Passive Monitoring:

A Guide to Sorbent Tube Sampling for EPA Method 325

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EPA 325 - Refinery perimeter monitoring

Revised Federal regulation (CFR 40, part 60 and 63) to be implemented September 2015, compliance within 3 years

- Requires continuous monitoring of vapour-phase organics (specifically Benzene) around the boundary of oil refineries
- US EPA Methods 325 A (Sampling protocol) and 325 B (Laboratory analysis)
- 2-week passive sampling using industry standard sorbent tubes.
- Subsequent analysis is by TD–GC(MS) analysis (MS recommended)

Target Compounds:
- **Benzene**
- Hazardous air pollutants (HAPs) VOCs
- Vapour-phase organics present in refinery air (light/ Middle fuel distillates)

Enhanced traceability throughout process
Sample tube cleaning
Tubes travel to field in '325 Container™'
Field sample deployment
Passive sampling
Tubes travel to laboratory in '325 Container™'
Sample & data analysis
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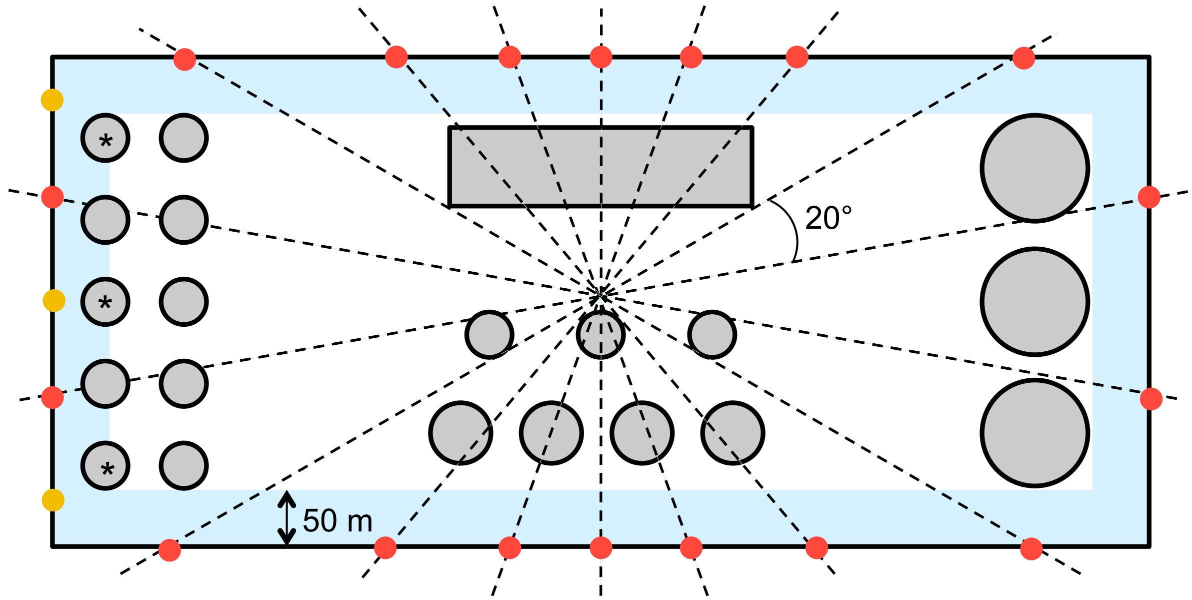
TubeTAG™ RFID
■ Minimise risk of litigation
■ Chain of custody from field to lab
■ Fully traceable audit trail

