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Polydimethylsiloxane-based permeation passive air sampler. Part II: Effect of temperature and humidity on the calibration constants

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ABSTRACT

Polydimethylsiloxane (PDMS) has low permeability towards water vapour and low energy of activation of permeation towards volatile organic compounds (VOCs) when compared to many other polymers. Suitability of the material for use in permeation-type passive air samplers was tested as it theoretically should reduce uptake rate variations due to temperature changes and eliminate or reduce complications arising from sorbent saturation by water vapour. The calibration constants of a simple autosampler vial-based permeation passive sampler equipped with a PDMS membrane (Waterloo Membrane Sampler®) were determined for various analytes at different temperatures. From the data, the activation energy of permeation for PDMS towards the analytes was determined. The analytes studied belonged to various classes of compounds with wide ranging polarities, including n-alkanes, aromatic hydrocarbons, esters and alcohols. The results confirmed Arrhenius-type relationship between temperature and calibration constant and the energy of activation of permeation for PDMS ranged from −5 kJ/mole for butylbenzene to −17 kJ/mole for sec-butylacetate. Calibration constants of the samplers towards n-alkanes and aromatic hydrocarbons determined at humidities between 30% and 91% indicated no statistically significant variations in the uptake rate with changes in humidity for 9 of the 11 analytes studied. The results confirmed the suitability of the sampler for deployment in high humidity areas and under varying temperature conditions.

1. Introduction

Passive sampling is defined as "any sampling technique based on the free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media" [1]. Based on this principle, passive air samplers have been designed with various geometries and materials of construction to suit different applications [2]. Irrespective of the sampler design, the ideal relative uptake rates of analytes into a specific sampler are defined by the fundamental transport properties such as the diffusion coefficient of the analyte in the air (for diffusive-type passive samplers) and permeability of the polymer towards the analytes (for permeation-type passive samplers). These fundamental transport properties are temperature-dependent and therefore the uptake rates change with variations in temperature. Diffusion coefficients of various organic molecules in air and their variations with temperature have been studied for many years, hence the dependence of the uptake rates on temperature for diffusive-type samplers is well understood and conveniently explained based on kinetic theory of gases [3]. This, however, is not the case for permeation-type passive samplers.

PDMS is characterized by high permeability towards volatile organic compounds (VOCs) and low permeability towards water molecules, making it an ideal membrane material for permeation passive samplers for pre-concentrating VOCs. The use of a PDMS membrane should potentially prevent non-ideal sampler performance due to sorbent saturation by moisture. Further, published research also indicates that PDMS has low energy of activation of permeation for various analytes as compared to many other polymers. Consequently, PDMS membrane permeability should theoretically be less affected by temperature than many other polymers. In the study reported in this paper, PDMS was used for the fabrication of a simple autosampler vial-based permeation passive sampler (Waterloo Membrane Sampler®, or WMS) and the effects of temperature and humidity on the uptake rates of the sampler were studied. The fundamental aspects of the sampler and determination of the uptake rates for 41 compounds of various polarities were presented in the first part of this paper [4].

2. Theory

The fundamentals of permeation-type passive samplers along with a brief discussion of the design of the passive sampler studied

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in this project were discussed by Seethapathy et al. in an earlier contribution [2]. A more detailed description was presented in the first part of this paper [4]. The WMS sampler is fabricated using a PDMS membrane in such a way that one side of the membrane is exposed to the sample matrix, while the other side is in contact with a sorbent which is isolated from the sample matrix. According to Fick's law, for such a permeation-type passive sampler the mass of analyte M (kg) collected in time t (min) by the sampler is given by [4]:

$$\left(\frac{M}{t}\right) = D\frac{A}{L_m}(C_{ma} - C_{ms}) \quad (1)$$

where D is the diffusion coefficient of the analyte in the membrane (cm^2/min), A is the surface area of the membrane (cm^2), L_m is the membrane thickness (cm), C_{ma} is the concentration of the analyte on the surface of the membrane exposed to the air (kg/cm^3) and C_{ms} is the concentration of the analyte on the membrane surface in contact with the sorbent (kg/cm^3). To maintain a concentration gradient between the two surfaces of the membrane, the concentration of the analyte at the membrane–sorbent interface should ideally be zero. This is typically achieved by using strong sorbents for trapping the analytes from the gas phase inside the sampler. At a given temperature, the concentration of the analyte on the membrane surface exposed to the air is related to the concentration of the analyte in the air by the following relationship:

$$C_{ma} = KC_0 \quad (2)$$

where K (dimensionless) is the partition coefficient of the analyte between the air and the membrane. Under the conditions of constant temperature, the diffusion coefficient, partition coefficient, as well as membrane area and thickness are all constant and can be replaced by a new constant, k.

$$k = \frac{L_m}{DKA} \quad (3)$$

where k is the calibration constant of the passive sampler. The inverse of k is often referred to as the uptake rate of the sampler towards a particular analyte. Using Eqs. (2) and (3), Eq. (1) can be reduced to,

$$C_0 = \frac{kM}{t} \quad (4)$$

The product of the analyte's diffusion coefficient D in the membrane and its partition coefficient K is defined as the permeability of the polymer (P, cm^2/min) towards that particular analyte, and defines the relative calibration constants of the passive sampler towards various analytes [1].

