


Effect of Exposure Time & Analyte Concentrations on the Uptake Rate of a Polydimethylsiloxane Based Permeation Passive Air Sampler

Effect of exposure time and analyte concentration on the uptake rate of a polydimethylsiloxane-based permeation passive air sampler

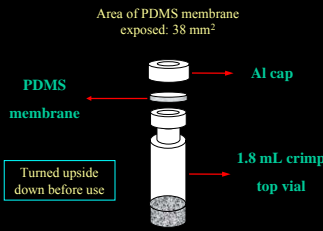

Suresh Seethapathy, Tadeusz Górecki
University of Waterloo,
Ontario, Canada



Measuring Air Pollutants by Diffusive Sampling and Other Low Cost Monitoring Techniques
Krakow, 15th – 17th Sep, 2009.

Passive sampler design

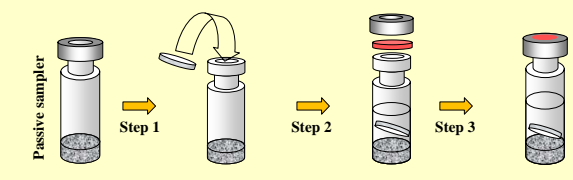
Area of PDMS membrane exposed: 38 mm²

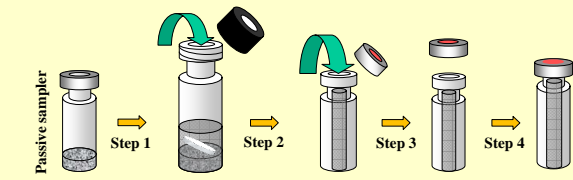
Disposable 1.8 mL crimp-top vial-based permeation passive sampler – **TWA-PDMS sampler**

Material cost < 1.00 \$ per sampler

Extraction scheme 1



Extraction scheme 2



The solution-diffusion model

- Dissolution of the analyte in the membrane material
- Diffusion of the dissolved analyte through the membrane
- Desorption of the analyte on the opposite side of the membrane

$$P = D K_p$$

P - Permeability
 D - Concentration-averaged diffusivity (cm²/min)
 K_p - Partition coefficient

Calibration constant

Theory: Fick's first law of diffusion

Rate of permeation of a gas across a fluid membrane is:

- Proportional to the difference in the concentration of the analyte on the opposite surfaces of the membrane.
- Proportional to the area of cross section of the membrane.
- Inversely proportional to the thickness of the membrane.

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

M = Amount of analyte collected by the sorbent
 D = Diffusion coefficient
 A = Membrane area
 C_{ma} = Concentration of the analyte on the membrane surface in contact with air
 C_{ms} = Concentration of the analyte on the membrane surface in contact with the sorbent
 t = Sampling time
 L_m = Membrane thickness

Calibration constant

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

$$C_{ms} = K C_o$$

$$\left(\frac{M}{t}\right) = (DK) \frac{A}{L_m} C_o$$

$$k = \frac{L_m}{PA} \quad C_o = \frac{kM}{t}$$

M = Amount of analyte collected by the sorbent
 D = Diffusion coefficient
 A = Area of the membrane
 C_{ma} = Concentration of the analyte on the membrane surface in contact with air.
 C_{ms} = Concentration of the analyte on the membrane surface in contact with the sorbent
 t = Sampling time
 L_m = Membrane thickness
 K = Partition coefficient of the analyte between the air and the membrane
 P = Permeability constant of the polymer towards the analyte
 C_o = Concentration of the analyte in the air

k = Calibration constant (time/volume)

k' = Uptake rate (volume/time)

Effect of Exposure Time & Analyte Concentrations on the Uptake Rate of a Polydimethylsiloxane Based Permeation Passive Air Sampler

Dynamics of the sampler response

Residence time for diffusive-type samplers

$$t_d = \frac{L^2}{2D_a}$$

- Residence time of toluene ($D_a = 8.6 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) for diffusive-type passive samplers:¹

GABIE - 4.05 s, Perkin Elmer - 25.5 s

Residence time for permeation-type samplers

$$t_p = \frac{L^2}{2D_p}$$

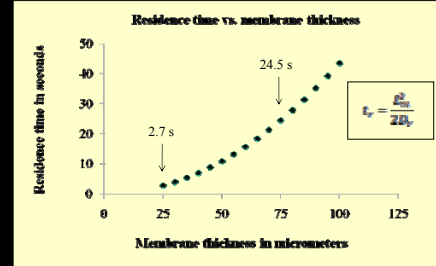
- Estimated residence time of toluene ($D_p = 1.15 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) for TWA-PDMS passive samplers:

for 75 μm thick PDMS membrane – 24.5 s

¹E. Langlois, Am. Occup. Hyg. 52 (2008) 239.

7

Estimated residence time of toluene for TWA-PDMS passive samplers



8

Water vapour diffusivity/permeability in diffusive- and permeation-type samplers

- Uptake rate of water vapor for diffusive-type passive samplers is roughly 3 times higher than that for toluene.
- Estimated uptake rate of water vapor for TWA-PDMS samplers is roughly 63 times lower than that for toluene.

