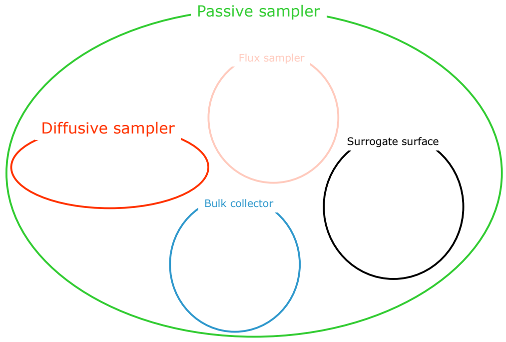
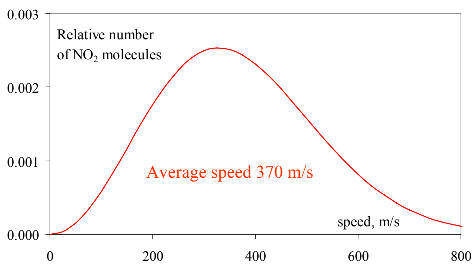
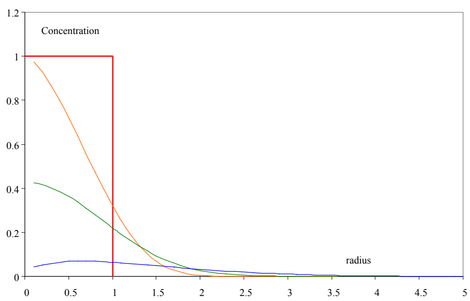
Principles of Diffusive Monitoring

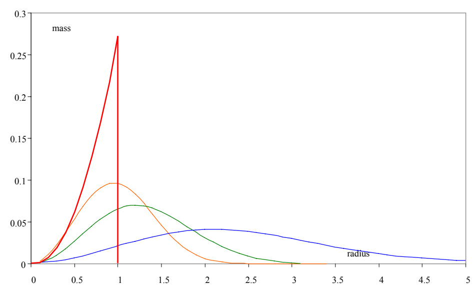
Martin Ferm, Kraków, 15 September 2009

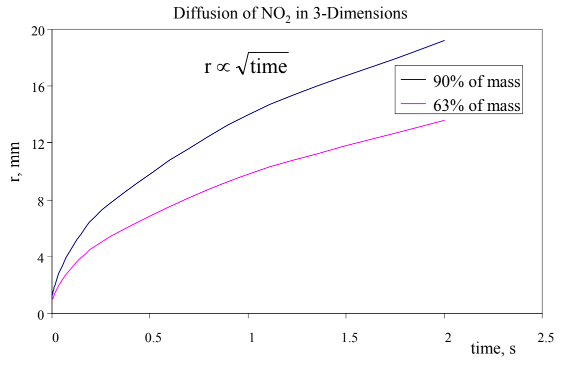




Molecular diffusion







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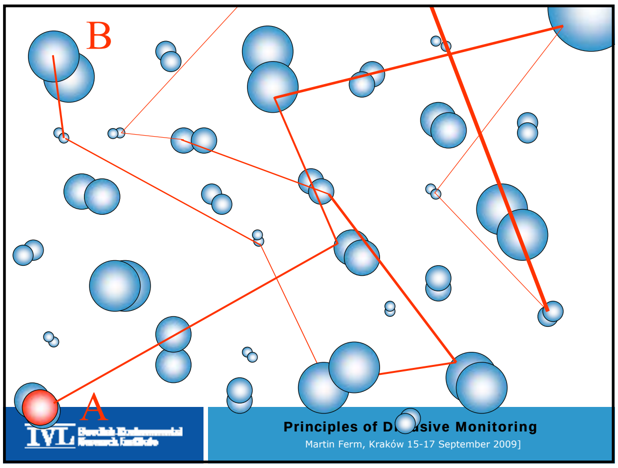

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Collision frequency, Z for a NO_2 molecule ≈ 4 ·10^9 s^{-1}

Mean free path, λ ≈ 0.1 µm

Average velocity, ū ≈ 370 m s^{-1}

Diffusion coefficient ≈ 1/3 λ ū

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Calculations for Palmes tube

Each NO_2 molecule travels on average 62 km in the tube.

