# Development of Miniature Mass Spectrometry for In-Situ Characterization of the Environment

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# Contents

1. Direct PAH analysis from soil

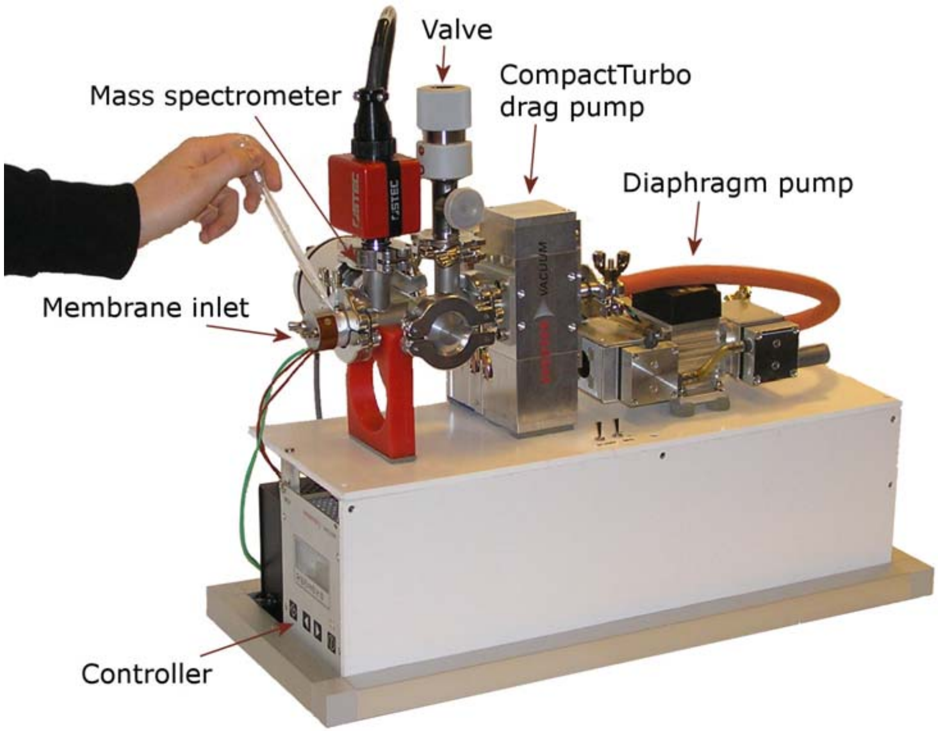
   AEC Group, Copenhagen

2. The moving sensors algorithm or dynamic FIA

   AEC Group and T. Short's group, USF

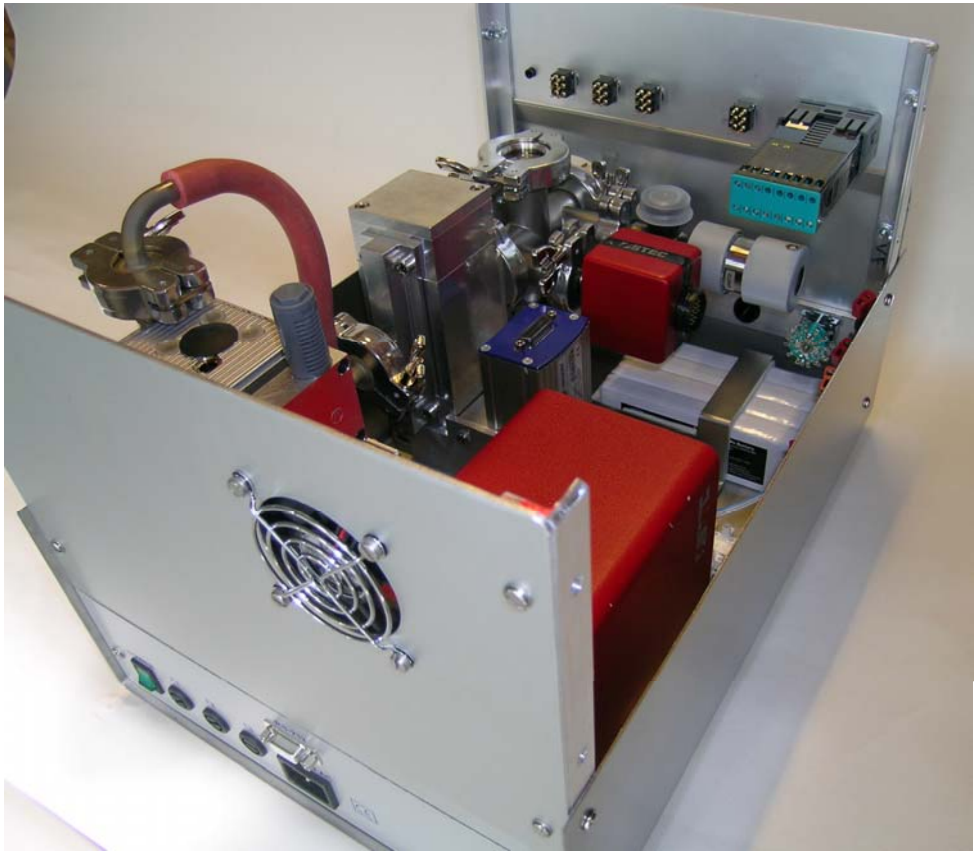
# The mini-MIMS at the AEC-Group
# Department of Chemistry, Copenhagen University

