Sampling, measurement and analysis of VOCs & SVOCs: What are the best tools for the job?

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THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

Agenda

- Sampling VOCs in air – The tools of the trade
  Focusing on:
  - Canisters and online sampling
  - Sorbent tubes
    - Active sampling
    - Passive sampling
  - When should each technique be used?

How on-line/canister analysis works

1. Air/gas focusing

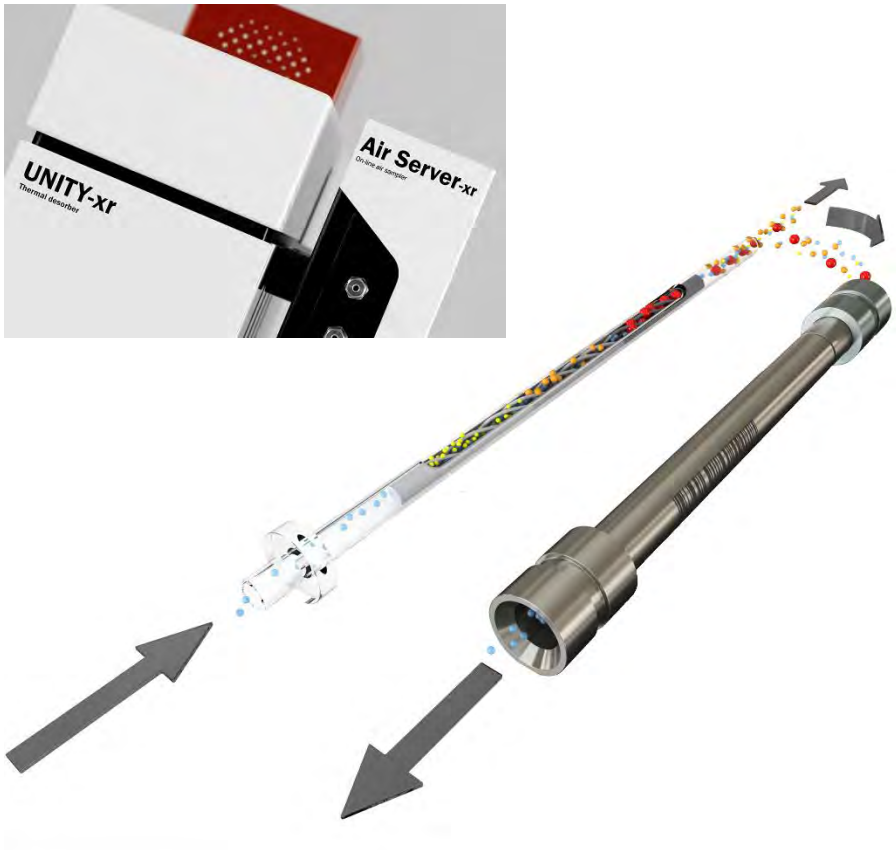
Samples are introduced directly onto the electrically-cooled, sorbent-packed focusing trap of the UNITY-xr thermal desorber, typically held between ambient and –30° C.

Quantitative retention of ultra-volatiles from up to 1.5 L volumes and efficient low-flow, splitless desorption ensure low detection limits.

Peltier-cooled focusing trap eliminates ice-plug formation, while fast trap cooling minimises cycle times.

