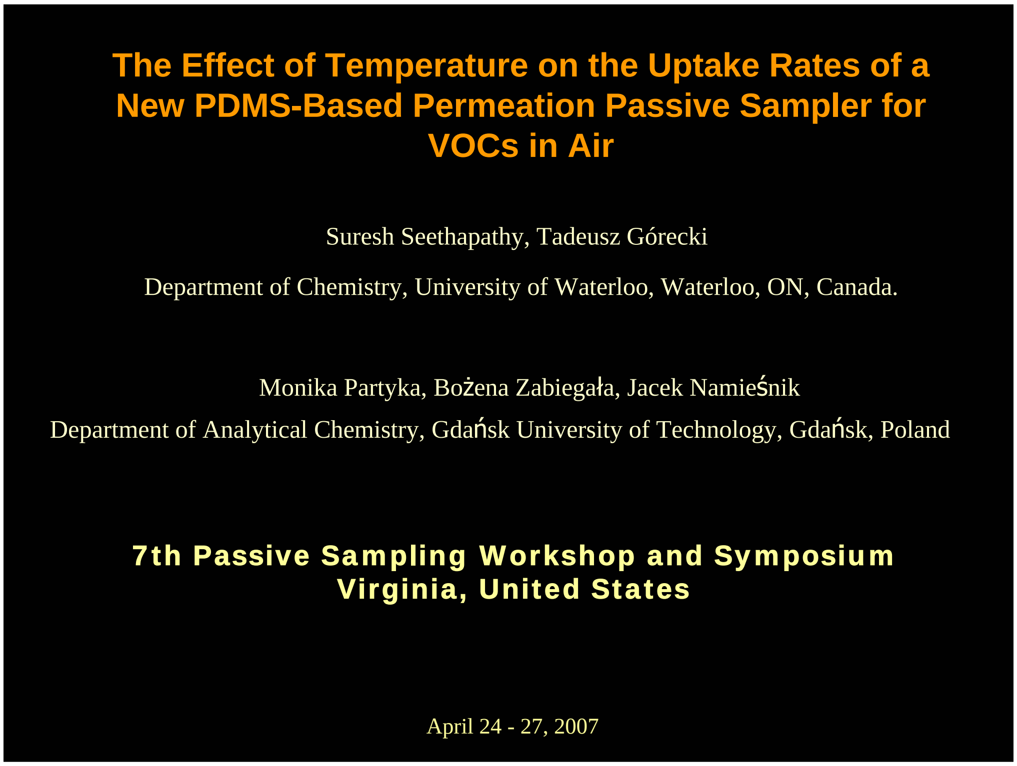

The Effect of Temperature on the Uptake Rates of a New PDMS-Based Permeation Passive Sampler for VOCs in Air

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7th Passive Sampling Workshop and Symposium
Virginia, United States

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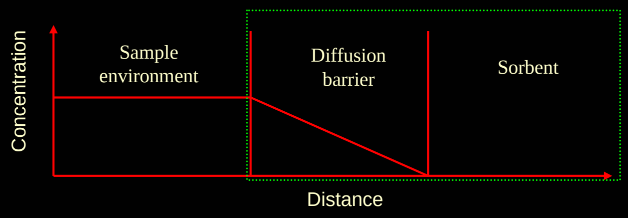
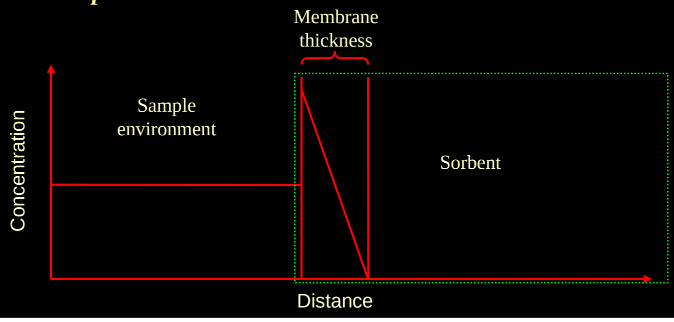
Concentration Profiles for the Two Types of Passive Samplers