## HEMS 2005



## HEMS 2007

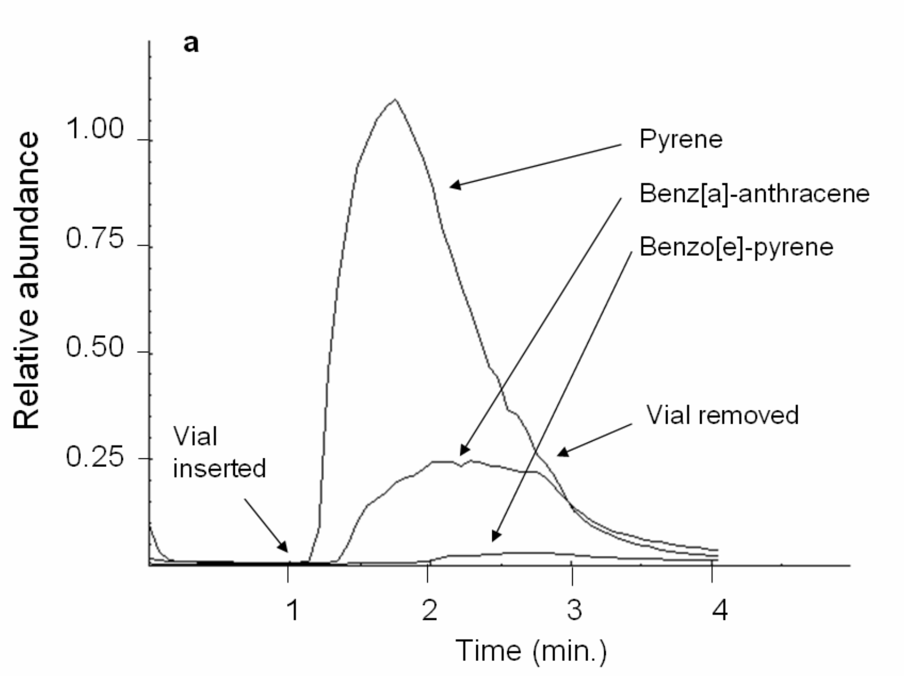
# Compact packing



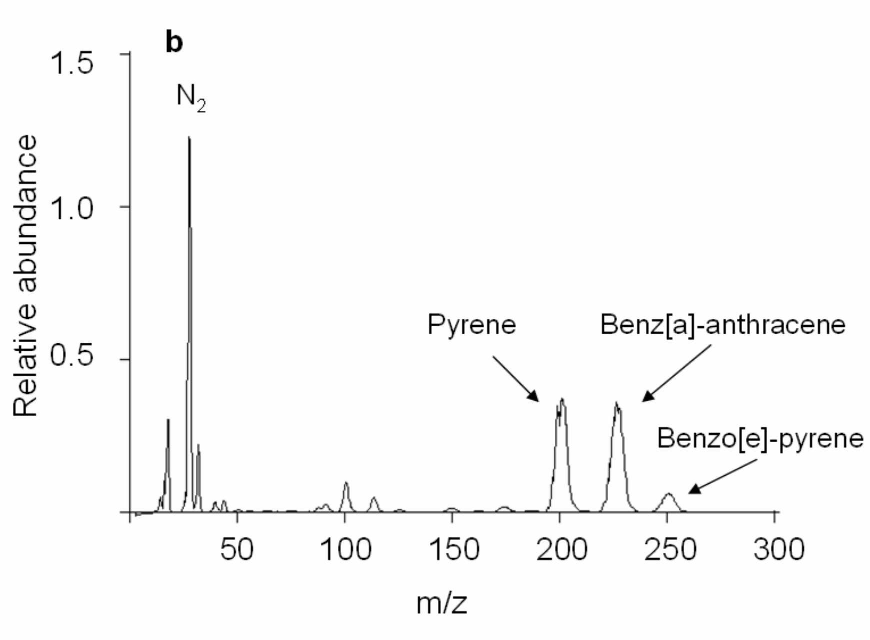
Sample cell for direct soil analysis

# PAH's analysed directly from sand and soil

## Monitoring of PAHs evaporating from the sample

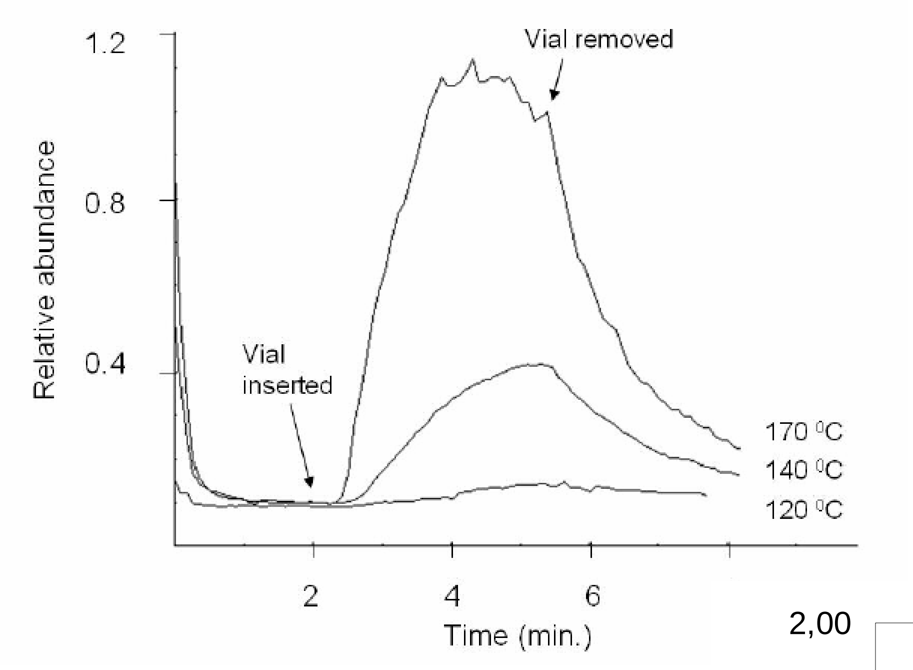