Monitoring method requirements

- 12–24 monitoring stations round each refinery

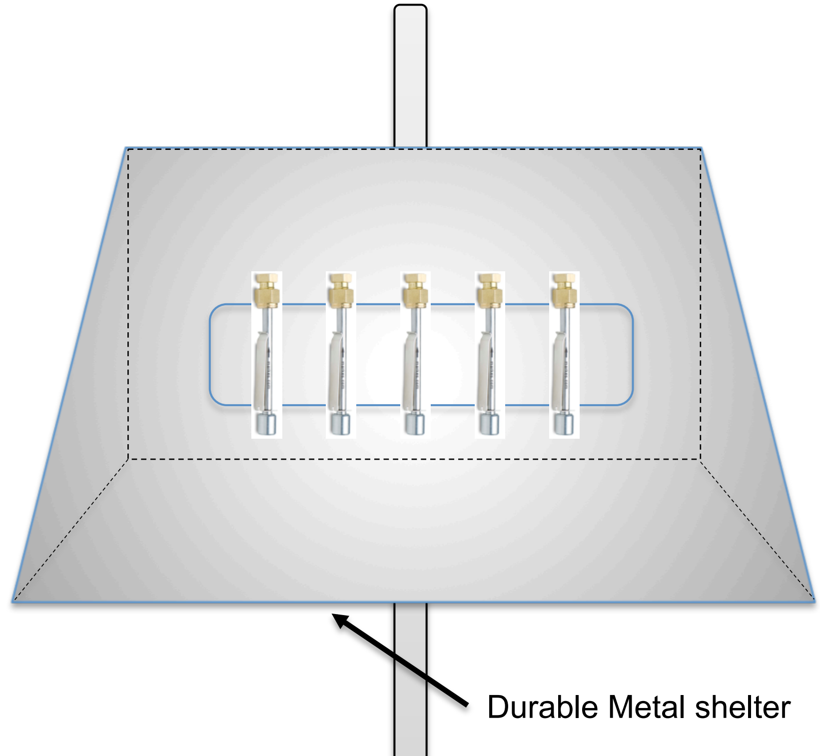
Further samplers:

- Replicates
- Blanks
- Calibration
- Alternative sorbents
- Additional shorter-term monitoring for pinpointing fugitive emissions



Example of monitoring stations on a rectangular site of 750–1500 acres.[2] Monitoring sites (●) are placed just beyond the boundary at 20° intervals. Sources between two monitoring stations and within 50 m of the boundary (★) require that additional monitoring stations (●) are installed.

Setting up the field stations
Monitoring industrial air using passive sorbent tubes



325 Field Station™

- Passive (diffusive) samplers deployed around the perimeter under weather proof hoods
- Housing up to five tubes: samples, duplicates, blanks and differing sorbents
- Robust, weather proof shelter
- Sample must sit 1.5-3 meters above the ground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Diffusive Sampler Theory

Ficks' 1st Law

- Diffusion is a molecular transport property. It is the process by which matter progresses along a concentration gradient until there is an equalisation of concentration within a single phase.
- Thus, as with any chemical system, a diffusing gas is spontaneously adopting its most probable energy distribution in its quest for an even, maximum dispersion and thus maximum entropy.
- The rate of this migration property is measured by its flux (J), which is the quantity of matter passing through a reference surface area per unit time.
- As J_x is the component of a vector and as matter flows down the concentration gradient away from its source, the coefficient of proportionality, D (the diffusion coefficient) in the matter flux expression must be negative.

$$J_x \propto \frac{dC}{dx}$$

therefore,

$$J_x = -D\frac{dC}{dx}$$

where:
Jx - rate of diffusion ($molcm^{-2}s^{-1}$);
dC/dx - concentration gradient ($molcm^{-2}$).
D - diffusion coefficient (cm^2s^{-1}).