Diffusion samplers



Permeation samplers



Comparison of Diffusion and Permeation Passive Samplers

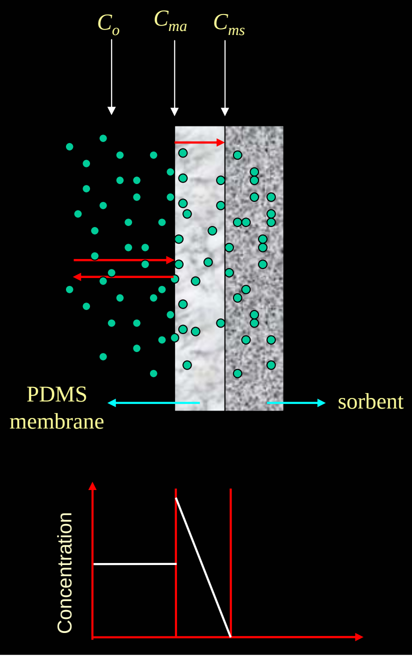
Permeation passive sampling – permeation through a membrane

Diffusive passive sampling – diffusion through air

- Diffusion samplers
  - sampling rate can be estimated based on the properties of the analyte
  - sensitive to moisture, air currents, temperature variations

- Permeation samplers
  - effective moisture elimination, much less sensitive to air currents and temperature changes
  - must be calibrated for each analyte

Calibration Constant / Uptake rate



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

M = Amount of analyte collected by sorbent

D = Diffusion coefficient

A = Area of 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 = Time of sampling

L_m = Membrane thickness

Theory

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

$$C_{ma} = KC_o$$

$$\left(\frac{M}{t}\right) = \textcircled{DK}\frac{A}{L_m}C_0$$

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

$$C_0 = \frac{kM}{t}$$

M = Amount of analyte collected by sorbent

D = Diffusion coefficient

A = Area of 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 = Time of sampling

L_m = Membrane thickness

K = Partition coefficient of the analyte between air and the membrane

P = Permeability constant of the polymer towards the analyte

C_o = Concentration of the analyte in air

<u>k = Calibration Constant (time/volume)</u>

<u>k^{-1} = Uptake rate (volume/time)</u>

Properties of PDMS

- Individual segmental motions even at –127 °C !!!
  - Nearly constant diffusion coefficient for most VOCs
  - Relative permeabilities are primarily decided by partition coefficients

- Temperature effects on permeability

increase in temperature results in

- decreased partition coefficient
- increased diffusivity

$$\left.\begin{array}{l}\text{- decreased partition coefficient}\\ \text{- increased diffusivity}\end{array}\right\} P = \text{Đ}K$$

$$P = P^{o} \exp\left(-E_{p}\left[\frac{1}{RT} - \frac{1}{RT_{o}}\right]\right)$$