How on-line/canister analysis works

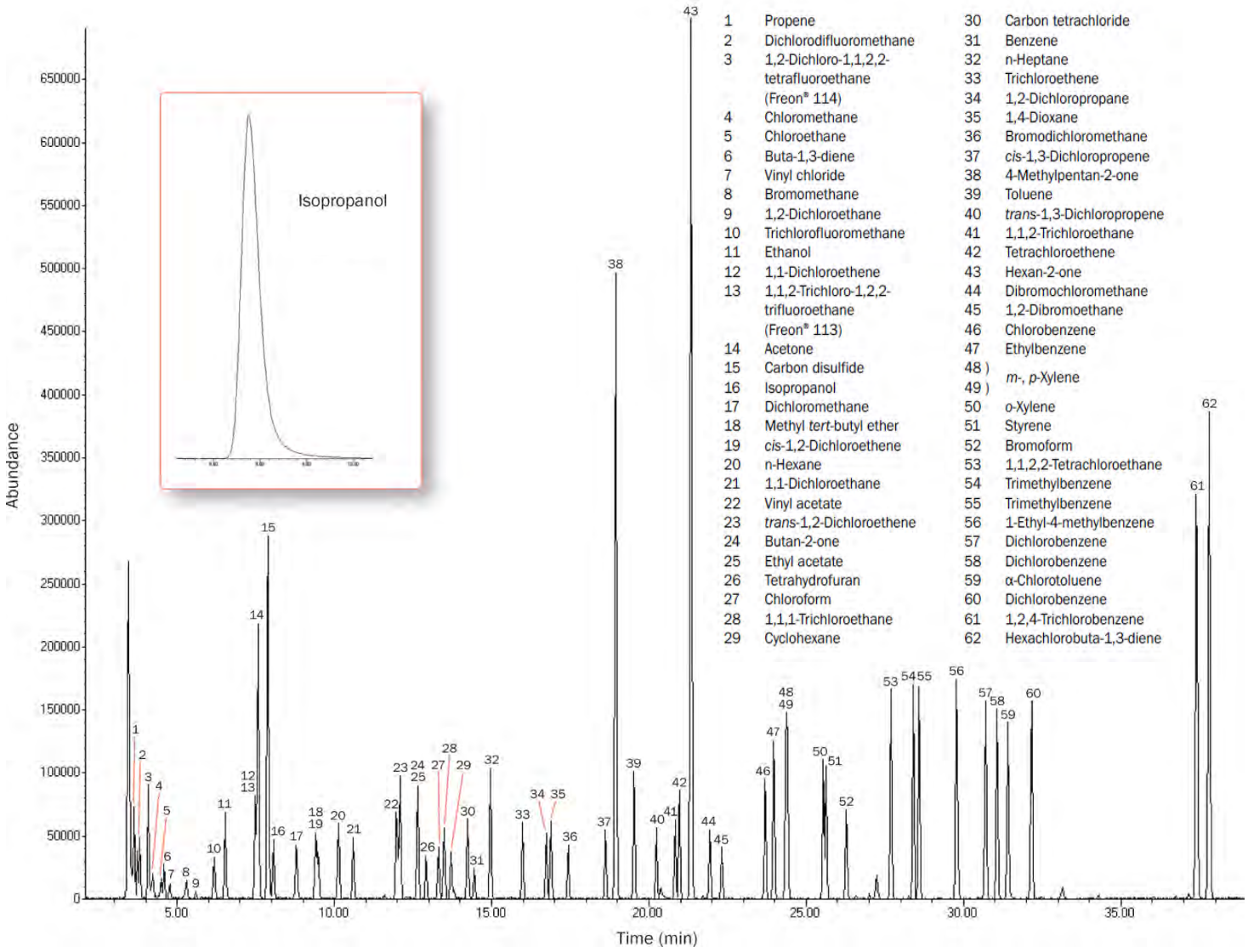
2. Trap desorption and outlet split



Focusing trap rapidly heated (up to 100° C/s) in a reverse flow of carrier gas ('backflush' operation), to transfer the analytes to the GC column.

- Fully automated sequences of air/gas (from a sample stream, calibration gas or zero air/gas) can be set at user-defined frequencies.
- During trap desorption, the flow of analytes can be split and re-collected onto a clean sorbent tube.
- Tubes and traps can contain multiple sorbents, for analysis of an extended range of analytes.