## Spectrum recorded just before the vial was removed



Rapid Commun. Mass Spectrom. 2007, 21, 1574-1578

# Influence of temperature

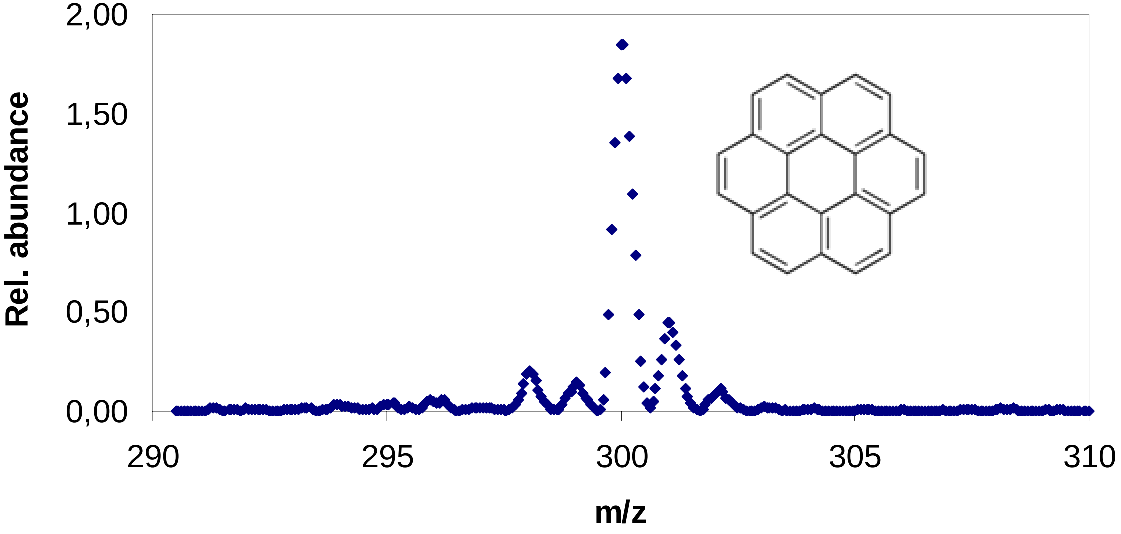


Benz[a]anthracene detected at different temperatures