2.1. Effect of temperature

Temperature dependence of polymer permeability towards a given analyte is determined by the temperature dependences of the diffusion coefficient of the analyte in the polymer and its partition coefficient between air and the polymer. The partition coefficient and diffusion coefficient of a molecule, and consequently the permeability of a polymer towards a particular analyte, can be expressed as a function of temperature using Van't Hoff's and Arrhenius equations [1]:

$$P = P_o \exp\left[-E_p\left(\frac{1}{RT} - \frac{1}{RT_o}\right)\right] \quad (5)$$

$$K = K_o \exp\left[-\Delta H_s\left(\frac{1}{RT} - \frac{1}{RT_o}\right)\right] \quad (6)$$

$$D = D_o \exp\left[-E_d\left(\frac{1}{RT} - \frac{1}{RT_o}\right)\right] \quad (7)$$

$$DK = D_oK_o \exp\left[-(E_d + \Delta H_s)\left(\frac{1}{RT} - \frac{1}{RT_o}\right)\right] \quad (8)$$

where P_o, K_o and D_o are the permeability constant, partition coefficient and diffusion coefficient at temperature T_o, E_p is the activation energy for permeation, ΔH_s is the enthalpy of sorption of the analyte in the membrane, and E_d is the activation energy for diffusion. Using Eqs. (5)–(8), one can express the activation energy of permeation as:

$$E_p = E_d + \Delta H_s \quad (9)$$

To understand how the temperature affects the calibration constant, theoretical relationship between the two parameters was derived as follows.

According to Eq. (5),

$$\ln P = \ln P_o - \frac{E_p}{RT} + \frac{E_p}{RT_o} \quad (10)$$

From the definition of the calibration constant, one can arrive at the following relationship:

$$\ln k = \ln\left[\frac{L_m}{A}\right] - \ln P \quad (11)$$

Eqs. (10) and (11) can then be used to derive the relationship between temperature and the calibration constant.

$$\ln k = \ln\left[\frac{L_m}{A}\right] - \ln P_o - \frac{E_p}{RT_o} + \frac{E_p}{R}\left[\frac{1}{T}\right] \quad (12)$$

According to Eq. (12), a linear relationship should exist between $\ln(k)$ and $1/T$. Further, it should be possible to calculate the activation energy of permeation from the slope of this linear relationship. Experiments were therefore performed to determine the calibration constants of the samplers towards various analytes at different temperatures, and E_p was determined from the slope of the $\ln(k)$ vs. $1/T$ line.

2.2. Effect of humidity

PDMS is a hydrophobic polymer, hence analyte partitioning into it is governed to a large extent by the hydrophobic surface area of the analyte [4]. Since water molecules are small and polar, they are characterized by K value lower by several orders of magnitude than those for most VOCs. Even though the diffusion coefficient of water molecules in PDMS is higher than that for many VOCs, permeability of PDMS towards water (the product of D and K) is low due to the dominant nature of K (see Part I of this contribution [4]).

3. Experimental

3.1. Chemicals

High purity CS_2 required for the preparation of standard solutions of the analytes for gas chromatographic quantification and for analyte desorption from sorption tubes and passive samplers was purchased from VWR CANLAB (Mississauga, ON). Anasorb 747® used as the sorption material inside the WMS passive sampler was purchased from SKC Inc. (Philadelphia, PA). Chromatography grade compressed air, helium, nitrogen, and hydrogen were purchased from Praxair (Kitchener, ON). All high purity, analytical grade chemicals were purchased from Sigma–Aldrich (Bellefonte, PA). The analytes included n-alkanes (n-hexane to n-decane), aromatic hydrocarbons (benzene, toluene, ethylbenzene, o-xylene, propylbenzene and butylbenzene), alcohols (n-butanol to n-octanol, 2-methyl-1-propanol, 2,3-dimethyl-3-pentanol, 2,4-dimethyl-3-pentanol, 2-ethyl-1-hexanol, 2-methyl-1-butanol, 6-methyl-2-heptanol, 2-hexanol, 2-octanol and 3-octanol), and

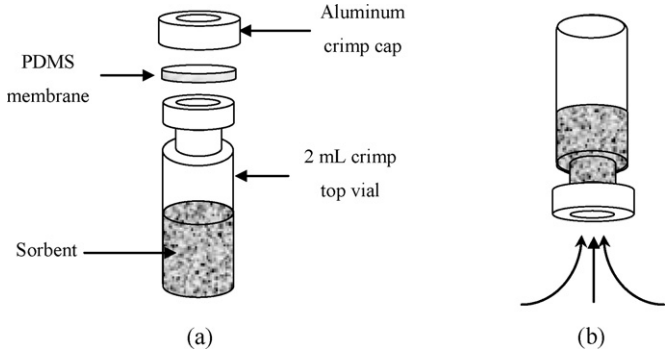

Fig. 1. (a) Components of the 2 mL crimp cap vial-based permeation passive sampler and (b) passive sampler configuration during sampling [4].

esters (ethylacetate, propylacetate, butylacetate, sec-butylacetate, methylbutyrate, ethylbutyrate, propylbutyrate and butylbutyrate).