Analysis of Air Toxic compounds – Canisters

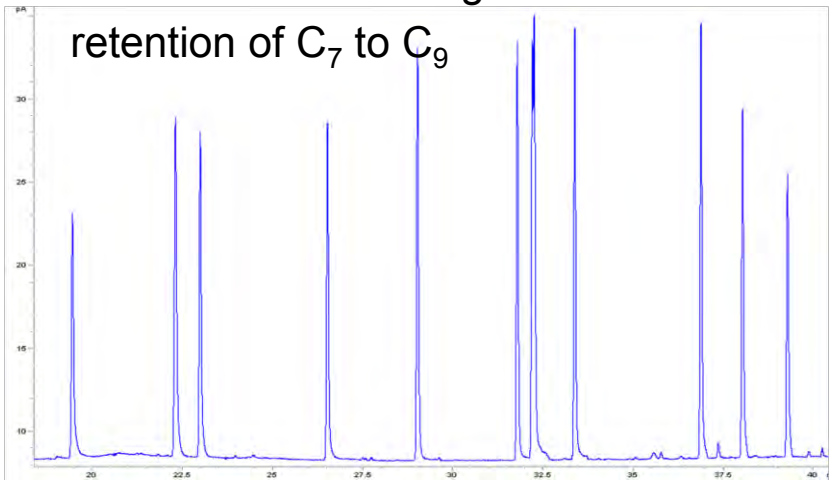


1	Propene
2	Dichlorodifluoromethane
3	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon® 114)
4	Chloromethane
5	Chloroethane
6	Buta-1,3-diene
7	Vinyl chloride
8	Bromomethane
9	1,2-Dichloroethane
10	Trichlorofluoromethane
11	Ethanol
12	1,1-Dichloroethene
13	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon® 113)
14	Acetone
15	Carbon disulfide
16	Isopropanol
17	Dichloromethane
18	Methyl *tert*-butyl ether
19	*cis*-1,2-Dichloroethene
20	n-Hexane
21	1,1-Dichloroethane
22	Vinyl acetate
23	*trans*-1,2-Dichloroethene
24	Butan-2-one
25	Ethyl acetate
26	Tetrahydrofuran
27	Chloroform
28	1,1,1-Trichloroethane
29	Cyclohexane
30	Carbon tetrachloride
31	Benzene
32	n-Heptane
33	Trichloroethene
34	1,2-Dichloropropane
35	1,4-Dioxane
36	Bromodichloromethane
37	*cis*-1,3-Dichloropropene
38	4-Methylpentan-2-one
39	Toluene
40	*trans*-1,3-Dichloropropene
41	1,1,2-Trichloroethane
42	Tetrachloroethene
43	Hexan-2-one
44	Dibromochloromethane
45	1,2-Dibromoethane
46	Chlorobenzene
47	Ethylbenzene
48) 49)	*m*-, *p*-Xylene
50	*o*-Xylene
51	Styrene
52	Bromoform
53	1,1,2,2-Tetrachloroethane
54	Trimethylbenzene
55	Trimethylbenzene
56	1-Ethyl-4-methylbenzene
57	Dichlorobenzene
58	Dichlorobenzene
59	α-Chlorotoluene
60	Dichlorobenzene
61	1,2,4-Trichlorobenzene
62	Hexachlorobuta-1,3-diene

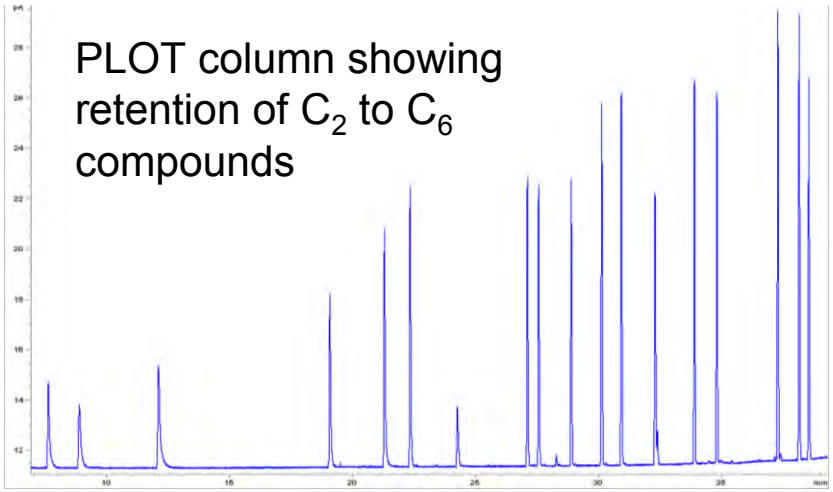
MARKES international 1 L of a 1 ppb air toxics mix analysed splitless & cryogen-free using TD-GC/MS scan