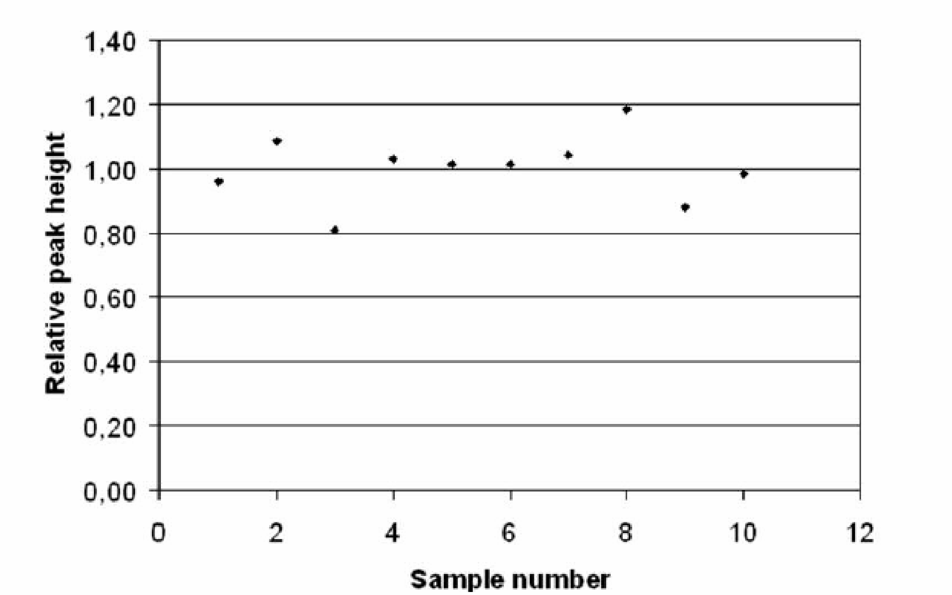
Coronene: $C_{24}H_{12}$

mp 430 $^{O}$C

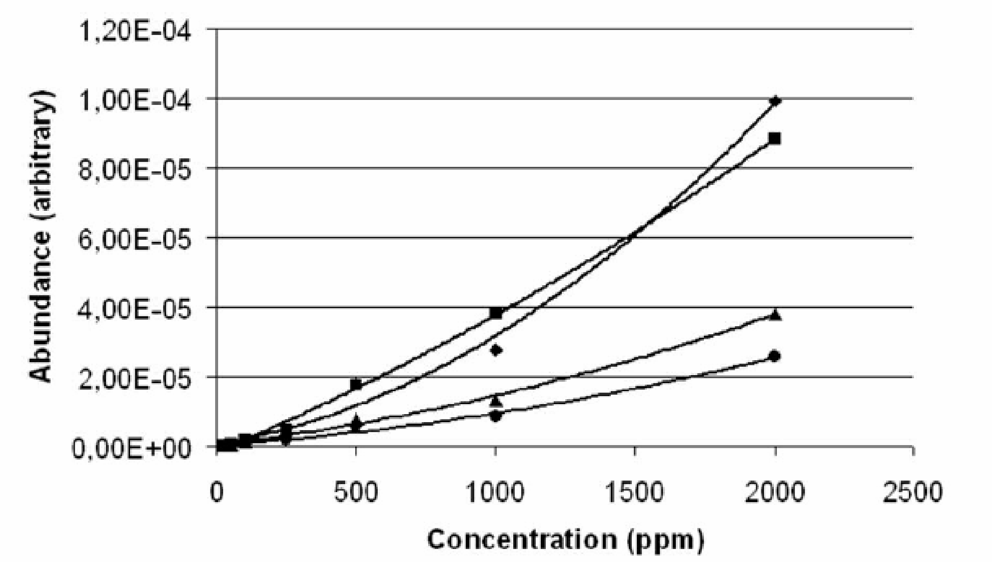
Inlet 200 $^{O}$C



# Quantification



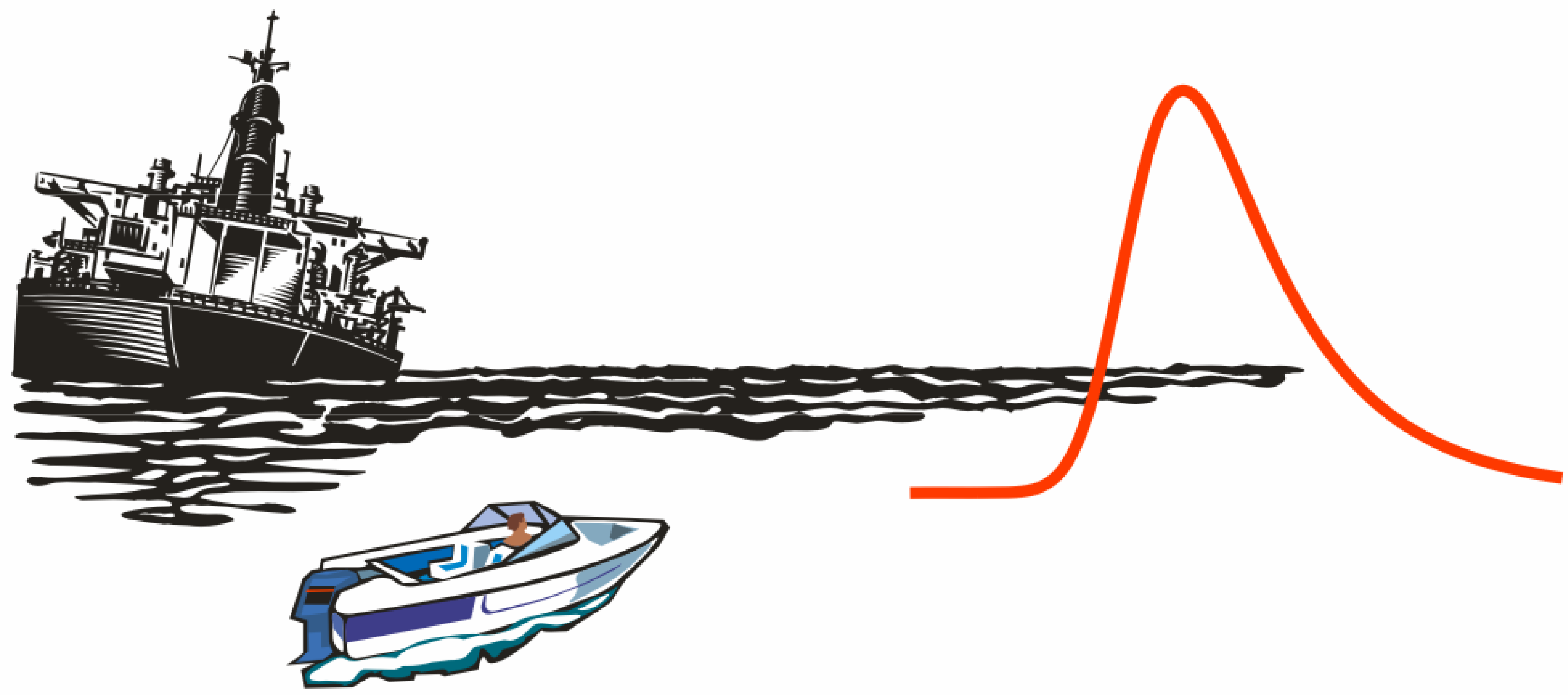
10 independently prepared sand samples spiked with benz[a]anthracene