3.2. Passive sampler design

The design of the WMS passive sampler is shown in Fig. 1. A detailed description of the design and the fabrication of the sampler were presented in Part I of this contribution [4].

For determining the effect of temperature and humidity on the uptake rates of analytes by the samplers, it was critical to keep all other variables affecting the uptake rate constant, including the membrane thickness. However, the sampler shown in Fig. 1 was not designed for re-use, and both the aluminum cap and the membrane had to be removed before analyte desorption was carried out. To overcome this limitation, a re-usable sampler was designed and fabricated in the glass shop at the University of Waterloo as shown in Fig. 2. The sampler fabrication involved cutting the bottoms of a crimp cap vial and a screw cap vial (both of the same internal and external diameters) and fusing the open vial ends together. This enabled removing the sorbent from the vials through the screw cap end without disturbing the membrane.

A set of 7 such samplers was used for exposure experiments at different temperatures. The average weight of each membrane used for the fabrication of these samplers was 8.6 mg ± 0.2 mg. Another set of 8 samplers was used for the experiments at different humidity levels, and the average weight of each membrane was 8.2 ± 0.3 mg in this case. Membrane weight was used as an indirect measure of the membrane thickness (see Part I [4]).

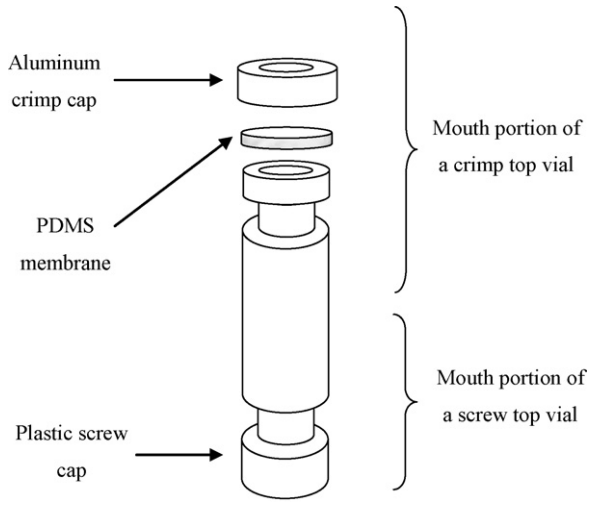

Fig. 2. Design of a re-useable WMS sampler.

3.3. Experimental setup

The schematic of the experimental setup is depicted in Fig. 3. High pressure nitrogen gas was first purified by activated charcoal scrubber and a flow rate of 1000 mL/min was set using a mass flow controller (model MDF-52000L0N-0L) purchased from Pneucleus Technologies Inc. (Hollis, NH). An MKS Instruments (Andover, MA) Type 247 4-channel readout system was connected to this mass flow controller for setting and monitoring the flow rate. The dry nitrogen gas was split into two streams prior to its delivery to the exposure chamber. One stream was saturated with water vapour by bubbling the gas through water in a 2.5 L glass jar, while the other was passed along sets of custom made permeation tubes placed in a flow-through cell. The cell was maintained at a constant temperature (between 30 and 60 °C, depending on the permeation rates of the analytes through the permeation tubes) inside a GC oven. The flow rates of the two streams, and hence the humidity at the outlet, could be controlled using needle valves A and B. The humidity of the resulting standard gas mixture was measured using a hygrometer (Model 11-661-7D) procured from Fisher Scientific, Inc. (Ottawa, ON). The nitrogen gas containing analyte vapours from the standard gas mixture generator was then introduced into a thermostatted exposure chamber described in Part I of this contribution [4].

