Sampling, measurement and analysis of VOCs; what are the best tools for the job?

Mr Heath Linnell – EMEAI Sales Manager

Agenda

Sampling VOCs in air – The tools of the trade,
When should each technique be used?

Focusing on:

- Canister Sampling
- Online Sampling
- Sorbent tubes
    - Active sampling
    - Passive sampling
- Expanding Your Thermal Desorption capabilities

Thermal desorption – One versatile technique for all vapour-phase air monitoring applications

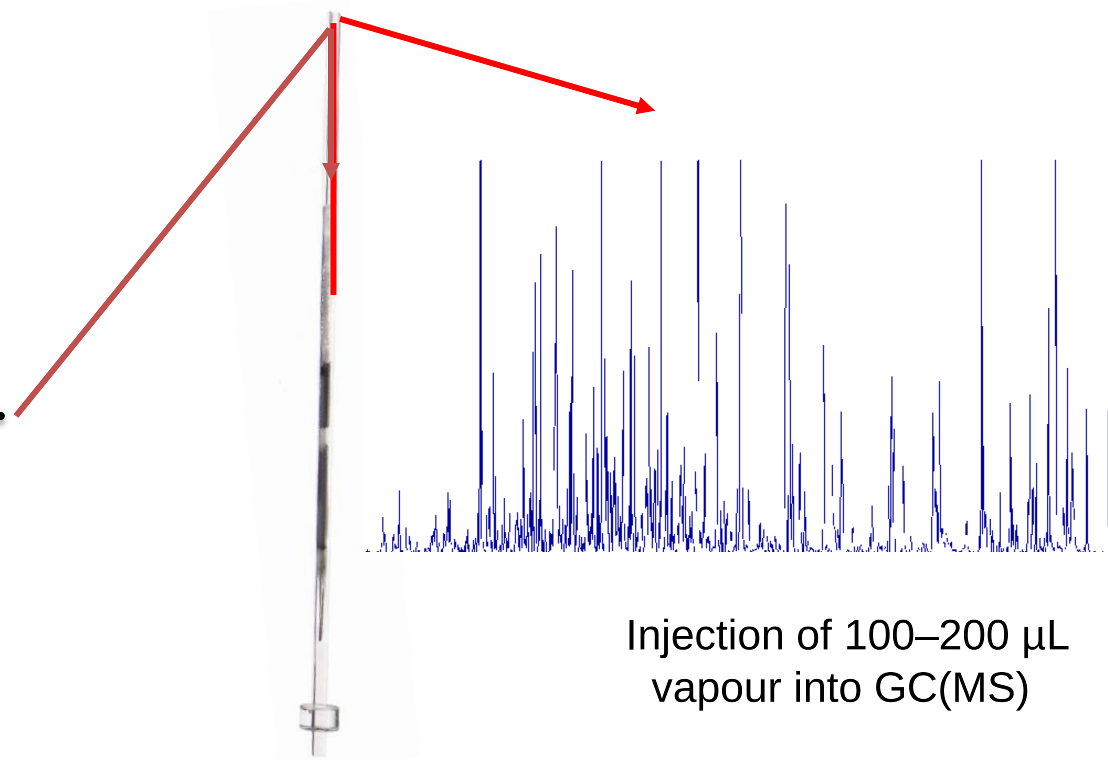
Canisters/bags

Sorbent tubes

Passive

Active

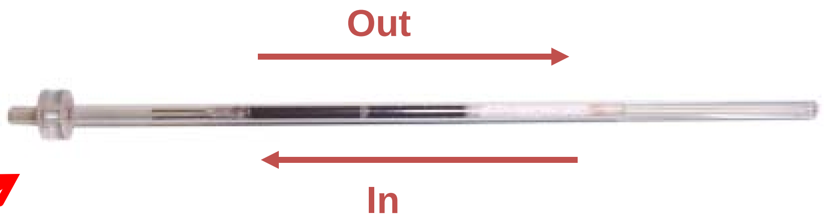
Electrically-cooled focusing trap



Injection of 100–200 µL vapour into GC(MS)

Water and volatile interferences can be purged to vent

Electrically-cooled & back-flushed focusing trap



- **Electrically cooled** - No liquid cryogen required
- Mixture of chemical (sorbent) & physical (temp.) trapping – maximises component trapping
- **Fast trap cooling/heating** reduces cycle times - Max heating rates approach 100ºC/s for sharp capillary peaks and high sensitivity
- Allows **selective purging of water or solvent**, thus reducing analytical interference
- Robust design **reduces dry gas consumption** (N_2 or air) to ~50 mL/min (*vs.* 500-600 mL/min on other systems) plus coolers turn off if dry gas runs low
- **Easy to change the trap without breaking it**

Canisters vs Tubes

- TO-15 vs TO-17

Canisters
Which sampling method is best?