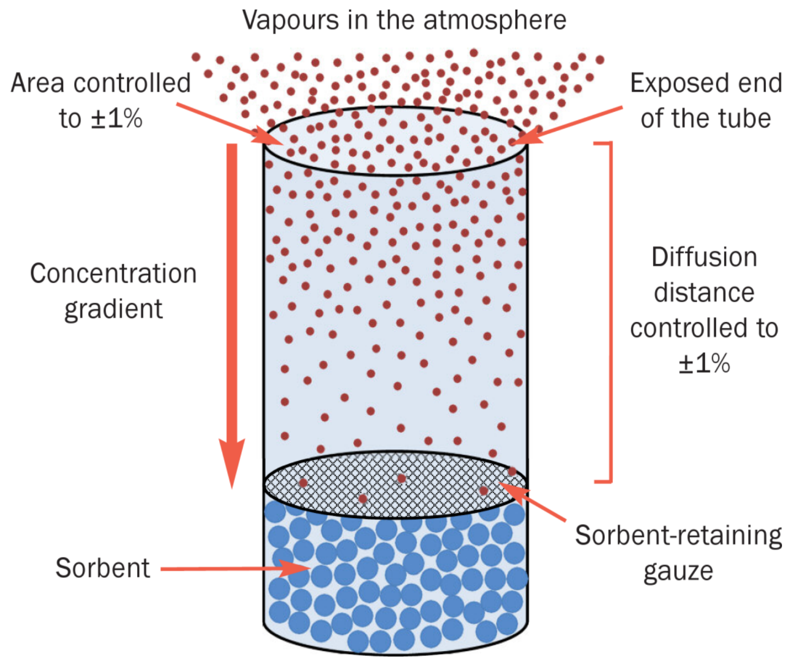
Application of Fick's First Law to passive samplers

Axial type samplers

- A passive sampler is essentially a collection medium, either
  - solid sorbent,
  - liquid sorbent,
  - or chemically impregnated inert support,

  which is separated from the atmosphere of interest by a zone of still air.

The driving force for matter flux across the still-air gap is the induced concentration gradient formed between the sampler opening and the air-adsorbent interface where vapour phase matter is scavenged.

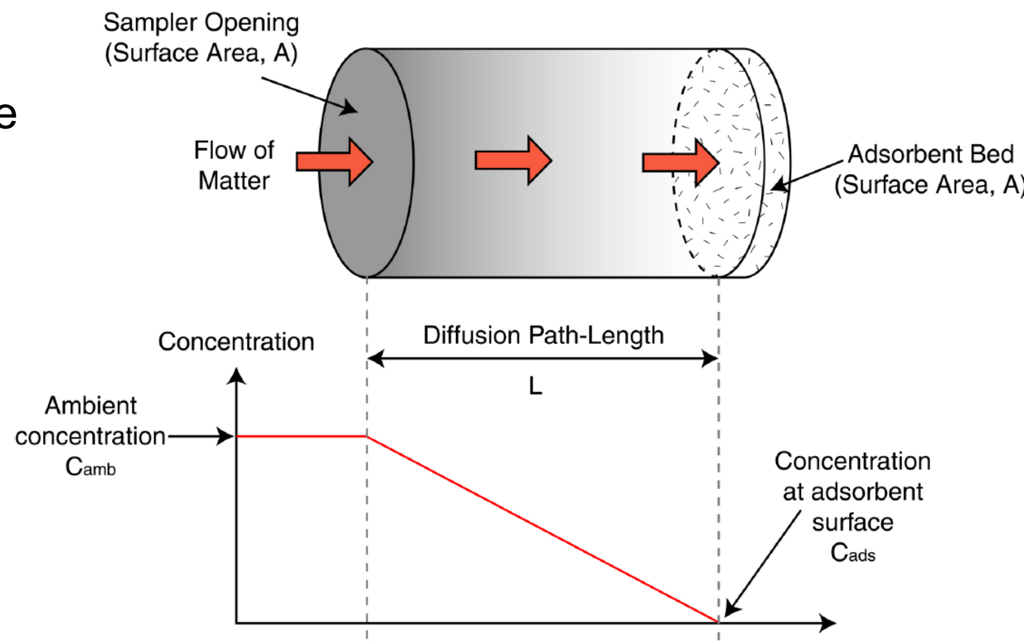


Application of Fick's First Law to passive samplers

Axial type samplers

For application of Fick's First Law to a diffusive sampler several simplifying assumptions are necessary:

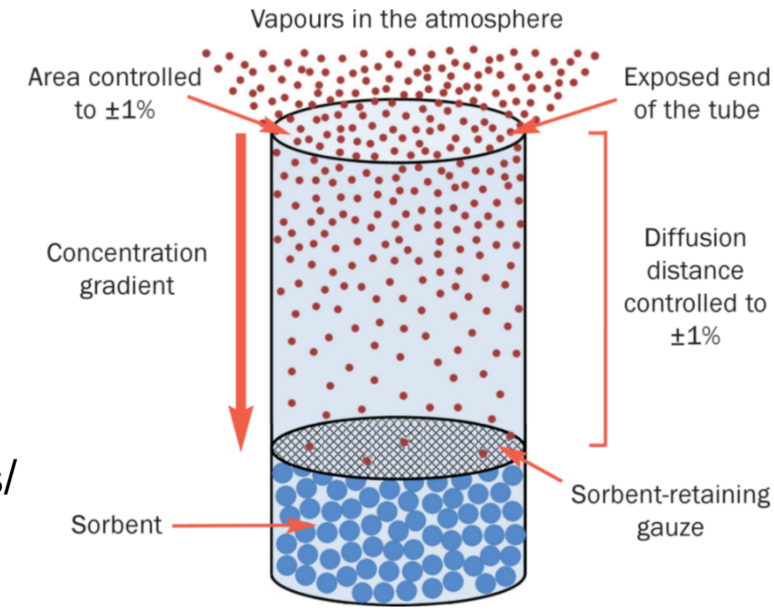
- Ambient concentration of the analyte at the surface of the monitor (C_{amb}) i.e. does not take matter from its surrounding environment faster than it can be replaced
- Zero concentration of the analyte at the surface of the sorbent, i.e. the adsorbent is a zero sink and therefore there is no saturation of the adsorbent (C_{ads} = 0)
- A linear concentration gradient between the two. steady state conditions always exist



Passive sampling of volatiles onto sorbent tubes

Passive (diffusive) sampling for workplace and environmental air monitoring

- Vapours migrate across the air gap at a constant "uptake rate"
- Diffusive sampling is a slow process, typically sample for :
  - Occupational Hygiene
  - Workplace exposure
  - Personal exposure
  - Environmental air monitoring (days/ weeks)
- One sorbent ONLY



Note: Diffusive (passive) sampling is gaining momentum and can drive TD-GC/MS system sales. It won't work with glass or SafeLok tubes. Use standard stainless steel or Silcosteel® tubes

Method 325 sampler

Sample geometry

The uptake rate is directly proportional to adsorbent bed surface area and inversely proportional to diffusion path length. Commercially available passive samplers fall into two main categories

- low uptake rate tube-type devices,

- high uptake rate badge-type devices.

Passive sampling of volatiles onto sorbent tubes

Uptake rate - a particular analyte being sorbed onto a particular sorbent under a set of monitoring conditions

Well validated for ambient air – 100’s published uptake rates ISO 16017-2, ASTM D6196, EN 14662-4

Robust – Variable ambient conditions (temperature, wind speed, humidity, interferences) have minimal impact on uptake rate

Low cost – Samplers are re-usable more than 50 times and are inexpensive to buy and transport

Versatile – Sorbent tubes can be used for pumped or passive sampling and offer quantitative sampling & release of compounds over a wide volatility range.

During passive sampling, a diffusion cap is fitted to the sampling end of the tube, while the other end is kept sealed (*Note penclip is optional*)