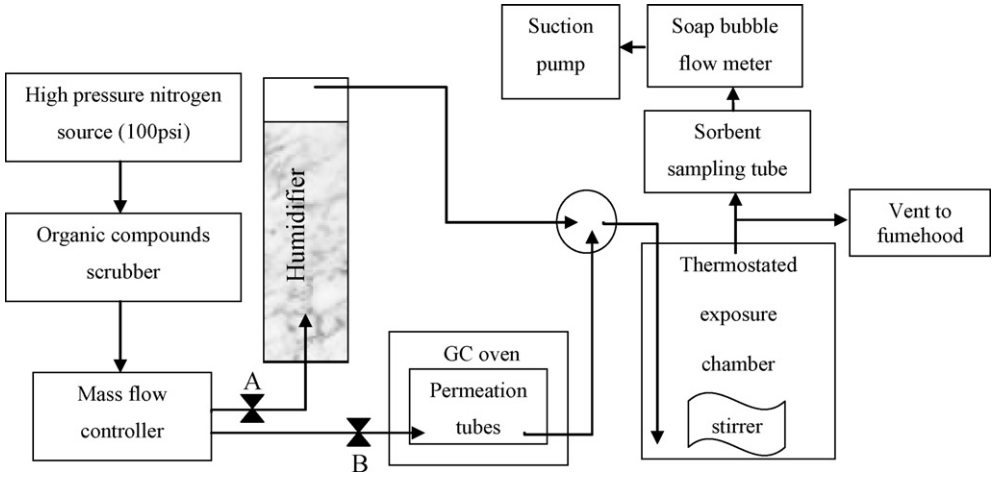

Fig. 3. Schematic of the experimental setup used for the determination of the calibration constants.

Table 1
Energy of activation of permeation of PDMS towards n-alkanes and aromatic hydrocarbons computed from calibration constants determined at 10, 19.7, 29.9 and 39.5 °C.

Analyte	k at 10 °C	% RSD[a]	k at 19.7 °C	% RSD	k at 29.9 °C	% RSD	k at 39.5 °C	% RSD	Slope of ln(k) vs 1/T line ($\times 10^{-3}$)	Standard error of the slope ($\times 10^{-2}$)	R^2	E_a (kJ/mole)
n-Hexane	0.804	6.4	0.960	5.4	1.099	6.2	1.106	10.3	−1	2.2	0.9082	−8
n-Heptane	0.356	7.2	0.440	4.7	0.517	6.4	0.556	10.1	−1.3	1.6	0.9721	−11
n-Octane	0.167	7.4	0.210	4.0	0.245	6.4	0.283	9.7	−1.6	1	0.9964	−13
n-Nonane	0.093	7.6	0.111	4.0	0.123	5.8	0.147	9.4	−1.3	1.2	0.9842	−11
n-Decane	0.065	8.1	0.073	5.1	0.080	5.2	0.087	8.7	−1	0	0.9985	−7
Benzene	0.428	5.4	0.510	5.0	0.569	6.1	0.588	9.8	−1	1.7	0.9431	−8
Toluene	0.194	5.9	0.230	4.0	0.273	6.0	0.297	10.1	−1.3	1.2	0.9833	−11
Ethylbenzene	0.115	7.1	0.140	3.8	0.161	5.8	0.183	9.7	−1.3	0	0.9985	−11
Propylbenzene	0.075	7.4	0.090	4.2	0.098	5.5	0.111	9.2	−1.2	0	0.9990	−9.7
Butylbenzene	0.055	7.9	0.060	5.4	0.064	4.9	0.068	8.5	−1	0	0.9960	−5
o-Xylene	0.097	6.6	0.110	3.9	0.130	5.8	0.150	9.8	−1.3	0	0.9970	−11

[a] RSD: relative standard deviation.

Analyte concentrations in the chamber were determined using active sampling by drawing a known volume of the gas exiting the chamber through a 1/8 in. stainless steel tubing inserted into the chamber (through the vent) and a custom made sorption tube. A suction pump (Model MB-21) procured from Metal Bellows Corp. (Shanon, MA) was used for this purpose. A soap bubble flow meter was used to measure the flow rate through the sorption tube (typically between 80 and 120 mL/min).

3.4. Methods

Experiments to determine the effect of temperature on the calibration constants of the sampler involved three sets of compounds: (1) alkanes and aromatic hydrocarbons, (2) linear and branched alcohols, and (3) esters. The experiments were performed at 0% relative humidity and 4 different temperatures ranging from approximately 10 °C to 40 °C for each set of compounds. The goal was to determine the energy of activation of permeation through PDMS without introducing any uncertainty related to non-zero humidity.

Experiments to determine the effect of humidity on the calibration constants involved n-alkanes and aromatic hydrocarbons as model compounds. They were performed at three relative humidity levels: 30%, 60% and 91%. The exposure time in these experiments was 9000 minutes in each case and the temperature of the calibration chamber was maintained at 25 ± 0.2 °C. For all these experiments, the fan blade inside the calibration chamber was rotated at high enough speed to maintain uniform analyte concentrations throughout the chamber. Consequently, the analyte concentration sensed by the passive samplers was expected to be same as the concentration sensed by the active sampling method at all times, and the starvation effect could be practically eliminated.

Prior to exposure studies, analyte recoveries from Anasorb 747® were determined and the respective recovery rates were applied for determining the analyte amounts trapped in the samplers, as well as in sorption tubes used for active sampling. Detailed description of the procedure was presented in Part I of this contribution [4].

