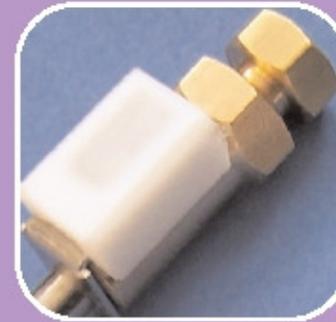


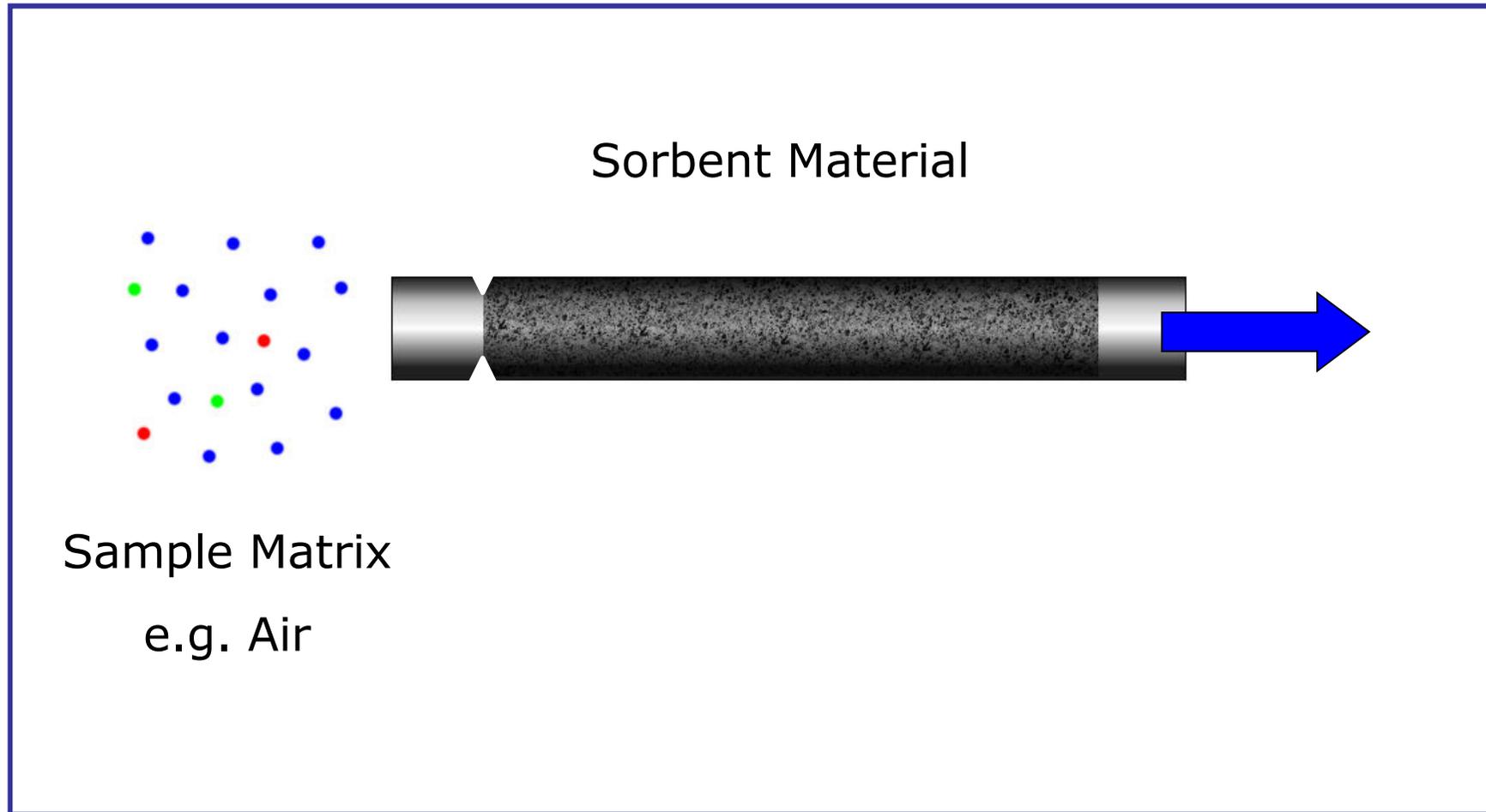
Markes International Thermal Desorption Training



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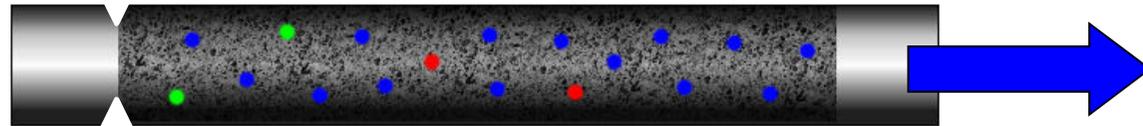
MARKES
international

What is Thermal Desorption?



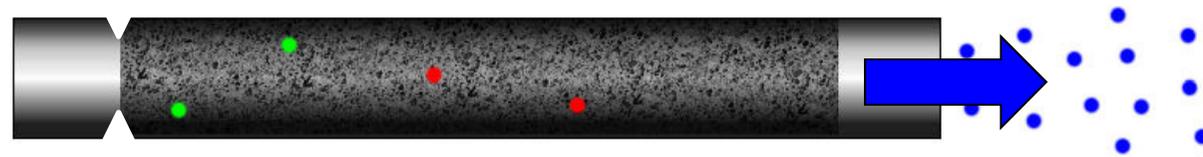
What is Thermal Desorption?

Sample passes onto the sorbent



Compounds of interest are adsorbed
on the sorbent surface

What is Thermal Desorption?



Lighter gases such as nitrogen, argon and carbon dioxide pass through the sorbent

What is Thermal Desorption?



The sorbent tube is now heated in a reversed flow of clean carrier gas (back flushed)

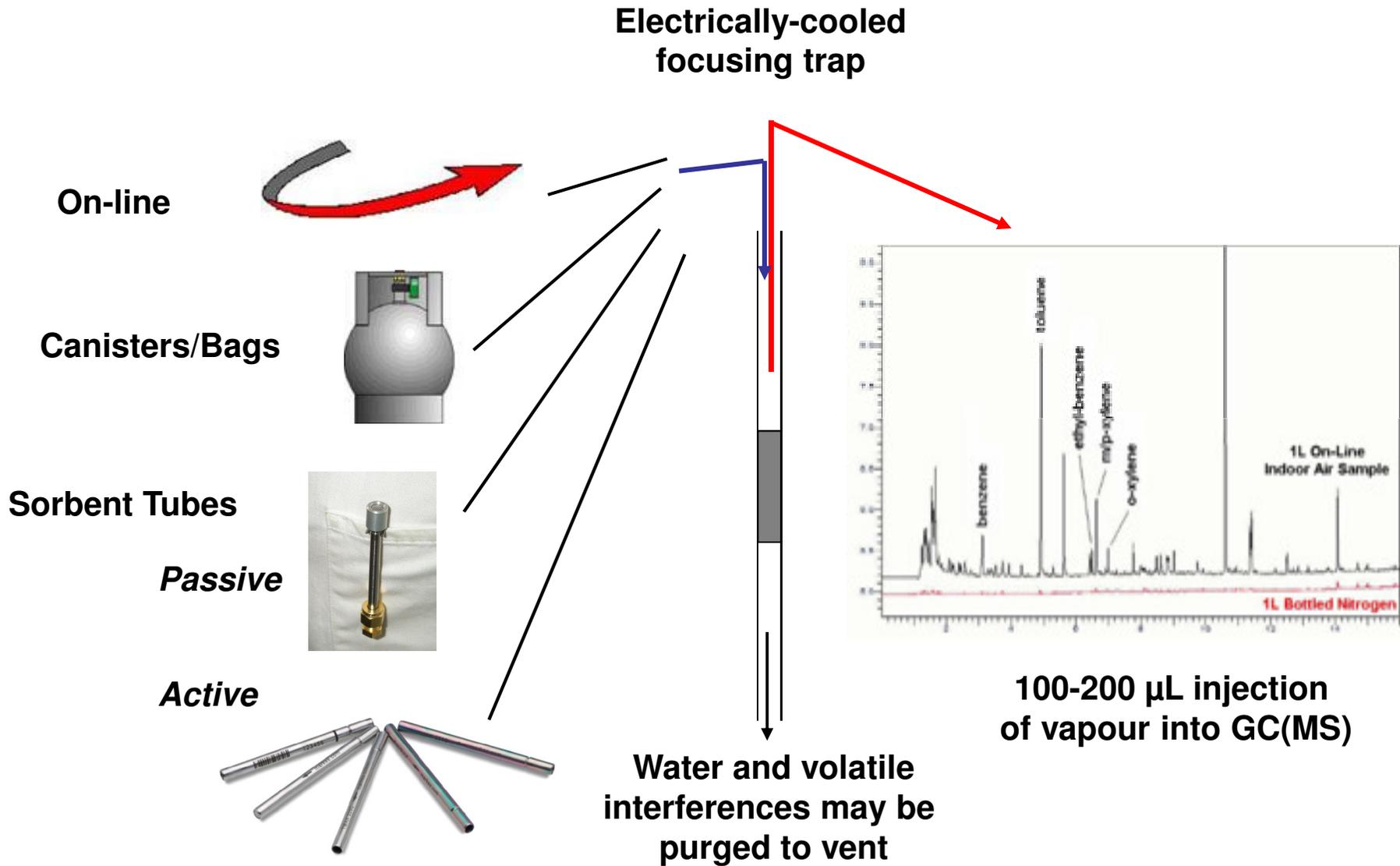
What is Thermal Desorption?

