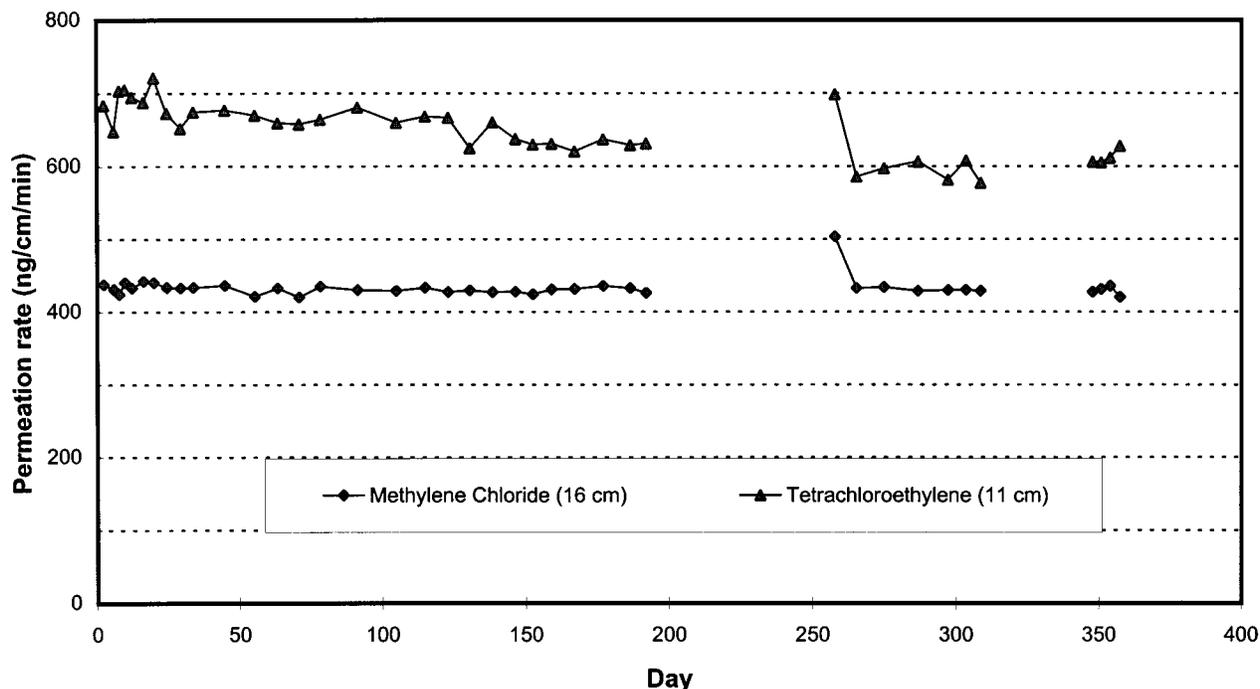


FIGURE 3. Change in permeation rate over time for methylene chloride and tetrachloroethylene tubes.