The samplers were exposed to the dynamic standard test gas atmosphere by inserting them, membrane end down, into the holes drilled into the top of the exposure chamber. Immediately after the exposure was started, active sampling was initiated as described above. The sorption tube was changed every 24–48 h throughout each exposure experiment.

After the exposure was complete, the sorbent from the samplers was removed via the screw cap end of the modified sampler and transferred into separate 4 mL vials. The analytes were quantified by extraction with 1 mL of CS_2 as described in Part I [4]. The analytes trapped in the sorption tubes used for active sampling were also quantified in this way. The average analyte concentrations in the chamber determined using the sorption tubes were used for calculating the calibration constants of the samplers.

4. Results and discussion

4.1. Effect of temperature

The results obtained from the experiments allowed the determination of the fundamental transport properties of PDMS (energy of activation of permeation) towards the model compounds used in the study and provided critical information on the variability of the calibration constants with temperature required for applying any corrections if necessary. The calibration constants of n-alkanes and aromatic hydrocarbons determined at 10, 19.7, 29.9 and 39.5 °C are listed in Table 1. The results indicated that the calibration constants (inversely proportional to the permeability of PDMS towards an analyte) increased with increase in temperature in all cases. This observation is in agreement with the permeability characteristics of PDMS membranes reported by Boscaini et al. [5] and LaPack et al. [6] (among others).

A plot of 1/T vs ln(k) for each of the n-alkanes and aromatic hydrocarbons, shown in Fig. 4, reiterated the earlier observations noted in the literature that the permeability was related to temperature through Arrhenius-type relationships for PDMS. The correlation was good for all the analytes studied with the exception of hexane and benzene, with the correlation coefficients ranging from 0.9082 to 0.9985 for n-alkanes and from 0.9431 to 0.9990 for aromatic hydrocarbons. The deviation from the exact correlation coefficient of 1 could either be due to experimental errors or to the temperature dependence of the heat of solution (ΔH). With the experimental setup and method used, it was impossible to determine which of the two contributed to the deviations from linearity observed for the most volatile analytes. Assuming that the enthalpy and entropy of solution were independent of temperature, the slopes of the regression lines were used to determine the energy of activation of permeation (using Eq. (12)). The calculated values are listed in Table 1 along with the standard errors of the slopes. Eq. (9) shows that the temperature dependence of permeability is a function of the analyte's heat of solution and its activation energy for diffusion. For PDMS, the diffusion coefficient of a molecule in the polymer increases with increase in temperature, and the partition coefficient of the molecule decreases with increase in temperature. In other words, E_d is greater than zero (positive), and ΔH_s is less than zero (negative) for the majority of volatile organic compounds. The net change in the permeability of the polymer membrane with temperature is decided based on which of these two parameters defining the activation energy of permeation prevails. In the case of PDMS, the results indicated that ΔH_s was the dominating factor. Since E_d and ΔH_s oppose each other, there is a trade-off in the net

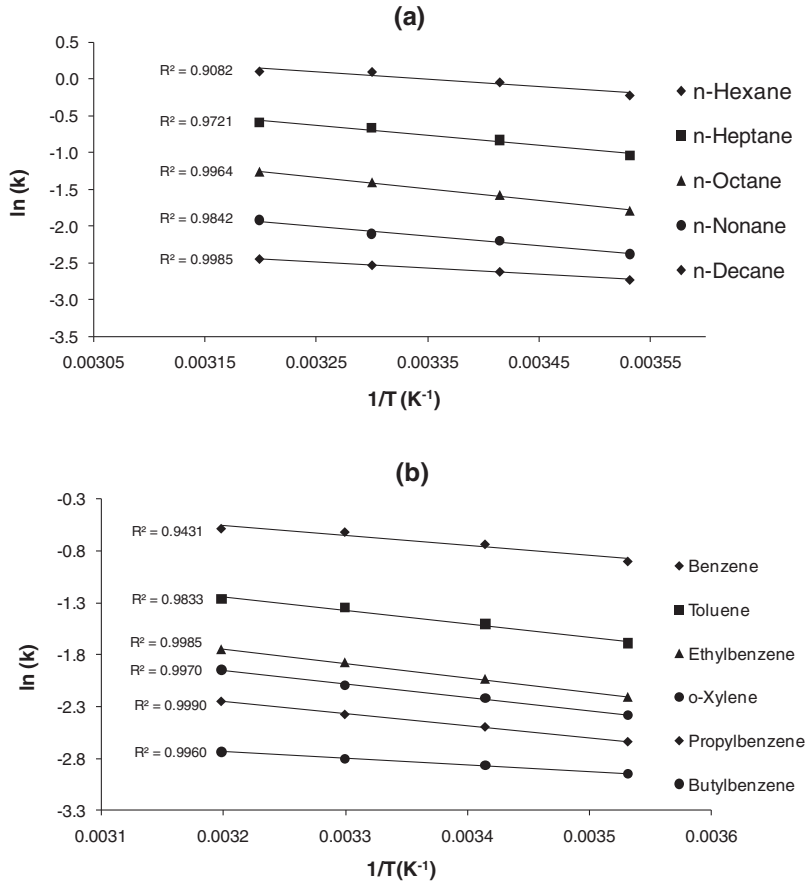

Fig. 4. Arrhenius-type relationship between ln(k) and 1/T for (a) n-alkanes and (b) aromatic hydrocarbons.

permeability with change in temperature. This eventually results in the permeability of PDMS generally being a weak function of temperature when compared to many other polymers.