Compounds are released from the sorbent into the flow of carrier gas



It is a simple extension of the technique of Gas Chromatography and is a **sample introduction technology** for difficult or real-world samples

Thermal Desorption; one versatile technique for all vapour phase air monitoring applications



What's it used for?

For sample matrices that cannot be directly introduced to the analyser (GC)

Dilute Vapour Samples



Food and drink



Solids – powders, granules



Resins, emulsions, pastes



What compounds are compatible with TD?

Any volatile or semi-volatile organic compounds which meet the following criteria:

- ✓ $\leq n\text{-C}_{40}$, bpt $\leq 525^\circ\text{C}$
- ✓ Compatible with 'standard' GC analysis
- ✓ The sorbent or matrix containing the compounds is compatible with the high temperatures required

- ✗ Inorganic compounds
- ✗ Most permanent gases (CO_2 , Ar, N_2 etc.) and other compounds with very low boiling points (methane)
- ✗ Compounds with volatility $> n\text{-C}_{40}$
- ✗ Compounds which are not compatible with gas chromatography (or which require on-column injection)

TD – the process

- 1) Collect / prepare sample
 - a. Passive (diffusive) sampling
 - b. Direct sampling
 - c. Active (pumped) sampling



Sorbent Tubes

Industry standard dimensions (3.5" long, ¼" I.D.)

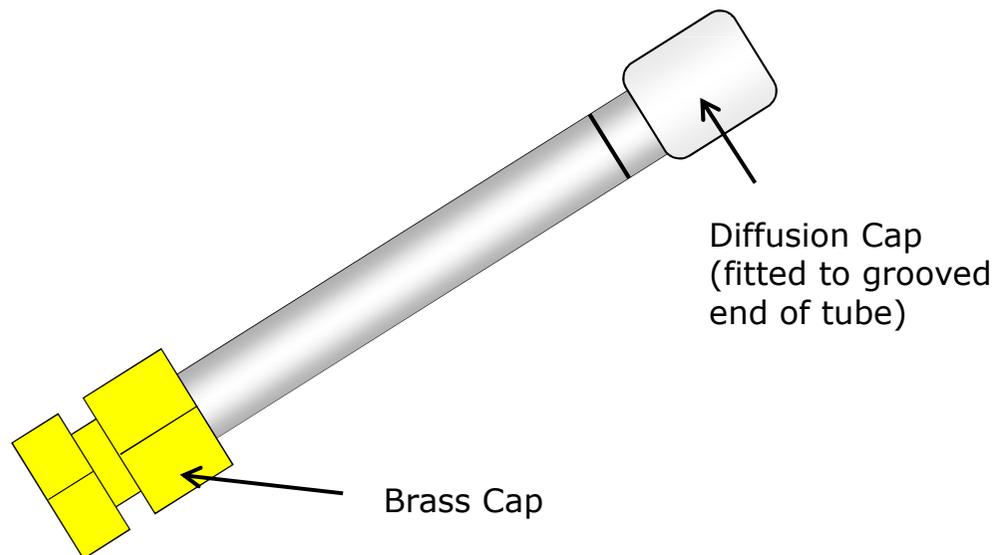
Each has a unique code

Groove on the sampling end of the tube



1a. Passive (diffusive) sampling

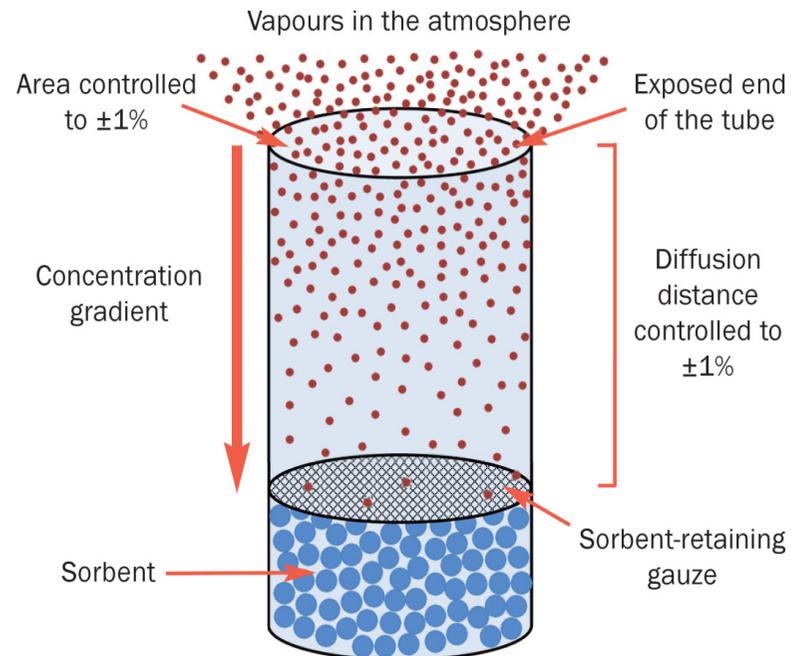
- Diffusive sampling = a simple and cost effective method of collecting the large number of samples required in many air monitoring programmes
- Vapours migrate across the air gap at a constant “uptake rate”
- Diffusive sampling is a slow process, typically sample for days



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-sorbent interface where vapour phase matter is scavenged.

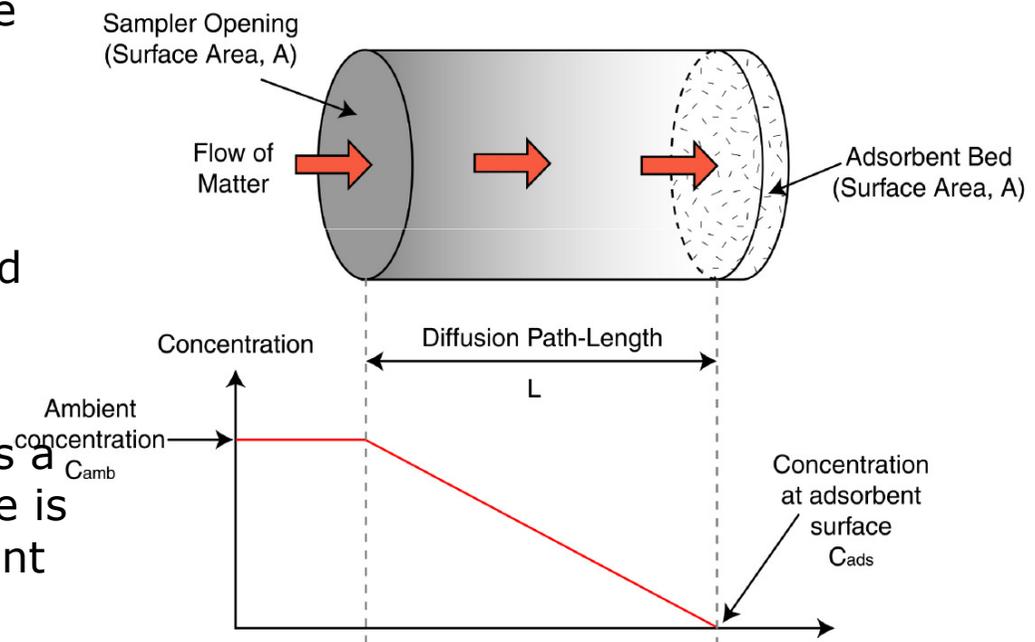


Application of Fick's First Law to passive samplers

- 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



Factors that influence sampler performance

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.