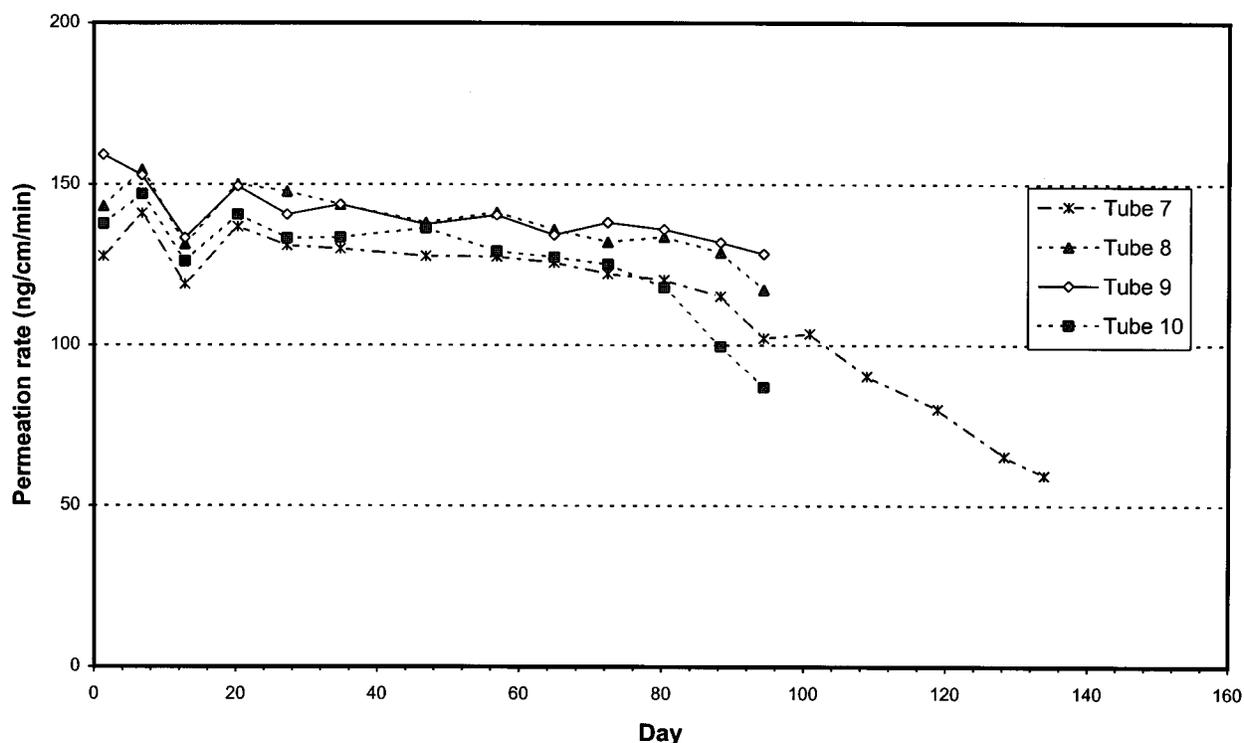


FIGURE 4. Change in permeation rate over time for styrene tubes (10 cm).

of approximately $430 \text{ ng min}^{-1} \text{ cm}^{-1}$ over 1 year, similar to that provided by the manufacturer. Tetrachloroethylene (Figure 3) also had a relatively stable permeation rate (approximately $630 \text{ ng min}^{-1} \text{ cm}^{-1}$) with a slight decline over time. The temporal permeation rate trends for benzene and carbon tetrachloride tubes (Figures S-2 and S-3) were similar to that of tetrachloroethylene in that the rates showed more variability than that of methylene chloride and slightly decreased over the experimental period. All tubes showed unstable permeation rates immediately after storage in a refrigerator, requiring a minimum of 3 weeks of conditioning in the U-tubes.

Figure 4 shows the permeation rate over time for four styrene tubes purchased from Kin-Tek. After approximately 20 days of equilibration, styrene permeation rates became stable, although they varied for different tubes. The rates showed a decreasing trend from 135 to $150 \text{ ng min}^{-1} \text{ cm}^{-1}$ at 20 days to $120\text{--}135 \text{ ng min}^{-1} \text{ cm}^{-1}$ at 80 days, followed by a more pronounced decay. The permeation rate for tube 7 decreased to $60 \text{ ng min}^{-1} \text{ cm}^{-1}$ after approximately 135 days, equivalent to 45% of the original rate. On the basis of these data, styrene tubes could be used for at least 3 months under these experimental conditions. According to the data provided by the manufacturer, the permeation rate should be

approximately 147 ng min⁻¹ cm⁻¹ with a useful life of 2–6 months.

The permeation rates for chloroform (Figure S-4), 1,4-dichlorobenzene (Figure S-5), and toluene (Figure S-6) tubes were generally lower than indicated by the manufacturer but stable for at least 200 days, at approximately 120, 220, and 330 ng min⁻¹ cm⁻¹, respectively. As with other VOCs, permeation rates were unstable immediately after refrigerator storage.

Temperature and RH control of the exposure chamber system met the passive sampler evaluation design requirements of this study. By carefully monitoring weight loss of the permeation tubes every 3–4 days over the length of the study, we were able to generate concentrations that approached the original targets. A minimum of 3 weeks of equilibration time in the U-tubes was necessary in order to obtain a stable permeation rate. While the permeation rate of 1,3-butadiene was not stable, it could be derived by a best-fit approach. The useful lifetime for the permeation tubes depends on the specific compound. For benzene, carbon tetrachloride, methylene chloride, tetrachloroethylene, and toluene, the useful lifetime was about 1 year, about 200 days for chloroform and 1,4-dichlorobenzene, and 80 days for styrene. The data suggest that the useful lifetime for 1,3-butadiene can vary between 40 and 60 days, depending on specific tubes, when the permeation rate is above 500 ng min⁻¹ cm⁻¹.

Acknowledgments

This study was supported by the Mickey Leland National Urban Air Toxics Research Center. The authors thank Mr. Steve Jones and especially Ms. Silvia Maberti for their assistance in the preparation of this manuscript.

Supporting Information Available

A detailed description of the exposure system including six figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review May 31, 1999. Revised manuscript received July 12, 1999. Accepted July 21, 1999.

ES990607J