Within the n-alkane homologous series, the E_p values decreased from −8 kJ/mole for n-hexane to −13 kJ/mole for n-nonane, and then increased again to −7 kJ/mole for n-decane. A similar trend within the aromatic hydrocarbons was noticed where the E_p decreased from −8 kJ/mole for benzene to −11 kJ/mole for ethyl benzene, and increased again to −5 kJ/mole for butyl benzene. Nevertheless, the E_p values were all within the same order of magnitude, as has been observed by other researchers. For n-hexane, the increase in temperature from 10 °C to 39.5 °C resulted in the uptake rate decreasing from 1.24 mL/min to 0.9 mL/min, a decrease of 27.3%. This corresponds to an average decrease in the uptake rate of about 0.9% per °C change within the temperature range studied. Within the n-alkane group, n-octane had the highest average decrease in the uptake rate of 1.4% per 1 °C increase in temperature. Mathematically, the closer the energy of activation of permeation is to zero, the smaller is the effect of a change in temperature on the calibration constant.

A similar trend of increasing calibration constants with increase in temperature (Table 2) was also observed for all esters. The linearity of the ln(k) vs. 1/T curve was good with the correlation coefficients greater than 0.98 for the five compounds. The energy of activation of permeation for all the esters was calculated, along with the standard error of the slope and is provided in Table 2. The experiments with alcohols also revealed an increasing trend in the calibration constants with temperature (Table 3). The E_p values were generally lower than those observed for the n-alkanes and aromatic hydrocarbons and the ln(k) vs. 1/T plots showed good correlations for all compounds. Within the n-alcohol group, there was also a similar trend of increasing energy of activation of permeation from −13 kJ/mole for n-butanol to −8 kJ/mole for n-heptanol, followed by a reversal in the trend with −9.3 kJ/mole for n-octanol. From the results observed for all the different groups of compounds and from the literature data it can be concluded

Table 2
Energy of activation of permeation of PDMS towards esters computed from calibration constants determined at 10, 20, 30.5 and 39.5 °C.

Analyte	k at 10 °C	% RSD[a]	k at 20 °C	% RSD	k at 30.5 °C	% RSD	k at 39.5 °C	% RSD	Slope of ln(k) vs 1/T line ($\times 10^{-3}$)	Standard error of the slope ($\times 10^{-2}$)	R^2	E_a (kJ/mole)
Propyl acetate	0.199	10.8	0.232	11.1	0.28	9.2	0.326	10.5	−1.8	1	0.9971	−15
Methyl butyrate	0.186	10.7	0.217	10.9	0.26	9.1	0.302	10.4	−1.8	1	0.9980	−15
sec-Butyl acetate	0.205	11.2	0.236	11.4	0.29	9.6	0.367	11.2	−2.1	1.7	0.9869	−17
Ethyl butyrate	0.135	9.8	0.153	10.3	0.18	8.5	0.209	9.9	−1.6	1	0.9940	−14
Butyl acetate	0.129	9.7	0.144	10.3	0.17	8.4	0.198	9.8	−1.6	1.1	0.9911	−13

[a] RSD: relative standard deviation.

Table 3
Energy of activation of permeation of PDMS towards alcohols computed from calibration constants determined at 10, 20.1, 29.9 and 40.1 °C.

Analyte	k at 10 °C	% RSD[a]	k at 20.1 °C	% RSD	k at 29.9 °C	% RSD	k at 40.1 °C	% RSD	Slope of ln(k) vs 1/T line ($\times 10^{-3}$)	Standard error of the slope ($\times 10^{-2}$)	R^2	E_a (kJ/mole)
n-Butanol	0.282	6.5	0.338	2.3	0.358	3.6	0.491	4.1	−1.5	2.9	0.9373	−13
n-Pentanol	0.140	5.8	0.165	2.5	0.175	3.1	0.226	2.9	−1.3	2.1	0.9554	−11
n-Hexanol	0.074	4.8	0.087	4.0	0.094	2.3	0.112	2.2	−1.1	1	0.9869	−9.6
n-Heptanol	0.052	3.2	0.059	4.5	0.062	2.2	0.074	2.2	−1	1.3	0.9700	−8
n-Octanol	0.046	3.8	0.046	6.7	0.047	2.5	0.052	3.1	−1.1	3.7	0.8139	−9.3
2-Methyl-1-propanol	0.391	4.6	0.455	2.7	0.465	1.9	0.611	3.2	−1.2	2.8	0.9074	−10
2,4-Dimethyl-3-pentanol	0.111	3.9	0.128	3.0	0.130	2.1	0.148	2.8	−1	1.3	0.9432	−6
2-Octanol	0.043	6.5	0.049	10.0	0.053	8.4	0.066	7.6	−1.2	1.7	0.9659	−9.7
2-Ethyl-1-hexanol	0.050	4.0	0.057	7.5	0.060	2.8	0.076	3.6	−1.2	2.0	0.9502	−9.9