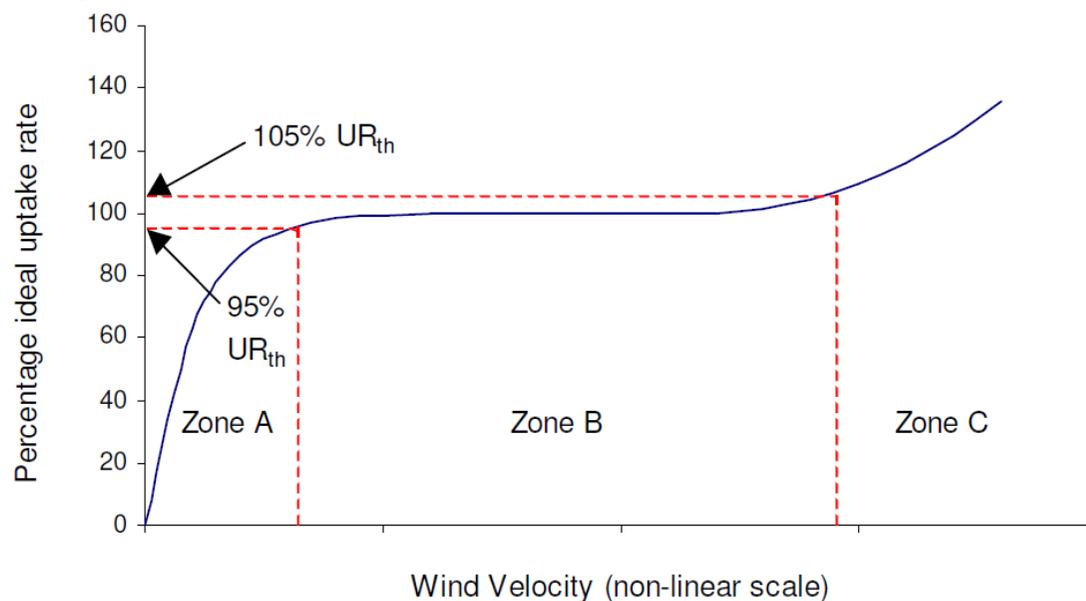
Factors that influence sampler performance

- Environmental factors
 - Temperature
 - A 20°C difference in temperature represents a five percent difference in sampled mass.
 - However increased temperature does not lead to faster matter transfer and thus a greater quantity of analyte being up taken, but the opposite, which is why sampling devices should be protected from heat sources, such as direct sunlight, in the field.
 - Relative humidity
 - This is more influential when using polar adsorbents. At high RH, water molecules may preferentially occupy adsorbent sites, leading to premature saturation. Secondly,
 - When the compounds of interest are water sensitive, hydrolysis or solution may take place on the adsorbent surface.
 - When sampling for prolonged durations from ambient atmospheres, where high relative humidities are commonly encountered, **a hydrophobic adsorbent is preferable.**

Factors that influence sampler performance

Environmental factors - Face velocity (air speed)

- **Zone A:** Represents stagnant, or slowly moving air. The main process by which this matter is replaced is by diffusion and it has been shown that under these conditions the replenishment rate is too low.
- **Zone C:** At the other end of the scale there is non-ideal behaviour through excessive face velocity. Here due to turbulence in the diffusion air gap, the effective diffusion path length is decreased and consequently the uptake rate increases.



Recommended minimum face air velocities are:

Badge type samplers 0.05 to 0.10 ms^{-1} .

Axial tube type samplers 0.001 ms^{-1} .

Factors that influence sampler performance

Sorbent selection

A poor choice of adsorbent can lead to unpredictable sampler behaviour and unusable results that no amount of subsequent calculation or careful laboratory procedure can correct.

Considerations when selecting a sorbent/compound pair:

- *Ensure that the sorbent is strong enough for the compound(s) of interest and also for the duration of the sampling event i.e. the sorbent must behave as a zero sink. This ensures a constant sampling rate and no loss of compounds prior to analysis.*
- If under extreme adsorbent loading conditions
 - extended exposure to high concentration atmospheres
 - misuse of high uptake rate devices
 - poor matching of an adsorbent to the target species

a build-up in the vapour phase concentration at the adsorbent surface may be observed. This can lead to deviation from theoretical uptake rates and even sample loss back to the atmosphere

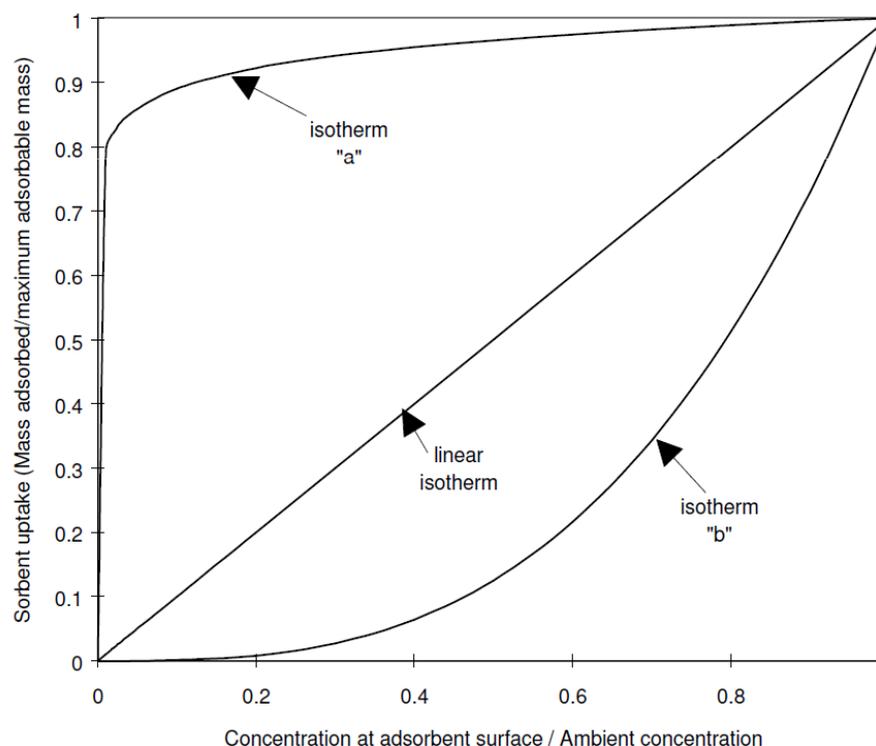
Factors that influence sampler performance

Sorbent selection – high concentration atmospheres

- *For air monitoring situations, where concentrations of targets are typically high, the most critical factor governing the suitability of an adsorbent for a given compound is its adsorption capacity. An adsorbent's capacity may be determined from its isotherm.*

Isotherm "a" is favourable for passive sampling.

The linear isotherm and isotherm "b" are unfavourable as they predict a rapid build up in the vapour phase concentration after only a minimal uptake of adsorbate.



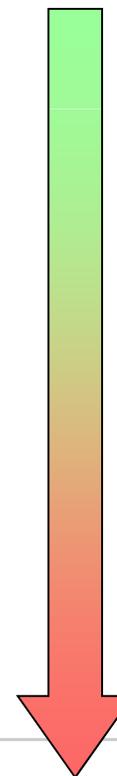
Factors that influence sampler performance

Sorbent selection – low concentration atmospheres

- *When monitoring low concentrations in ambient atmospheres, sampler blanks and adsorbent inertness to interference from humidity and reactive atmospheric species also become governing factors for adsorbent choice*

Sorbent name	Volatility range
Tenax TA	C ₇ – C ₃₀
Carbograph 2TD	C ₈ – C ₂₀
Carbograph 1TD	C _{5/6} – C ₁₄
Carbograph 5TD	C _{3/4} – C _{6/7}
SulfiCarb	C ₃ – C ₈
Carboxen 1003	C ₂ – C ₅