Application: Monitoring of C_2–C_{10} hydrocarbons (ozone precursors) in ambient (TD–GC dual FID)

DB-1 column showing retention of C_7 to C_9



PLOT column showing retention of C_2 to C_6 compounds



- **Target compounds:**
  - **C_2 to C_{10} hydrocarbons (ozone precursors)**
  - 'Ozone precursors' focusing trap at –30°C and flow path at 120°C
- **Performance in field operation:**
  - Detection limits: <0.05 ppb
  - Retention time stability: <0.2% RSD across all compounds
  - Standard reproducibility: 0.2–5% RSD
  - Excellent peak shape for splitless injection

Can canisters do everything?

- ✓ 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 suitable for high-concentration samples
- x Time-weighted average sampling is NOT as easy with a canister

How thermal desorption works

1. Tube desorption and inlet split

Sample tubes and traps can contain multiple sorbents, for analysis of a wide range of analytes.

During desorption of the tube the flow of analytes can be split and re-collected onto a clean sorbent tube.

Sample tube heated in flow of carrier gas and analytes swept onto an electrically cooled focusing trap, typically held between ambient and –30° C.

How thermal desorption works

2. Trap desorption and outlet split

Focusing trap rapidly heated (up to 100° C/s) in a reverse flow of carrier gas (‘backflush’ operation), to transfer the analytes to the GC column.

Extended re-collection

Quantitative re-collection allows:

- Valuable samples to be re-analysed, overcoming the historic ‘one-shot’ limitation of thermal desorption.
- Allows complete analyte transfer to be validated, ensuring compliance with standard methods.
- Aids method development and troubleshooting.

Sorbent tubes: Sampling techniques

- Active sampling
- Passive sampling

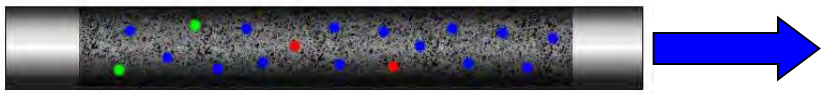
Which method to use?

Pumped sampling

Sample collection

- Sample (*e.g.* air) is collected

- Compounds of interest are adsorbed on the sorbent surface



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

Flow rate = 20–100 mL/min

Volume = 500 mL to 100 L

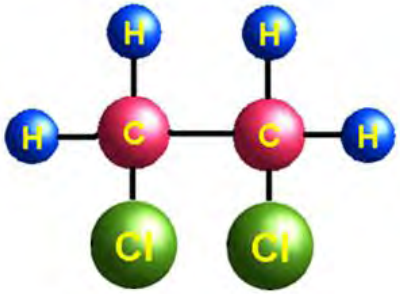
Important – do not exceed breakthrough volume for a compound on a given sorbent

Air monitoring - pumped

Sorbent selection for both tubes and focusing trap are very important

Semi-volatile compounds – Weak sorbent
Helps prevent retention of unwanted compounds

Very volatile compounds – Strong sorbent
Prevents breakthrough of light compounds



A complex example (US EPA TO-17)