[a] RSD: relative standard deviation.

that for most VOCs, the energy of activation of permeation through PDMS is indeed mainly governed by the heat of solution of the analyte in the membrane, and to a much smaller extent by the energy of activation of diffusion. Further, the results also indicate that the energy of activation of permeation is typically of the same order of magnitude for all compounds irrespective of their polarities.

The temperature variations of the uptake rates observed for the model compounds studied in this project were somewhat higher than the theoretically calculated ~0.4%/°C change for diffusive-type passive samplers reported in the literature [7]. It should be noted that when the temperature increases, the uptake rates increase for diffusive-type passive samplers, whereas they decrease for the sampler described in this paper. In practice, diffusive-type passive samplers have been reported to be dependent on temperature to various degrees by different researchers. For example, Penniquin-Cardinal et al. found that the uptake rate decreased by 0.6%/°C for benzene, while it increased by 0.35%/°C for toluene and 0.5%/°C for ethyl benzene and xylenes for the diffusive-type Radiello® samplers [8]. Piechocki-Minguy et al. observed an average 2%/°C change in the uptake rate of nitrogen dioxide between 5 °C and 30 °C using their custom-made diffusive-type passive sampler [9]. The variations in the uptake rates with temperature for the WMS samplers are still relatively small compared to other variabilities involved under field conditions, such as linear flow velocity of air across the sampler, temporal concentration variations, etc. Furthermore, for typical applications in indoor air and soil gas analysis, the temperature of the air is usually nearly constant. Consequently, temperature variations are expected to play only a minimal role in field applications. When more accurate results are desired, appropriate corrections to the calibration constants can be made based on the knowledge of temperature variations in the field.

4.2. Effect of humidity

Prior to interpreting the data, it is important to note that sampler-to-sampler variations in the uptake rates within a single exposure experiment might be due to variations in extraction efficiencies, as well as minor differences in the thicknesses of the membranes used in the fabrication of the individual samplers (the effect of membrane thickness will be reported in a subsequent publication). In this case, the same average analyte concentration in the chamber (determined over the duration of the exposure) was used for the calculation of the calibration constant for that specific analyte for all the individual samplers deployed in the chamber. On the other hand, variations in calibration constants between different exposure experiments might also be due to uncertainties involved in the determination of the concentration of the analyte in the calibration chamber between different exposures.

The calibration constants obtained for the n-alkanes and aromatic hydrocarbons at 3 different humidity levels are listed in Table 4. For each of the analytes, a single factor one-way ANOVA was performed using 24 data points in total obtained from the experiments at 3 different humidities with 8 replicates at each humidity level. The summary of the ANOVA test at 95% probability level ($\alpha = 0.05$) is shown in Table 5. The results indicated that there were no statistically significant differences between the mean calibration constants determined at the three relative humidity (R.H.) levels for all analytes except propylbenzene and butylbenzene. The small but statistically significant differences between the calibration constants of these two compounds determined at different R.H. levels could be attributed, e.g. to the uncertainties in the measurement of their concentrations in the chamber arising from their tendency to sorb onto the walls and/or to the effect of moisture on the sorbent in the active sampling tube. Most importantly, even though the differences were deemed statistically significant, they

Table 4
Average calibration constants for n-alkanes and aromatic hydrocarbons at 3 different humidity levels.

Analyte	Humidity					
	30% R.H.		0% R.H.		90% R.H.	
	Average k	SD[a] ($n = 8$)	Average k	SD ($n = 8$)	Average k	SD ($n = 8$)
n-Hexane	0.664	0.026	0.676	0.021	0.643	0.084
n-Heptane	0.319	0.014	0.334	0.018	0.306	0.047
n-Octane	0.154	0.010	0.159	0.007	0.145	0.022
n-Nonane	0.087	0.005	0.088	0.003	0.081	0.010
n-Decane	0.061	0.003	0.059	0.002	0.057	0.005
Benzene	0.367	0.018	0.371	0.031	0.354	0.055
Toluene	0.178	0.011	0.187	0.010	0.168	0.022
Ethylbenzene	0.099	0.006	0.109	0.006	0.104	0.013
o-Xylene	0.087	0.004	0.085	0.003	0.083	0.011
Propylbenzene	0.068	0.002	0.072	0.002	0.065	0.007
Butylbenzene	0.051	0.002	0.053	0.002	0.048	0.004

[a] SD: standard deviation for n observations.