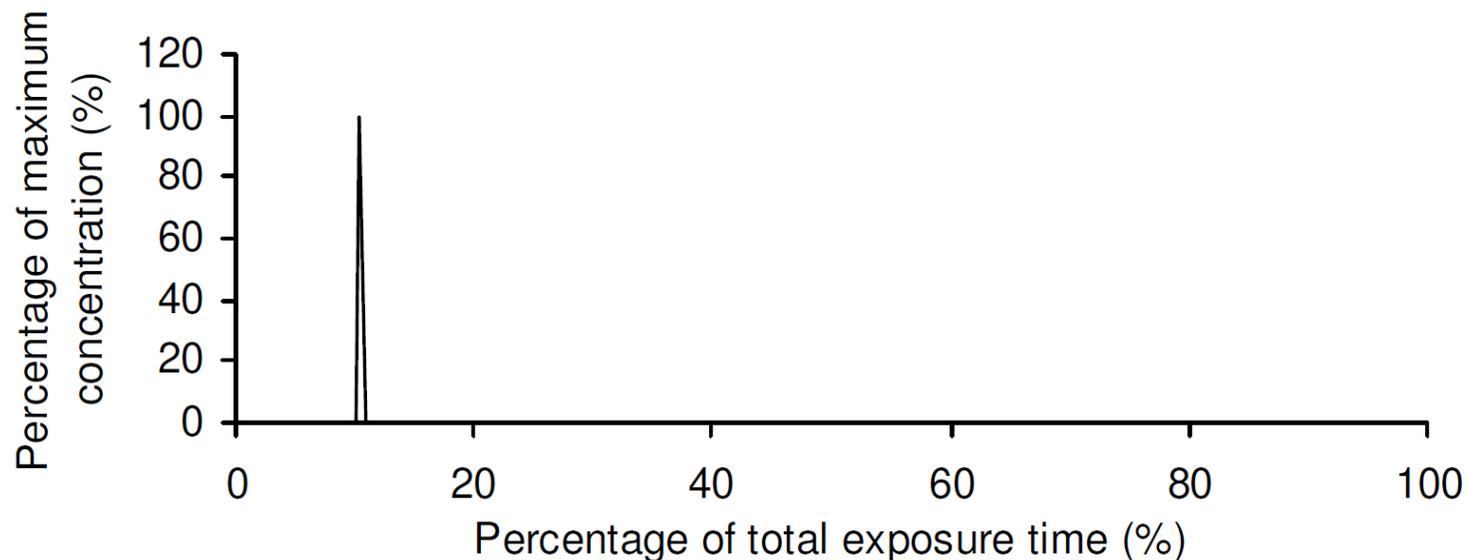
Water retention



Effects of poor sorbent/compound pairings

Sample losses i.e. back diffusion

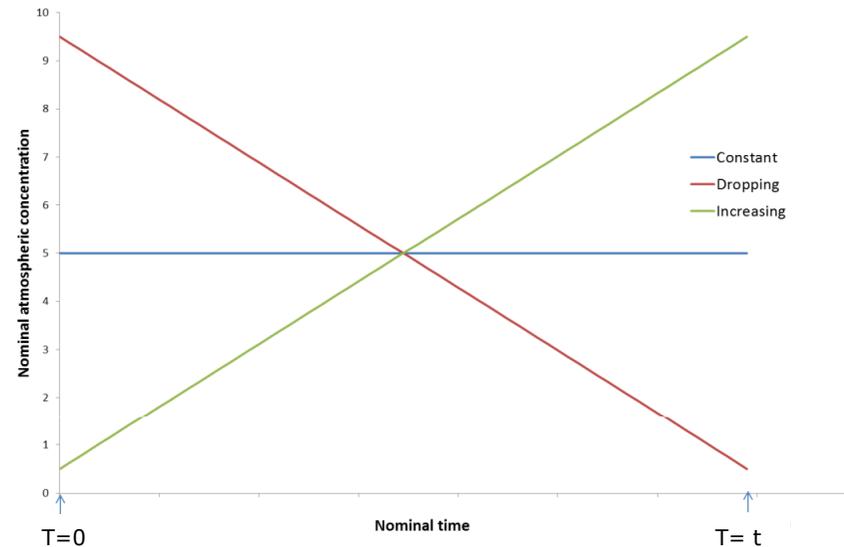
- This occurs due to the inversion of the concentration gradient within the sampler air-gap. It occurs when the vapour phase concentration within the sampler becomes greater than the vapour phase concentration in the surrounding air. This is particularly acute when sampling poorly retained compounds from transient atmospheres.



Sampling complex atmospheres

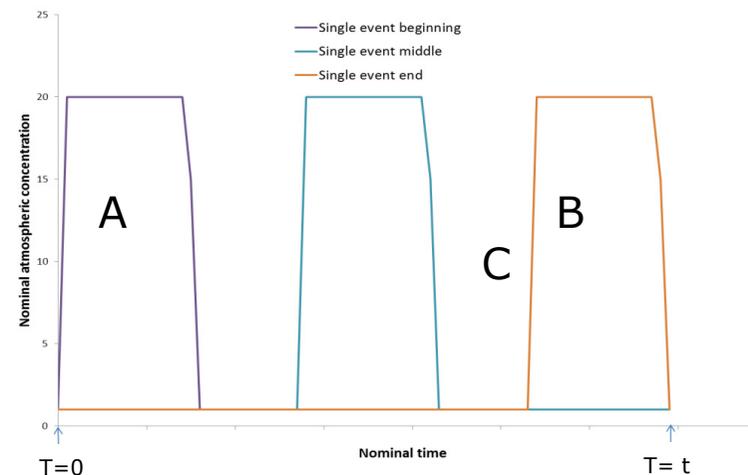
- Why is it important to ensure a constant sampling rate?

- Three VOC atmospheres – with the concentration a) static (blue), b) falling (red) and c) increasing (green) over the monitoring period – but with the same time weighted average concentration overall

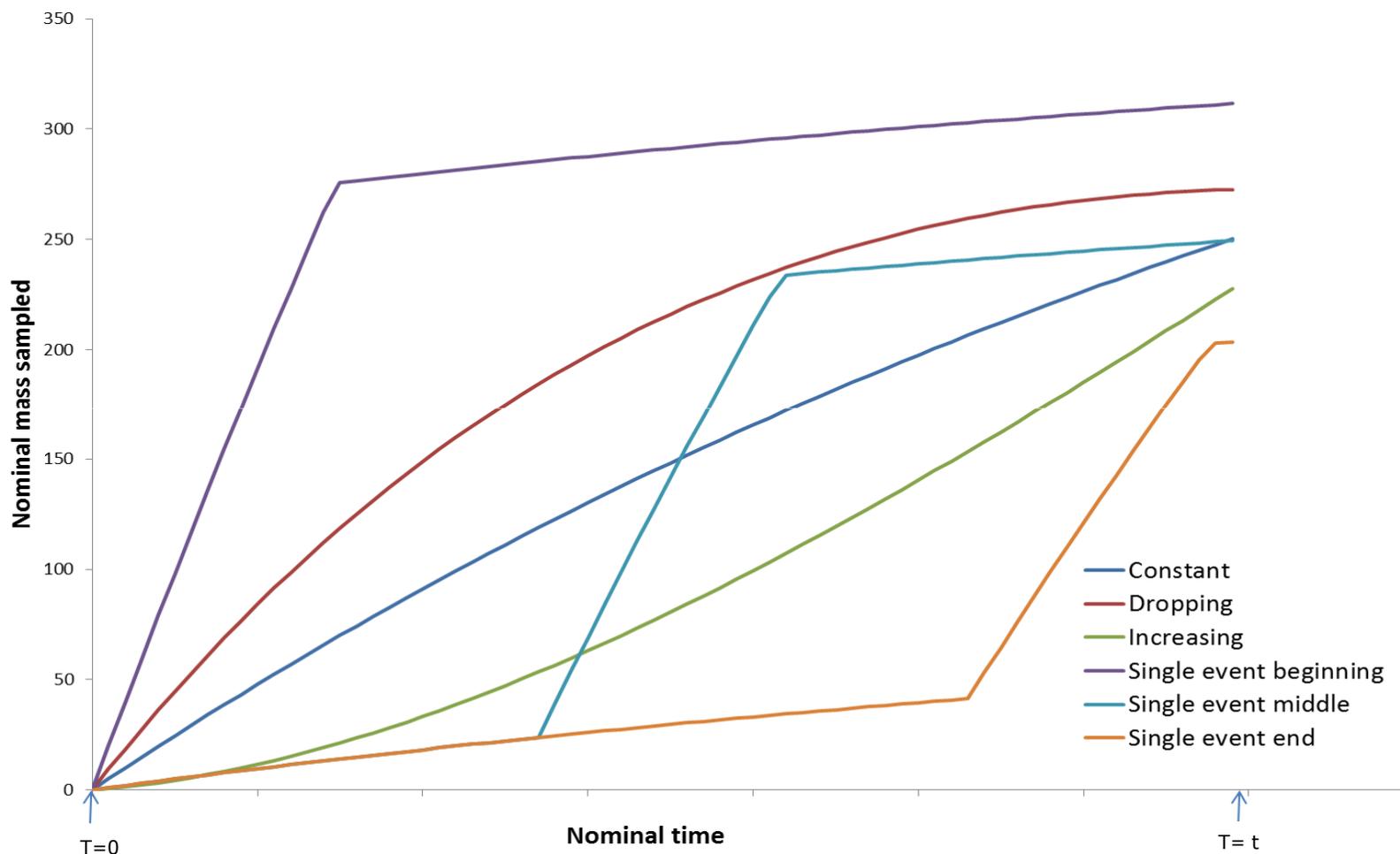


- Three more VOC atmospheres with an emission event occurring

- a) early-, b) mid- and c) late- in the monitoring cycle, but with the same time weighted average concentration overall.