1	Propene	30	Carbon tetrachloride
2	Dichlorodifluoromethane	31	Benzene
3	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon® 114)	32	n-Heptane
		33	Trichloroethene
		34	1,2-Dichloropropane
4	Chloromethane	35	1,4-Dioxane
5	Chloroethane	36	Bromodichloromethane
6	Buta-1,3-diene	37	*cis*-1,3-Dichloropropene
7	Vinyl chloride	38	4-Methylpentan-2-one
8	Bromomethane	39	Toluene
9	1,2-Dichloroethane	40	*trans*-1,3-Dichloropropene
10	Trichlorofluoromethane	41	1,1,2-Trichloroethane
11	Ethanol	42	Tetrachloroethene
12	1,1-Dichloroethene	43	Hexan-2-one
13	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon® 113)	44	Dibromochloromethane
		45	1,2-Dibromoethane
		46	Chlorobenzene
14	Acetone	47	Ethylbenzene
15	Carbon disulfide	48)	*m*-, *p*-Xylene
16	Isopropanol	49)	
17	Dichloromethane	50	*o*-Xylene
18	Methyl *tert*-butyl ether	51	Styrene
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20	n-Hexane	53	1,1,2,2-Tetrachloroethane
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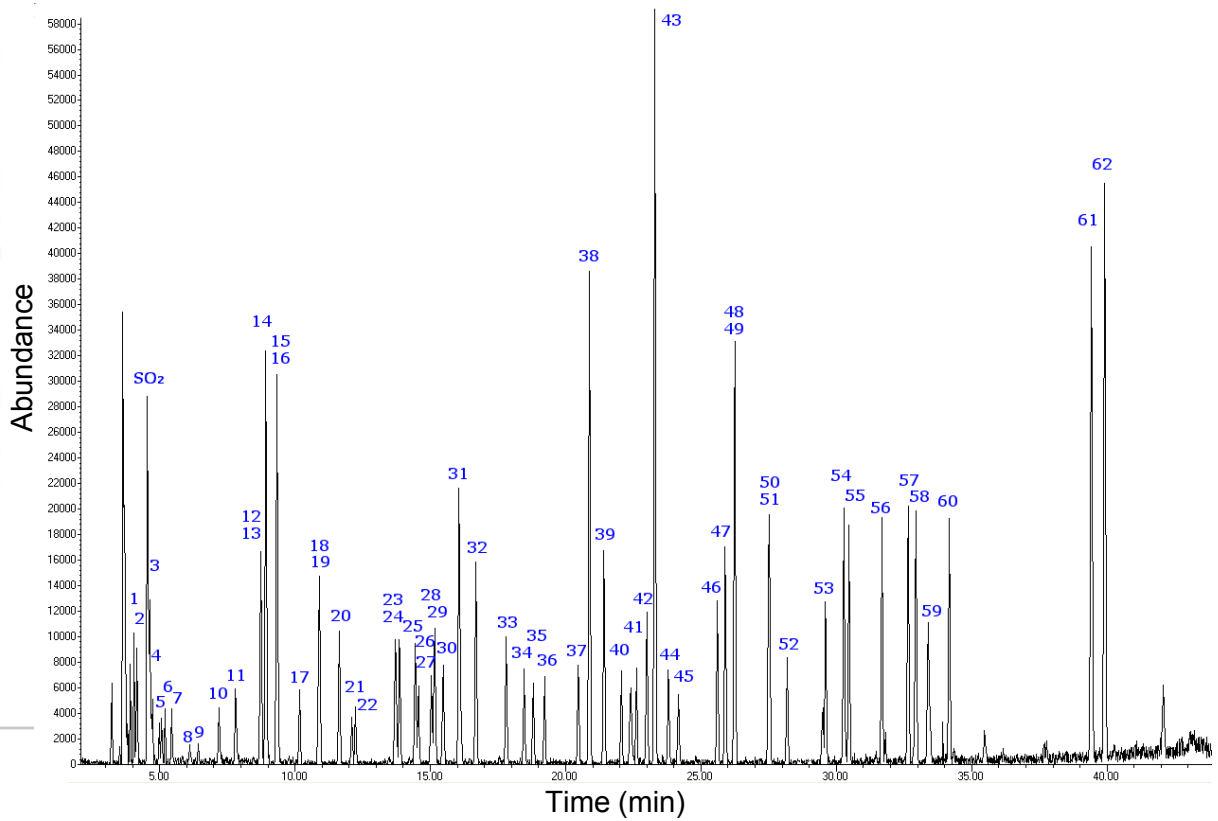
23	*trans*-1,2-Dichloroethene	56	1-Ethyl-4-methylbenzene
24	Butan-2-one	57	Dichlorobenzene
25	Ethyl acetate	58	Dichlorobenzene
26	Tetrahydrofuran	59	α-Chlorotoluene
27	Chloroform	60	Dichlorobenzene
28	1,1,1-Trichloroethane	61	1,2,4-Trichlorobenzene
29	Cyclohexane	62	Hexachlorobuta-1,3-diene