Consequence

- Sorbent saturation with moisture is quicker for diffusive-type samplers when compared to TWA-PDMS samplers.
- Should allow for extended period of sampling at higher analyte concentrations in vapor phase for TWA-PDMS samplers without sorbent saturation.

9

Determination of calibration constants

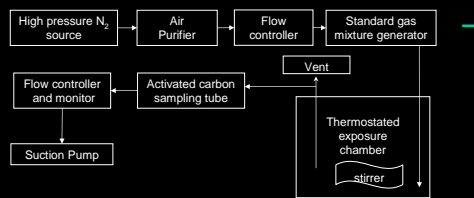
- Generation of standard gas mixture.
- Exposure of the passive sampler to this mixture for a pre-determined time at constant temperature.
- Quantification of the analytes trapped by the sorbent.

$$k = \frac{C_0 M}{t}$$

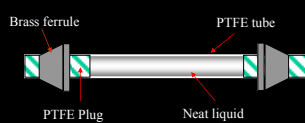
Where $\frac{1}{k} = \frac{PA}{L_m}$

10

Experimental setup



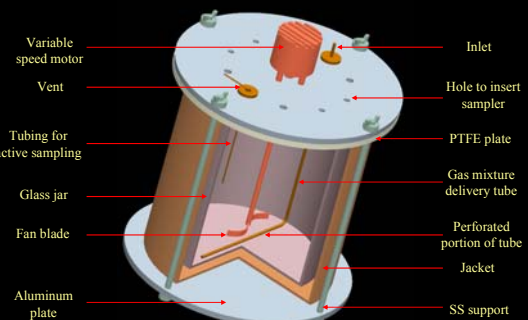
Laboratory made permeation tube^e



^eProf. Jacek Namieśnik, Technical University of Gdańsk, Private communication.

11

Calibration chamber design



12

Effect of Exposure Time & Analyte Concentrations on the Uptake Rate of a Polydimethylsiloxane Based Permeation Passive Air Sampler

Calibration constants of n-hexane for different exposure durations

Concentration ($\mu\text{g}/\text{m}^3$)	Exposure duration (days)	Average constant (min/mL)	STDev (n=6)	%RSD
806.3	1	0.850	0.072	8.5
759.2	3	0.835	0.018	2.2
923	5	0.862	0.052	6.0
605.2	7	0.842	0.019	2.3
700.2	9	0.860	0.082	9.5

- No observable effects of exposure duration on calibration constant.
- Long term TWA sampling made possible.

13

Experimentally determined and estimated calibration constants of selected chlorinated compounds

Analyte	Calibration constant (min/mL)
c-DCE	0.524
TCE	0.305
PCE*	0.187

* PCE concentration estimated based on physicochemical properties of the analytes.

A good correlation between TWA-PDMS samplers and standard methods over a wide range of analyte concentration indicates non-variability of k with concentration.

14

Comparison of results obtained from SUMMA™ canisters and TWA-PDMS samplers (location 1)

- TWA PDMS samplers deployed inside vent pipes and just above ground level when there was upward air flow in the pipes.
- The flow in the vent pipe was expected to reduce any starvation effect.
- The TWA-PDMS samples and the SUMMA™ canisters samples were both taken over a period of 24 hours for TWA concentration determination.



Passive vent pipe

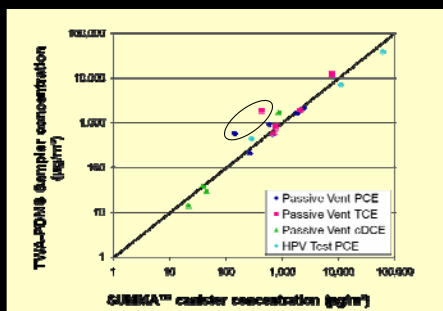
15

Comparison of results obtained from SUMMA™ canisters and TWA-PDMS samplers (location 2)

- TWA PDMS samplers deployed inside a flow-through cell in the effluent path.
- The forced flow in the vent pipe was expected to reduce any starvation effect.
- TWA-PDMS samplers were deployed in the flow cell for half an hour to an hour.
- SUMMA™ canister samples were collected over a period of 5 minutes during the period the TWA-PDMS sampler was deployed.

16

Comparison of results obtained from SUMMA™ canisters and TWA-PDMS samplers (locations 1 and 2)



17

Comparison of results obtained from SUMMA™ canisters and TWA-PDMS samplers (locations 1 and 2)

- Very strong correlation between the two methods over two to three orders of magnitude for each analyte
- A good overall correlation over ~4 orders of magnitude for all the analytes put together.
- Exception – A deviation from the 1:1 correlation line for two data points.
- No negative bias in the concentrations obtained from TWA-PDMS samplers which indicated that there was no starvation effect.