Application Note 001: Uptake rates for tube-type axial diffusive samplers

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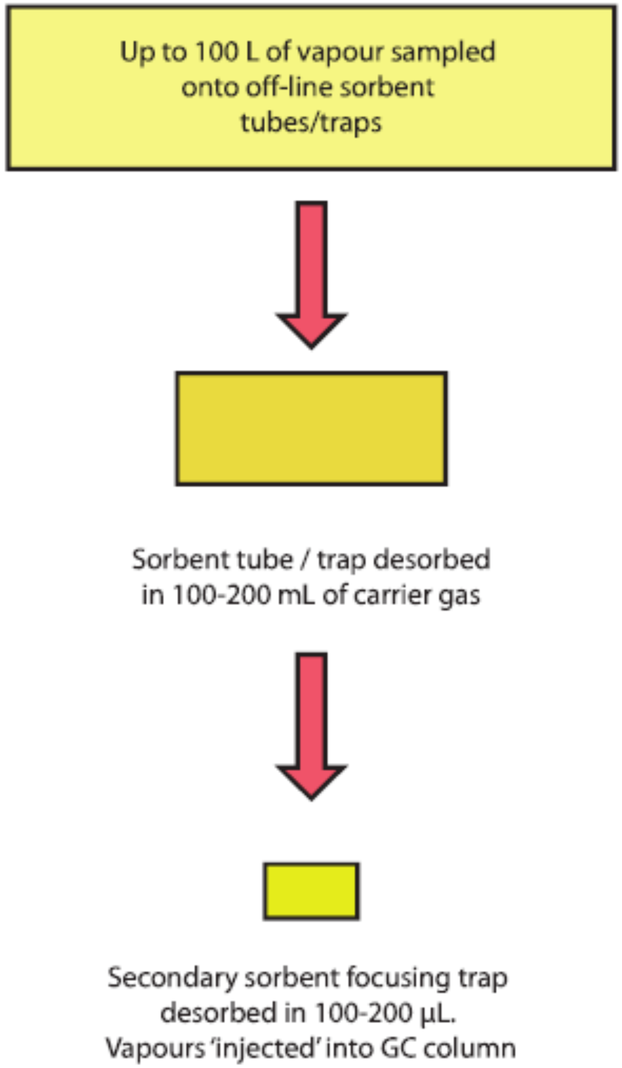
Analysis by TD-GC/GCMS