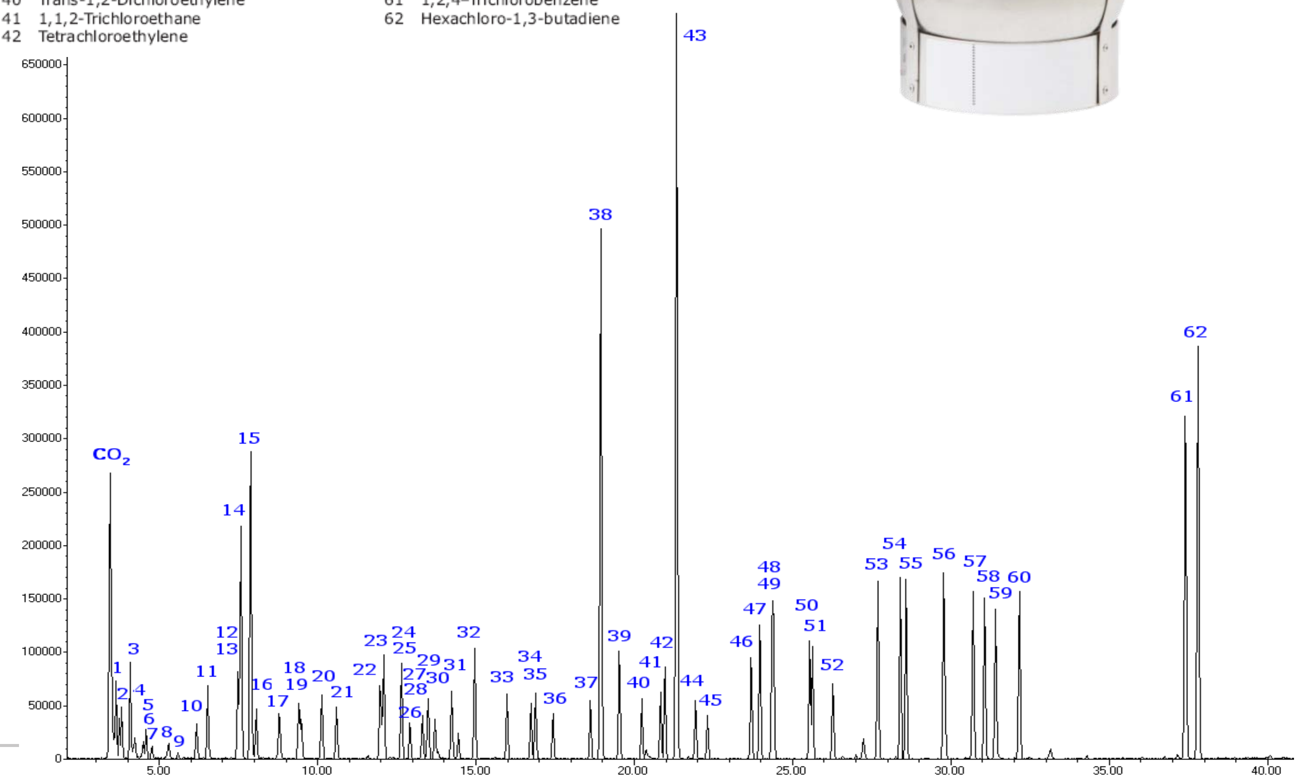
- ✓ Great for C_2 to C_{12} compounds
- ✓ Suitable for rapid transfer (not storage) of ultra-volatile reactive compounds such as H_2S
- ✓ Ideal for simple grab-sampling

- x NOT suitable for compounds with volatility less than $C_{10/12}$
- x NOT recommended for high-concentration samples
- x Time-weighted average sampling is NOT easy with a canister

