The Development Of Low-Flow Pump Tubes And Their Potential As A Tool For Simplifying The Validation Of Axial Diffusive Tubes

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Overview

- Introduction to diffusive sampling including principles of diffusion
- Methods to validate uptake rates
- Diffusion locking technology and its use to calculate/confirm uptake rates for sorbent/analyte combinations.
- Parallel study results

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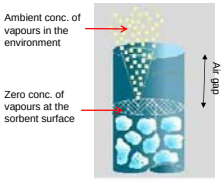
Sorbent Tubes - Diffusive Sampling

- A simple and cost effective method of collecting the large number of samples required in many air monitoring programmes
- Vapors migrate across the air gap at a constant "uptake rate"
- Uptake rates for common compounds and sorbents available in the literature
- Diffusive sampling is a slow process, typically sample for days
- Only single bed tubes can be used



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Human Exposure Monitoring

1,3-Butadiene and benzene are criteria air pollutants cited in many regulations

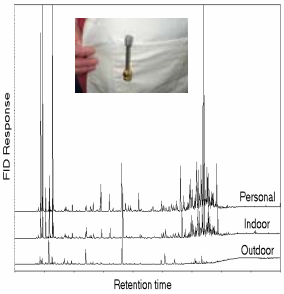
Butadiene

- Pumped sampling of butadiene onto Carbopack X or Carbograph 5TD
- Diffusive sampling on Carbopack X:
  - 8 hour: 1.64 pg/ppb/min
  - 1 week: 1.19 pg/ppb/min
  - (2 week: 1.02 pg/ppb/min)

Benzene

- Validated for pumped and diffusive sampling at ambient and workplace levels. Optimum sorbent Carbograph 1TD.

Diffusive sampling facilitates personal exposure monitoring



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Principles of Diffusive Sampling

- Diffusive Monitors must be capable of maintaining the following conditions during sampling
  - Ambient concentration of the analyte at the surface of the monitor
  - Zero concentration of the analyte at the surface of the sorbent
  - A linear concentration gradient between the two
- When these conditions are met, Fick's First Law of Diffusion applies

$$J = -D\frac{\partial \phi}{\partial x}$$

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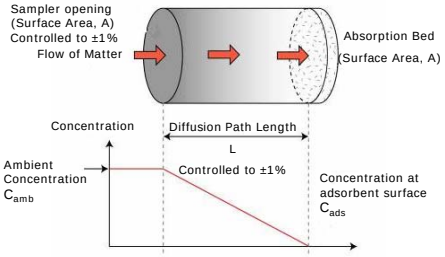
Axial Diffusive Sampling



- Using an Industry standard tube (typical diffusion path length of ~1.5 cm) atmospheric concentration of a compound is determined by using the following equation.

$$ppm = \frac{\text{Mass of sample on tube(ng)}}{Up_i(\text{ng/ppm/min}) \times T_s(\text{min})}$$

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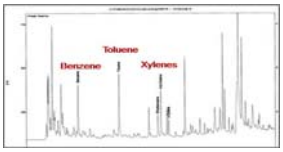
Axial Diffusive Sampling

- Many actual uptake rates for a variety of compounds are now published in the literature.
- However, if an uptake rate is not available then there are several options,
  - Calculate ideal uptake rate using Fick's 1st law.
  - Predict the uptake rate by combining simple short experiments and modelling studies.
  - Determine the uptake rate experimentally.



14-day diffusive sampling of BTX in ambient air

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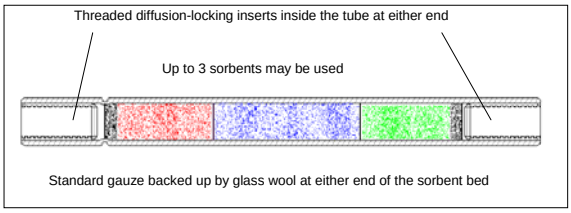
Specialist Safe-Lok Sorbent Tubes



- Why use low flow pumped tubes ?
  - Validation of uptake rates using an active flow similar to the natural rate of diffusion, normal axial tubes have errors associated with diffusion
  - Parallel sampling of air using diffusive tubes and low-flow pumped tubes can be a way to validate uptake rates

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Sorbent Tubes – Specialist tubes

- **Safelok tubes facilitate pumped sampling at low flow rates (< 1 ml/min)**
- Reduces risk of contamination
- Prevents necking caused by over tightening
- Safer to handle toxic compounds
- Same mass of sorbent and same external dimensions as standard tubes