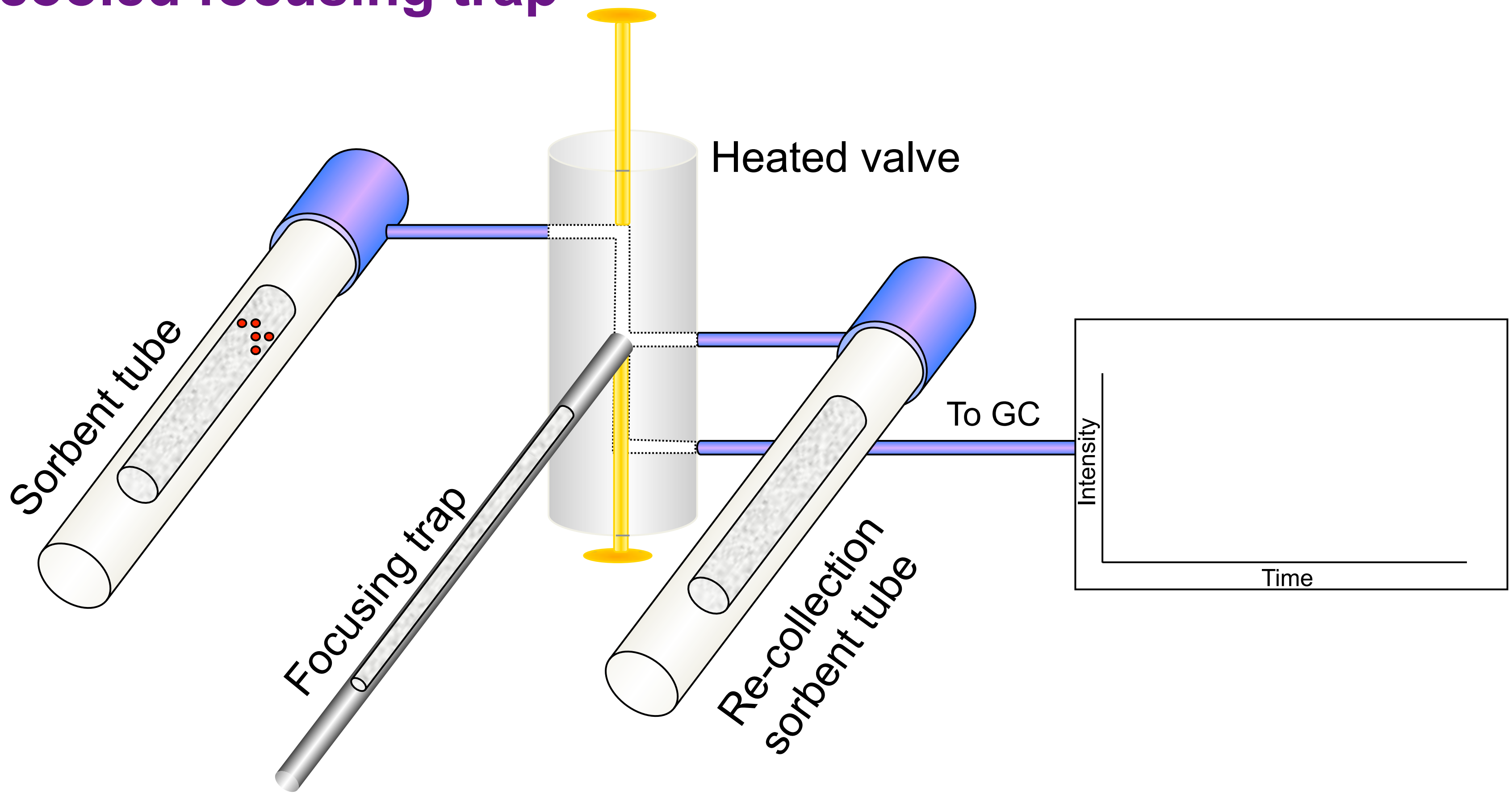
- Passive sampling sorbent tubes are analysed using a thermal desorption device.
- This works by heating the sample tube and releasing the compounds in to a flow or inert gas.
- This process is slow, so a focusing step is needed to retain the compounds.
- Once the sample is focused, it is heated again and rapidly injected in to the GC column in a narrow band of vapour.

Sensitivity Enhancement

- VOCs from 100 L of air or gas can be introduced to the GC column in as little as 100 µL of carrier gas
- 10^6 concentration enhancement means ppt and sub-ppt detection limits depending on detector sensitivity



During stage 1, trapped analytes are desorbed from the heated sample tube and transferred to the electrically-cooled focusing trap



- The TD-100 heated valve is inert and low volume allowing quantitative recovery of high & low volatility compounds plus reactive species
- It also isolates the TD system allowing compliance with standard methods: leak testing, backflush trap desorption, purge to vent, overlap mode, *etc.*