$$E_p = E_d + \Delta H_s$$

E_p: Energy of Activation of permeation

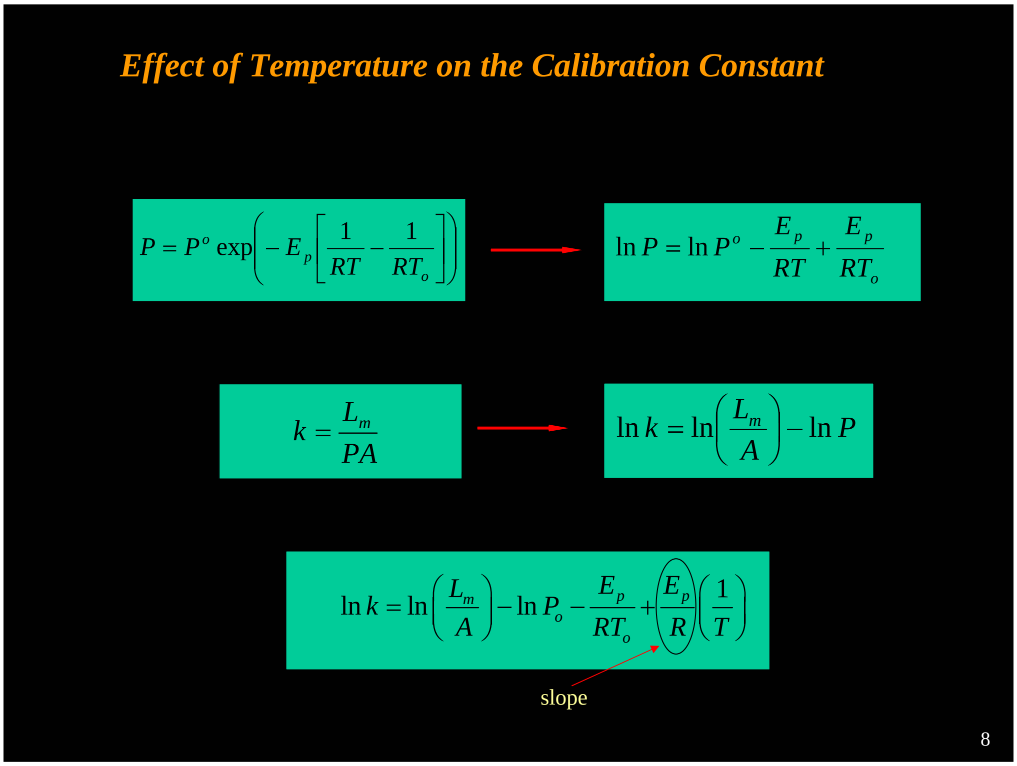
E_d: Energy of activation of diffusion

ΔH_s: Heat of solution

For PDMS, towards most volatile organic compounds

$\Delta H_s < 0$

$E_d > 0$

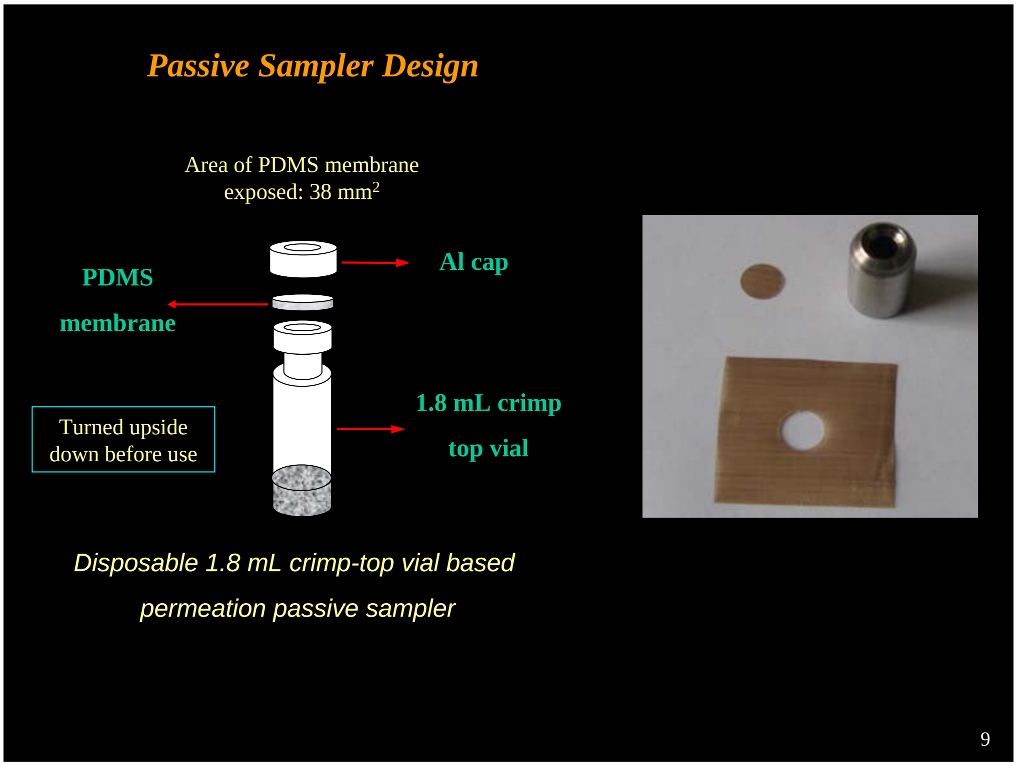


Effect of Temperature on the Calibration Constant

$$P = P^o \exp\left(-E_p\left[\frac{1}{RT} - \frac{1}{RT_o}\right]\right) \longrightarrow \ln P = \ln P^o - \frac{E_p}{RT} + \frac{E_p}{RT_o}$$

$$k = \frac{L_m}{PA} \longrightarrow \ln k = \ln\left(\frac{L_m}{A}\right) - \ln P$$

$$\ln k = \ln\left(\frac{L_m}{A}\right) - \ln P_o - \frac{E_p}{RT_o} + \underbrace{\left(\frac{E_p}{R}\right)}_{\text{slope}}\left(\frac{1}{T}\right)$$



Passive Sampler Design

Area of PDMS membrane exposed: 38 mm^2

PDMS membrane

Al cap

Turned upside down before use

1.8 mL crimp top vial

Disposable 1.8 mL crimp-top vial based permeation passive sampler

1. Desorption in the same vial – If proper solvent volume is used in combination with non-powdery, spherical sorbent like anasorb 747, direct introduction into autosampler without filtration is possible – HAS BEEN VARIFIED TO BE WORKING.
2. Very simple – perhaps use and throw, avoiding all sample contaminations involved during reusage of a sampler.

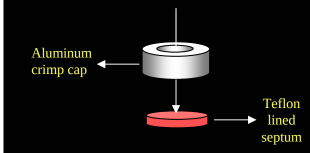
2mL crimptop vial – 15$/100 vials

Membrane area required for each vial ~ 1sq cm – for 100 samplers – 100 sq cm ~

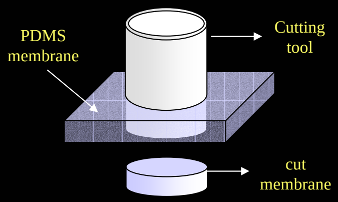
Cost of membrane per square feet (30cm x 30cm) – 25$ ---→ cost of membrane for 100 sq cm ~ 10$

Total material cost for making 100 samplers – 25$!!