Sampling complex atmospheres



Sampling considerations

Compound target concentration

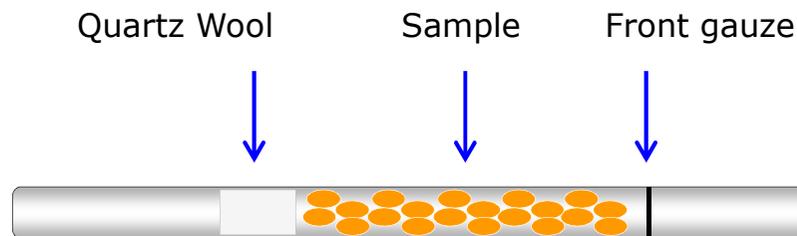
- When designing a passive sampling study, the target compounds and typical concentrations should be known.
- This will help define
 - the type of sampler to use
 - the sorbent
 - the exposure period
- As a general rule, concentration ranges are,

	8 h	Four week
Axial	2 $\mu\text{g m}^{-3}$ to 10 mg m^{-3}	0.3 $\mu\text{g m}^{-3}$ to 300 $\mu\text{g m}^{-3}$

- Sampling over shorter periods is possible (30 minutes) for higher concentrations, as is sampling over longer periods (six weeks) for much lower atmospheric concentrations (sub-ppb), providing the correct sorbent is used.
- However, when atmospheric concentrations are very low (<1 ppb) **and** when a result is required within a few hours, in these instances high uptake rate samplers provide a better solution.

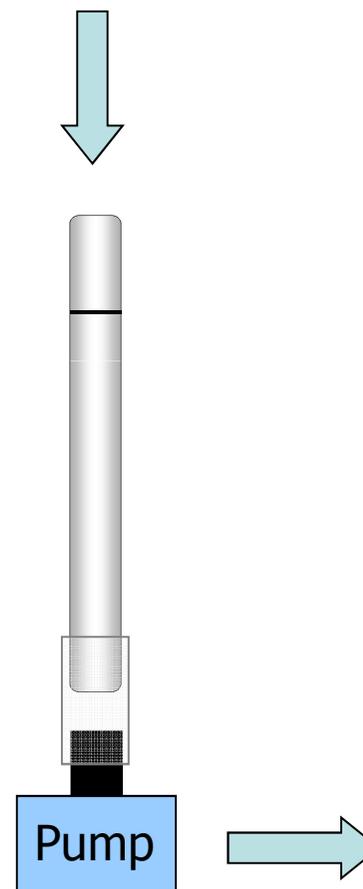
1b. Direct sampling

- Place sample directly into the tube
- Need a homogeneous sample
- Only 50 – 100 mg of (representative) sample is needed
- Weigh into empty tube
- Use gentle heating conditions to release VOC content

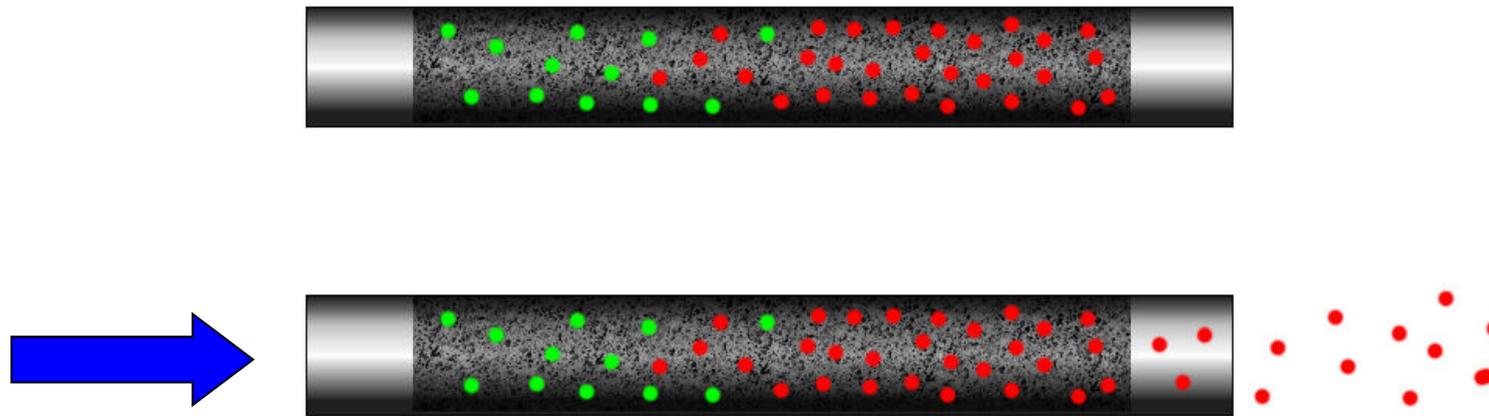


1c. Active (Pumped) Sampling

- TO17 specifies “The monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs”
- Flow rate typically 20 – 100 ml/min
- Volume taken is typically in the range 5 ml – 100 L, depending on expected concentration
- Much faster technique compared to diffusive sampling
- **Important** do not exceed breakthrough volume for a compound on a given sorbent



Breakthrough



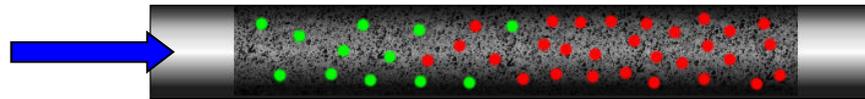
Affected by:

- | | |
|-----------------|--|
| Temperature | lower temp. = stronger interaction |
| Sample volume | lower volume = less risk of breakthrough |
| Mass or sorbent | more sorbent = more surface area |
| Type of sorbent | stronger sorbent = stronger interaction |

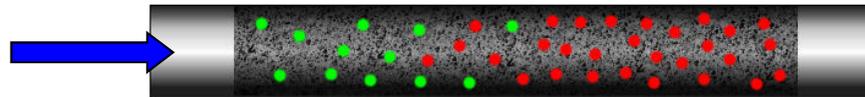
Breakthrough

Can test for breakthrough by either:

Sampling two tubes at different times or flows to achieve 1 and 4 litre sample volumes

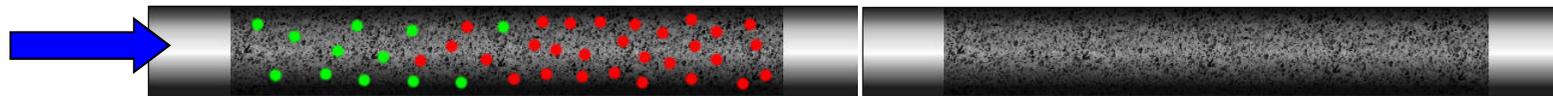


1 L sample



4 L sample

Sample with two tubes attached in series

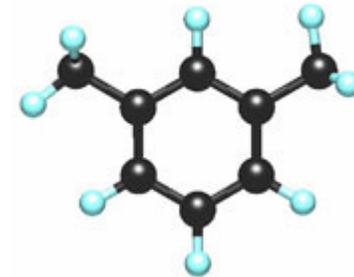


Air Monitoring - Pumped

Sorbent selection for both tubes and cold trap are very important

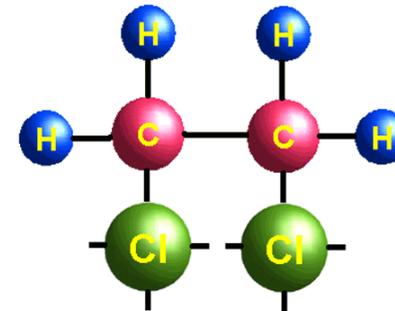
Semi volatile compounds - Weak sorbent

Helps prevent retention of unwanted compounds (such as water and CO₂) by allowing them to breakthrough the sorbent



Very volatile compounds - Strong sorbent

Prevents **breakthrough** of the lighter compounds but will retain more of the unwanted lighter compounds

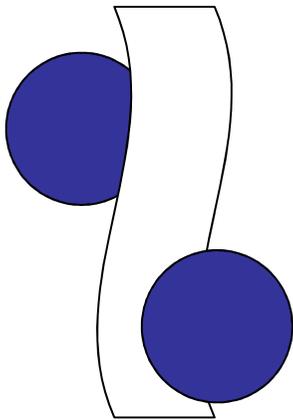


Sorbent selection

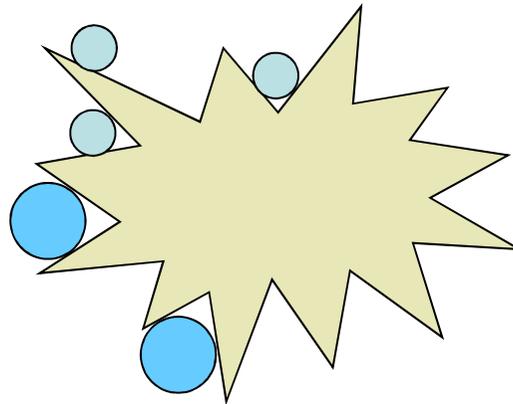
The sorbent(s) selected must quantitatively retain the compounds of interest from the volume of air / gas sampled **and** must then release those compounds as efficiently as possible during the desorption process.