Non-linearity at high concentration caused by membrane swelling

# The moving sensors algorithm or dynamic FIA

C. Janfelt, S.K. Toler, R.J. Bell, R.T. Short and F.R. Lauritsen

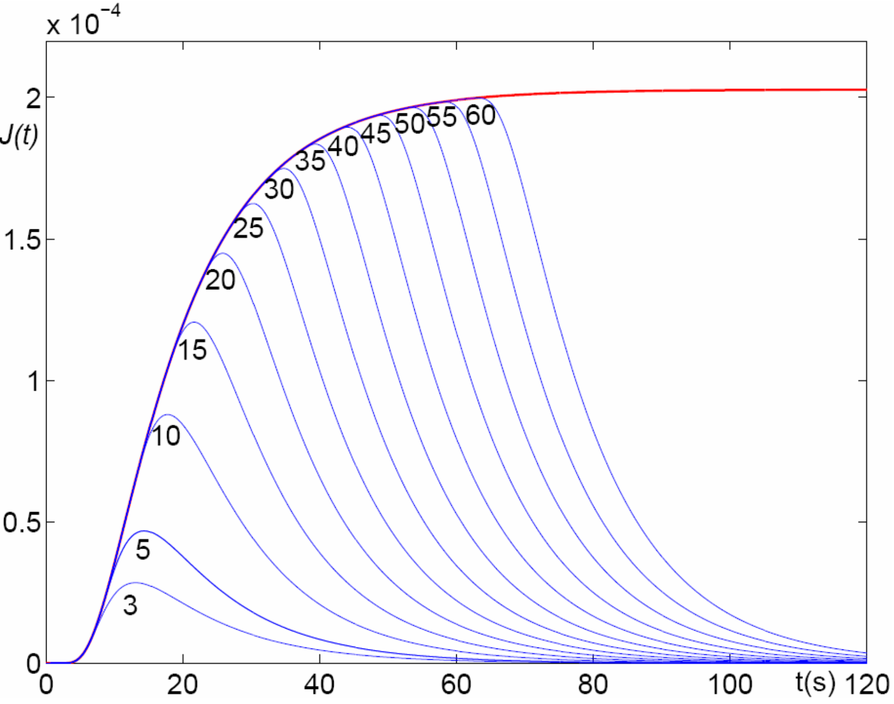


*Anal. Chem.* **2007,** *79,* 5336−5342

# The problem of an unknown exposure time

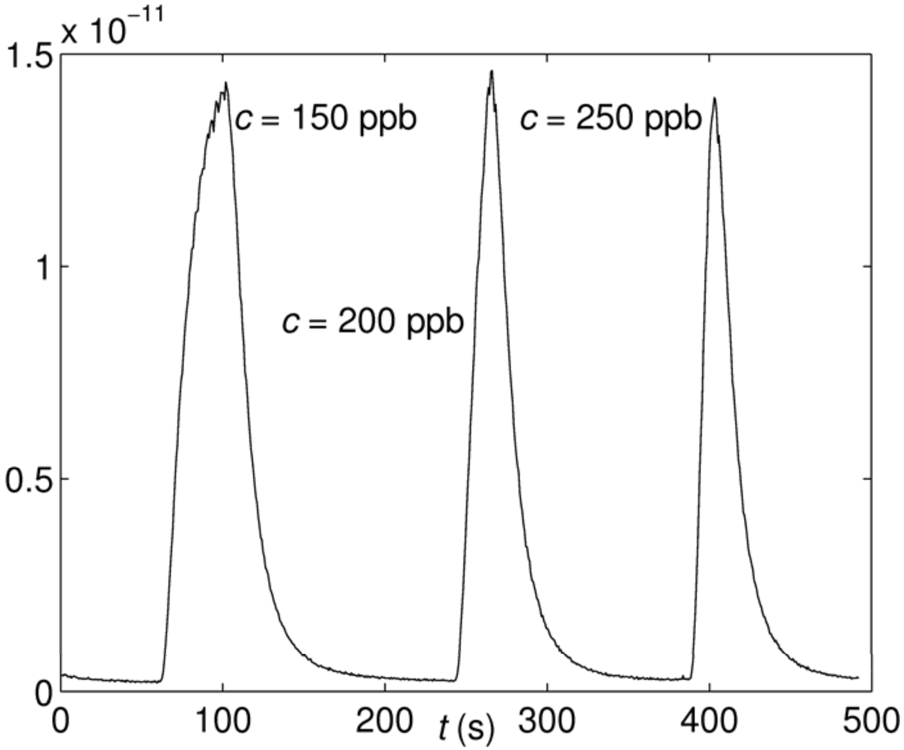
Steady state versus flow injection

Simulation



Flow injection with varying exposure times

Experimental



# Solving the diffusion equation

$$j(x,t) \quad = \quad -D\frac{\partial}{\partial x}c(x,t) \qquad\qquad \frac{\partial}{\partial t}c(x,t) \quad = \quad D\frac{\partial^2}{\partial x^2}c(x,t)$$