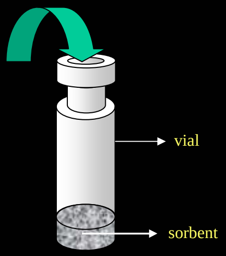
Sampler Preparation



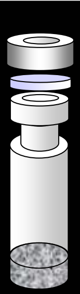
1. Remove septum from crimp cap



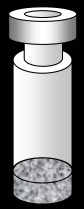
2. Cut PDMS membrane



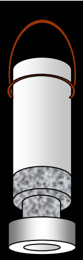
3. Add sorbent to the vial



4. Assemble membrane and cap

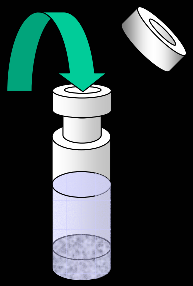


5. Crimp to seal

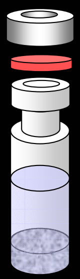


6. Attach support/turn upside down for sampling

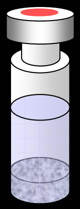
Analyte extraction/analysis



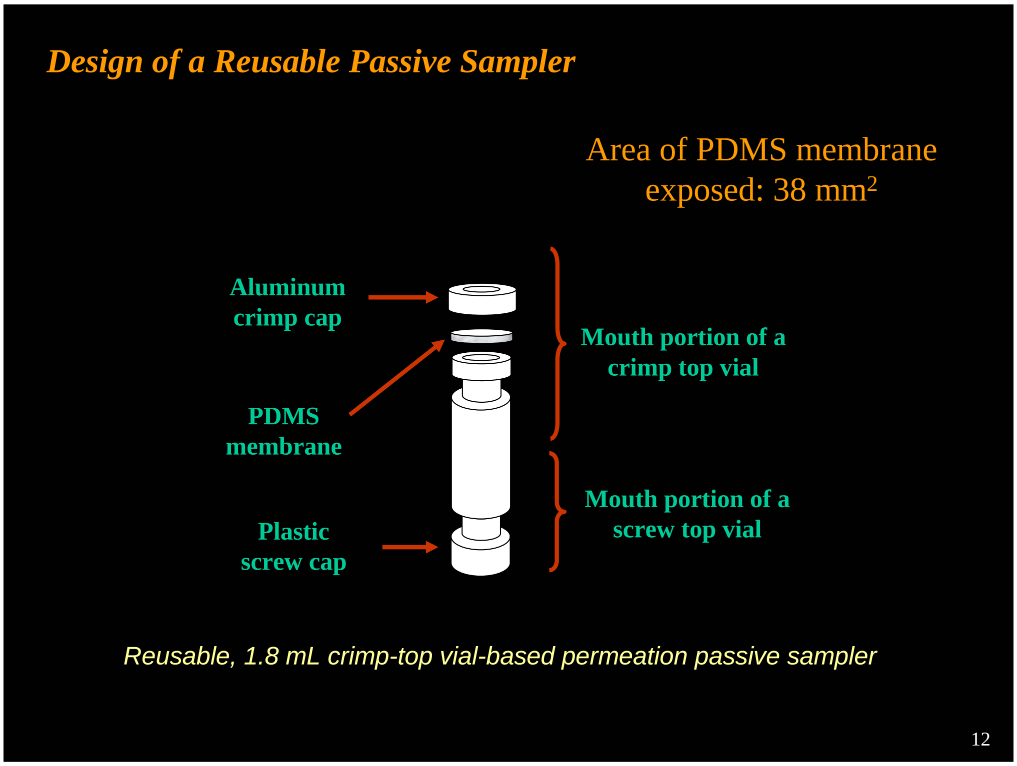
7. De-crimp cap, add desorption solvent



8. Crimp with aluminum crimp cap/teflon lined septum and shake



9. Introduce into GC auto sampler – **either directly** or after transferring the extract into a different vial



Design of a Reusable Passive Sampler

Area of PDMS membrane exposed: 38 mm^2

Aluminum crimp cap

PDMS membrane

Plastic screw cap

Mouth portion of a crimp top vial

Mouth portion of a screw top vial

Reusable, 1.8 mL crimp-top vial-based permeation passive sampler

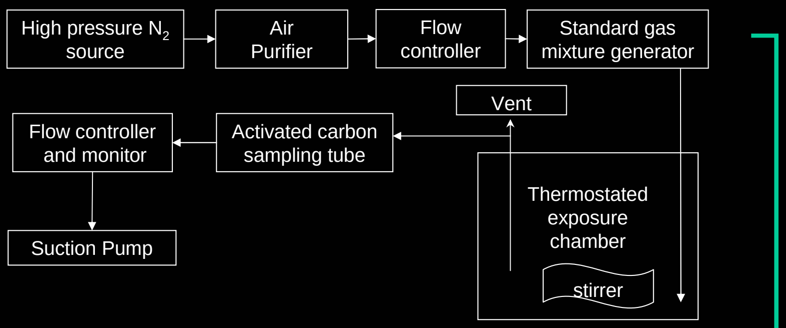
Double headed vials.

Advantages:

Keyword: membrane thickness

1. Membrane is reusable
2. Sampler can be calibrated and the same sampler can be utilized for passive sampling
3. Important to keep the membrane properties constant when studying the effect of environmental factors on the calibration constant
4. In the case of single headed passive sampler, if the membrane is changed, it has to be ensured that the membrane thickness is the same as the membrane thickness with which the calibration was performed.. This can be done by cutting the membrane using a die to ensure constant area of membrane. By doing this, the membrane can then be weighed and a constant weight will indicate the same thickness of the membrane.