Sorbent selection principally depends upon the volatility of the analyte(s) concerned –***the more volatile the analyte to be trapped, the stronger the sorbent must be.***

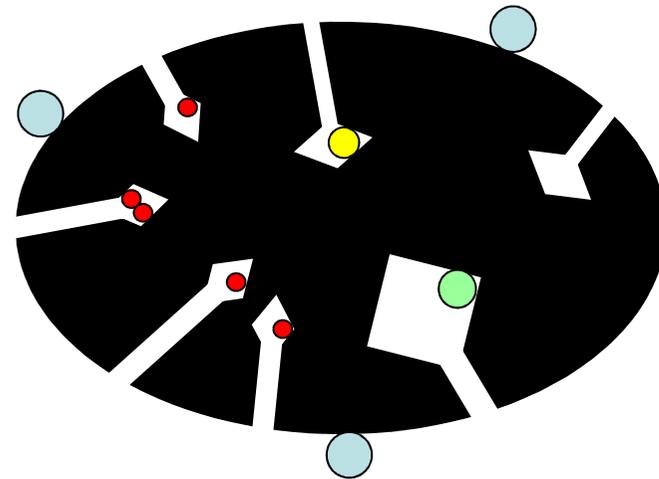
Quartz Wool



Porous Polymer



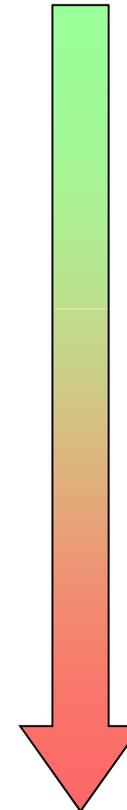
Carbon Molecular Sieve



Common Sorbents

Sorbent Name	Volatility Range
Quartz wool / silica beads	C ₃₀ - C ₄₀
Tenax TA	C ₇ - C ₃₀
Carbograph 2TD	C ₈ - C ₂₀
Carbograph 1TD	C _{5/6} - C ₁₄
Carbograph 5TD	C _{3/4} - C _{6/7}
SulfiCarb	C ₃ - C ₈
Carboxen 1003	C ₂ -C ₅
Carbosieve SIII	C ₂ -C ₅

Water retention



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Sorbent selection

Sorbents have a number of characteristics that must be taken into account when selecting the best choice for the compound(s) of interest:

Strength

Look at the boiling point of the compound of interest

- | | |
|------------------|--|
| Bpt > 100 °C | use a 'weak' strength sorbent (e.g. Tenax TA/GR, Carb 2TD) |
| Bpt 30 to 100 °C | use a 'medium' sorbent (e.g. Carbograph 1TD) |
| Bpt -30 to 50 °C | use a 'strong' sorbent (e.g. Carb X, Unicarb, Carboxen 1000, CS III) |

Thermal stability

Consider the maximum operating temperatures of porous polymers which varies considerably

- Tenax TMAX = 350°C,
- Porapak/Chromosorb/Hayesep TMAX ranges from 190 °C to 280 °C.
- Graphitised carbon blacks >400°C,
- Carbonised molecular sieves >400°C

Sorbent selection

Inertness

Some sorbents are completely inert – e.g. porous polymers (Tenax etc.) and carbonised molecular sieves – these sorbents are suitable for analysis of thermally labile / reactive compounds such as; mercaptans and other sulphur containing species, phosphorous pesticides, terpenes, phthalates etc.

Hydrophobicity

Some sorbents are very hydrophobic and therefore useful when sampling in humid environments. Others are extremely hydrophilic and will collect water (sometimes several mg) during sampling – this water then has to be “managed” during the thermal desorption process in order to avoid analytical problems.

Artefact Levels

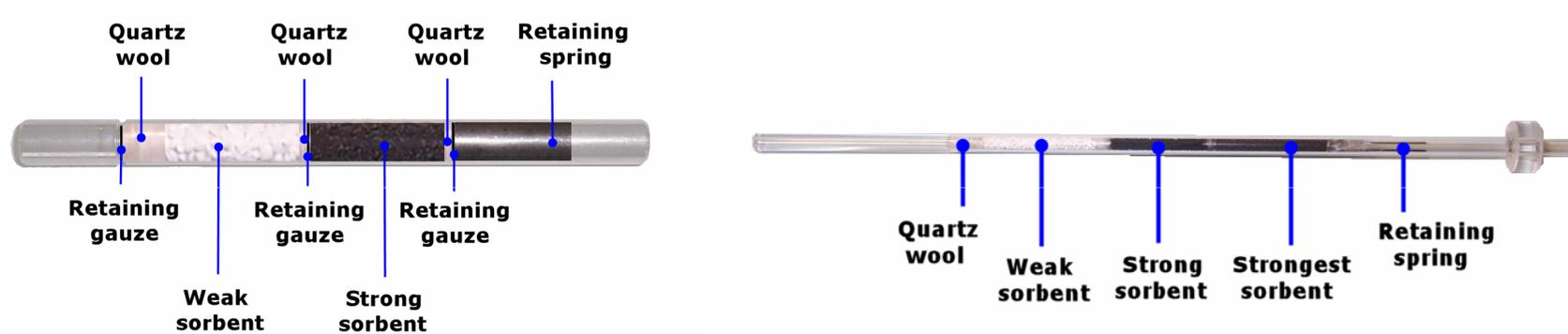
Carbonised molecular sieves (UniCarb, Carboxen, Carbosieve) and graphitised carbon blacks (Cargograph) exhibit minimal artefact levels ($< 0.1\text{ng/component}$) if rigorously conditioned.

Tenax TA / GR exhibits low artefact levels of $< 1.0\text{ ng/component}$ (including benzene) when new and freshly conditioned, but these rise as the sorbent ages.

Combining Sorbents

What if you have a wide range of compounds you wish to trap?

Answer: Use multiple sorbent beds in tube / cold trap



How should sorbents be combined?

What will happen if I have the wrong combination?

Sorbent Care

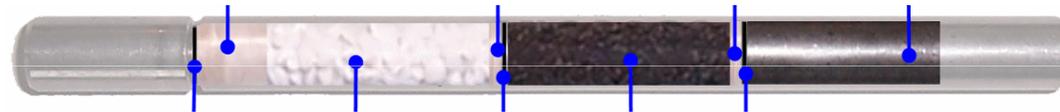
- Be careful not to damage your tubes / trap by exceeding the sorbent maximum temperature
- Tenax melts at temperatures above 340°C
- Graphitised carbons and molecular sieves are stable to > 400°C
- Graphitised carbons and molecular sieves are sensitive to mechanical damage i.e. they form small particles that impede cold trap flow
- Excessive moisture can also cause impedance problems



Tube Repacking

The lifespan of a freshly packed tube will depend upon the following:

- The sorbent type
- The maximum temperature the tube has been desorbed at
- The temperature the tube has routinely been desorbed at
- The number of desorption cycles (analytical and tube conditioning)