During that process it hits the wall on average 5.3 million times.

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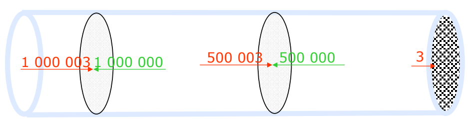
Calculations for Palmes tube
10 µg NO_2 m^{-3}, Δt= 1 ns, at steady state



Net flux:	3	3	3

Fick's first law of diffusion   Net flux: $\varnothing = -D\frac{dC}{dx}$

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Diffusive sampling (If C_s=0): $\overline{C}_a = \frac{S \cdot L}{D \cdot A \cdot \Delta t}$

Active sampling: $\overline{C}_a = \frac{S}{F \cdot \Delta t}$

$F = \frac{D \cdot A}{L}$ [ml/min]

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Changing the lower detection limit

$$S = \frac{\overline{C}_a \cdot D \cdot A \cdot \Delta t}{L}$$

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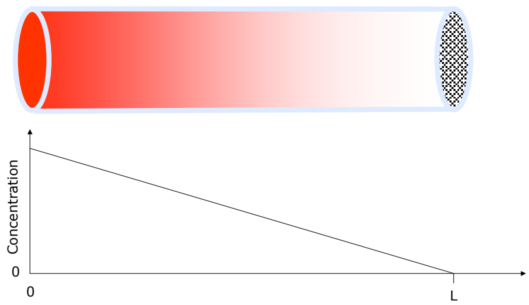

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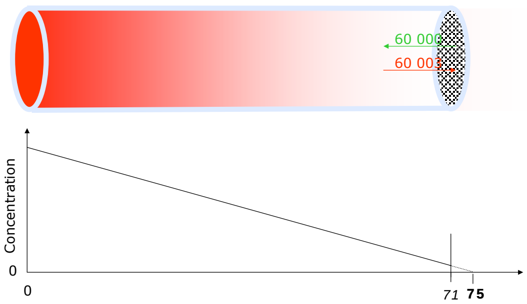
$$\frac{A_{sorbent}}{A_{sampler}} = 2.0$$



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Comparing diffusive sampling with active sampling

Diffusive sampling:

- The sorbent does not have to be very efficient
- The tube material must be very inert to the gas
- Interference from other gases is severer

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Except for **molecular diffusion**, gas molecules can also be transported by:

- **Turbulent (Eddy) diffusion**
- Permeation (Knudsen diffusion), effusion
- Convection
- *Advection*
- *Sound waves, Explosion*

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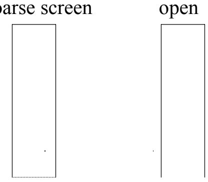
Turbulent diffusion

INDOOR SAMPLING

coarse screen | open



30.5±2.7 | 31.1±0.6 µg NO_2 m^{-3}

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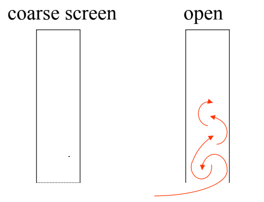
OUTDOOR SAMPLING



30.0±2.1   55.6±8.0 $\mu g\ NO_2\ m^{-3}$

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Permeation

When the pore size is similar or less than the mean free path of the gas

Teflon membrane filters have a pore size > the mean free path of NO_2

high porosity (>80 %)

and a thickness < 0.2 mm

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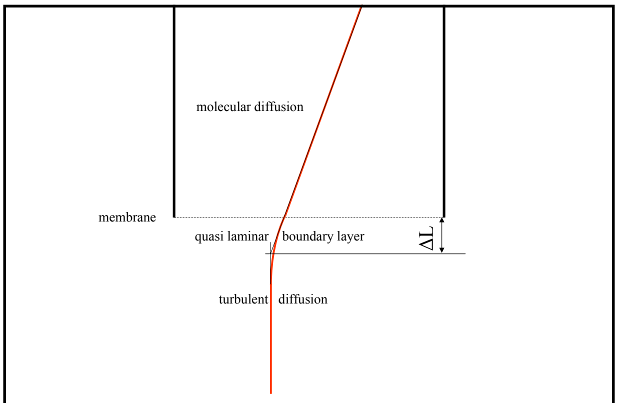