Experimental Setup



High pressure N_2 source

Air Purifier

Flow controller

Standard gas mixture generator

Vent

Flow controller and monitor

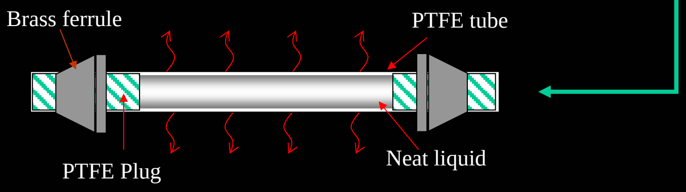
Activated carbon sampling tube

Thermostated exposure chamber

stirrer

Suction Pump

Laboratory made permeation tube[a]



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[a] Prof. Jacek Namieśnik, Technical University of Gdańsk, Private communication.

Effect of Temperature on the Calibration Constant

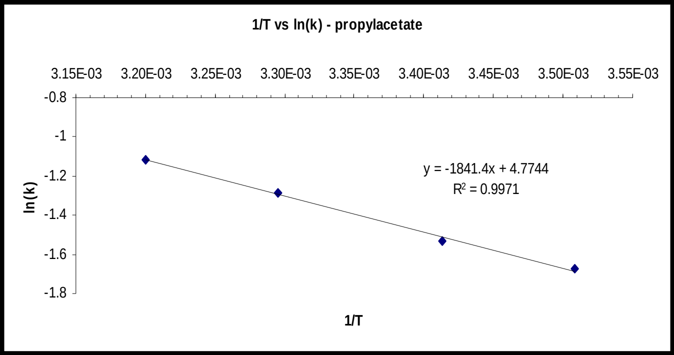
- Experiments were conducted over a temperature range of 285 to 312.5 K

- Model compounds included n-nonane, n-decane, ethyl acetate, propyl acetate, methyl butyrate, sec-butyl acetate, ethyl butyrate, butyl acetate, propyl butyrate, butyl butyrate.

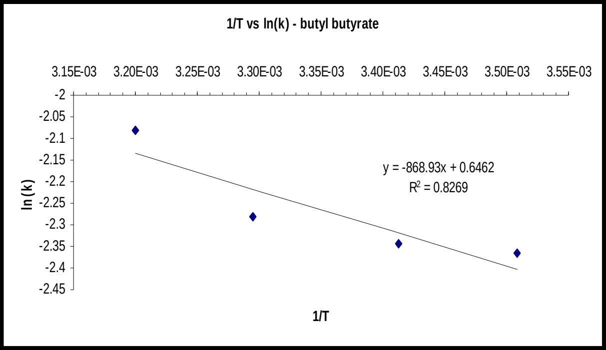
- n-nonane and n-decane used as references.

- Experiments started with esters as they have polarity between that of highly polar alcohols and highly non-polar alkanes and aromatic hydrocarbons.