Typical Application: 'Air toxics' in canisters – US EPA Method TO-15

1 Propylene
2 Dichlorodifluoromethane
3 1,2-Dichlorotetrafluoroethane
4 Methyl chloride
5 1,2-Dichloroethane
6 1,3–Butadiene
7 Vinyl chloride
8 Methyl bromide (bromomethane)
9 Chloroethane
10 Trichlorotrifluoroethane (Freon® 113)
11 Ethanol
12 1,2,-Dichloroethylene
13 1,1,2-Trichlorotrifluoroethane
14 Acetone
15 Carbon disulfide
16 Isopropyl alcohol
17 Methylene chloride
18 Tert-butyl methyl ether
19 *n*-Hexane
20 1,1-Dichloroethane
21 Vinyl acetate
22 Cis-1,2-Dichloroethylene
23 Methyl ethyl ketone
24 Ethyl acetate
25 Tetrahydrofuran
26 Chloroform
27 1,1,1-Trichloroethane
28 Cyclohexane
29 Carbon tetrachloride
30 Benzene
31 *n*-Heptane
32 Trichloroethylene
33 1,2-Dichloropropane
34 1,4-Dioxane
35 Bromodichloromethane
36 Trans-1,3-dichloropropene
37 Methyl isobutyl ketone
38 Toluene
39 Cis-1,3-Dichloropropene
40 Trans-1,2-Dichloroethylene
41 1,1,2-Trichloroethane
42 Tetrachloroethylene
43 Methyl *n*-butyl ketone
44 Dibromochloromethane
45 1,2-Dibromoethane
46 Chlorobenzene
47 Xylene
48 Xylene
49 Xylene
50 Styrene
51 Tribromomethane
52 1,1,2,2-Tetrachloroethane
53 1,2,4-Trimethylbenzene
54 1,3,5-Trimethylbenzene
55 1-Ethyl-4-methyl benzene
56 Ethylbenzene
57 1,2-Dichlorobenzene
58 1,3-Dichlorobenzene
59 Chloromethylbenzene (alpha)
60 1,4–Dichlorobenzene
61 1,2,4–Trichlorobenzene
62 Hexachloro-1,3-butadiene

1 L of a 1 ppb air toxics mix analysed splitless and cryogen-free using TD–GC/MS scan



MARKES international

CIA *Advantage* systems

- State of the art automated VOC analysis for air in canisters or bags
- Increased sample throughput
  - Optional humidified purging of internal sample lines means very low carry over and reduced need for blanks
  - Mix high and low concentration samples in a single sequence*
  - Options for 4, 14 or 27 channels
- Operates cryogen-free thus reducing costs
- Compatible with TO-17 compliant tube analysis
  - Can be upgraded for tube automation

Outcome: Just 5 more runs/day could mean ~€1000 extra/day (i.e. >€100K extra revenue per year) while saving ~€10K per year in Liquid N_2

* *Range from low ppm to sub-ppb for similar pressure canisters*

MARKES international

CIA *Advantage*: Accessories & options

- **CIA Satellite**
  - The satellite module increases sample capacity by 13 channels, providing extra capacity for canister processing

- **Canister cleaner**
  - The TO-14/15-compliant TO-Clean canister cleaning system cleans up to twelve 6 L canisters as standard (accessories for smaller canisters are available)

- **Racks**, bench or floor mounted
  - To hold up to 15 canisters (14 samples and one internal standard)

- **Diluter & humidifier**
  - Markes' humidification and dilution accessories allow efficient purging and mean a single gas standard can be diluted into multiple different calibration levels

Tubes:
Which sampling method is best?

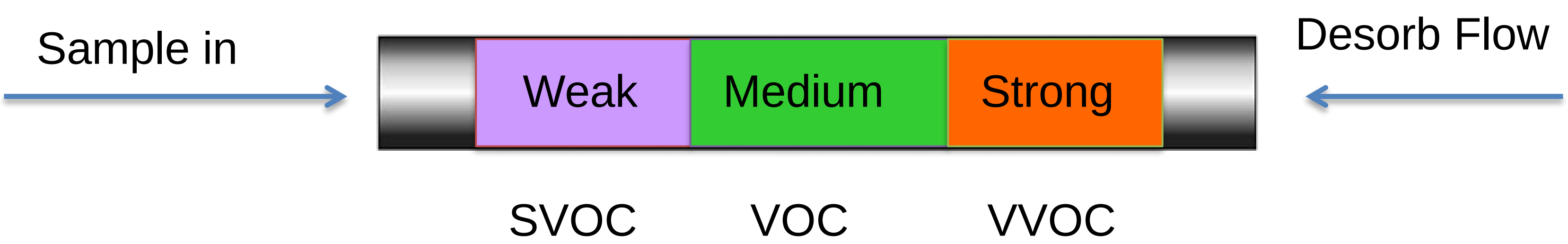
- ✓ Great for C_3 to n-C_{40} compounds
- ✓ Suitable for short or long term monitoring, using either passive or active techniques.
- ✓ Ideal for time-weighted average samples

- x NOT suitable for ultra volatile compounds such as CF_4, C_2H_2, H_2S
  - Ambient temperature trapping is not enough, sorbents require cooling to retain these compounds

Sampling parameters (flow, volume, type of tube etc) require thought before deployment.