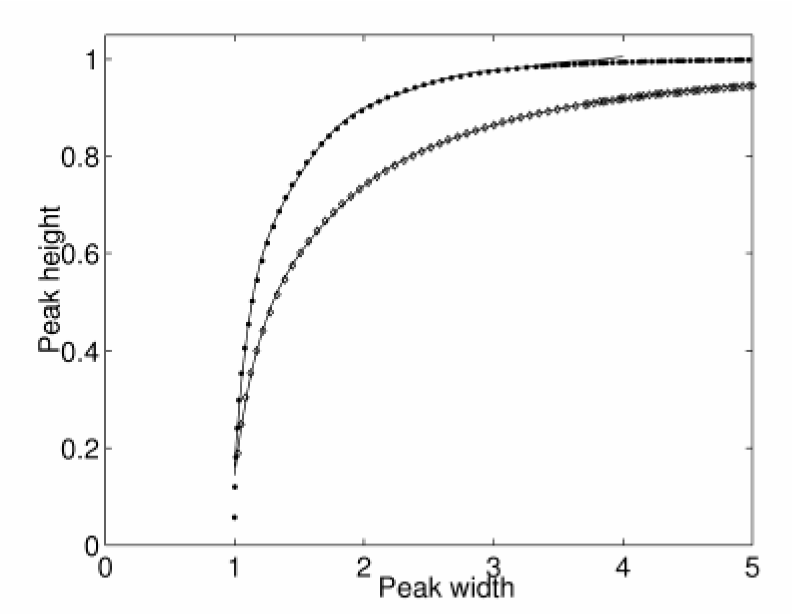
## Typical exposure conditions

$$c_{step}(t) \quad = \quad \begin{cases} 0 & t < t_0 \\ c_0 & t \geq t_0 \end{cases} \qquad\qquad c_{rectangular}(t) \quad = \quad \begin{cases} 0 & t < t_0 \\ c_0 & t_0 \leq t \leq t_0 + \Delta t \\ 0 & t > t_0 + \Delta t \end{cases}$$

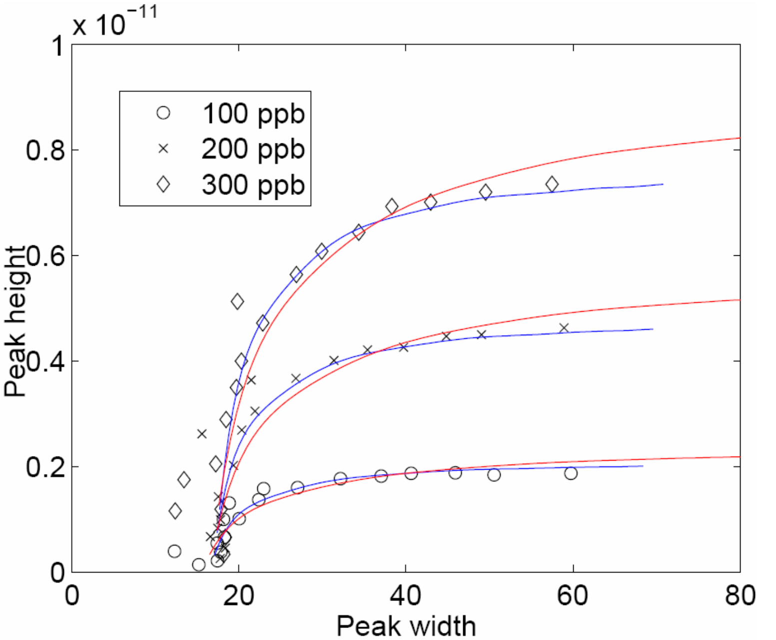
$$c_{Gaussian}(t) \quad = \quad c_0 \cdot \exp\left( -\frac{4 \cdot \ln 2}{\Delta t^2} \cdot (t - t_0)^2 \right)$$