Splitless desorption of 'Air toxics' tube loaded with 1 L of 1 ppb std
GC/MS

Source: Markes Application Note TDTS 86



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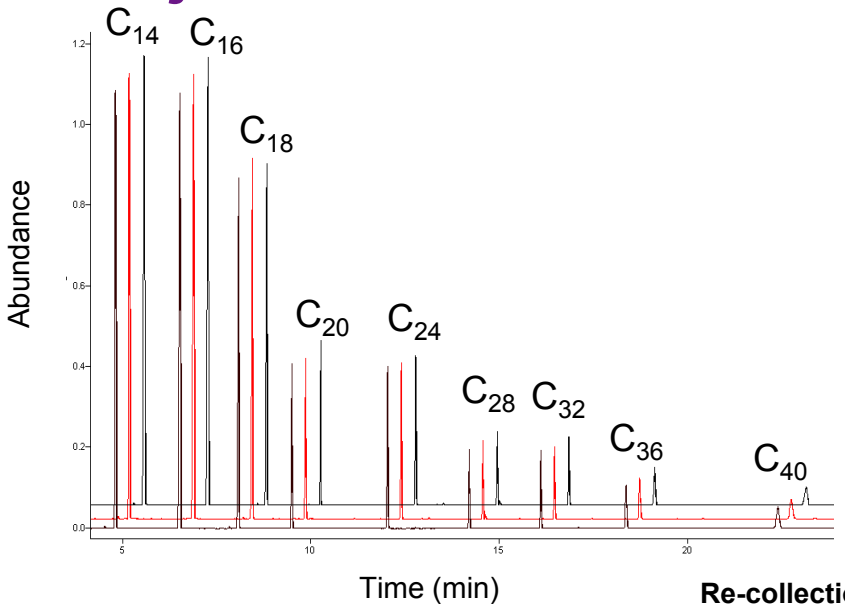
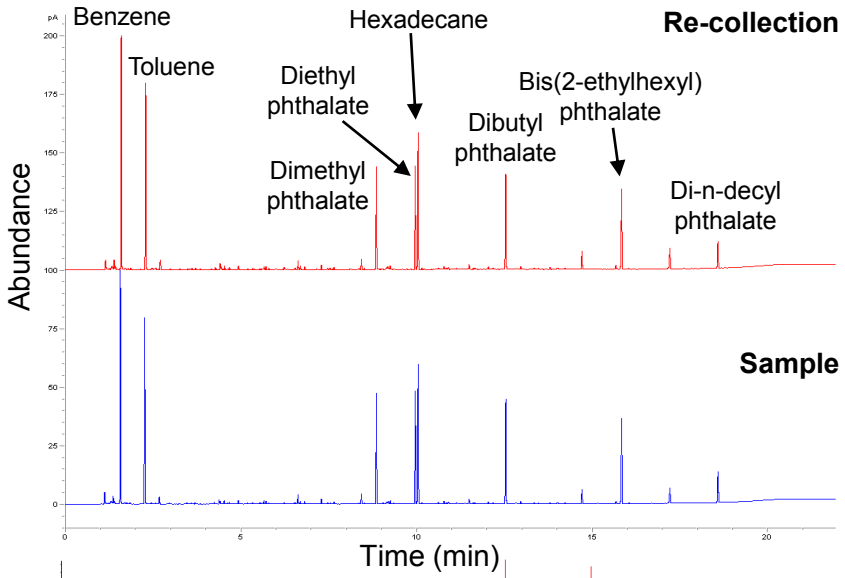
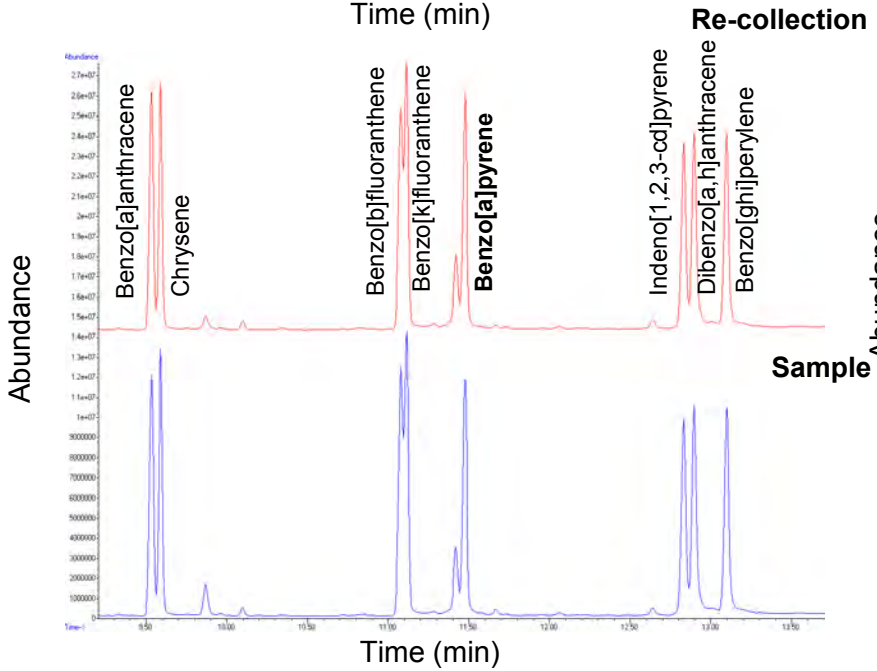
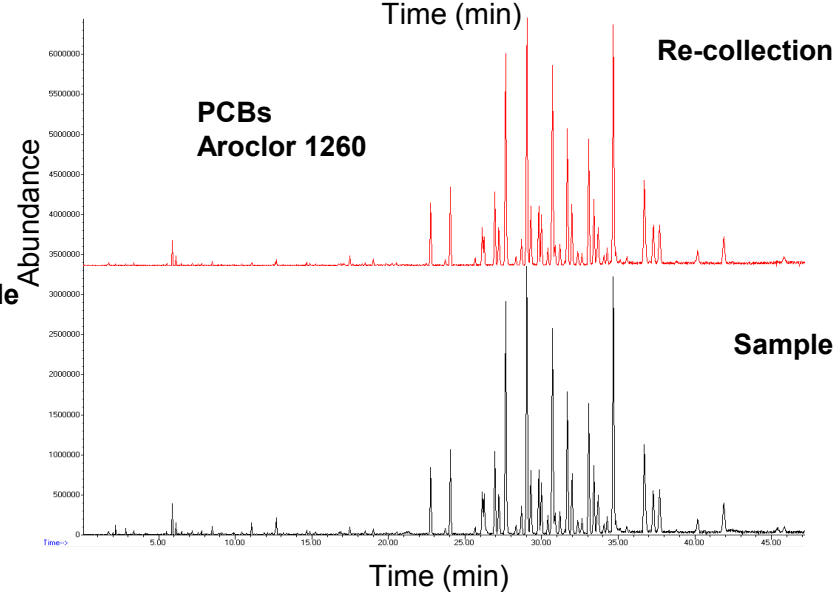
Not just volatiles...