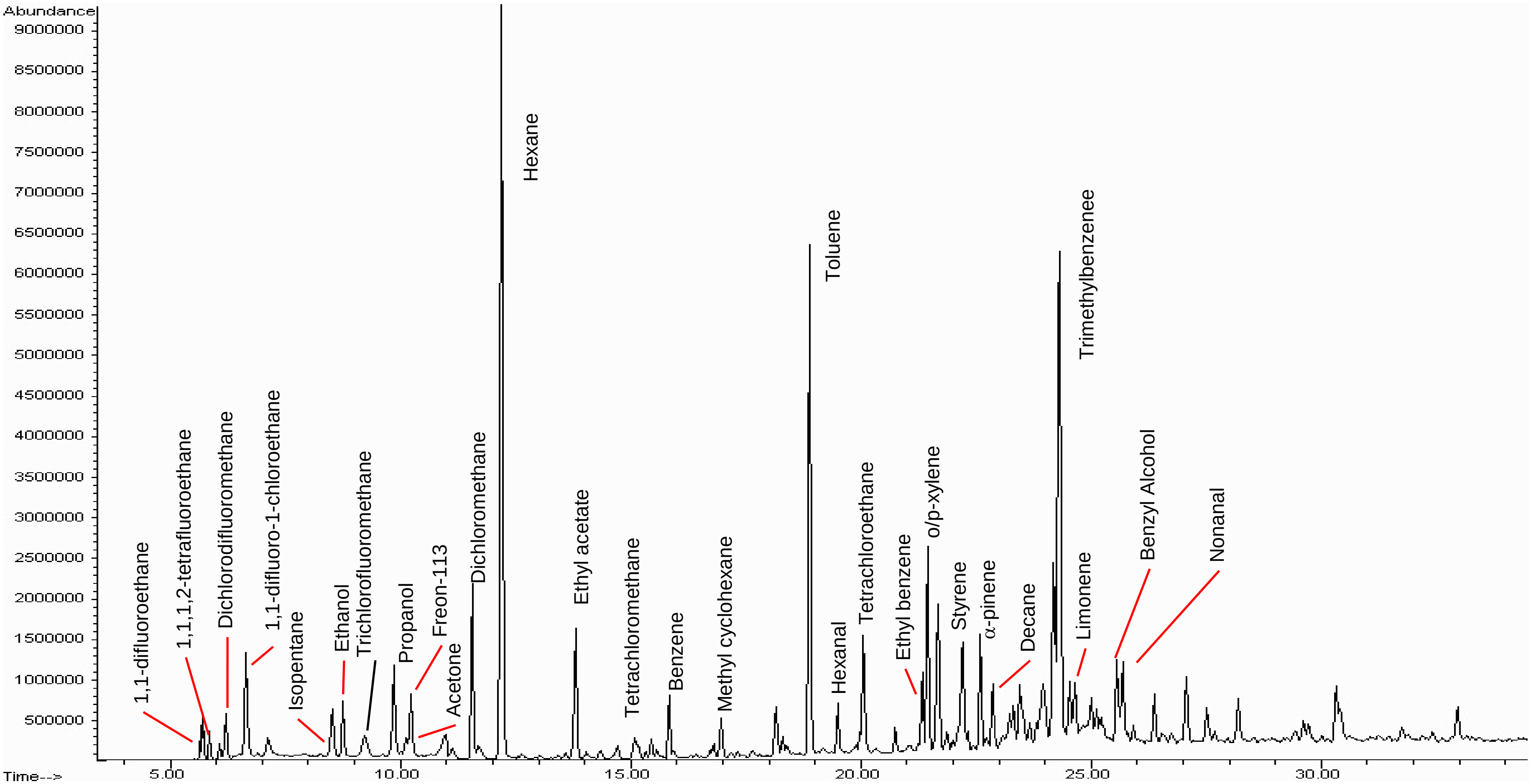
Active (pumped) sampling

- Pump air through sorbent tube
- Flow rate = 20–100 ml/min
- Volume = 500 ml to 100 L
- Important – do not exceed breakthrough volume for a compound on a given sorbent
- Multiple sorbents enable a wider volatility range