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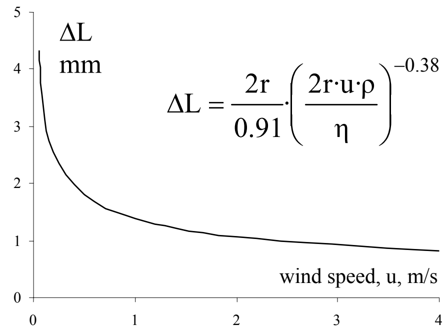

$$\Delta L = \frac{2r}{0.91} \cdot \left(\frac{2r \cdot u \cdot \rho}{\eta} \right)^{-0.38}$$

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Within tube chemistry: $NO + O_3 \rightarrow NO_2 + O_2$

Residence time: $t_r = \frac{L^2}{2D}$

L	t_r
71 mm	2.5 min
30 mm	30 s
10 mm	3 s

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Transient response

The diffusion equation

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

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Fick's second law of diffusion

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

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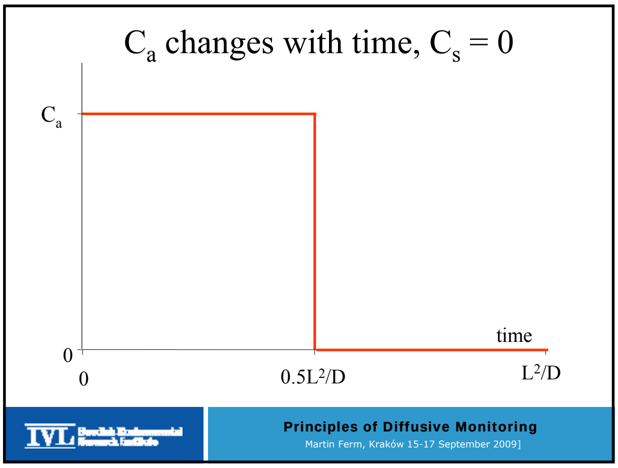