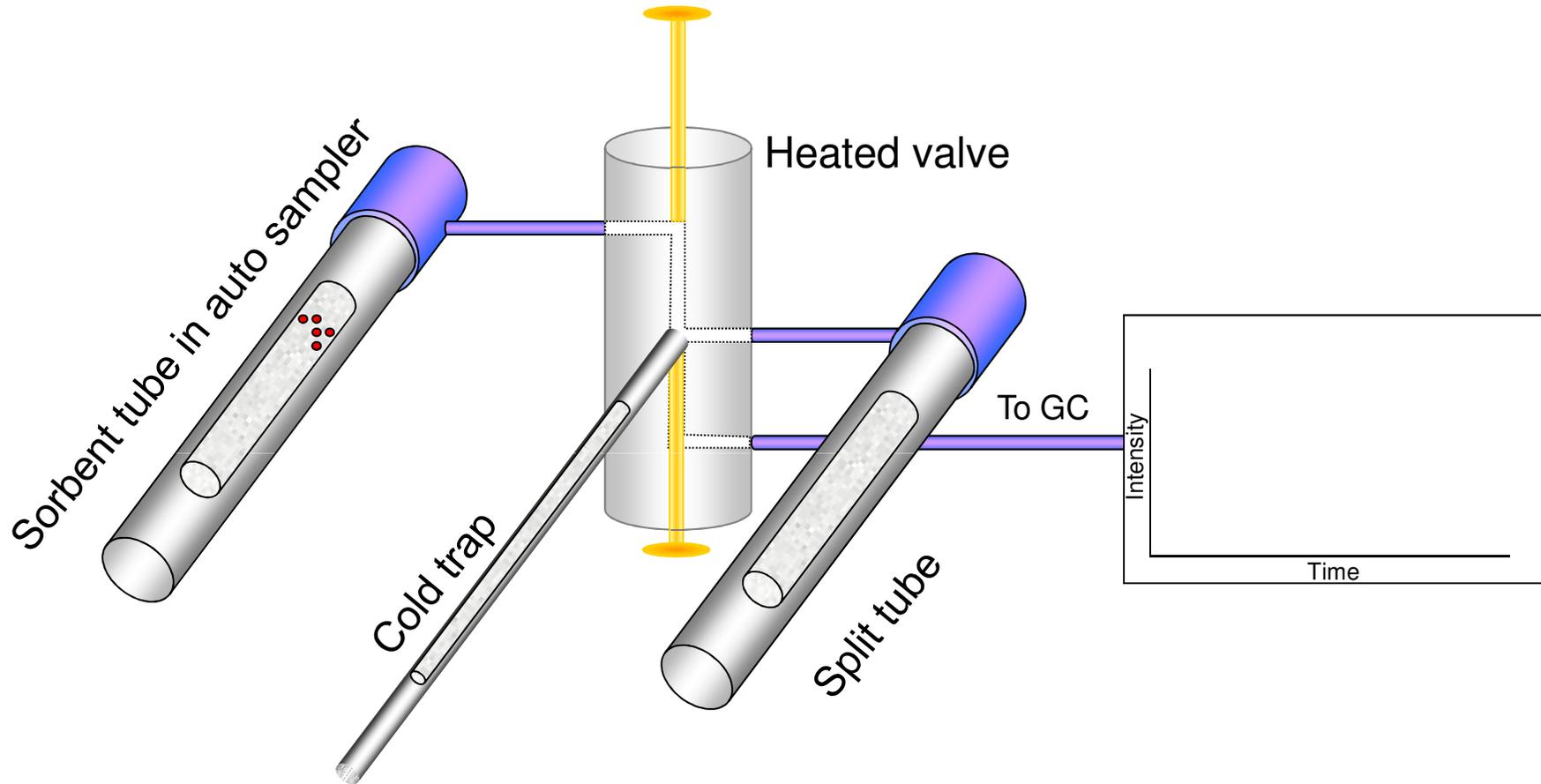
Tenax TA tubes and tubes packed with carbon based sorbents are good for 100 - 200 cycles.

Other porous polymers such as Chromosorb, Porapak and HayeSep tubes should be repacked once they have undergone 100 thermal cycles.

Same applies to cold traps - performance degrades over time. High boiling or sulfur applications require more frequent maintenance.

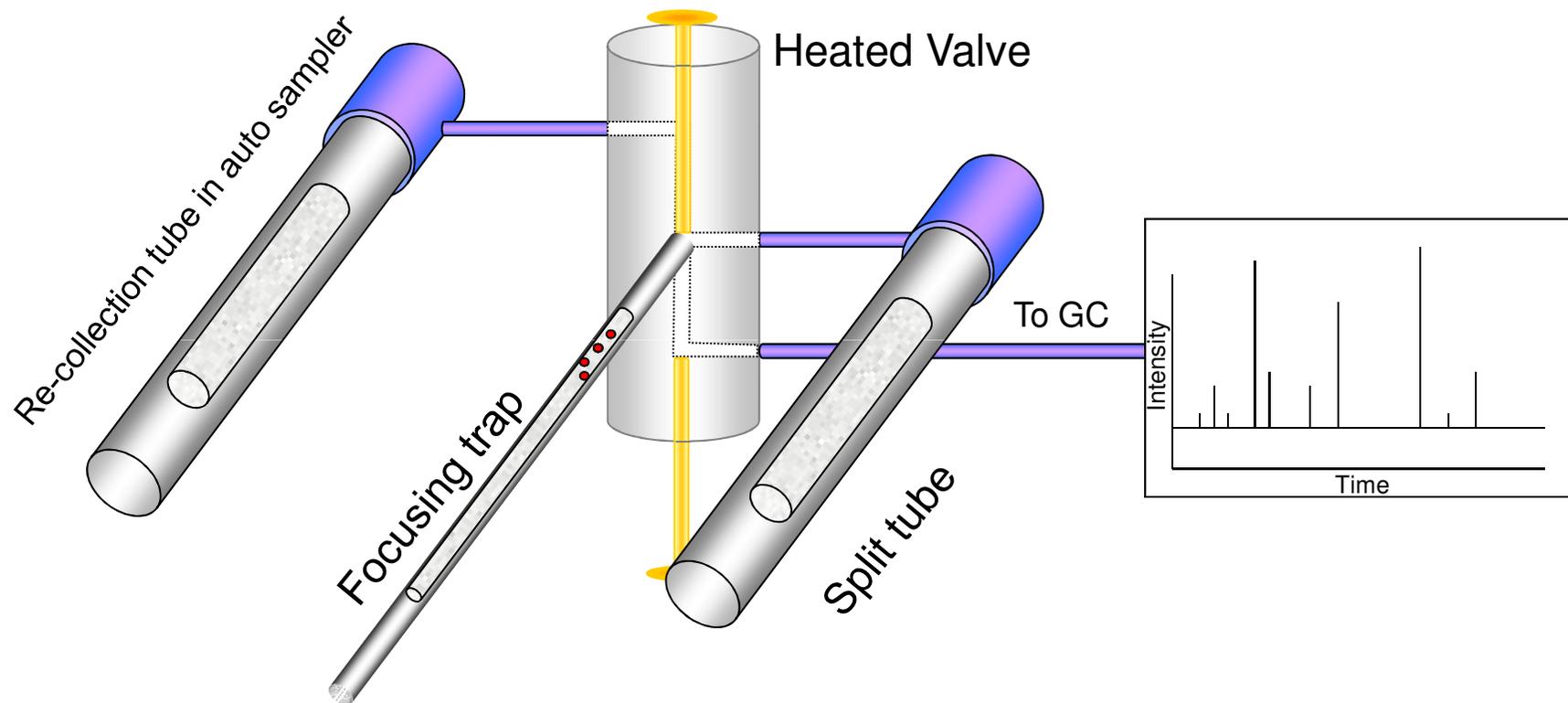
ANALYTICAL CONSIDERATIONS

Tube Desorption on TD-100



- Sample transferred from tube to cold trap, using heat & flow of inert carrier gas (in the opposite direction to sampling flow)
- Split available at this point for high concentration samples

Trap Desorption on TD-100 (with re-collection)

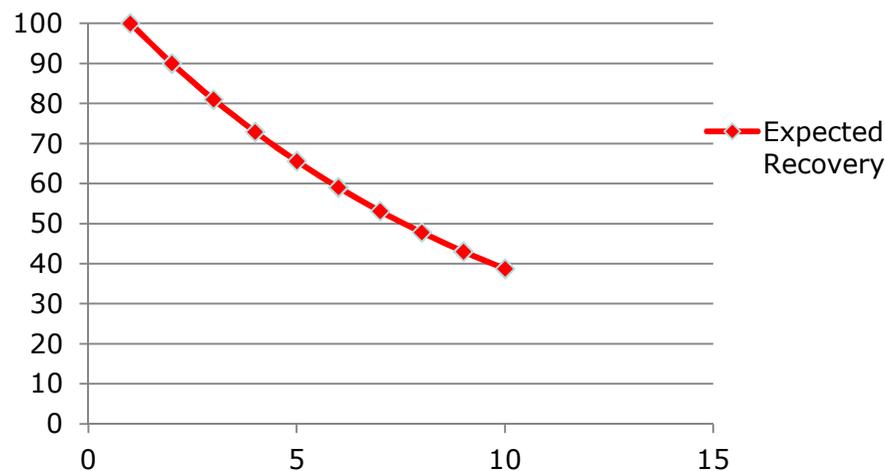


- Cold trap heated rapidly (up to 100°C/second)
- Dimensions of cold trap allow splitless desorption for trace (ppt) analysis
- Split / re-collection available at this point for high concentration samples