At 50ml/min a 1L sample of Air takes 20mins to collect

Typical Application: ISO 16017 part 1
"Clean" indoor air sampled onto multi-sorbent tube



MARKES international

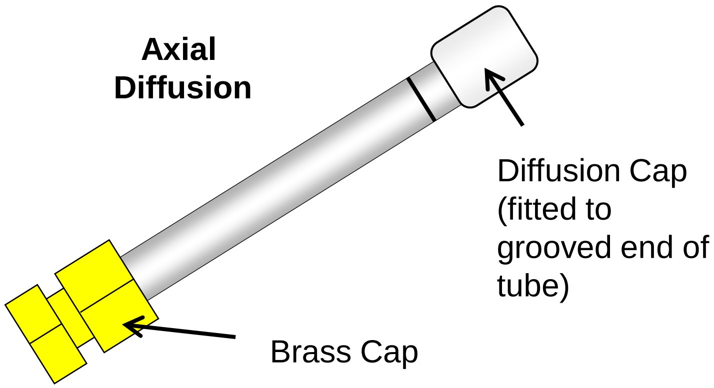
Passive (diffusive) sampling

A simple and cost effective method of collecting the large number of samples required in many air monitoring programmes

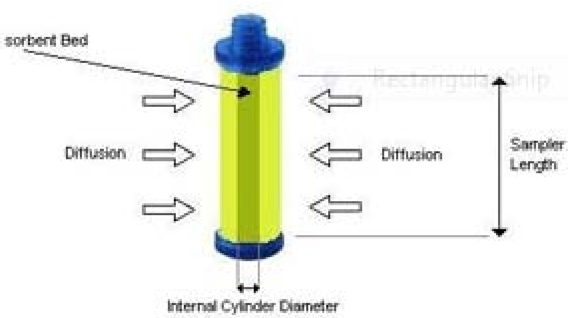
- A passive sampler is essentially a collection medium, either
  - solid sorbent,
  - liquid sorbent,
  - or chemically impregnated inert support,

  which is separated from the atmosphere of interest by a zone of still air.
- Vapours migrate across the air gap at a constant "uptake rate"
- Typically used in:-
  - Occupational Hygiene
  - Workplace Exposure
  - Personal Exposure
  - Environmental Air Monitoring (days/weeks)

Axial Diffusion



Radial Diffusion



When should I use diffusive sampling?

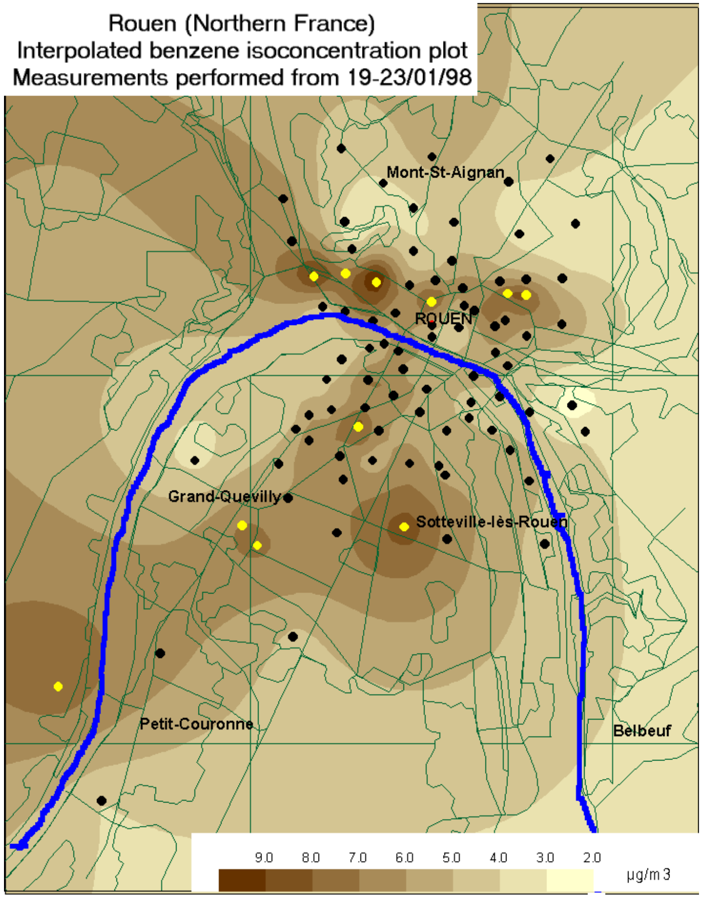
- ✓ You know the compound that you are looking for
- ✓ There is a validated uptake rate available for that compound
- ✓ The test atmosphere is not heavily contaminated with a wide range of other organic compounds at much higher concentrations
- ✓ The expected concentration of analyte in the atmosphere is such that the desired sampling time (usually between 4–8 hours (occupational) and 1–4 weeks (environmental)) will result in a mass on the tube which is above the limit of detection of the TD–GC(MS) method
- ✓ You are looking for several compounds of the same volatility