# Calculating the concentration from the peak height and width

## Theory: Computer simulation



## Experimental

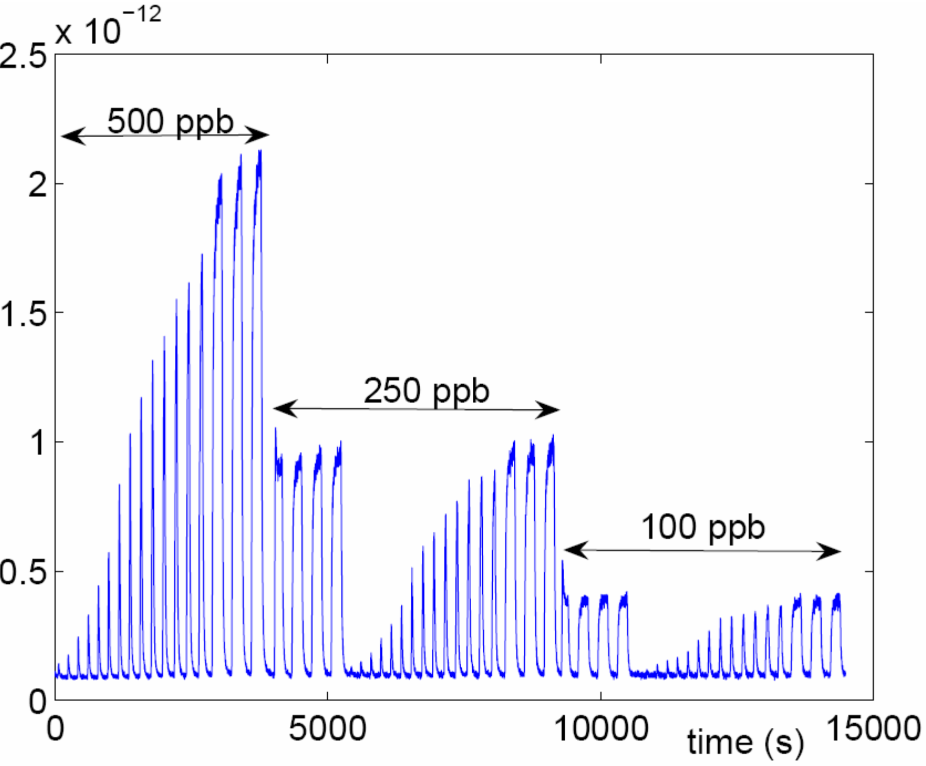


## A simple solution

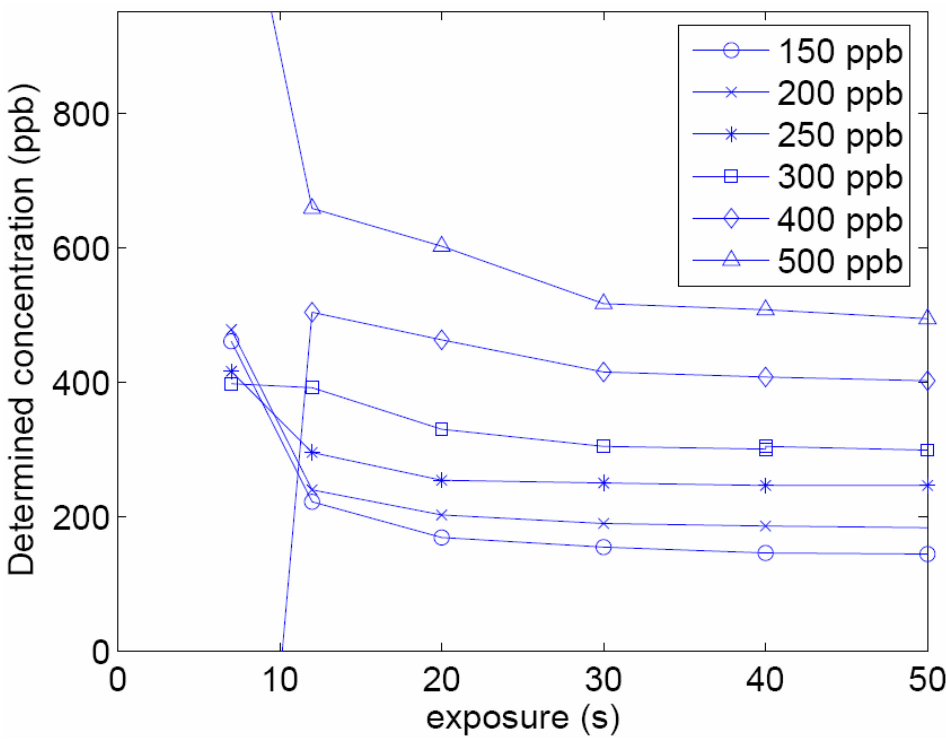
$$c = \frac{A \cdot H}{P\left(\frac{W}{B}\right)}$$