18

Effect of Exposure Time & Analyte Concentrations on the Uptake Rate of a Polydimethylsiloxane Based Permeation Passive Air Sampler

TWA-PDMS samplers and TAGA for the quantification of PCE in indoor air (location A)



US EPA Trace Atmospheric Gas Analyser (TAGA) mobile laboratory

- Indoor air sampling was performed at two buildings at a former military arsenal in New Jersey to quantify PCE concentrations.
- TWA-PDMS samplers were deployed for a 2-week period, and the analyte concentrations compared to those obtained a week earlier from US EPA TAGA mobile laboratory.

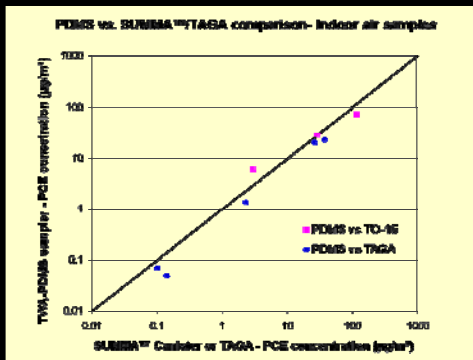
19

TWA-PDMS samplers and SUMMA™ canisters for the quantification of PCE in indoor air (location B)

- TWA-PDMS sampling was performed over a period of 3 days.
- Compared to samples collected over a period of 8 hours using SUMMA™ canisters (analyzed by EPA Method TO-15).
- The SUMMA™ canister samples were taken immediately after the TWA-PDMS samplers' deployment period.

20

TWA-PDMS samplers and TAGA for the quantification of TCE and PCE in indoor air (locations A and B)



21

TWA-PDMS samplers and SUMMA™/TAGA for the quantification of PCE in indoor air (locations A and B)

- Excellent correlation between TWA-PDMS samplers and other reference methods.
- The correlation indicates a wide dynamic range of the TWA-PDMS samplers (over 4 orders of magnitude).
- The correlation was good for 3 days to 14 days exposure.
- Considering that the samples from TWA-PDMS samplers were collected over 3 days, SUMMA™ canisters over 8 hours and TAGA measured the concentrations instantaneously, the correlation observed can be considered excellent.

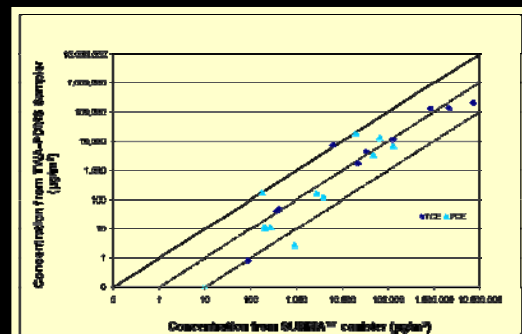
22

Sub-slab vapor sampling with TWA-PDMS samplers and SUMMA™ canisters

- SUMMA™ canister samples were collected one week prior to the deployment of the TWA-PDMS samplers.
- The vapour samples were collected from 13 mm holes drilled into the floor for a period ranging between 5 and 10 minutes at 200 mL/min using the flow controller in the SUMMA™ canister.
- The TWA-PDMS samplers were introduced into holes of 19 mm diameter (of varying depths depending on the thickness of the concrete).
- The samplers were hung from a rigid metal wire at approximately an inch from the bottom of the bore hole, and sealed with a rubber stopper wrapped with aluminum foil.

23

Sub-slab vapor sampling with TWA-PDMS samplers and SUMMA™ canisters



24

Effect of Exposure Time & Analyte Concentrations on the Uptake Rate of a Polydimethylsiloxane Based Permeation Passive Air Sampler

Sub-slab vapor sampling with TWA-PDMS samplers and SUMMA™ canisters

- Negative bias in the concentrations of both TCE and PCE determined by the TWA-PDMS samplers compared to those obtained using the SUMMA™ canister method.
- Approximately one order of magnitude for most of the samplers.
- A direct consequence of the starvation effect.

25

Sub-slab vapor sampling with TWA-PDMS samplers and SUMMA™ canisters

- Positive correlation between the two methods over ~ 4 orders of magnitude sufficient for routine use of the TWA-PDMS sampler.
- Application in determining the relative concentrations of various pollutants at different locations.
- Starvation effect is unavoidable for not just the sampler discussed here, but for any other passive sampler in general.

26

Conclusions

- Calibration constant of n-hexane did not vary over exposure duration ranging from 1 day to 9 days.
- Comparison of analyte concentrations from TWA-PDMS samplers and TAGA/SUMMA™ canisters indicated excellent dynamic range of over 6 orders of magnitude concentrations for selected chlorinated compounds.
- The advantages can be attributed to permeability properties of PDMS.
- TWA-PDMS samplers can be used for long term (~ two weeks) exposure studies.

27

Acknowledgments

- University Consortium for Field-Focused Groundwater Contamination Research.
- **Todd McAlary, Hester Groenevelt**, David Bertrand, Robin Swift, Todd Creamer, Chapman Ross, and Duane Graves of Geosyntec Consultants, Inc., Guelph, ON, for performing the field exposure experiments.

28