SafeLok Tubes

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Experimental

- Tube types
  - **Safelok tubes**: Carbograph 1TD/Carbopack-X
  - **Diffusive tubes**: Carbopack-X
  - **Safelok tubes** pumped at 2 ml/min for 14 days
  - **Diffusive tubes** exposed for 14 days
- Analysis conditions
  - Tube desorption temp: 400ºC for 15 min
  - Flow path temp: 200ºC
  - Cold trap low: –30ºC
  - Cold trap temp high: 300ºC for 2 min
  - Trap Split: 18 ml/min
  - Cold trap packing: TENAX GR
  - Column pressure: 12.2 psi
  - Column used OV-1701
  - GC temp program 50ºC for 6 mins then 10ºC/min to 90ºC then 10ºC/min to 200ºC for 10mins (31 mins total)

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RESULTS FROM THE ANALYSIS OF SAFELOK TUBES

Diffusive Tubes

Tube		Duration	Benzene	Toluene	Ethylbenzene	m/p-Xylene	o-Xylene	Total Hydrocarbons
		min	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v
CX-90	BLK	18691	<0.1	<0.3	<0.3	<0.3	<0.3	<5
CX-537		18691	0.5	1.1	<0.3	0.5	<0.3	10
CX-587		18691	0.4	1.0	<0.3	0.5	<0.3	8
CX-3750		18691	0.4	0.9	<0.3	0.5	<0.3	10
CX-502		18691	0.4	1.0	<0.3	0.5	<0.3	9

Pumped Tubes

Tube		Volume	Benzene	Toluene	Ethylbenzene	m/p-Xylene	o-Xylene	Total Hydrocarbons
		ml	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v
M-029485	BLK		<0.1	<0.3	<0.3	<0.3	<0.3	<5
M-029480	P37	34140	0.4	1.13	<0.3	0.5	<0.3	7
M-029489	PL7	33094	0.4	1.03	<0.3	0.5	<0.3	7
M-0.2481	P46	30591	0.4	1.07	<0.3	0.5	<0.3	7
CX-140	P37 B/U	34140	<0.1	<0.3	<0.3	<0.3	<0.3	<5
CX-102	PL7 B/U	33094	<0.1	<0.3	<0.3	<0.3	<0.3	<5
CX-3253	P46 B/U	30591	<0.1	<0.3	<0.3	<0.3	<0.3	<5

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Calculating uptake rates

- For example Benzene has a concentration of 0.4 ppb on the pumped tube which also relates to 0.4 ppb on the diffusive tube.
- Given this, we can now calculate the uptake rate by

$$\text{Uptake rate} = \frac{\text{Mass (pg)}}{\text{Concentration (ppb)} \times \text{Time (min)}}$$

Which gives a value of 1.99 $pg.ppb^{-1}.min^{-1}$ for benzene on carbopack-x

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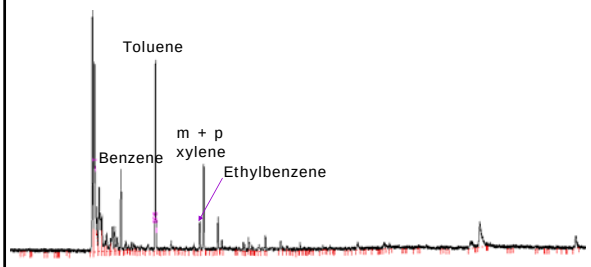
Diffusive tube – CX587



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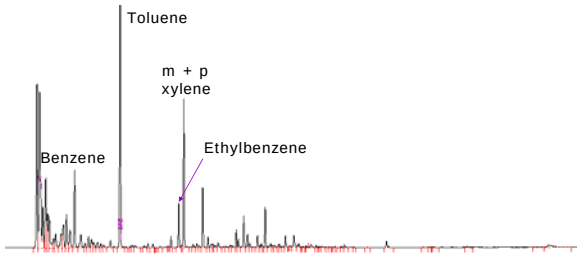
Safelok Tube – M-029489



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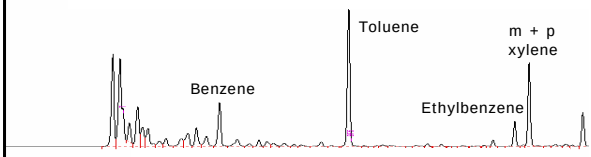
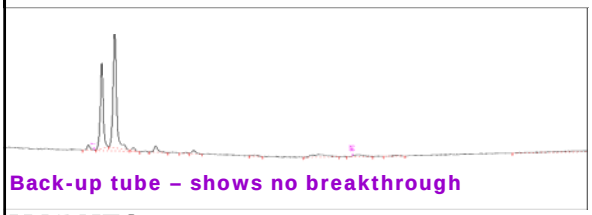


Pumped Safelok tube



Back-up tube – shows no breakthrough

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Summary

- Demonstrated how low flow pumped sampling can be used as a confirmation of uptake rates for variety of sorbent analyte combinations.
- Diffusion locking technology facilitates low flow sampling by minimising the error related to simultaneous diffusive ingress.
- Acknowledgements
  - Malcolm Henderson and Bob Lipscombe – NPL, Teddington

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