# Experimental verification of the model

## Recording desorption profiles

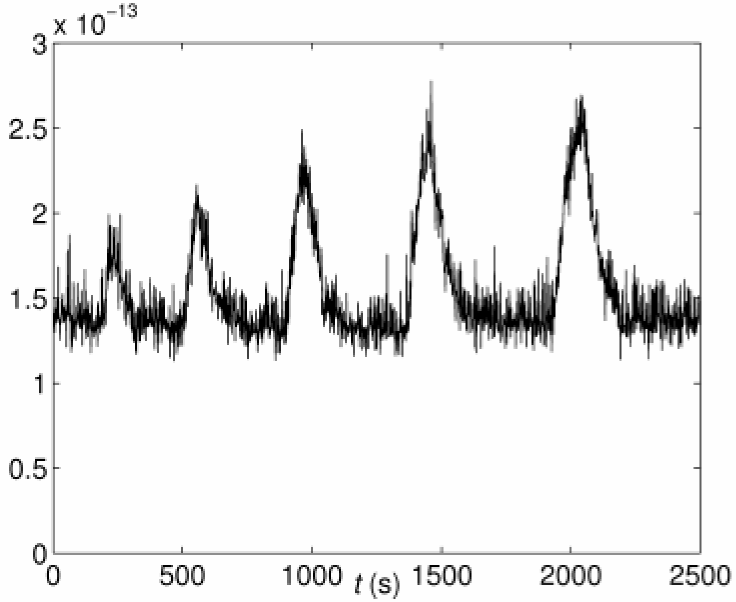


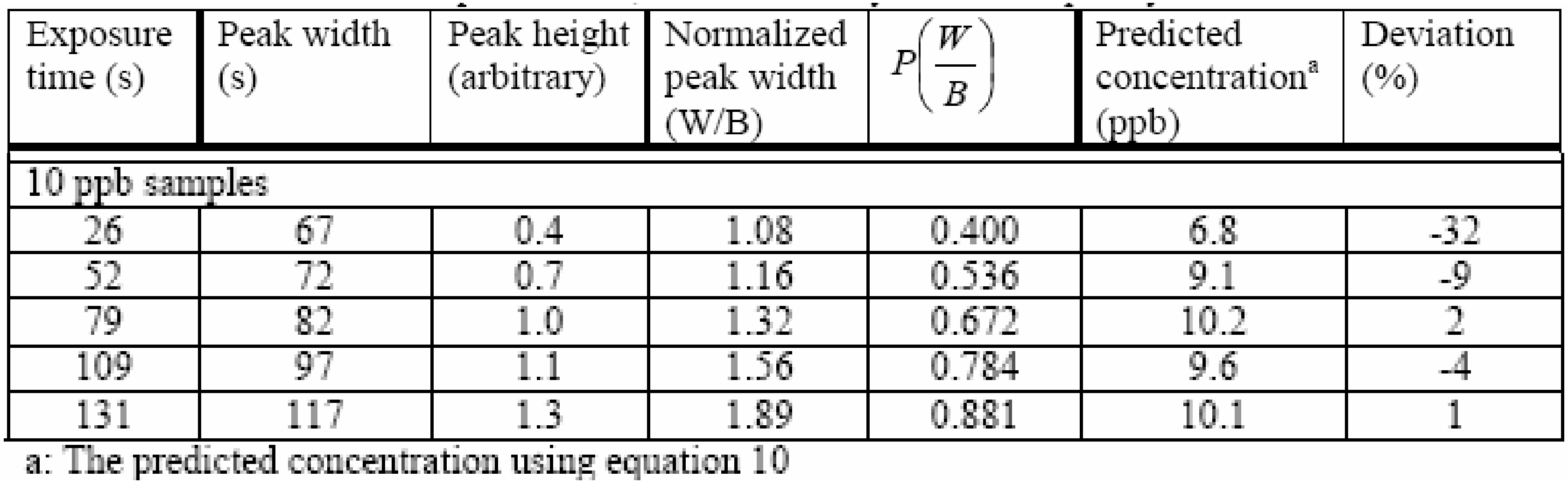
## Determination of concentrations



# Low level detection

Peak shapes following a 10 ppb exposure of the membrane to 2,2-dichloroethylene at varying durations





| Exposure time (s) | Peak width (s) | Peak height (arbitrary) | Normalized peak width (W/B) | $P\left(\frac{W}{B}\right)$ | Predicted concentration[a] (ppb) | Deviation (%) |
|---|---|---|---|---|---|---|
| 10 ppb samples | | | | | | |
| 26 | 67 | 0.4 | 1.08 | 0.400 | 6.8 | -32 |
| 52 | 72 | 0.7 | 1.16 | 0.536 | 9.1 | -9 |
| 79 | 82 | 1.0 | 1.32 | 0.672 | 10.2 | 2 |
| 109 | 97 | 1.1 | 1.56 | 0.784 | 9.6 | -4 |
| 131 | 117 | 1.3 | 1.89 | 0.881 | 10.1 | 1 |

a: The predicted concentration using equation 10

# Conclusion on the dynamic-FIA approach

We have developed and experimentally tested a 2-dimensional calibration model that makes it possible to predict the concentration of a chemical in a sample, even though the exposure time to the membrane-covered sensor is unknown.

The model is easy to use, since the concentration is simply given by a calibration factor multiplied with the peak height and divided by the value of a polynomial, determined at a normalized peak width.

Good results are obtained as long as the exposure time exceeds 1/10 of the time it takes to reach a steady state response.

# Acknowledgement

**The AEC Group, Copenhagen**

Christian Janfelt
Christian S. Pedersen
Rune Græsbøll
Pia Kammeyer

**USF, Skt. Petersburgh**

Tim Short (SRI)
Strawn Toler
Ryan Bell

**Mikrolab Aarhus A/S**

Construction of fully field portable version of the Mini-MIMS

**Funding**

The Danish Natural Science Counsil