- x You are using a multi-bed sorbent tube
- x You are sampling a completely unknown atmosphere
- x You want to sample two (or more) compounds of widely differing volatilities (*e.g.* acetone and toluene)
- x There are no uptake rates available for the compounds of interest

Typical Application: Using sorbent tubes for diffusive sampling of outdoor air

Mapping urban pollution concentrations with low-cost diffusive (passive) sampling[1]

- Black dots = 100 sampling sites
- Yellow dots = pollution hotspots



[1] Application Note TDTS 10 – Use of diffusive sampling with TD–GC for ambient air monitoring

Factors that influence sampler performance

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.

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 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)

- 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.

- 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 are 0.05 to 0.10 ms^{-1}
  - 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.*
- Under extreme adsorbent loading conditions e.g.
  - 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

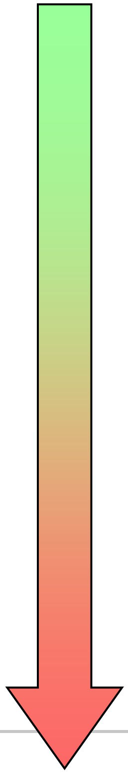
Factors that influence sampler performance

Sorbent selection

- *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	$C_2 – C_5$

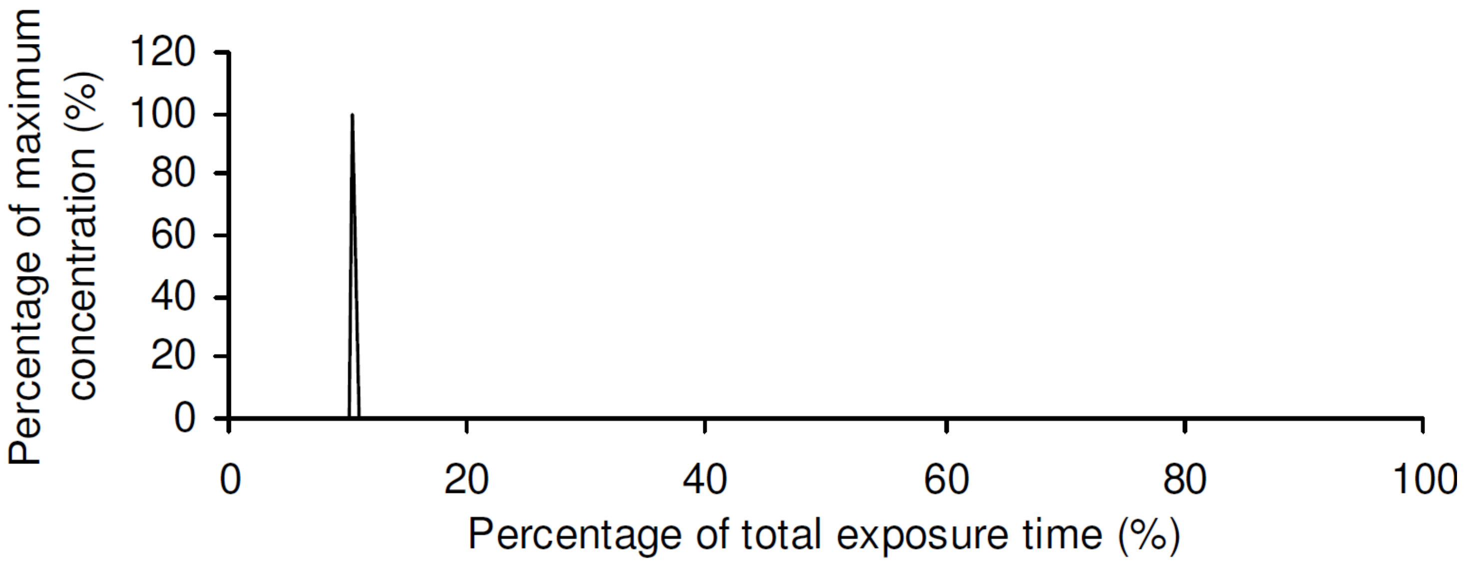
Water retention



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.