Table 5
Single factor ANOVA performed using 24 data points in total obtained from the experiments at 3 different humidities and with 8 replicates at each humidity.

Analyte	SS	df	MS	*F*	*P*-value	*F* crit
n-Hexane	0.004641	2	0.00232	0.84	0.445	3.47
Benzene	0.001352	2	0.00068	0.47	0.629	3.47
n-Heptane	0.003049	2	0.00152	1.71	0.205	3.47
Toluene	0.001462	2	0.00073	3.12	0.065	3.47
n-Octane	0.000782	2	0.00039	1.90	0.175	3.47
Ethylbenzene	0.000379	2	0.00019	2.26	0.129	3.47
n-Nonane	0.000221	2	0.00011	2.50	0.106	3.47
o-Xylene	0.000078	2	0.00004	0.78	0.470	3.47
Propylbenzene	**0.000206**	**2**	**0.00010**	**4.79**	**0.019**	**3.47**
n-Decane	0.000054	2	0.00003	2.05	0.154	3.47
Butylbenzene	**0.000111**	**2**	**0.00006**	**6.51**	**0.006**	**3.47**

SS: sum of squares, df: degrees of freedom and MS: mean of squares.
Bold values indicate analytes for which there was a statistically significant difference between the mean calibration constants at the 3 different humidity levels.

were in fact minor compared to other possible sources of variability in the field: for propylbenzene the maximum deviation from the mean calibration constant value was ~7% (at 60% R.H.), whereas for butylbenzene it was only ~5% (at 91% R.H.). Thus, from the practical point of view, these differences would be inconsequential in field measurements. The RSDs of the calibration constants determined at 30 and 60% humidity levels were within 8.5% ($n = 8$) for all analytes, and at 91% humidity they were within 16%. Further, the RSDs of the average calibration constants determined at the 3 humidity levels for each analyte ($n = 4$) were within 6% for all analytes. In practice, this can be considered insignificant when compared to other measurement uncertainties under field conditions.

The diffusion coefficients of water vapour and toluene in the air at atmospheric pressure and 25 °C are 0.251 cm^2/s and 0.0827 cm^2/s, respectively [10,11]. Consequently, the uptake rate of water for a diffusive-type passive sampler is roughly 3 times higher than that for toluene. On the other hand, the permeability of toluene in PDMS is approximately 63 times higher than that of water vapour [12]. Accordingly, the uptake rate of water should be only about 0.0157 times that of toluene when using the WMS sampler. Consequently, the chance of the sorbent getting saturated with water (eventually leading to non-linear sorption of the analyte molecules) should theoretically be very small when compared to diffusive-type passive samplers.

The fact that the variation in calibration constants at different humidity levels is either statistically insignificant or minimal is advantageous when using the WMS samplers for soil gas sampling applications, as the relative humidity in such matrices is typically close to 100%. Further, the samplers can be deployed for a longer time than diffusive samplers (to reduce the limits of detection and quantification), as the saturation of the sorbent by moisture does not occur as early as it does for the latter.

5. Conclusions

It is important to consider the effect of environmental factors such as temperature and humidity on the uptake rates of any passive sampler for accurate determination of the analyte concentrations in the gas phase. Increase in temperature resulted in decreased uptake rates for the vial-based samplers, indicating that the heat of solution played the major role in determining the net energy of activation of permeation, while the energy of activation of diffusion played only a minor role. The trend in uptake rate changes with temperature for the WMS sampler (uptake rates decreasing with increasing temperature) was opposite of that observed for diffusive-type passive samplers, for which they increased with increase in temperature. Experiments performed to determine the variation in the calibration constants with temperature allowed the determination of the energy of activation of permeation of various analytes through PDMS. Such fundamental transport properties can be used for techniques using PDMS membranes such as membrane extraction with a sorbent interface (MESI) or membrane inlet mass spectrometry (MIMS).

Statistically significant differences in the means of the calibration constants determined at different humidities were observed for only 2 out of 11 analytes, and even the two significant differences were so small as to be inconsequential when compared to other sources of variability in field measurements. The possible sources of the difference could be the uncertainty in the measurement of analyte concentrations in the chamber due to sorption onto the walls of the chamber and/or the effect of moisture on the sorbent in the active sampling tube.

The WMS sampler has high potential for applications such as soil gas vapour monitoring, as the temperature in the borehole where the sampler is deployed is expected to vary little with time and the sampler is insensitive to high humidity often found in soil gas. Calibration constant of the sampler towards an analyte is also a function of the sampler's geometry, linear flow velocity of air across the surface of the sampler, exposure duration and analyte concentration among others, and hence their study is important for the overall validation of the sampler. These studies are currently in progress and will be published shortly.

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