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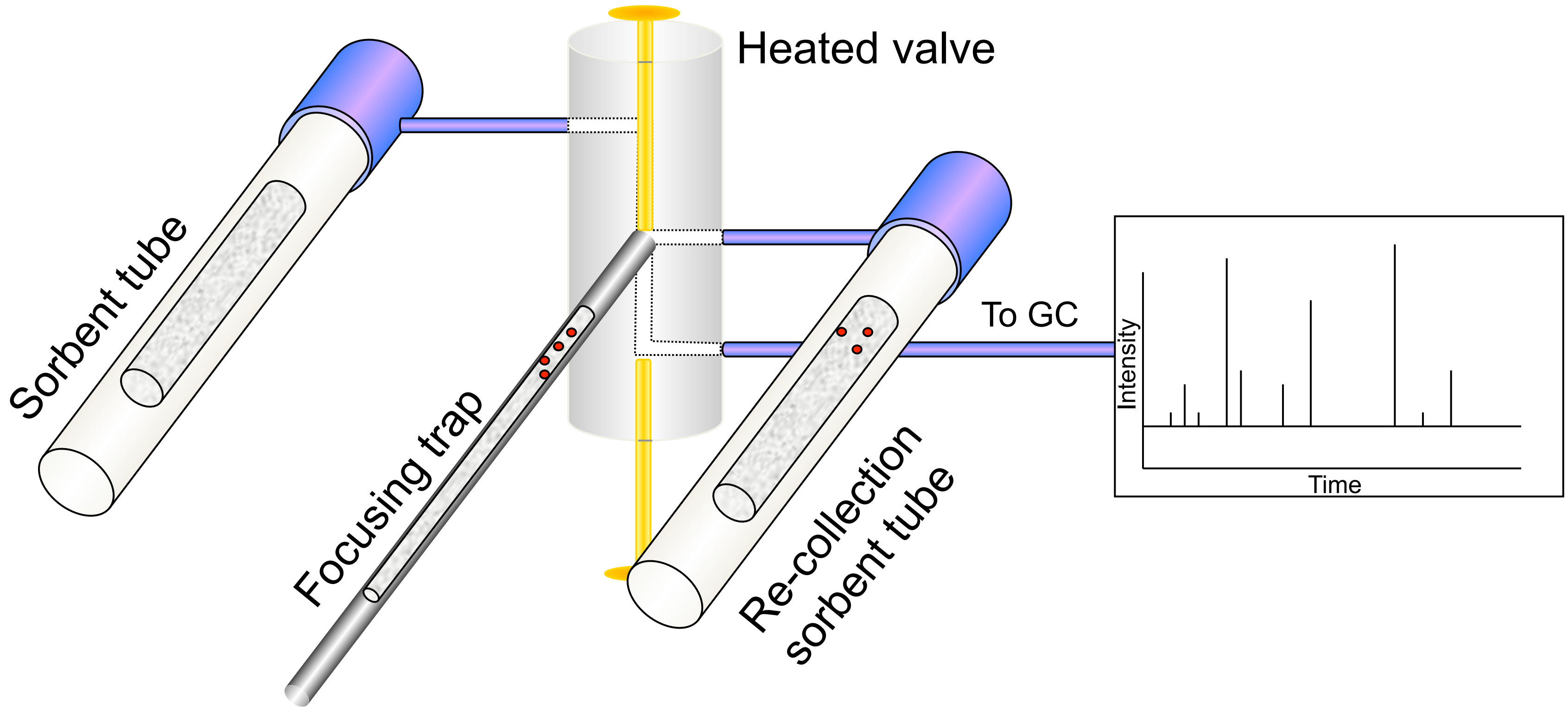
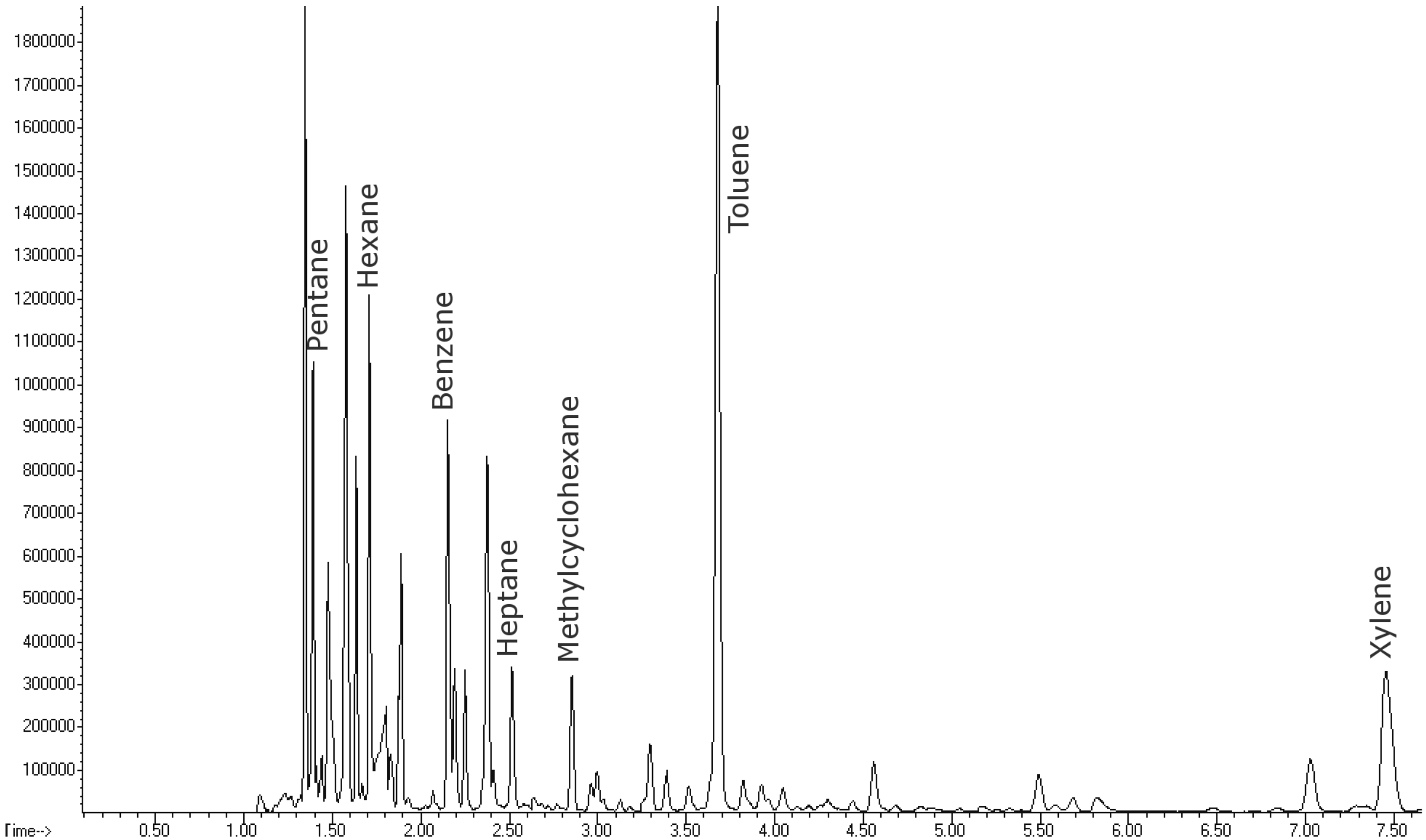
During stage 2, the trap heats rapidly to transfer/inject analytes into the GC column. Split effluent is quantitatively re-collected on a clean tube ready for repeat analysis