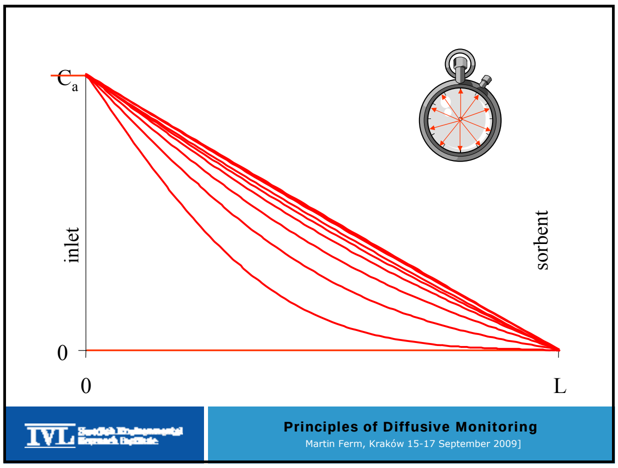

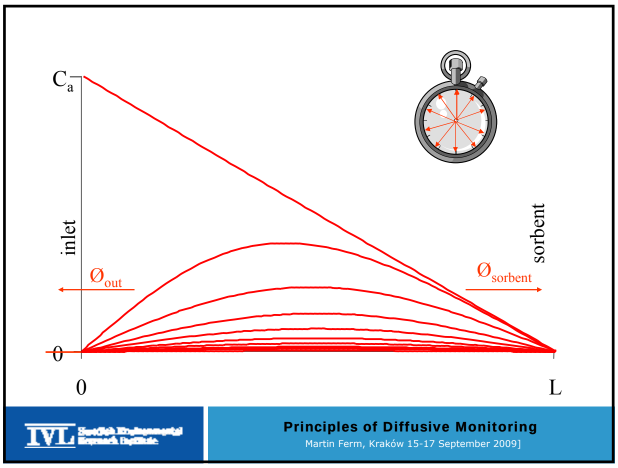

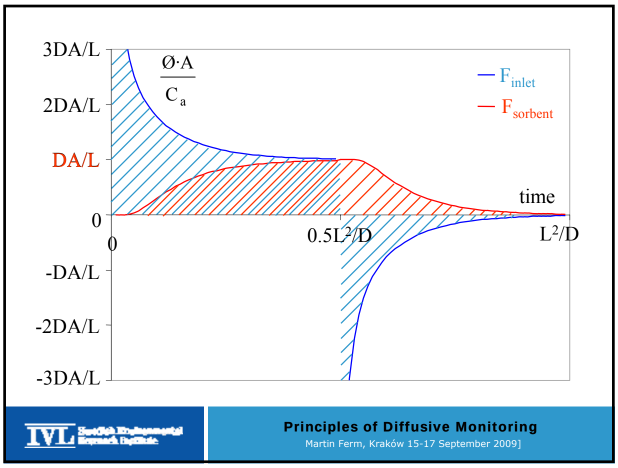

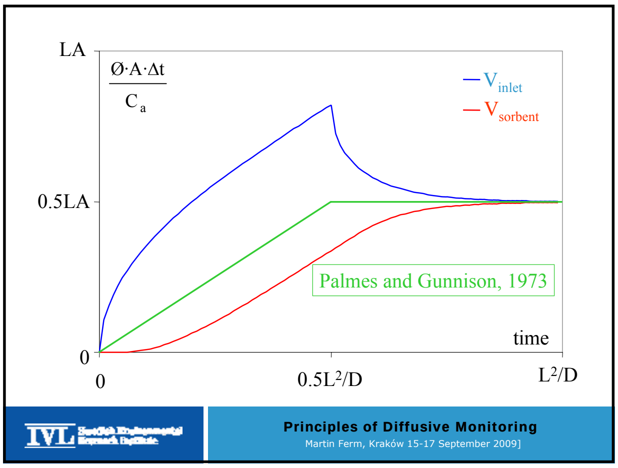

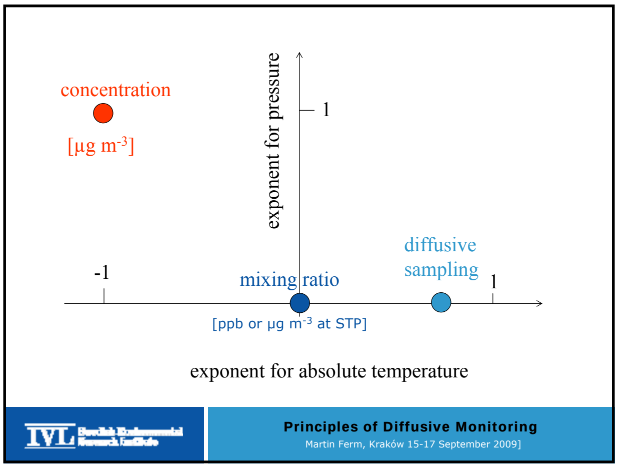
concentration
[µg m-3]
exponent for pressure
1
-1
mixing ratio
[ppb or µg m-3 at STP]
diffusive sampling
1
exponent for absolute temperature
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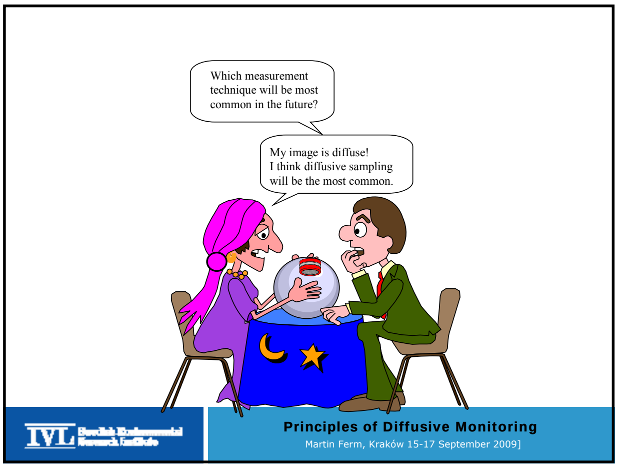
Which measurement technique will be most common in the future?
My image is diffuse! I think diffusive sampling will be the most common.
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