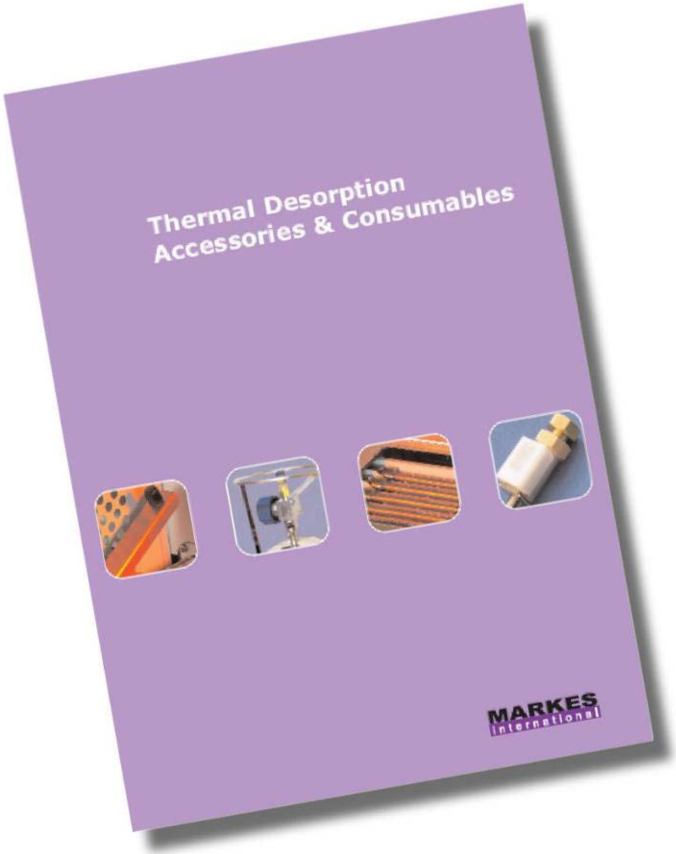
Sampling considerations

Things to remember when using Passive Samplers

- This will help define
  - the type of sampler to use, axial or radial
  - the sorbent
  - the exposure period
- Constant sampling rate
- Zero sink
- Protect your sampler from adverse atmospheric conditions
  - Temperature
  - Wind Speed
  - Relative humidity

Innovative TD accessories from Markes

Extending the TD application range



TC-20™

Multi-tube conditioning & dry-purge unit

- While all Markes TD systems feature a tube conditioning mode, the TC-20 offers cost-effective, simultaneous conditioning of up to 20 tubes
- Conditioning temps from 50 to 400°C
- The TC-20 also allows ambient temperature dry purging of up to 20 tubes simultaneously - in the sampling direction
- Delivers same flow through all tubes, however many or few are attached
- Allows use of low cost N_2
- Frees up TD–GC–MS analytical capacity

Micro-Chamber/Thermal Extractor™ (µ-CTE™)

For screening chemical release/emissions from products & materials and for odour profiling

One of GC's most versatile sampling tools

Barcoded sorbent sampling tubes

- Standard features: unique serial number, barcode (code 128), sampling flow direction arrow
- Reusable 100–1000 times

Options:

- Special tube labelling: up to 5 bands and/or up to 10 alphanumeric characters and/or TubeTAG
- Pre-packed with up to 3 sorbent beds or empty
- Pre-conditioning/capping (ready to use)
- Stainless steel, inert coated steel or fritless glass. Steel tubes also available in **SafeLok** 'diffusion limiting' format

Easy-to-use bar code reader. Read tubes directly into sequence table

SafeLok™

Peace of mind for pumped sampling

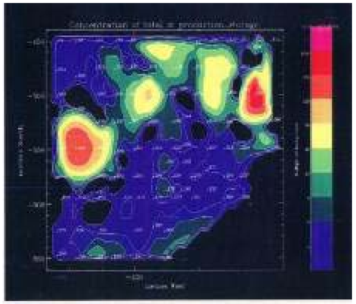
- Patented diffusion-locking technology protects samples from contamination and sample loss from diffusion (*e.g.* when incorrectly capped or uncapping in contaminated lab air)
- Also enables accurate low flow pumped sampling (<10 mL/min)
- Tube dimensions and sorbent mass identical to standard tubes, so easy to switch
- NB – Metal tubes only and not suitable for diffusive sampling
- Compatible with standard TD-compatible sampling pumps like **ACTI-VOC**