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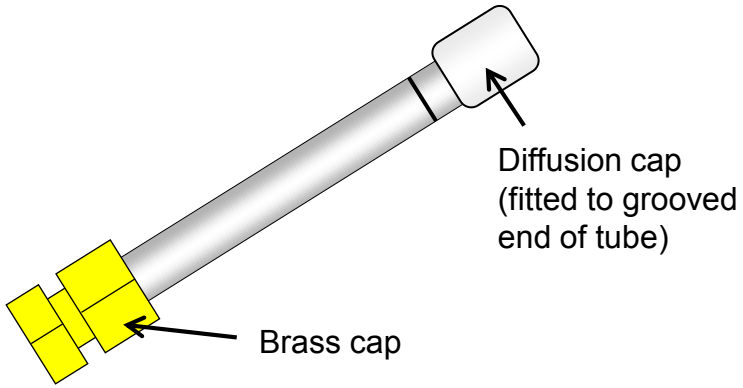
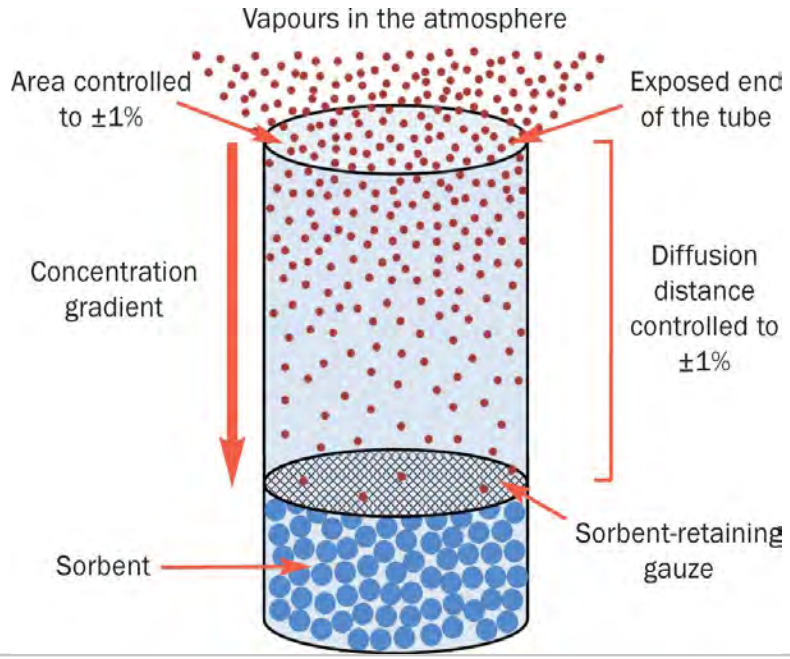
Passive (diffusive) sampling

- 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





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

EPA 325 – Refinery perimeter monitoring

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

- Requires continuous monitoring of vapor-phase organics around the boundary of oil refineries. Target analytes:
  - Benzene
  - Hazardous air pollutants (HAPs)
  - VOCs in refinery air (light/middle distillate fuels)
- **US EPA Methods:**
  - 325 A (Sampling): 2-week passive sampling using sorbent tubes.
  - 325 B (Analysis): TD–GC(MS) determination (MS recommended)

~~Which sampling method is best?~~

How do I get the right results?

- What are the compounds of interest?
- What is the expected concentration?
- How long is the monitoring period?
- Is the matrix compatible?
- Etc…..

- You can not determine which method is best until you know the sampling situation.

- ***Define the problem, before finding the solution,*** or as Einstein is quoted as having said

" If I had one hour to save the world, I would spend fifty-five minutes defining the problem and only five minutes finding the solution."

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Questions?

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Acknowledge the work of the Markes Application Team

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