Temperature – Calibration constant relationship for esters

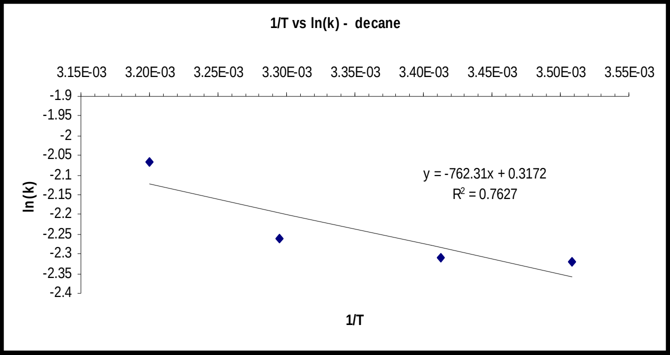


Temperature – Calibration constant relationship for esters

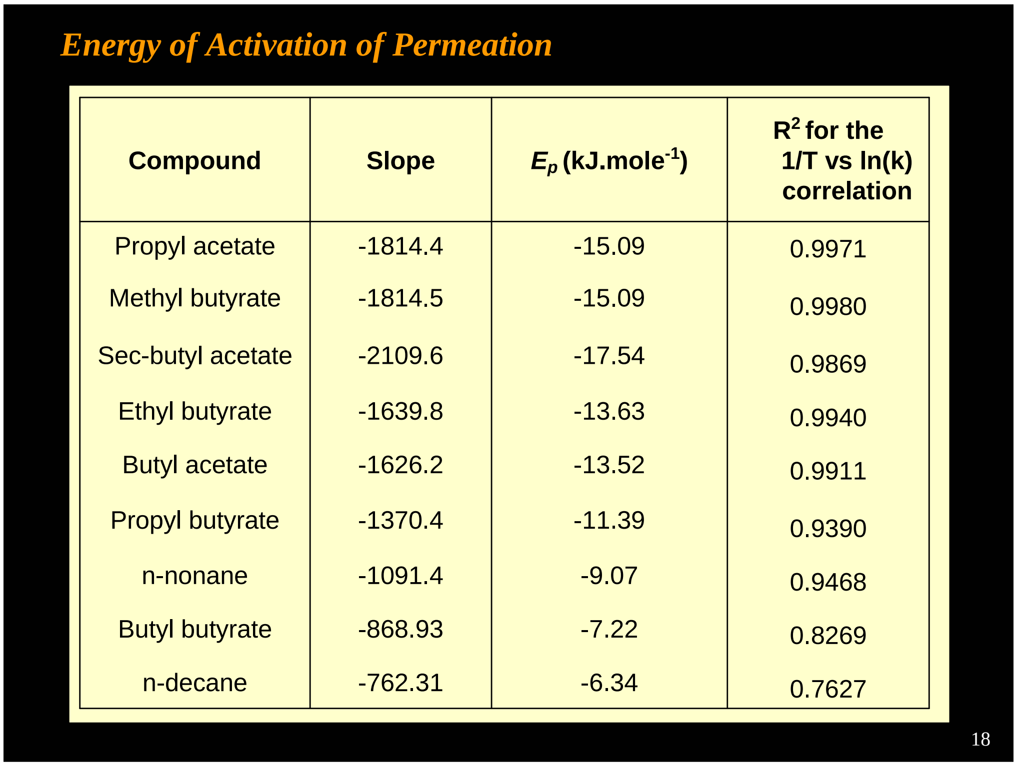


- average variation for moderately polar esters - 1.4% per ^{o}K

Temperature – Calibration constant relationship for n-alkanes



- non-polar n-nonane and n-decane - 0.9% per ^{o}K



Energy of Activation of Permeation

Compound	Slope	E_p (kJ.mole^{-1})	R^2 for the 1/T vs ln(k) correlation
Propyl acetate	-1814.4	-15.09	0.9971
Methyl butyrate	-1814.5	-15.09	0.9980
Sec-butyl acetate	-2109.6	-17.54	0.9869
Ethyl butyrate	-1639.8	-13.63	0.9940
Butyl acetate	-1626.2	-13.52	0.9911
Propyl butyrate	-1370.4	-11.39	0.9390
n-nonane	-1091.4	-9.07	0.9468
Butyl butyrate	-868.93	-7.22	0.8269
n-decane	-762.31	-6.34	0.7627

Conclusions

- A simple, cost effective passive sampler and sampling procedure have been devised to quantify VOCs in air.
- Temperature effects on calibration constant have been studied for esters, n-nonane and n-decane.
- Fundamental transport properties like energy of activation of permeation can be determined using the data.
- Temperature effects are usually negligible in indoor air environments.

Stress on point 2

Acknowledgments

- Natural Sciences and Engineering Research Council (NSERC Canada).
- University Consortium for Field-focused Groundwater Contamination Research.
- Workplace Safety and Insurance Board of Ontario (WSIB)

Questions?