Specialist sampling from Markes

Markes' unique range of innovative TD accessories

Breath sampling

***In situ* monitoring of VOCs in soil**



Sorbent tubes in soil probes for low-cost mapping of ground contamination

Complete Application focused Solutions

EPA 325 - Refinery perimeter monitoring

New federal regulation (CFR 40) to be implemented mid 2015, compliance within 3 years

- Requires continuous monitoring of vapour-phase organics around the boundary of oil refineries
- US EPA Methods 325 A (Sampling) and 325 B (Analysis)
- 2-week passive sampling using sorbent tubes. *Pumped monitoring onto sorbent tubes may also be allowed.*
- 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)


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

TubeTAG™

- Sample and tube tracking

Patent # US 6.446,515 B2. Priority: 2002

TubeTAG™ : How it works

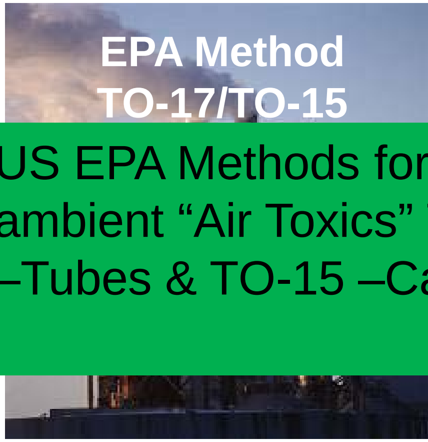
RFID tag permanently attached to tube, and tube-related information uploaded using TAG*SCRIBE*

Tagged tube sent to field. Sample details written to tag using TAG*SCRIBE*

Sample details written to tag using TAG*SCRIBE*

Data retrieved using TD instrument. Sample analysed, and tag information automatically updated

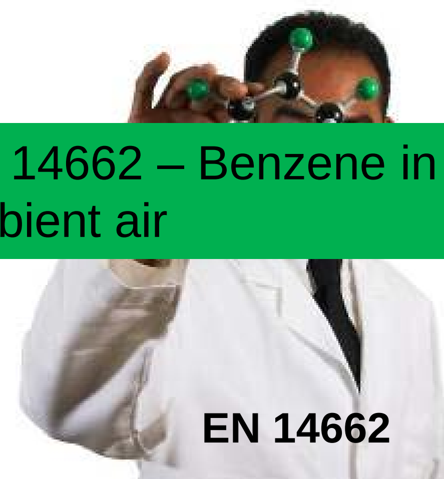
Complete compliance with international standard methods



US EPA Methods for ambient “Air Toxics” TO-17 –Tubes & TO-15 –Canisters

ISO EN 16017 & ASTM D-6196- Pumped or diffusive sampling of ambient, indoor and workplace air, plus materials

EN ISO 16000 – TD-GC/MS/FID materials emissions collected using emission cells or chambers



EN 14662 – Benzene in ambient air

Example Publications/Methods available

- ASTM D6246 - 08(2013) Standard Practice for Evaluating the Performance of Diffusive Samplers
- ASTM D4597 – 10, Standard Practice for Sampling Workplace Atmospheres to Collect Gases or Vapors with Solid Sorbent Diffusive Samplers
- ASTM D6306 – 10, Standard Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air
- Protocol for assessing the performance of a diffusive sampler (Method for the Determination of Hazardous Substances No. 27), UK Health & Safety Executive.
- CEN EN 838: Workplace atmospheres – Requirements and test methods for diffusive samplers for the determination of gases and vapours.
- EN ISO 16017: Air quality – Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/ capillary gas chromatography. Part 2: Diffusive sampling.
- MDHS 80: Volatile organic compounds in air. Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography (August 1995).
- E.R. Kennedy *et al., Protocol for the evaluation of* passive monitors, US National Institute for Occupational Safety and Health (NIOSH), published in: ‘Diffusive sampling: An alternative approach to workplace air monitoring’ (CEC Publication No. 10555EN), 1986.

Typical Application areas for TD

Thank You

Environmental air quality monitoring & workplace air

Military, forensic & counter-terrorism

Residual volatiles & materials emissions testing

Food, flavour & fragrance profiling