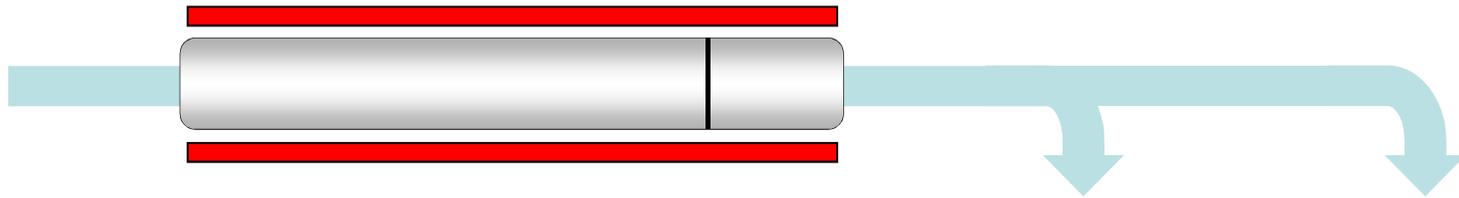
Uses for Re-collection

- Re-collection experiment where we load a standard and re-collect it multiple times between two tubes
- Compare results to expected recovery as a means of verifying instrument performance

Set	TYPE	Method	Tube	Injection	Re-collection
Set_01		Single split Tenax tube desorption.mth	1-2	1	Yes
Sample01_1	Sample	C:\Program Files\Markes TD\methods\Single split Tenax...	1	1	2
Sample01_2	Sample	C:\Program Files\Markes TD\methods\Single split Tenax...	2	1	1



Analytical Objectives – primary desorption

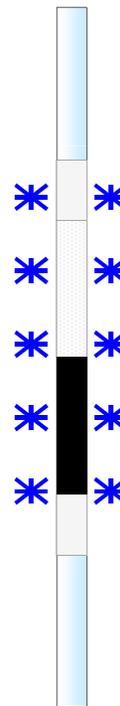


1. TUBE: Complete (representative) desorption of all target analytes from the sorbent tube

i.e. Everything desorbed from the Tube

2. TRAP: Complete (representative) retention of all target analytes for the duration of primary desorption

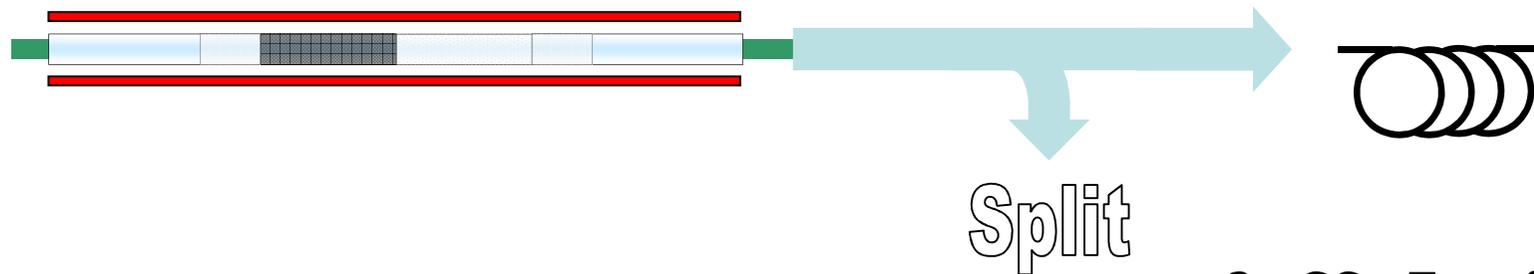
i.e. Everything retained on the Trap



Split

3. SPLIT: Optional (quantitative) split of portion of sample and / or selective elimination of unwanted volatiles

Analytical Objectives – secondary desorption (trap fire)



1. TRAP: Complete desorption of all target analytes from the trap

i.e. Everything desorbed from the trap

2. SPLIT: Optional (quantitative) split of portion of sample

3. GC: Transfer of all analytes (or a representative portion of them) to the analytical system in a narrow band of vapour

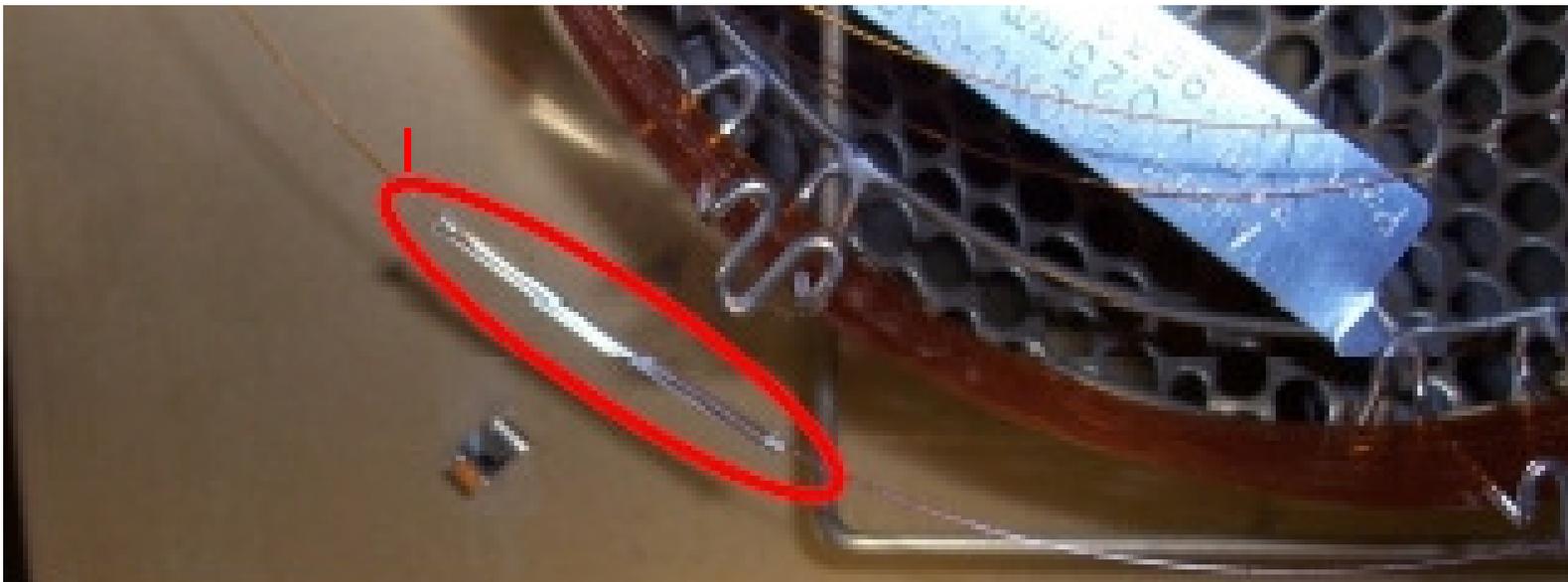
i.e. Injection onto column in a narrow band of vapour

Unexpected results?

- Check your sampling conditions
 - Correct sorbent?
 - Sampling flow rates appropriate?
 - Sampling duration?
 - Field blanks, trip blanks, correct caps?
- Check your method conditions
 - Flows, temperatures, times, splits
 - Are they optimised for the application?
 - Reactive sulfur compounds require a low flow path temperature
 - High boiling phthalates require a high flow path temperature
 - Correct flows?
 - Correct cold trap?
- Check TDTS application notes for guidance
 - 109 different application notes covering all sorts of application areas
- Check for any system leaks

Typical Leak

This leak is not detected during the tube leak test - but can be detected from the total flow reading of the GC (on electronic carrier controlled systems)



Fused silica transfer line connection to GC
- inside GC oven

Further Information

- Thermal Desorption application notes, especially notes 6 & 86
- Markes website
 - www.markes.com
- Applications books
 - Environmental
- Myself, nwatson@markes.com
 - Based in the Cincinnati, Ohio Laboratory

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international

Technical Support

Application Note 006

Troubleshooting analytical thermal desorption applications

Introduction

Thermal desorption-gas chromatography (TD-GC) is now a well-validated and widely used technology. However, in common with most analytical techniques, troubleshooting is still important, especially during method development.

This document describes some of the most commonly encountered concerns and how best to address them. Advice given relates specifically to Markes' UNITY™-based systems and the TD-100™.

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