- Repeat analysis of re-collected samples makes it easy to validate analyte recovery through the TD flow path
- A change to the overall VOC profile indicates any bias

Long-term passive sampling of ambient and industrial air

2-week passive sampling of light hydrocarbons monitored around the perimeter of a major petrochemical installation



Data interpretation

Two-week diffusive sampling uptake rates for benzene on a variety of sorbents

Sorbent	Uptake rate (mL/min)	Uptake rate (ng/ppm/min)
Carbograph™ 1TD or Carbopack™ B	0.64	2.02
Carbopack™ X	0.61	1.99

To determine the concentration of benzene, five-point calibrations are used to calculate the mass on tube from the peak abundance. The following equation is then used to determine the airborne concentration.

$$\text{Concentration (ppm)} = \text{Mass of sample on tube (ng)} / \text{Uptake Rate (ng/ppm/min)} \times \text{Sampling time (min)}$$

Summary

- Method 325 is due to be released September 2015, with compliance needed within three years
- Sampling protocol is dependant on the size of the site, with each size bracket requiring a different number of sample sites
- Passive sampling is a widely used technique for occupational monitoring, but is gaining ground in ambient air as an alternative to TO-15 longer term sampling
- Many uptake rates are published for method 325, others can be determined through experimentation.

Questions?

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